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On the plasticity mechanisms of β metastable Ti alloys, towards enhanced work hardening

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Abstract

Owing to a unique profile of properties like high specific strength and excellent corrosion resistance, titanium alloys are more and more used for various medical, chemical and especially aerospace applications. β -stabilised Ti alloys have attracted a large attention since this particular class of alloys exhibits the widest panel of performances. However, these alloys show a plasticity driven by dislocation glide so that they generally suffer from a lack of work hardening, which is most of the time a major drawback.

The present thesis aimed at assessing how the triggering of a combination of different plasticity mechanisms by a fine tuning of the chemical composition can enhance the work-hardening rate of β titanium alloys. The present work shows that such designed alloys exhibit work-hardening rates never reached before, as a result of the synergetic activation of α'' stress-induced martensitic (SIM) phase as well as from mechanical twinning.

Each mechanism has been thoroughly characterised in order to estimate its contribution to the overall work-hardening rate. Specific characterisation techniques such as synchrotron-based X-ray diffraction, HR-TEM and HR-EBSD used during *in situ* tensile loading of a Ti-12wt.%Mo alloy, brought the monitoring of the deformation mechanisms from the nano to the mesoscopic scale. Furthermore, incremental oligo-cyclic shear tests brought some insight in the influence of strain path changes on the mechanical response of the material.

Résumé

De par leur combinaison unique de propriétés telles qu'une haute résistance spécifique et une excellente résistance à la corrosion, les alliages de titane sont de plus en plus utilisés dans des domaines aussi variés que le biomédical, l'industrie chimique et le secteur aéronautique. En particulier, les alliages de titane stabilisés sous forme β attirent de plus en plus l'attention car ils couvrent le panel de performances le plus large. Cependant, la plasticité de ces alliages est gouvernée par glissement de dislocations qui, dans ce cas précis, n'entraîne pas d'écrouissage lors de la déformation plastique, ce qui constitue un inconvénient majeur pour la plupart des applications.

Cette thèse a pour but d'évaluer comment l'activation d'une combinaison de différents mécanismes de plasticité, obtenue par un réglage fin de la composition chimique, peut améliorer le taux d'écrouissage des alliages de titane β . Ce travail montre que les alliages correctement sélectionnés montrent un taux d'écrouissage exceptionnel, résultant de l'activation synergique de la transformation martensitique sous contrainte et du maclage activé mécaniquement.

Chaque mécanisme a été caractérisé en profondeur afin d'estimer sa contribution au taux d'écrouissage global. Des techniques de caractérisation spécifiques telles que la diffraction des rayons X sous rayonnement synchrotron, le MET à haute résolution et l'EBSA à haute résolution angulaire utilisés lors de tests mécaniques *in situ* ont permis de suivre les mécanismes de plasticité tout au long de la déformation, de l'échelle du nanomètre à l'échelle mésoscopique. Enfin, des tests de cisaillement cycliques avec incréments de déformation ont amenés les premiers résultats

relatifs au comportement mécanique de ces alliages lors de changements de chemin de déformation.

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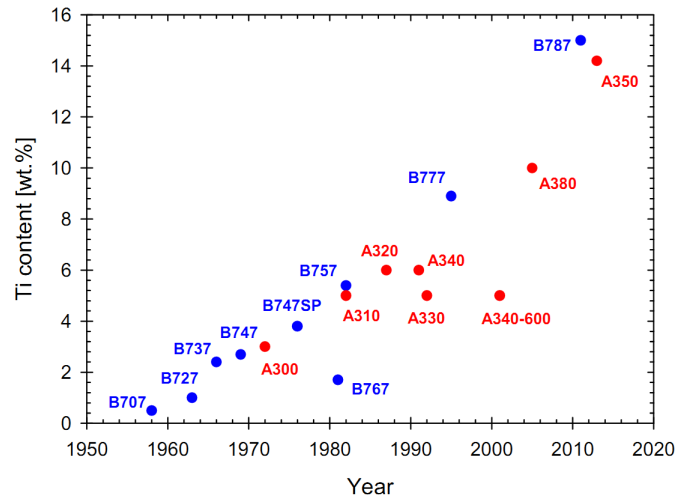
“Ah, not in knowledge is happiness, but in the acquisition of knowledge!”

- Edgar Allan Poe

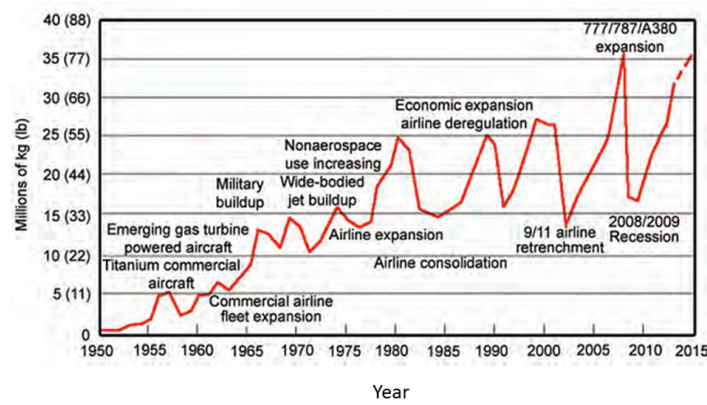
Chapter 1

Introduction and context

Since their first introduction on the market of structural materials in the 1950s, titanium and its alloys experience a constant growing use in a wide range of applications due to their excellent combination of properties and despite their high cost (see Figure 1.1(a)). Among their remarkable properties, one can cite their very high strength-to-weight ratio, their corrosion resistance and their biocompatibility. These properties render them particularly attractive for aeronautic and biomedical applications, but new application fields like energy, chemistry, jewellery or sport gears are also constantly emerging. However, as suggested by Figure 1.1(b), the global Ti market is still dependent on the aerospace market, which will thus regulate the price of Ti alloys. The main parts of aircrafts made of titanium alloys are illustrated in Figure 1.2, where the materials in use must fulfill the following heavy combination of requirements : a high specific strength, high fatigue and crack propagation resistance, as well as heat and corrosion resistance. Nowadays, at least 15% of the overall weight of a modern aircraft is made of titanium alloys.



(a)



(b)

Figure 1.1: (a) Growth of Ti alloys use as a percentage of total weight in commercial aircrafts [1,2] ; (b) U.S. Ti industry shipments since the introduction of Ti alloys on the market [2].

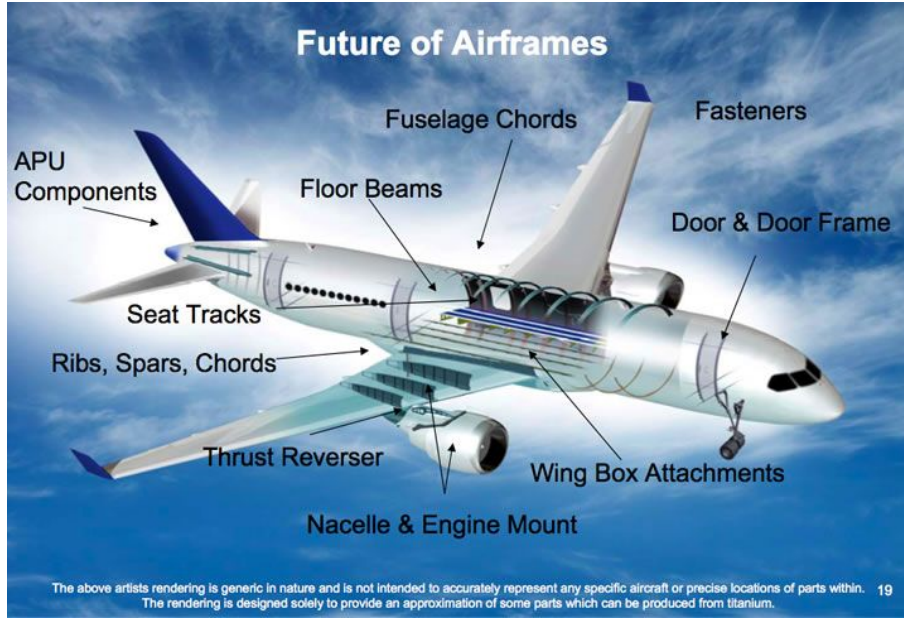


Figure 1.2: *Main parts of modern aircrafts made of titanium alloys. Taken from [3].*

β -stabilised Ti alloys are particularly attractive due to their wider range of achievable properties. However, their development remained rather limited during the XX^{th} century due to several factors. Firstly, they are generally heavily alloyed, which increases their production cost. Secondly, they exhibit nearly no work hardening capacity, which drastically limits their use in advanced applications where a combination of high strength and ductility is a major requirement. As an example, Ti alloys containing non-cytotoxic elements such as *Nb*, *Ta* or *Mo* (which are β stabilisers) are excellent candidates for biomedical applications where superior biocompatibility and low Young's modulus are required. However, these drawbacks do not allow them to currently compete with austenitic steels or *Cr – Co* alloys for evident reasons.

These considerations define the first objective of the present work, i.e. the development of new Ti alloys exhibiting a good combination of strength and ductility, owing to the improvement of the work hardening

capacity. Such kind of improvements have been achieved in the steel industry by the development of first and second generations of advanced high strength steels (AHSS). Among these steels, two particular cases are of great interest : the Transformation Induced Plasticity (TRIP) steels and the Twinning Induced Plasticity (TWIP) steels. Thanks to these particular mechanisms of accommodation of plastic deformation, these materials exhibit the aforementioned combination of desired properties expected for Ti alloys. Indeed, any microstructural feature that inhibits or delays dislocation motion influences the work hardening rate of a metallic material. Such microstructural features can be grain boundaries, other dislocations, interfaces (twin or second phase boundaries), strain-gradients, etc.

In order to meet the target described above, a design strategy based on electronic orbital calculation has been successfully applied for designing a new type of metastable β -Ti alloys exhibiting combined TRIP and TWIP effects. It is shown that the simultaneous activation of martensitic transformation and mechanical twinning leads to an improvement of the work hardening rate compared to conventional β Ti alloys deforming by dislocation glide. Moreover, a synergy between each deformation mode is observed. This observation brings about the second major objective of this work, the determination of the impact of each activated plasticity mechanism on the global work hardening behaviour of the designed alloy. To achieve this goal, the microstructural evolution has been examined by various characterisation techniques such as X-ray diffraction (XRD) and electron microscopy. Finally, insights in the behaviour of the material under complex stress path such as load direction reversal have been performed.

The manuscript is thus organised in the following way :

- **Chapter 2** presents the general concepts relative to titanium and its alloys, with a focus on the deformation mechanisms observed in β -Ti alloys.
- In **Chapter 3**, the d -electron design strategy applied in this work is presented, followed by the experimental methods and the validation of the design strategy in the case of Ti-12wt.%Mo alloy.

- **Chapter 4** focuses on the microstructural evolution during plastic straining. Based on these results, the amount of deformation products and the work hardening are related with a sequence of activation between $\{332\}\langle 113 \rangle$ mechanical twins and α'' stress-induced martensite.
- In **Chapter 5**, the onset of plasticity is investigated. Transmission Electron Microscopy (TEM) characterisation was performed on both post-mortem samples and *in situ* tensile tests. The $\{112\}\langle 111 \rangle$ mechanical twinning mechanism operating in Ti-12Mo is carefully analysed.
- In **Chapter 6**, the evolution of the internal stress state in the β matrix during plastic straining is followed *in situ* during tensile tests with synchrotron diffraction. The evolution of the martensite content is also estimated, as well as its hardening behaviour.
- **Chapter 7** introduces an emerging high resolution characterisation technique based on Electron Back-Scattered Diffraction (EBSD) capable of estimating in an absolute way the local internal stress state in a crystalline material, as well as the density of Geometrically Necessary Dislocations (GND). It is then applied on stress-induced interfaces in the Ti-12Mo alloy.
- In **Chapter 8**, the behaviour of the material during simple shear experiment is studied and compared to uniaxial tension. Cyclic shear-reverse shear experiments have been carried out to observe the evolution of internal stresses arising within the material during plastic straining.
- Finally, the main results obtained through this thesis are summarised in the **general conclusion**, and prospects concerning the development and optimisation of the TRIP/TWIP titanium alloys are given.

Chapter 2

State of the art

This chapter aims at summarising the basic principles necessary for the understanding of the present work. A brief historical overview of the development of titanium alloys, closely related to the widening of their application fields, will be followed by a description of the classification depending on the type and amount of alloying elements. Since this work focuses on the mechanical behaviour of a particular β -Ti alloy, a description of the commonly observed deformation mechanisms in this family of alloys will be then presented. Finally, a brief description of the strain hardening formalism of Kocks-Mecking will be introduced.

2.1 Historical perspective and fundamental concepts

Titanium and its alloys constitute a young class of engineering materials. Indeed, their use as structural materials started in the early 1950s [1, 4]. In the beginning, the high cost of Ti limited its use to military applications. As time passes, its metallurgy became more understood and mastered, and aeronautic industry began to add titanium alloys in an increasing number of structural parts of aircrafts, as illustrated in Figure 1.1(a). Nowadays, these materials can be found in various other application fields, like biomedical industry for prothesis or stents, chemical industry for heat exchangers and corrosion resistant pipes, luxury and sport industries, etc.

2.1.1 Pure titanium

Titanium is an element from the transition metals class (IVB column of the Mendeleev table). In its pure form, titanium exhibits 3 stable crystallographic packing depending on the temperature and pressure (see the $P - T$ diagram on Figure 2.1). At atmospheric pressure, the allotropic transformation between high temperature body-centered cubic (BCC) phase (called β phase) and low temperature hexagonal close packed (HCP) α phase takes place at $882^\circ C$. The high pressure stable phase has a non-compact hexagonal structure and is called ω phase. More details about this phase will be given in Section 2.1.3.

The transformation $\beta \rightarrow \alpha$ follows the Burgers mechanism and is partially displacive, since the change from the BCC structure to the HCP structure can be achieved with atomic displacements smaller than interatomic distances. Figure 2.2 illustrates the transformation from β to α phase, the orientation relationship being the following one :

- directions : $\langle 111 \rangle_\beta \parallel \langle 11\bar{2}0 \rangle_\alpha$
- planes : $\{110\}_\beta \parallel \{0001\}_\alpha$

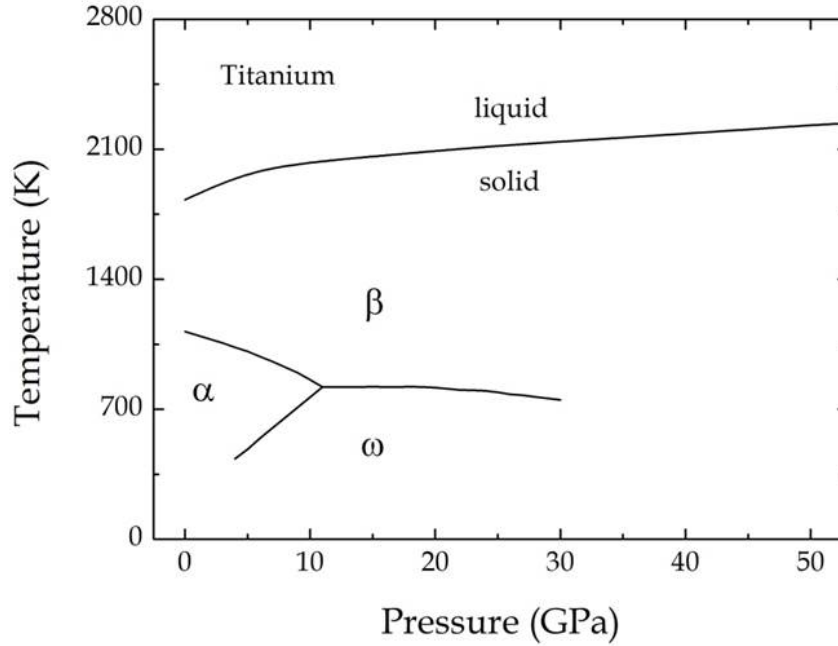


Figure 2.1: *The $P - T$ diagram of pure titanium [5].*

If titanium has become such an attractive metallic material, it is definitely due to its particular combination of properties. Indeed, in addition to its high specific strength (that is the strength-to-weight ratio), it is highly corrosion resistant as well as biocompatible. These two last properties come mainly from the fact that a dense oxide passivation layer forms at its surface, preventing oxidation of the bulk material. It is also non-cytotoxic, meaning that human cells can grow and proliferate on its surface. These properties, combined with a relatively low Young's modulus, explain its wide use in biomedical industry.

2.1.2 Classification of titanium alloys

Like in steels, one can separate alloying elements in titanium depending on their α - or β -stabilising character. The effect of common alloying

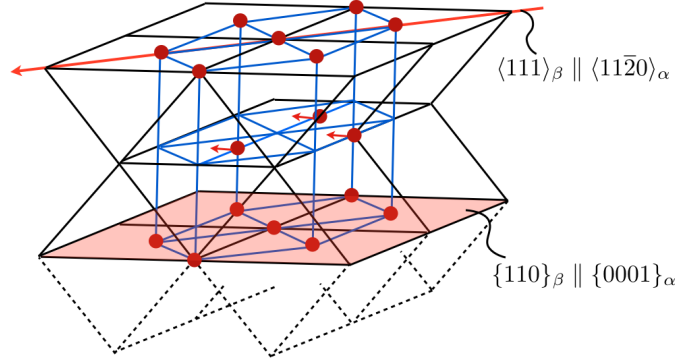


Figure 2.2: Schematic representation of the allotropic transformation between β and α phases in pure titanium. Redrawn from [6].

elements on phase stabilities are summarized in Figure 2.3. The fact that titanium presents an allotropic transformation brings the opportunity to harden alloys by phase transformation upon heat treatments through introducing numerous internal interfaces. A wide range of mechanical properties is thus reached by titanium alloys. The main features of each family of alloys are briefly listed in the following paragraphs. In order to easily classify titanium alloys, two indices have been introduced : the Mo_{eq} and Al_{eq} (Equations 2.1) [7,8], the coefficient of each alloying element depicting the strength of its effect on the system thermodynamics.

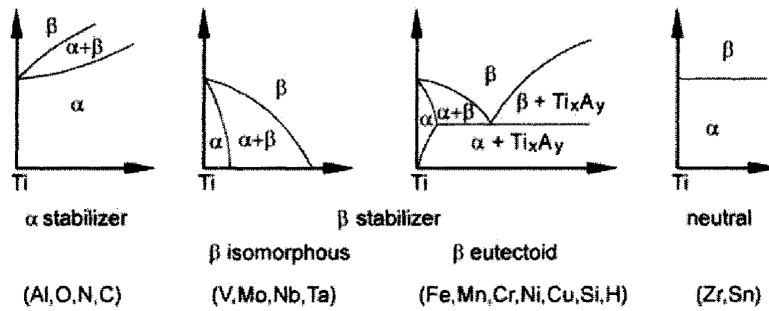


Figure 2.3: Illustration of different phase diagrams achieved in titanium alloys depending on alloying elements [4].

$$\begin{cases} Mo_{eq} = Mo + 0.67V + 0.44W + 0.28Nb + 0.22Ta + 2.9Fe + \dots - Al \\ Al_{eq} = Al + 0.33Sn + 0.17Zr + 10(O + C + 2N) \end{cases} \quad (2.1)$$

It is thus possible to classify the titanium alloys in three main classes depending on their chemical composition and the microstructure obtained upon quenching from high temperature β field, as illustrated in the pseudo-binary phase diagram in Figure 2.4. Titanium alloys can be classified as α or near α , $\alpha + \beta$ or β alloys if enough β -stabilising elements are added to retain completely the β phase at room temperature. This last class can be subdivided in “stable” and “metastable” subclasses depending on the mechanical behaviour of the alloy under an applied stress.

α and near- α alloys

α titanium alloys are mainly used in chemical and process industries due to their large corrosion resistance and high formability. These alloys can be strengthened by small addition of interstitial oxygen, but with a loss in ductility [10]. Achievable microstructures are highly dependent on the thermomechanical processing (TMP) of the material. Among these ones, one can highlight martensitic microstructure upon quenching, equiaxed α grains after annealing in highly α -stabilized alloys or Widmanstätten structures (basket-weave) in low alloyed grades [1].

Near- α alloys are used in high temperature applications owing to their excellent creep resistance combined with strengthening effect of dual-phase material [8]. Indeed, a small amount of β phase is retained at room temperature between the α platelets of the Widmanstätten structure.

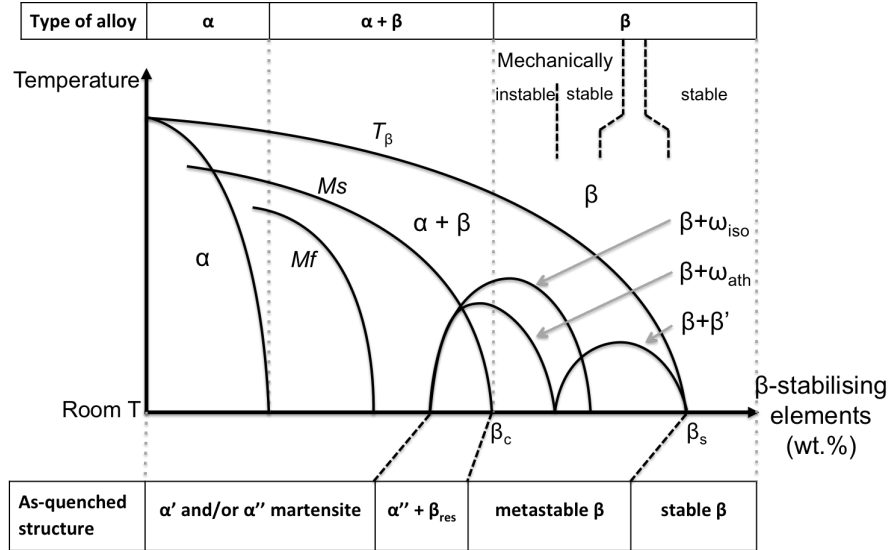


Figure 2.4: Pseudo-binary phase diagram of titanium alloys illustrating the influence of the amount of β -stabilising elements on the decomposition products of the β phase upon quenching (adapted from [9]). β_c is the minimal amount of elements to retain 100% of β phase upon quenching ; β_s is the minimal amount to retain 100% of β phase during slow cooling ; T_β , M_s and M_f are the β -transus, the martensite start and martensite finish temperatures, respectively.

$\alpha + \beta$ alloys

This class of alloys contains the most known titanium alloy, the $Ti - 6Al - 4V$. It represents the major part of the overall titanium alloys production [11]. The massive use of this alloy is mainly due to the combination of two facts : (i) it can reach a large range of mechanical properties by playing on phase proportions and morphologies ; (ii) it is by far the most studied titanium alloy and its metallurgy is well known. $Ti - 6Al - 4V$ alloy can readily be forged and welded, is heat-treatable to levels of ultimate tensile strength of the order of $1200MPa$ and has stable mechanical properties up to $360 - 400^\circ C$ [], explaining its use in low temperature compressor parts of aircraft engines [12].

β alloys

Until the 1990s, these alloys were scarcely used since the commercially available alloys suffered from a lack of ductility in their high-strength conditions and they exhibit the highest density among titanium alloys. These two disadvantages restrained their use despite their superior reachable strength, formability and corrosion resistance. Bania listed the advantages and disadvantages of this family of alloys, reproduced in Table 2.1 [13]. Nevertheless, the recent progresses in β -metastable titanium alloys metallurgy should induce an increasing use of these promising engineering materials.

Advantages	Disadvantages
high strength-to-density ratio	high density
low modulus	low modulus
high strength/high toughness	poor low and high temperature properties
high fatigue strength	small processing window (s. a.)
good deep hardenability	high formulation cost
low forging temperature	segregation problems
low-cost TMP	high springback
cold formable (s. a.)	microstructural instabilities
easy to heat treat	interstitial pick up
excellent corrosion resist. (s. a.)	poor corrosion resistance (s. a.)
excel. combustion resist. (s. a.)	

Table 2.1: *Advantages and disadvantages of β titanium alloys [13].*
(s. a. = some alloys)

2.1.3 The ω phase

ω phase is a metastable phase that can be found in some Ti alloys in two distinct forms : athermal ω (ω_{ath}) and isothermal ω (ω_{iso}). ω_{ath} is similar to a martensitic phase, *i.e.* a diffusionless transformation that brings nanometric precipitates. It occurs upon quenching in alloys containing

sufficient amount of β stabilizing elements to avoid thermally induced α'' martensitic transformation (see Section 2.2.2). It has a hexagonal symmetry (space group $P6/mmm$) and is reported as a brittle phase. However, in the as-quenched state, ω_{ath} domains are small and do not interfere with β phase mechanical properties. It has the highest Young's modulus among the phases occurring in titanium alloys. The amount of ω phase will thus have an effect on the mean Young's modulus of the alloys. The formation of ω_{ath} is due to the collapse of two successive $\{111\}$ planes as illustrated in Figure 2.5.

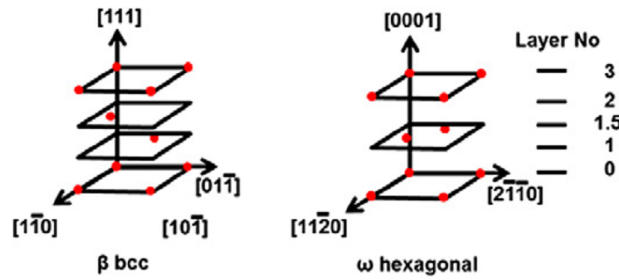


Figure 2.5: Illustration of collapse of $\{111\}_{\beta}$ planes to form ω_{ath} phase [14].

The aging of a β titanium alloy containing athermal ω phase leads to the formation of ω_{iso} . β -stabilising elements diffuse out of growing ω particles resulting in a stabilisation of the β matrix [15]. These precipitates are very brittle and lead to high yield strength, but nearly no ductility [16, 17].

The composition ranges where ω_{ath} can be observed depend on the β -stabilising strength of alloying elements, but also on the quenching rate and the impurity level [18].

2.2 Deformation mechanisms in β -Ti alloys

2.2.1 Dislocation glide

Perfect dislocations

Dislocations are one dimensional defects whose existence was independently suggested in the 1930s by Orowan, Polanyi and Taylor to explain the deformation of crystalline materials [19]. Their existence has been confirmed with the appearance of the Transmission Electron Microscope (TEM). They are responsible for the high ductility of metals compared to other crystalline materials like ceramics. These defects correspond to discontinuities in the periodic arrangement of atoms. Dislocations are characterised by two vectors : the Burgers vector $\vec{b}$, which corresponds to the direction and the distance of slip in the crystal and the dislocation line $\vec{l}$, which can be view as its core. Depending on the relative orientation of the two vectors $\vec{b}$ and $\vec{l}$, one can distinguish two main types of dislocations :

- Edge dislocation : the two vectors $\vec{b}$ and $\vec{l}$ are perpendicular, and this defect can be easily described as the insertion of a half atomic plane between two planes of the perfect crystal lattice.
- Screw dislocation : the two vectors $\vec{b}$ and $\vec{l}$ are parallel, the nearest nodes from the core being shifted to the neighbouring position in the lattice, forming a screw around the dislocation line.

Figure 2.6 illustrates both types of dislocations in their more common form, a dislocation loop, where the curved part of the loop combines the character of both edge and screw dislocations since the orientation of the dislocation line changes continuously along the loop.

Dislocations will not form on random planes of the material. Indeed, for energetic reasons, they will glide on the most closely packed planes and along the most closely packed directions of the crystal lattice. There exists thus a finite number of slip systems for each type of crystal lattices. In the case of *BCC* lattices, there are no close-packed planes.

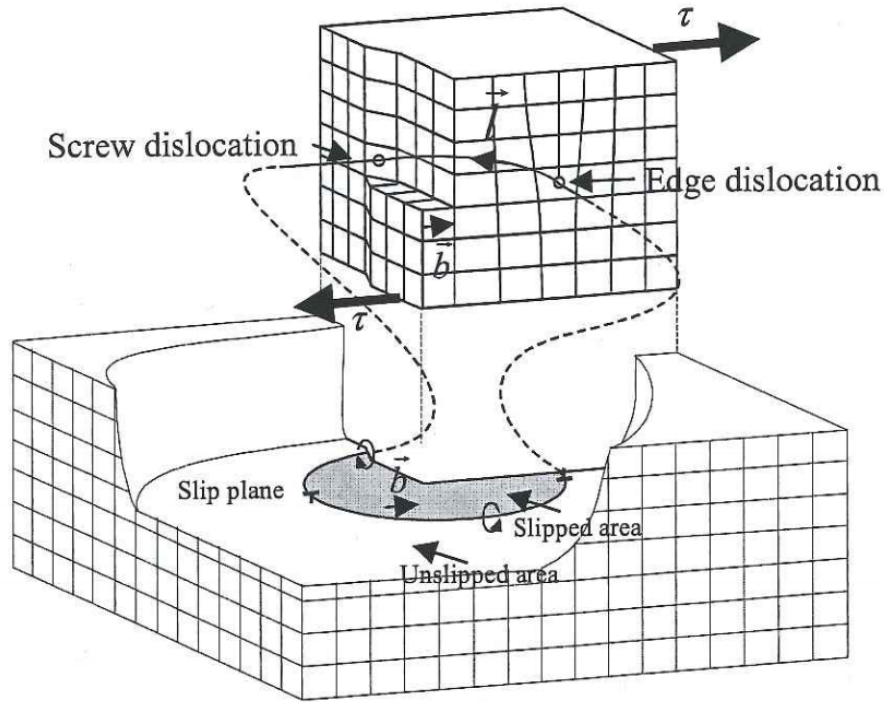


Figure 2.6: Schematic representation of a dislocation loop in a crystal [20]. Both pure edge and pure screw dislocations are indicated.

Dislocations can glide along the $\langle 111 \rangle$ directions on different families of planes containing these directions, generally the $\{110\}$, $\{211\}$ and $\{321\}$. This multiplicity of slip planes is responsible for the cross-slip phenomenon : dislocations can easily change of slip plane, which results generally in a lower strain hardening than in *FCC* metals for example.

Dislocation motion mechanics in *BCC* lattices is more complex than in *FCC* ones. Indeed, the core of the screw dislocations is spread in a 3D configuration due to the non close-packing [21], as illustrated in Figure 2.7. Depending on the stacking fault energy, and thus on the chemical composition of the alloy, the core will be more or less spread on the $\{110\}$ or on the $\{112\}$ planes of the lattice. It is thus necessary to “recombine” the dislocation in order to trigger its motion. This

fact explains why the plasticity of *BCC* materials is mostly driven by the screw dislocations. Also, the aforementioned spreading will have a huge impact on the capabilities of the dislocations to dissociate into the partials needed for mechanical twinning. An interesting difference between the behaviour of dislocations in *FCC* and *BCC* lattices is the tension/compression asymmetry exhibited by *BCC* single crystals at low temperature [22]. This asymmetry is another consequence of the spreading of the core. Indeed, in addition to the increase of the Peierls forces to overcome, the core distorts asymmetrically upon an applied shear stress [23]. The motion of the dislocation is therefore affected by the stress components outside the highest Schmid factor slip plane. This results in a “non-Schmid” behaviour of the *BCC* lattice, as illustrated in Figure 2.8.

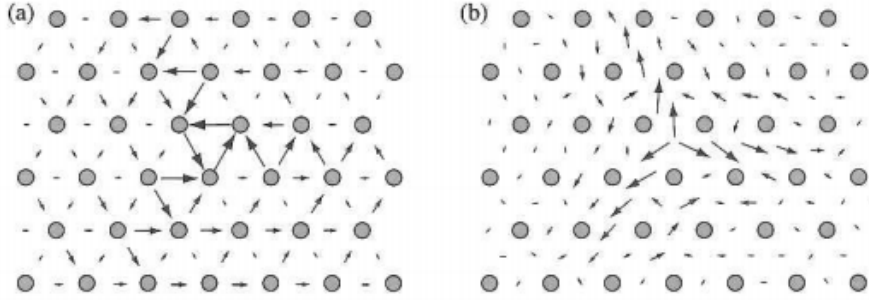


Figure 2.7: *Equilibrium configuration of (a) atomic displacements in BCC lattice around a screw dislocation line normal to the plane of the paper and (b) distribution of the small edge components perpendicular to the direction of the screw dislocation (Taken from [24]).*

Partial dislocations

Perfect dislocations can dissociate in several partial dislocations if this dissociation results in a lowering of the total energy associated to this defect :

$$\vec{b}_{perfect}^2 > \sum \vec{b}_{partial}^2 \quad (2.2)$$

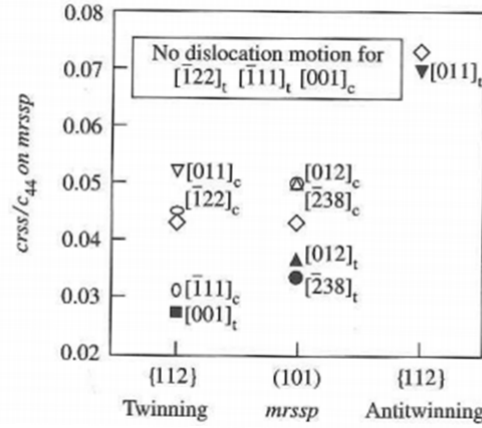


Figure 2.8: Results of simulation of tensile and compressive straining in Mo along six orientations, showing the critical resolved shear stress necessary to trigger dislocation motion on the $\{112\}$ -twinning and -antitwinning sense planes and on a $\{110\}$ plane. It is shown that an asymmetry exists in the behaviour of dislocation motion in BCC lattices (Taken from [24]).

Unlike perfect dislocations, partial dislocations do not connect two equivalent point of the lattice. The formation of partial dislocations is thus associated to another crystalline defect, the stacking faults. Indeed, the glide of a partial dislocation will induce a stacking change in the crystal, which is restored to its perfect stacking sequence after the glide of all partials. Although these defects are well-known and common in *FCC* and *HCP* materials, they have been scarcely observed in *BCC* alloys. Fourdeux *et al.* managed to observe stacking faults in annealed pure niobium crystals [25]. Nevertheless, several authors studied the theoretical dissociation possibilities on $\{110\}$ and $\{112\}$ planes in *BCC* lattice based on energetic and geometrical considerations [26–30].

The concepts of partial dislocations and stacking faults are of primary importance due to their close relationship with twinning, which will be briefly described in Section 2.2.3.

SSDs and GNDs

Beside their slip systems, the dislocations can also be differentiated depending on their origin. Two cases can be distinguished : the Statistically Stored Dislocations (SSD) and the Geometrically Necessary Dislocations (GND). Basically, the first type refers to the dislocations that are created and slip during plastic deformation, while the second type refers to the dislocations that are needed to accommodate the heterogeneous local deformation of the lattice. This concept has been introduced by Ashby [31, 32] and is of application in all polycrystalline material. These dislocations do not contribute to plastic strain, but will act as obstacles to the aforementioned SSDs and thus will contribute to the strain hardening of the material (see Section 2.3).

2.2.2 Martensitic transformation

Initially, the word “martensite” relates to the German metallurgist Martens who observed a needle-shaped microstructure in some quenched steels. It results from a displacive phase transformation, the carbon atoms being trapped in interstitial sites of *BCC* lattice during the allotropic transformation of iron. The concept of martensite has been further extended to other metallic materials presenting an allotropic transformation, allowing the formation of metastable phases with different mechanical properties. Since titanium exhibits such a transformation, it is possible to obtain martensitic microstructures.

Martensitic transformation as a deformation-induced mechanism has emerged during the 1960s in steels. The acronym TRIP (TRansformation Induced Plasticity) refers to the fact that mechanical properties are dictated by the stress-induced phase transformation occurring during plastic deformation. In order to exhibit a TRIP effect, the high temperature phase must be (meta-)stabilized at room temperature, that is its martensitic start temperature (M_s) must be lower than room temperature. Then, sufficient loading can induce the phase transformation, leading (generally) to a higher strain hardening than in the case of simple dislocation glide. The chemical stability of the parent

phase is thus the key parameter for designing an alloy exhibiting the TRIP effect [33, 34].

Since the work of Bain on martensitic transformation, this subject remains a very prolific research topic. A more global theory called Phenomenological Theory of Martensite Crystallography (PTMC) was proposed in the 1950s. Among others, Bowles and MacKenzie elaborated a theory to relate the transformed lattices to the parent ones [35]. They argued that two component strains are needed to explain correctly the transformations. They managed to apply their theory to different systems, even if it was not the case for $Ti - 11wt.\%Mo$ due to conflicting results in the literature [36]. In their work, they also highlighted that stress-induced martensite is generally twinned, and in the case of α'' martensite in titanium alloys, the invariant plane should be the $(0\bar{1}1)_{\alpha''}$. Inamura *et al.* [37] showed later that the twinning relationship between the α'' variants was dependent on the mismatch between the β matrix and the martensite. They proposed the $\{111\}_{\alpha''}$ type I twinning, the $\langle 211 \rangle_{\alpha''}$ type II or the $\{011\}_{\alpha''}$ compound twinning as achievable twinning relationships in β -Ti alloys.

α'' phase is a martensitic phase arising in mechanically instable β -Ti alloys or upon quenching in insufficiently β -stabilised alloys (see Figure 2.4). Recently, this phase has received a lot of attention due to its possible reversibility, inducing shape memory effect and pseudoelasticity with large strain recovery while unloading. It has an orthorhombic symmetry, the space group being $Cmcm$, and can be viewed as a distorted HCP lattice. This phase appears after quenching and/or under mechanical loading depending on the β -stabiliser content. Unlike in martensitic steels, this phase is thought to be softer than the matrix. Its mean Young's modulus is the smallest among the different phases in titanium alloys.

The transformation from β to α'' is schematically illustrated in Figure 2.9. The orientation relationship between the phases is the following :

- directions : $\langle 110 \rangle_\beta \parallel [001]_{\alpha''}$
- planes : $\{110\}_\beta \parallel (001)_{\alpha''}$
- planes : $\{112\}_\beta \parallel (110)_{\alpha''}$

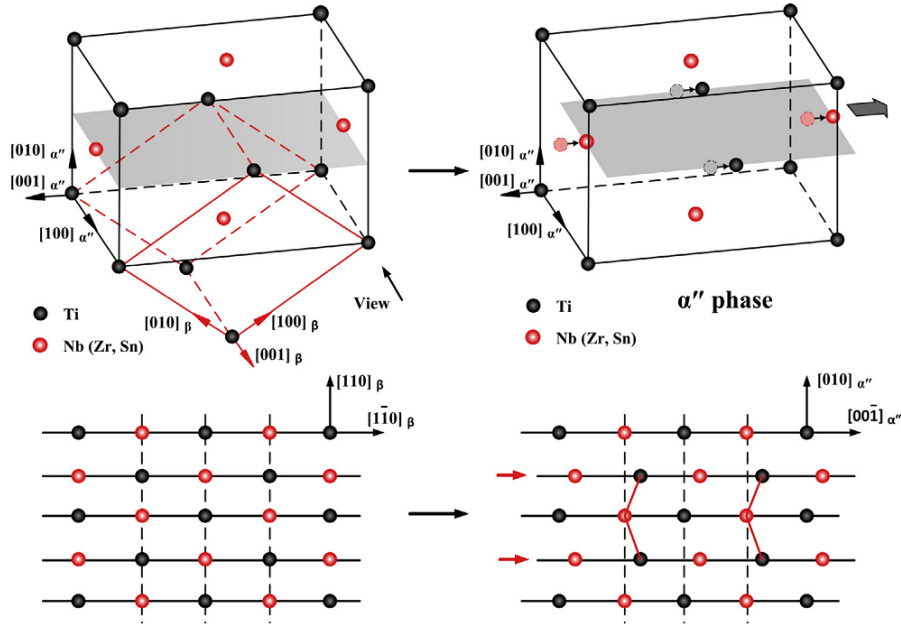


Figure 2.9: Illustration of lattice correspondence between β and α'' phases. Redrawn from [38].

Most of the studies carried out on α'' phase focus on the associated pseudo-elastic behavior in titanium alloys. Very few authors looked at the possible benefits on strain hardening that could be induced by the occurrence of this stress-induced martensitic (SIM) phase transformation.

The trigger stress necessary for inducing phase transformation will depend on several factors. Bhattacharjee *et al.* have shown that a too large initial β grain size could inhibit the SIM transformation [39], stating that the internal friction becomes too high for large grain size compared to the current stress state. Also, the testing temperature has an effect, since the trigger stress is proportional to the difference between M_s and the testing temperature. Recently, Neelakantan *et al.* applied the Kocks-Mecking formulation to model the SIM transformation in a near β alloy during compressive loading in a range of temperature ranging from room temperature to 213°C . They showed that the amount of α'' martensite created depends on the testing temperature [40].

The impact of SIM transformation on mechanical properties of β Ti alloys is qualitatively sketched in Figure 2.10. First, β phase deforms elastically up to a level of stress corresponding to the trigger stress for the martensitic transformation. Well-oriented β grains then start to transform, the amount of transformed phase depending on several parameters like chemical composition, grain size, initial texture, etc. A secondary linear zone follows the transformation plateau, where the remaining β phase as well as α'' phase deform elastically, up to the yielding point where those two phases deform plastically.

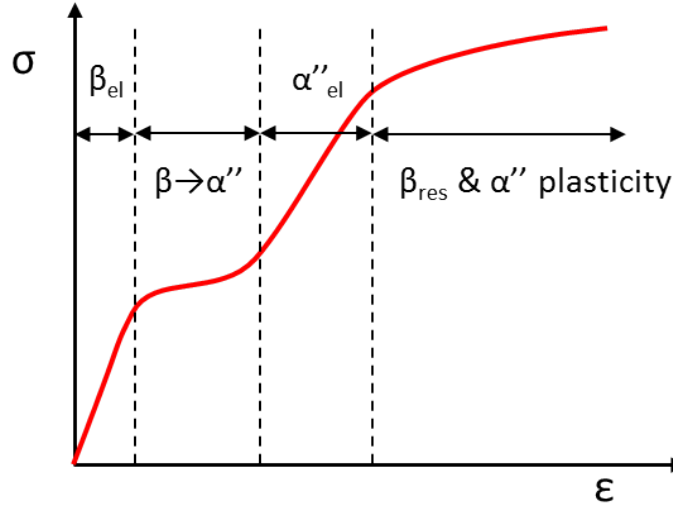


Figure 2.10: Qualitative stress-strain curve of a β -Ti alloy showing SIM α'' phase transformation. The curve shows the typical double yielding and transformation plateau due to massive β phase transformation. The difference of slopes between the two elastic regimes depends on the amount of α'' phase formed.

2.2.3 Mechanical twinning¹

The concept of mechanical twinning is known for a long time in various crystallographic systems [42]. It was discovered by Reusch in calcite [43]. The theory of deformation twinning is very close to the theory of martensitic transformation. Indeed, both mechanisms need the collective movement of atoms and the passage from the matrix to the deformation products can be expressed in terms of shear directions and habit planes. Some authors reported that *FCC* single crystals show mechanical twinning after appreciable slip plastic deformation, while in *BCC* single crystals twins arise in the elastic regime [41].

Among the different theoretically possible twinning modes, the operat-

¹This section is partly inspired by [41].

ing one will generally be the one with the better compromise between complexity of shuffling and magnitude of shear.

Crystallography of twinning

The complete description of a particular twinning mode is done by specifying the invariant plane of the shear $\mathbf{K}_1$ and the shear direction η_1 , as well as the conjugate plane $\mathbf{K}_2$ and the conjugate shear direction η_2 . The magnitude of shear is generally noted s . The four twinning elements are illustrated in Figure 2.11.

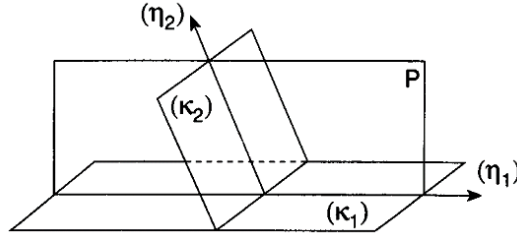


Figure 2.11: *The twinning elements : the twinning and conjugate planes ($\mathbf{K}_1$ and $\mathbf{K}_2$), and the twinning directions η_1 and η_2 [41].*

Bilby and Crocker established a generalised theory of deformation twinning [44]. They predicted all possible twinning modes for all crystal types by considering combinations of shear and shuffle. They concluded that the general guidelines for the occurrence of a twinning mode are, in order of importance :

1. a small twinning shear ;
2. a simple shuffle ;
3. a small shuffle ;
4. a shuffle parallel to twinning direction rather than perpendicular to it.

This theory is able to predict a wide number of experimentally observed twinning systems. Among all the twinning modes predicted in the *BCC*

lattices, two of them are reported in the literature to occur in *BCC* titanium alloys with the components listed in Table 2.2.

s	K_1	K_2	η_1	η_2	q
$2^{-\frac{1}{2}}$	$\{112\}$	$\{\bar{1}\bar{1}2\}$	$\langle\bar{1}\bar{1}1\rangle$	$\langle111\rangle$	2
$2^{-\frac{1}{2}}/2$	$\{332\}$	$\{11\bar{2}\}$	$\langle11\bar{3}\rangle$	$\langle111\rangle$	4

Table 2.2: *Twinning modes observed in β -Ti alloys. s denotes the magnitude of shear, K_i and η_i are the twinning elements and q corresponds to the smallest number of lattice planes parallel to the twinning plane for reproducing the lattice in the twin.*

Generally, the models of deformation twinning are separated in two stages, namely the nucleation and growth stages as in the case of first order phase transformations. Among the nucleation stage, two types of nucleation are also considered : homogeneous nucleation if twins form within a defect-free crystal and heterogeneous nucleation if the mechanism of formation is defect-assisted. Some cases of homogeneous nucleation have been reported in the literature in the case of carefully prepared *HCP* single crystals [45–47]. The authors reported much higher levels of trigger stress for twinning compared to bulk samples containing defects. It was therefore suggested that the presence of initial particular defect configuration is a driving force for nucleation of twinning.

The $\{112\}\langle111\rangle$ twinning system

The most common twinning system in *BCC* systems is the $\{112\}\langle111\rangle$ one. It has been observed in several systems like Fe-based alloys [48] and Nb-based alloys [49], for example.

Several authors explained theoretically the formation of such mechanical twins by dissociation of perfect $\frac{1}{2}\langle111\rangle$ screw dislocations to form three-layer twins in *Mo – Re* alloys [50], and occurrence of such mechanism in β titanium alloys have been reported [51].

A model of $\{112\}\langle111\rangle$ twinning based on experimental evidences has been proposed by Hsiung *et al.* in the case of *BCC* tantalum [52]. It

involves the presence of initial sources of dislocations, which are supposed to be grown-in thermal jogs. These jogs are vestiges of the dislocation structures developed in the material during thermomechanical treatments. Some parts of these dislocations are very stable and remains in the material even after recrystallisation treatments. An example of such initial sources is depicted in Figure 2.12 in the case of recrystallised niobium.

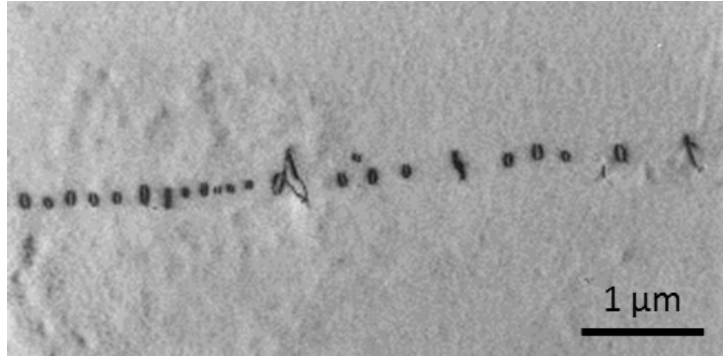


Figure 2.12: *Coaxial dislocation segments remaining after recrystallisation treatment in BCC niobium. Courtesy of H. Idrissi.*

Once the critical resolved shear is reached in the grain, dislocation are emitted. The perfect dislocations will decompose in partial dislocations following the reaction :

$$\frac{1}{2}[111] = \frac{1}{6}[111] + \frac{1}{6}[111] + \frac{1}{6}[111] \quad (2.3)$$

The partials are one-plane apart from each others and form a micro-twin domain. Since the stacking sequence in the $\langle 211 \rangle$ directions is composed of six different atomic layers, the dissociation of two dislocations is required to generate the complete stacking sequence in the twins. The final atomic stacking is illustrated in Figure 2.13 with the implied shear magnitude on each atomic layer.

It is worth noting that the same authors explain the formation of platelets of stress-induced ω phase with the same mechanism, the only difference being the involved dislocation core dissociation. Since anti-twinning

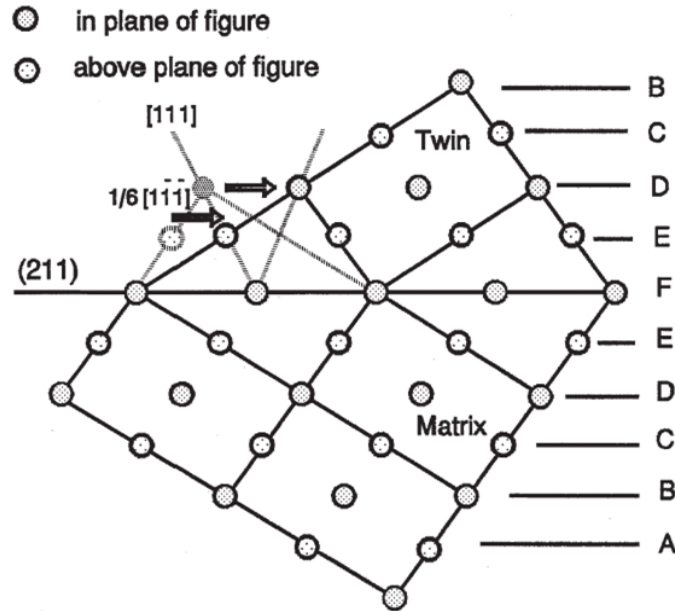


Figure 2.13: *Deformation twinning due to successive shear on $\{112\}$ planes [52].*

dislocations are involved in that case, much higher stresses are required to trigger the $\beta \rightarrow \omega$ transformation.

An interesting fact concerning the $\{112\}$ twins is that slip dislocations can theoretically easily traverse the coherent twin boundaries of these twins [53]. It thus means that the formation of these twins upon loading will have a limited effect on the hardening of the material. Figure 2.14 shows the consequence of the passage of a dislocation across a twin. The twin boundaries do not act as barrier to dislocation motion (even if a small hardening effect exists due to the change of slip system inside the twin), but it can be seen that each dislocation will create a step in the boundaries, and that new dislocations will be emitted along the boundaries.

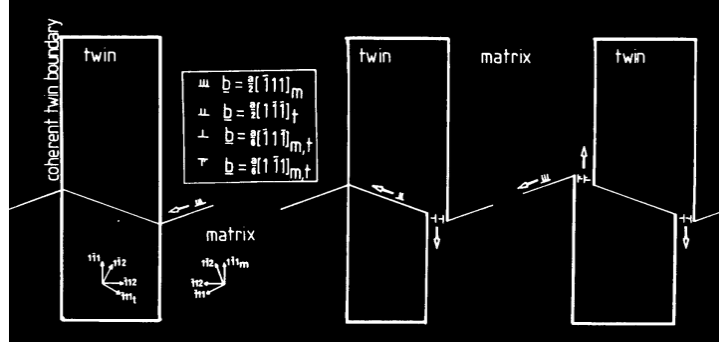


Figure 2.14: Passage of a dislocation through a $\{112\}$ coherent twin boundary [53]. The suscripts “m” and “t” refer to matrix and twin, respectively. All dislocations lines are parallel to $[\bar{1}\bar{1}0]_{M,T}$.

A last twinning type, called transformation twinning, can be found in the product structures of martensitic transformations. This kind of twinning is schematically drawn in Figure 2.15. Martensite twins due to geometrical constrains, and the habit plane of such twins is generally glissile.

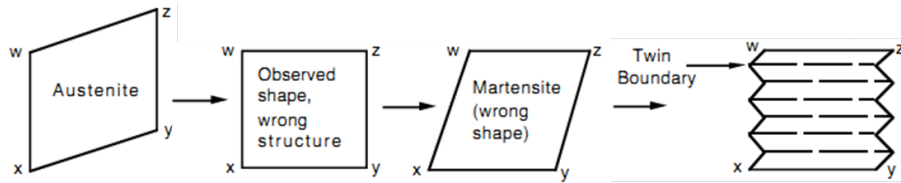


Figure 2.15: Schematic illustration of transformation twinning (adapted from [53]). The martensite has to twin to fulfil the geometrical constrains of the surrounding grains.

The $\{332\}\langle 113 \rangle$ twinning system

This second twinning system is much less common than the previous one. Like explained before, this twinning system has been predicted to be a possible twinning mode in *BCC* lattices [44, 54], even it had not been reported yet at that time. Since then, it has only been reported to

occur in metastable β -Ti alloys [55–57]. It is interesting to see that first investigations on similar β titanium grades led to wrong characterization of deformation products [58], presumably due to lack of diffraction analysis in a TEM. The lattice correspondence of a $\{332\}$ twin is illustrated in Figure 2.16.

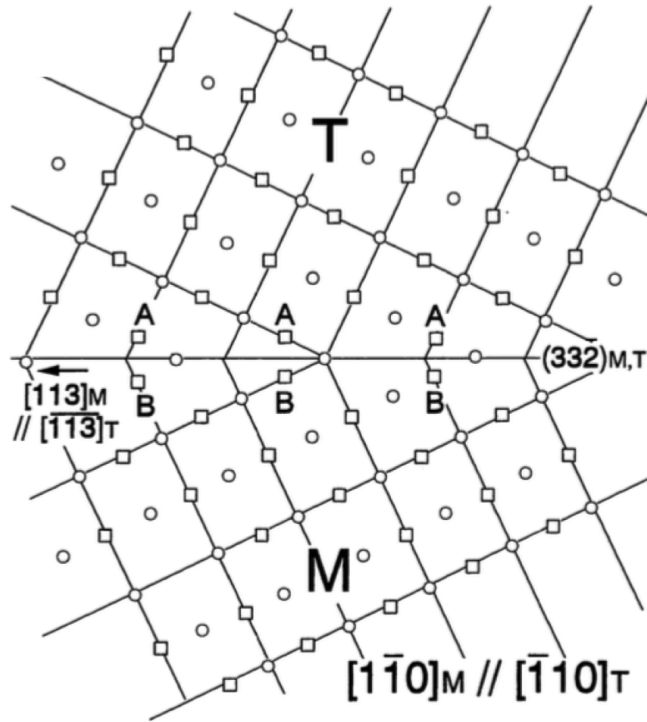


Figure 2.16: Schematic drawing of the $\{332\}\langle 113 \rangle$ twinning (taken from [59]). Circles are atoms in the projection plane, while squares are $\sqrt{2}/2a_0$ above or below the projection.

Different models have been proposed to explain this particular twinning mode. Crocker suggested a combination of shear and shuffle [54]. Later, Kawabata *et al.* [60] proposed a dislocation-based mode in order to take into account the dislocation structure they observed in *TiNbTa* single crystals containing such twins.

Recently, Tobe *et al.* [61] suggested that the low stability of β phase

could be the origin of the change from $\{112\}$ to $\{332\}$ twinning system. They considered the occurrence of lattice instabilities during straining due to the very low shear modulus C'^2 of β -metastable Ti alloys, which suppress $\{112\}$ twinning while promoting $\{332\}$. The lattice instabilities bring small shifts in atomic positions on $\{110\}_\beta$ planes, leading to a pseudo-tetragonal structure. This theory can be seen as if the quenched BCC lattice was in an intermediate state between the stable BCC case and the α'' martensitic state, with its particular twinning mode.

2.3 Strain hardening

The strain hardening concept refers to the generally observed strengthening of a material appearing during plastic deformation. Indeed, if a material is loaded up to a stress level σ^* higher than its elasticity limit σ_y in order to deform it permanently, this stress level becomes the new elasticity limit of the material. This strengthening is a consequence of the new dislocation configuration reached in the microstructure. The current strain hardening models are related to the dislocation creation and annihilation mechanisms. Kocks and Mecking published an extensive review on the strain hardening in [62], and the major concepts of their model are briefly exposed hereunder.

2.3.1 Kocks-Mecking model of strain hardening

In the Kocks-Mecking formalism, all events concerning the dislocation density in the material are gathered in the strain hardening rate parameter :

$$\Theta = \frac{\partial \sigma_y}{\partial \varepsilon_y^p} \quad (2.4)$$

where σ_y is the flow stress and ε_y^p is the accumulated plastic strain. During loading, dislocations move to accommodate the imposed plastic

² $C' = \frac{C_{11}-C_{12}}{2}$

deformation, leading to interactions with each other as well as with all kinds of obstacles within the microstructure. Depending on the mechanisms and their dominance, different hardening stages can be observed. Stages I and II are only observed in monocrystalline samples and will not be presented in this work. Stage III hardening is by far the most studied stage of strain hardening since it controls the response of the material in most practical levels of deformation. In classical materials where plastic deformation is driven by dislocation glide only, the variation of the strain hardening rate exhibits a linear decrease with increasing imposed stress, as schematised in Figure 2.17.

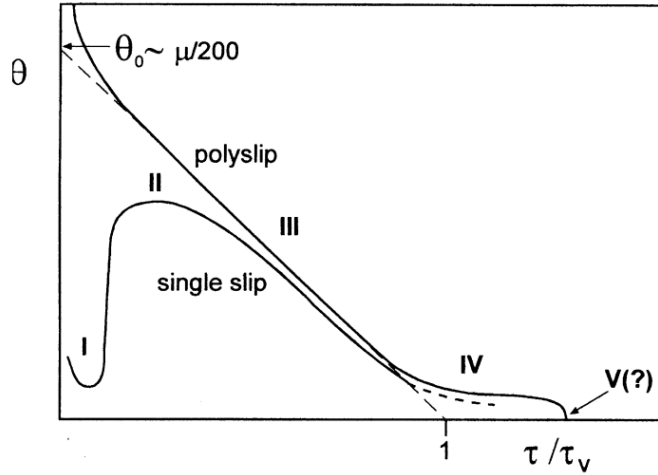


Figure 2.17: Schematic variation of strain hardening rate coefficient versus flow stress illustrating the difference between polycrystals and single crystals. Taken from [62].

The basic Kocks-Mecking approach assumes that the main contribution to hardening during plastic deformation comes from the dislocation-dislocation interactions, called forest hardening. Introducing the Taylor equation for flow stress evolution :

$$\Delta\sigma_w = M\mu b\alpha\sqrt{\rho} \quad (2.5)$$

where M is the Taylor factor, μ is the shear modulus, b is the Burgers vector, α is a geometric constant and ρ is the dislocation density in Equation 2.3.1, the hardening rate can be expressed as :

$$\Theta = \frac{M\alpha\mu b}{2\sqrt{\rho}} \frac{\partial \rho}{\partial \varepsilon^p} \quad (2.6)$$

During stage III, a competition between forest hardening (dislocation interactions and accumulation) and dynamic recovery takes place and determines the density of dislocations available for accommodating the imposed plastic deformation. The first term depends on the plastic deformation increments $d\gamma$ imposed :

$$\frac{\partial \rho^+}{\partial \varepsilon^p} \propto \frac{M}{b\Lambda} = M \frac{\sqrt{\rho}}{b\beta} \quad (2.7)$$

where $\partial \rho^+$ is the increment of mobile dislocation density, b is the Burgers vector of the dislocations and Λ their mean free path. The second term, referring to dynamic recovery, is dependent on the strain rate and the temperature and is generally expressed as a function of the dislocation density :

$$\frac{\partial \rho^-}{\partial \varepsilon^p} \propto Mk(T, \dot{\varepsilon}^p) \rho \quad (2.8)$$

The resulting strain hardening rate should thus take into account all the mechanisms that impact the dislocation storage or annihilation processes. Even if this model has mainly been developed for *FCC* materials, the principles can be applied for other systems while keeping in mind the characteristics of the lattice. Concerning *BCC* materials, two main facts must be kept in mind : (i) the larger dependence of the lattice resistance with temperature due to larger Peierls forces than in *FCC* lattices and (ii) the straighter shape of the dislocation due to huge difference of velocities between edge and screw parts and the easiness of cross-slip, rendering the storage process less effective.

2.3.2 Strain hardening in β titanium alloys

To our knowledge, hardly any studies have been carried out on the strain hardening of β titanium alloys in full β conditions. In hardened conditions, the microstructure of these alloys consists in a mixture of fine α particles (platelets) in the residual β matrix. These alloys exhibit very high strength level but suffer from a lack of strain hardening. This is due to the fact that it is nearly impossible to avoid the formation of a continuous layer of α phase along the β grain boundaries during annealing treatments below the β -transus. Indeed, this layer dominates the plastic deformation process since it acts as a preferential site of deformation, leading to quick localisation and failure of the material.

The tensile curves some full β alloys are gathered in Figure 2.18(a), as well as the corresponding strain-hardening rate evolution with applied stress in Figure 2.18(b). β Ti-5553 and β -LCB are metastable, mechanically stable, β alloys (refer to Figure 2.4) while Ti-24.5wt.%Mo is a stable β alloy. For comparison, the behaviour of $\alpha + \beta$ Ti-6Al-4V alloy is also presented. Results of Ti-5553, LCB and Ti-64 are extrapolated from [63] while the ones of Ti-24.5Mo are extrapolated from [58].

Figure 2.18(b) clearly illustrates the lack of strain hardening exhibited by mechanically stable β -Ti alloys. It is believed that this behaviour comes from a low level of forest hardening, as suggested by the straight parallel slip lines in a deformed LCB sample in Figure 2.19. The Ti-15Mo alloy exhibits $\{332\}\langle 113\rangle$ mechanical twinning. It is believed that mechanical twinning delays the plastic localisation phenomenon in this alloy, as largely observed in austenitic TWIP steels [65]. This will be discussed in more details in Chapters 3 and 4.

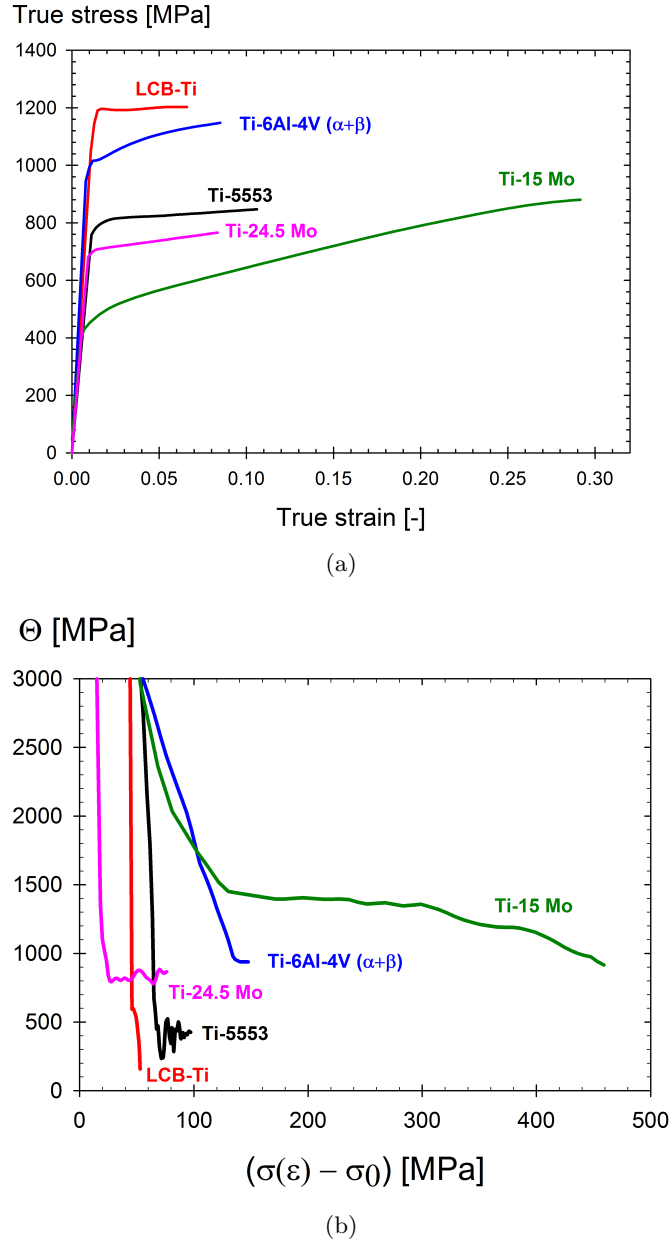


Figure 2.18: (a) True strain - true stress curves and (b) Θ -($\sigma(\varepsilon) - \sigma_0$) plots of several β -Ti alloys extrapolated from [63], [58] and [64].

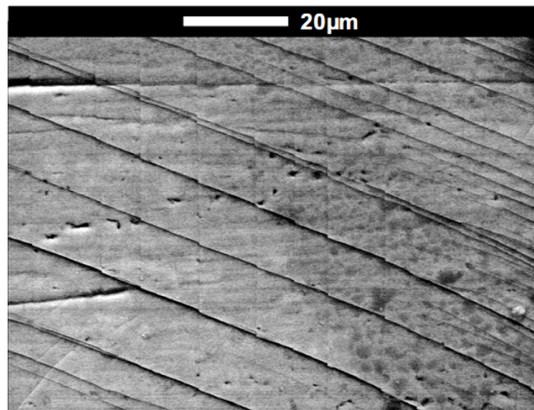


Figure 2.19: *Slip bands on the surface of a strained LCB titanium alloy in full β condition. Taken from [63].*

Chapter 3

Alloy design strategy for Ti alloys with improved work hardening

This work is part of a collaboration with Pr. Frédéric Prima from ChimieParisTech and has partially been published in [66, 67].

Over the past five decades, design of new alloys, compounds and composite materials has been attempted by numerous modelling approaches that allowed the prediction of an increasing number of materials properties like electronic and thermal conductivities, solubilities, phase stability and mechanical properties [68–70]. Until the 1990s, most of these theoretical approaches were based on the concept of molecular orbitals, while more recently, atomic potentials were considered with the easier access to *ab initio* simulations [71, 72]. The extensive use of computer-assisted design methods brings a faster and mainly less material-consuming screening of a large range of compositions. However, like in every numerical approach, a compromise between calculation time (“costs”) and accuracy of results (“benefits”) have to be considered depending on the purpose of the calculation.

3.1 Motivation

Before the emergence of computers and numerical calculation techniques, the design of new metallic materials was mostly based on trials and errors experiments and subsequent characterisation. It is useless to say that this method is both time-consuming and expensive.

In order to guide materials design, numerous parameters have been proposed to attempt to describe the behaviour of (unknown) alloys. The most used of them are the average number of valence electrons per atom (e/a), the atomic radius, the electronegativity and the number of electronic vacancies [73]. Some of these guidelines are known as the *Hume-Rothery rules* and are still very popular. These rules, which are empirical, state necessary conditions for inter-species solubilities. They are however not sufficient and only quantum chemistry can precisely predict the actual solubilities, especially in multi-components systems. Moreover, these rules give no clue about the mechanical properties of the resulting solid solutions.

The emergence of high performance computation facilities, as well as the maturation of theories modelling condensed matter, render the calculation of a variety of important quantities obtainable with enough accuracy to be used in design approaches. Among these quantities, one can quote equilibrium molecular geometries, electronic band structures, catalysis efficiency, phase stability, etc [74]. However, it is still difficult, not to say impossible, to deal with large systems without the use of several approximations. The choice of the formalism will be directly related to the accuracy of the results, and it is generally the first step in the selection of a design method. The chosen design method in this work, the "*d*-electron design strategy", is briefly outlined in the following section. The combination of this strategy with an empirical classification of existing titanium alloys leads to the choice of new alloy compositions exhibiting outstanding plasticity properties.

3.2 *d*-electron design strategy

3.2.1 Basic concepts

This strategy is related to the so-called Discrete-Variational (DV)– $X\alpha$ cluster method. This method is based on the Hartree-Fock molecular orbital theory, directly related to the Schrödinger equation :

$$\hat{H}\Psi = E\Psi \quad (3.1)$$

which is only solvable for the one-electron case and needs several approximations to be used in practical cases. As a reminder, E is the total energy of the system and Ψ is the n -electrons wave function. This function depends on the nature and positions of the nuclei, as well as on the number of electrons. The Hamiltonian $\hat{H}$ is the operator which specifies the kinetic and potential energies for each particle of the system :

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i^{electrons} \nabla_i^2 - \frac{\hbar^2}{2} \sum_A^{nuclei} \frac{1}{M_A} \nabla_A^2 \\ & - \frac{e^2}{4\pi\epsilon_0} \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A}{r_{iA}} \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_i^{electrons} \sum_{j<i}^{electrons} \frac{1}{r_{ij}} \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_A^{nuclei} \sum_{B<A}^{nuclei} \frac{Z_A Z_B}{R_{AB}} \quad (3.2) \end{aligned}$$

where $\hbar$ is the reduced Planck constant, m_e is the electron mass, ∇^2 is the Laplace operator, M_A is the mass of the atomic species A , e is the electron charge, ϵ_0 is the vacuum permittivity, Z_A is the atomic number of species A and r_{ij} is the distance between i and j .

The approximations that are made in modern quantum mechanics to reach a solution are the following :

- The **Born-Oppenheimer approximation** : nuclei are assumed to be stationary with respect to the electrons, resulting in the second term of Equation 3.2 being equal to zero and the last one being a constant ;
- The **Hartree-Fock approximation** : electrons move independently from each other, which is equivalent to state that each electron is confined in a spin orbital ;
- The one-electron solution for the many-electrons case is very close to the wave function of the hydrogen atom.

However, the Hartree-Fock approximation results in solutions with too large levels of energy of the systems. Indeed, instead of taking instantaneous interactions between neighbouring pairs of electrons into account, each electron interacts with a cloud formed by other electrons. This leads to solutions where the total repulsion energy is much larger than what it is in reality.

Finally, Walter Kohn and Lu Sham solved this problem by adding a term of exchange-correlation energy, named the Kohn-Sham potential (V_{KS}). The addition of this term approximates the electron-electron interaction forces, and thus renders the resolution of the Schrödinger equation for a N constituents system possible.

Atomic orbitals are numerically generated by resolution of this system, and molecular orbitals are then constructed by their linear combinations [75], resulting in the **LCAO** (*Linear Combination of Atomic Orbitals*) **approximation**. This approximation was first published by Lennard-Jones in 1929 [76]. It is worth noting that in the limit of an infinite basis set, this approximation leads to the exact solution.

A last, but crucial aspect concerning the calculations in this framework is the variational principle : if Ψ is the true wavefunction, then for any approximated one (Φ), we have :

$$E(\Phi) > E(\Psi)$$

Therefore, the whole problem reduces to a minimisation problem of the total energy of the system [77].

These molecular orbitals are then used to calculate the density of occupied electronic states in a « cluster », which is a representative element of the crystal like those ones shown in Figure 3.1.

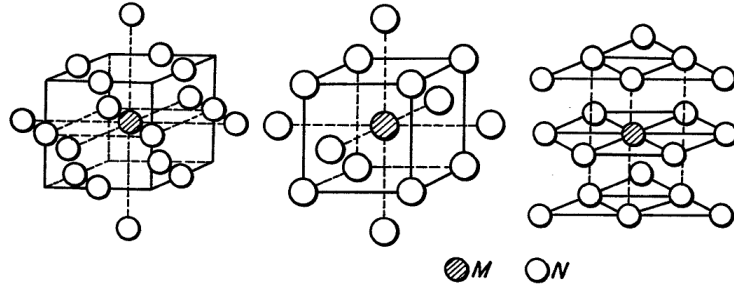


Figure 3.1: *Clusters in FCC, BCC and HCP crystalline systems [68].*

The density of states is the starting point of the design strategy. It is first calculated for a cluster of the pure studied element, then the work is repeated by substituting the central atom by another atomic species. From all these data, two electronic parameters are calculated [73] : the ***d*** orbital energy level, Md , and the bond order, Bo . The values calculated in the case of a *BCC* cluster of Ti are listed in Table 3.1.

***d* orbital energy level Md :** This parameter reflects the addition and/or the modification of the energy levels allowed for electrons due to the substitution of an atom by an alloying element in the cluster. This is schematically represented on Figure 3.2 in the case of a matrix of iron. It can be seen that the Fermi level is modified, as well as some energy levels as indicated by the dotted lines. It is interesting to see that Md is correlated to the electronegativity [78] and to the atomic radius [73]. Indeed, Md increases when electronegativity decreases and atomic radius increases. The units of Md are *eV*.

Bond order Bo : Since a molecular orbital is a linear combination of atomic orbitals, there exists a superposition phenomenon between

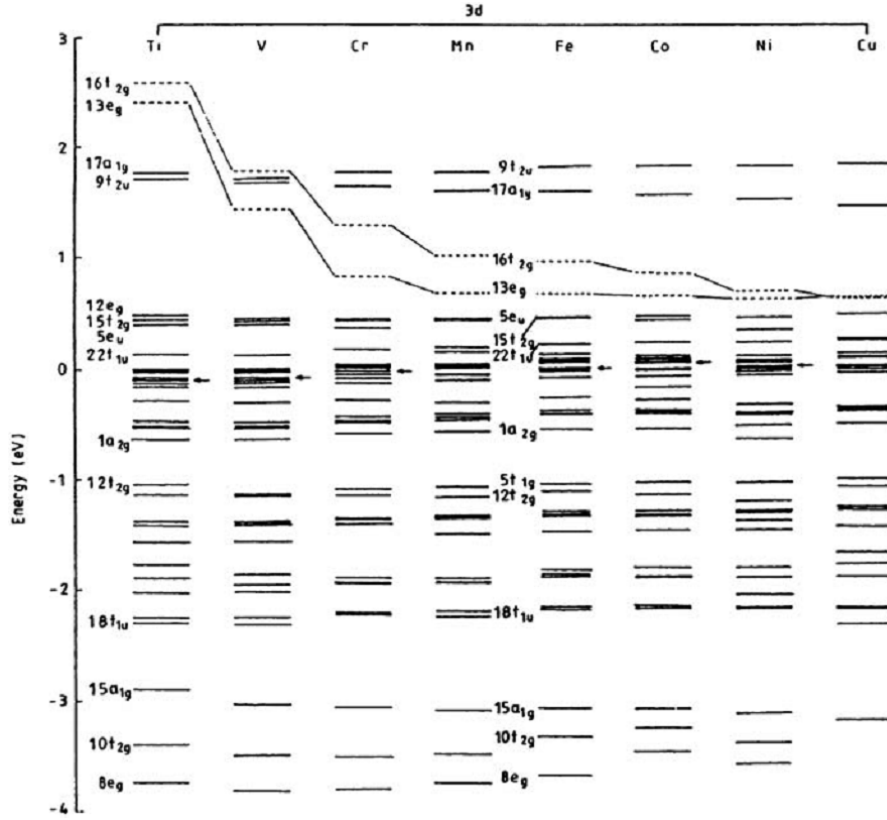


Figure 3.2: Energy level structures of pure and alloyed Fe. The arrows indicate the Fermi level of each cluster [73].

electrons within the orbital. The electron population involved in this superposition is defined by

$$Q_{\nu\nu'} = \sum_l \sum_{ij} C_{il}^{\nu} C_{jl}^{\nu'} \int_V \psi_i^{\nu} \psi_j^{\nu'} dV \quad (3.3)$$

$$\text{with} = \begin{cases} \psi_i^{\nu} & \text{the wave function of the } i^{th} \text{ orbital of atom } \nu \\ C_{il}^{\nu} & \text{a weighting term for the } i^{th} \text{ orbital of atom } \nu \\ & \text{in the } l^{th} \text{ molecular orbital} \end{cases}$$

$Q_{\nu\nu'}$ is called the bond order and will be noted Bo from now. An easy way to understand this parameter is to consider it as a measurement of the strength of the covalent bond between atoms of the matrix and the heterogeneous atom.

		Bo	Md [eV]			Bo	Md [eV]
3d	Ti	2.790	2.447	5d	Hf	3.110	2.975
	V	2.805	1.872		Ta	3.144	2.531
	Cr	2.779	1.478		W	3.125	2.072
	Mn	2.723	1.194		Re	3.061	1.490
	Fe	2.651	0.969		Os	2.980	1.018
	Co	2.529	0.807		Ir	3.168	0.677
	Ni	2.412	0.724		Pt	2.252	0.146
	Cu	2.114	0.567		Au	1.953	0.258
4d	Zr	3.086	2.934	other	Al	2.426	2.200
	Nb	3.099	2.424		Si	2.561	2.200
	Mo	3.063	1.961		Sn	2.283	2.100
	Tc	3.026	1.294				
	Ru	2.704	0.859				
	Rh	2.736	0.561				
	Pd	2.208	0.347				
	Ag	2.094	0.196				

Table 3.1: List of Bo and Md values for alloying elements in β -Ti (taken from [79]).

3.2.2 Use of Bo and Md parameters

The calculation presented above is valid for a particular stoichiometry since it is performed for a very restricted number of atoms. In practical cases, one needs to extrapolate the Md and Bo values for any possible stoichiometry. An hypothesis of the present approach is simply to state that these values are a mathematical mean of all atomic species present in the alloy, weighted by their atomic fractions like in Equation 3.4 [68].

$$\overline{Md} = \sum_i x_i (Md)_i \text{ and } \overline{Bo} = \sum_i x_i (Bo)_i \quad (3.4)$$

A graphical representation of the effect of alloying elements on Bo and Md values is shown in Figure 3.3. The straight lines starting from pure titanium are called the **alloying vectors** of species X , and one can theoretically reach any point of the map by linear combination of these alloying vectors. It is worth noting that the different kinds of β -stabilising elements in titanium (see Section 2.1.2) are gathered in the upper part of the map for isomorphous β -stabilising elements, and in the lower part for eutectoid β -stabilizing elements. This gathering of stabilizing effects can be viewed as another proof that these two electronic parameters are relevant for alloy design purpose.

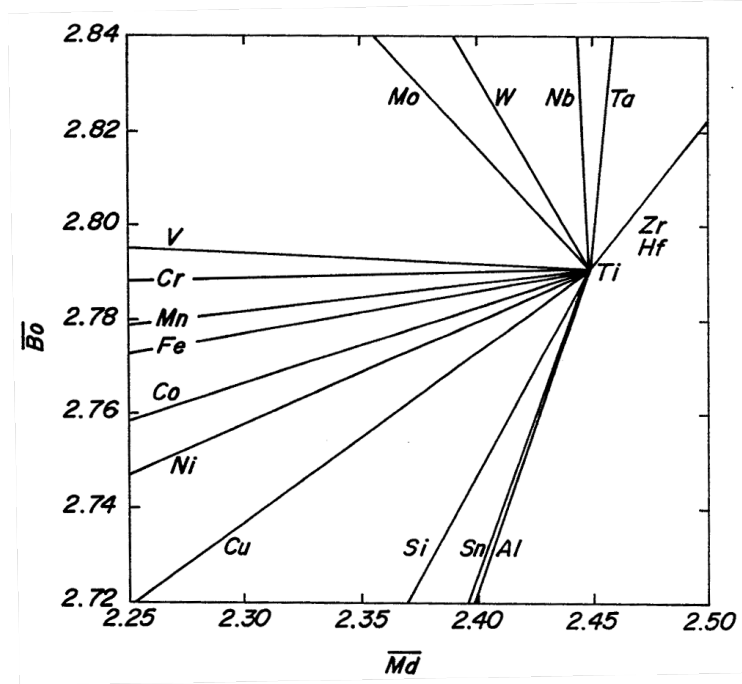


Figure 3.3: Original $\overline{Bo}$ – $\overline{Md}$ map of Morinaga et al. [68], showing the alloying vectors of most common alloying elements in titanium.

It is worth noting that the hypothesis included in Equation 3.4 is very strong and could induce large errors in $\overline{Md}$ and $\overline{Bo}$ values in the case of heavily alloyed systems since it does not take into account the interactions between different alloying species in the calculation of the density of states. It also means that it is not possible to predict the formation of intermetallic phases during the solidification of the alloy. However, like suggested in the previous paragraph, it seems that alloying elements promoting the formation of intermetallics containing titanium atoms are all pointing towards the same area in the map (i.e. lower left corner). It could be interesting to check this hypothesis in order to enhance the prediction capacities of such an alloying design tool.

The original goal of this design approach was the prediction of the stability of phases containing multiple atomic species while getting rid of the use of binary phase diagrams. Morinaga *et al.* succeeded to correlate experimental data to their calculations in several systems like *Ni*-based superalloys, titanium alloys, high-*Cr* ferritic steels, hydrogen storage alloys, etc [73].

The strength of this approach in the present case relies on the fact that a correlation seems to exist between particular combinations of *Bo* and *Md* values and the dominant plasticity mechanisms activated in the β phase during straining. Indeed, Morinaga managed to combine its phase stability map with a phenomenological map of deformation modes [80]. An important implicit hypothesis of the method is thus this chemically related deformation modes : if one designs a new composition leading to a couple *Bo* – *Md* located in the region of a particular deformation mode, this composition should exhibit this deformation mode. Abdel-Hady *et al.* have also shown that general trends in the modification of the elastic properties of the β phase with chemistry could also be mapped on this diagram, as shown in Figure 3.4. Indeed, this design method has been extensively used in the last decades to design new *Ti* alloys exhibiting superelasticity and low apparent Young's modulus [78, 81–85]. Reaching this combination of particular elastic mechanical properties combined with natural biocompatibility

of titanium is the main guideline for developing new materials for biomedical applications such as bone implants and coronary stents.

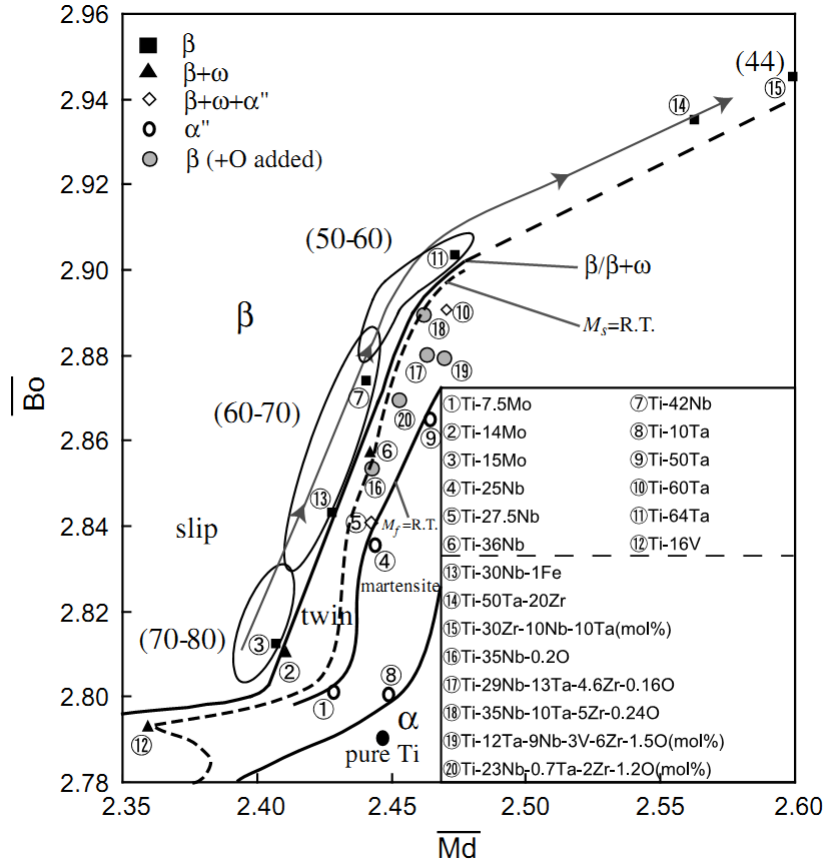


Figure 3.4: Recent extension of the Bo-Md diagram of Morinaga by Abdel-Hady et al. [79], emphasizing the effect of electronic parameters on Young's modulus (values in brackets) in β -Ti alloys.

Up to now, this method has been mainly applied on elastic properties, and very few studies deal with the enhancement of plasticity properties of β -Ti alloys. As a reminder of Section 2.2, β titanium alloys with plasticity driven by dislocation glide suffer from a lack of strain

hardening, resulting in a quick failure after yielding. It was also reported that mechanical twinning and martensitic transformation were common deformation modes in unstable β -Ti alloys. Each of these mechanisms present its own advantages and counterparts. In the present study, the idea of designing compositions exhibiting all these mechanisms in competition has been developed. Indeed, if their effects could be synergetic, an improvement of their mechanical properties could result from their simultaneous activation. A clever choice of a range of $Bo - Md$ couples is necessary to achieve this goal. A quick look at the $Bo - Md$ diagram directly suggests that molybdenum could be a potential candidate for this approach, since its alloying vector passes through all successive domains of activated mechanisms.

The chosen composition is $Ti - 12wt.\%Mo$, as shown on Figure 3.5. It lies between the domains of mechanical twinning and stress-induced martensitic (SIM) transformation, and has a $\overline{Bo}$ value of 2.807 and a $\overline{Md}$ value of 2.4158.

It is interesting to note that, despite a large amount of studies focusing on the $Ti - 15wt.\%Mo$ binary alloy through the last fifty years [57, 58, 64, 86–91], no complete investigation has been carried out on $Ti - 12wt.\%Mo$. Blackburn and Williams reported the occurrence of mechanical twinning and ω phase precipitation in cold rolled samples of $Ti - 11.6wt.\%Mo$ [92], but without any measurement of the mechanical properties. Holden *et al.* [58] as well as Williams *et al.* [93] have screened the mechanical behaviour of several $Ti - Mo$ alloys ranging from 0 to $\sim 25wt.\%$, but without barely any microstructural characterisation. The unusual mechanical behaviour of $Ti - 12wt.\%Mo$ had in fact already been observed for a long time, but no or wrong explanation of its mechanical properties were attempted, which will be the purpose of this work.

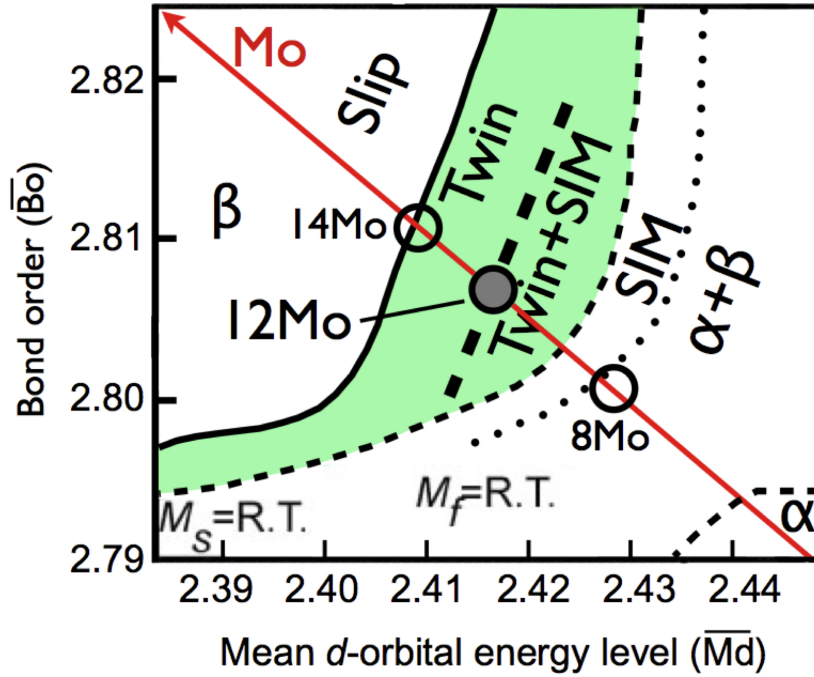


Figure 3.5: Magnified part of interest of Bo-Md diagram with alloying vector of molybdenum (red line). The thick dashed line represents the location aimed in this study [66].

3.3 Material and experimental procedure

Standard experimental techniques and preparation procedures are presented here. More specific techniques will be presented in the relevant chapters.

3.3.1 Material processing and machining

The binary alloy $Ti-12wt\%Mo$ has been chosen as a model grade of the new family of high work-hardening Ti alloys. It has been processed from commercially pure titanium and molybdenum by the self-consumable melting technique in an ingot of 9 kg. The chemical composition after

casting has been evaluated by Inductively Coupled Plasma (ICP) technique and is presented in Table 3.2. 10 mm thick slices were cut out of the ingot, wrapped in stainless steel sheets to limit oxygen intake and solution treated in resistive air furnace at 1173 K for 30 minutes, followed by a water quench to obtain a fully $\beta + \omega_{ath}$ microstructure. Prior to cold rolling, the thin oxide scale present at the surface was mechanically removed to avoid cracks during the process.

Species	Mo	Cu	Fe	O	Ti
[wt.%]	11.8	0.01	0.02	0.0115	Balance

Table 3.2: ICP analysis of the composition of the processed alloy.

Tensile specimens The slices were cold rolled down to 1 mm thick sheet, resulting in a 90 % reduction level. Tensile specimens were machined out of the rolled sheets by Electrical Discharge Machining (EDM) following the dog bone shape illustrated in Figure 3.6. Finally, the specimens were reheated at 1173 K for 15 minutes and water quenched to reach complete recrystallisation and homogeneous grain size. Again, the thin oxide layer was mechanically removed prior to tensile testing.

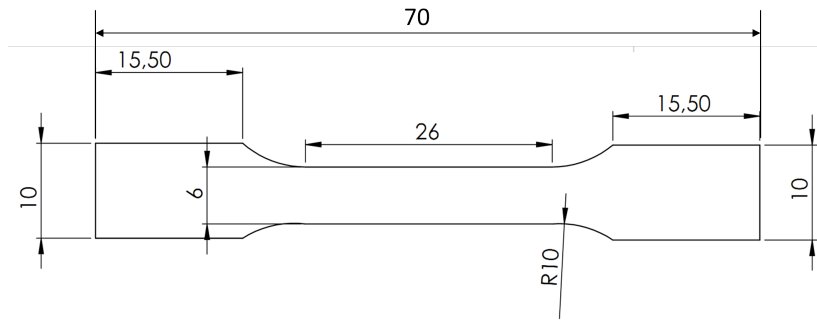


Figure 3.6: Drawing of the tensile samples used in this work. The dimensions are in mm.

3.3.2 Experimental procedure

Mechanical testing

Tensile tests were performed on a Zwick Roell Z250© machine at room temperature at a speed of 1 mm/min, corresponding to an average strain rate of $4.25 \cdot 10^{-4} \text{ s}^{-1}$. Strain was measured with a mechanical extensometer. Unless otherwise indicated, all tensile tests in this work were performed with tensile direction parallel to the rolling direction.

Microstructure characterisation techniques

Light and Scanning Electron Microscopy (SEM) Observations by light microscopy need a topographic contrast. Strained samples were mounted in a conductive resin and mechanically polished using SiC papers with decreasing granulometry from grit 320 to 1200. Diamond polishing with granulometry of 9 and 3 μm was then applied prior to the last polishing step. The final hardened layer was then removed by a mix of 100ml colloidal oxide suspension (OP-S from Struers) with 40ml H_2O_2 . Finally, microstructures were revealed by chemical etching with a solution of 4% HF - 10% HNO_3 - H_2O for a few seconds. A OLYMPUS microscope was used for observations. The grain size has been calculated by the mean linear intercept method and evaluated at about $50\mu\text{m}$. This β grain size is actually quite small for titanium alloys since it can easily reach 1 mm during forming processes [94]. It is believed that Mo has a high limiting effect on grain growth in titanium alloys due to both solute drag effect and low diffusivity compared to other alloying elements [95, 96]. Otherwise indicated, all analysed samples presented this grain size. Scanning Electron Microscopy was performed with a field emission gun (FEG) Zeiss Ultra55 operating at 20 kV. Secondary electron detector (SE2) was used for etched samples, and back-scattered electron detector (AsB) was used for non-etched samples.

X-Ray Diffraction (XRD) X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer equipped with a 1D LynxEye

detector and operating at 20kV with a $CuK\alpha$ radiation. The wavelength of the produced photons was $1.5406 \cdot 10^{-10}$ m. The 2θ range was always $30-125^\circ$ with an angular step of 0.02° . The data were analysed with the DIFFRAC.EVA software (V2.1) of Bruker. The $K\alpha_2$ contribution has been stripped from the raw data, followed by a background subtraction. The background subtraction method used for conventional XRD measurements is the one provided by the DIFFRAC.EVA software, with the Threshold and Curvature values set to 1¹. The theoretical diffraction patterns of the various phases observed in this thesis have been simulated with the CaRine Cristallographie (version 3.1) software.

Electron Back-Scattered Diffraction (EBSD) EBSD is another technique based on Bragg's law. When electrons of a fixed energy (or at least with the narrowest energy window achievable) penetrate a crystalline sample (usually tilted at 70°), they diffract on lattice planes according to Bragg's law and form diffraction cones. These Back-Scattered diffracted electrons hit a CCD camera placed at a calibrated working distance from the sample, and the complete Kikuchi pattern is then analysed by a software through a Hough transform in order to match a theoretical pattern. The angular resolution of this technique is typically of $0.5 - 1^\circ$.

In this work, EBSD scans with an energy of 15 or 20 kV were performed with a step size ranging from $1 \mu\text{m}$ to $0.05 \mu\text{m}$.

Transmission Electron Microscopy (TEM) Disks with a diameter of 3 mm were cut out of strained samples with an appropriate diamond drill. They were then mechanically thinned down to $200 \mu\text{m}$. Electron transparent areas were obtained by twin-jet electropolishing with a solution of 4% $HClO_4$ in methanol at -20°C . TEM observations were performed in a Philips CM30 operating at 300 kV and a FEI Tecnai G2 operating at 200 kV. Defects such as dislocations, twins and martensite needles were analysed by selected area diffraction (SAD) and dark field (DF) techniques.

¹The method is explained in details in the software documentation, document number DOC-M88-EXX200 V2

3.4 Validation of the design strategy

In this section, the microstructure of the $Ti-12wt.\%Mo$ grade in (i) the as-quenched state and (ii) after a plastic deformation will be briefly characterised in order to validate the design strategy presented above. The mechanical behaviour will then be highlighted and discussed together with the plasticity mechanisms activated during straining.

3.4.1 XRD analysis

As expected, the initial microstructure after cold rolling and recrystallisation treatment is a mix of β and ω_{ath} phases as confirmed by X-Ray Diffraction (XRD) pattern shown in Figure 3.7. β phase peaks also suggest some texture since diffracted intensities are rather different from the theoretical intensities of a randomly oriented sample, particularly for the $\{211\}$ reflection. The lattice parameter of the β matrix has been calculated by Rietveld refinement and is equal to 3.266 Å. The ω_{ath} phase lattice parameters are $a = 4.63\text{\AA}$ and $c = 2.84\text{\AA}$. Compared to the sharp peaks of the β phase, peaks of ω_{ath} phase are broad and weak.

Diffraction pattern of the specimen deformed to $\varepsilon = 0.1$ is also plotted in Figure 3.7. Extra peaks compared to the initial diffraction pattern are observed, even if their intensity is relatively low. These peaks have been indexed as α'' martensitic phase, which is a commonly observed stress-induced phase in metastable β -Ti alloys as already depicted in Chapter 2. The structural parameters of the indexed phases are gathered in Table 3.3. The theoretical XRD patterns simulated with these parameters are given in Figure 3.8.

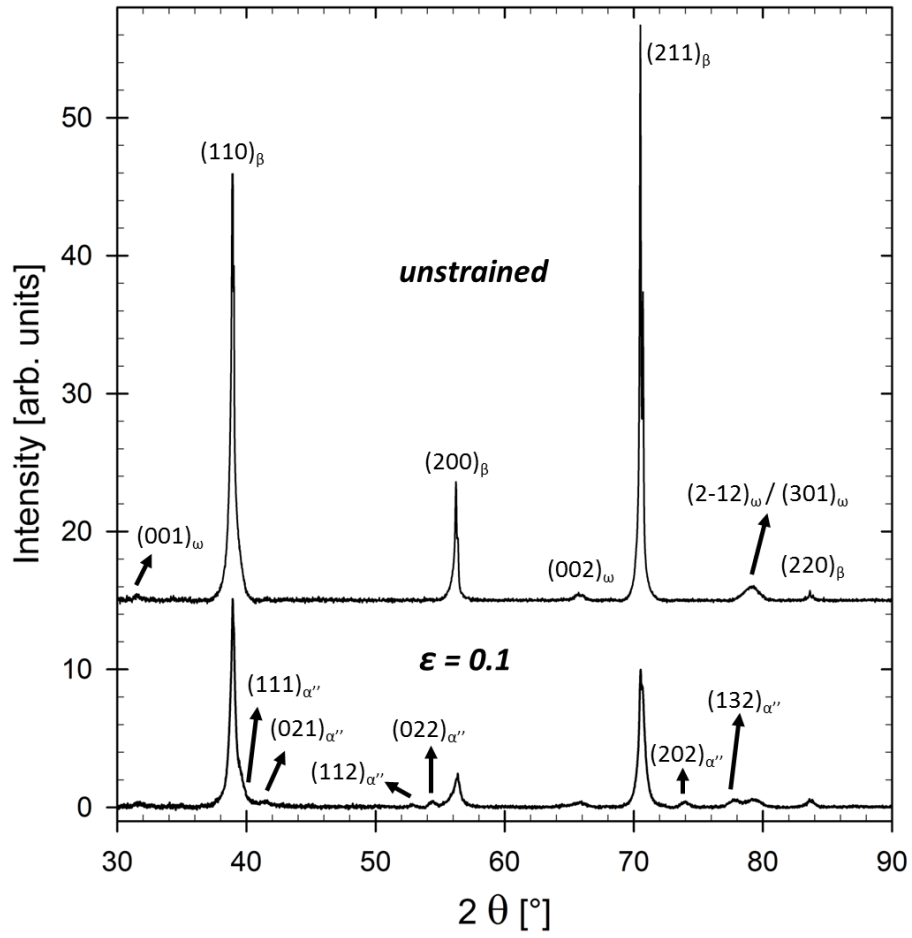


Figure 3.7: X-Ray Diffraction (XRD) pattern of Ti-12wt.%Mo alloy after a strain of $\epsilon = 0.1$ (Cu K_α radiation).

Theoretical
relative
intensity [-]

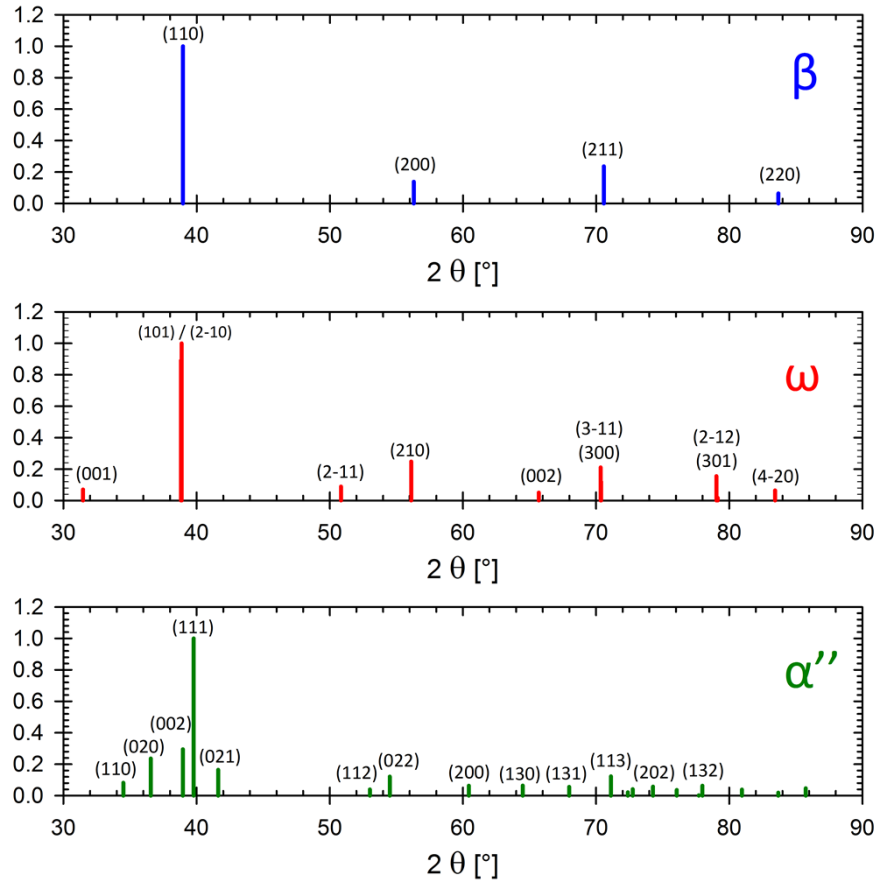


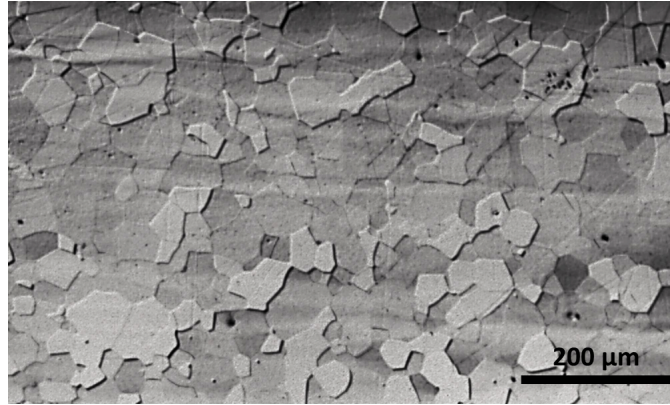
Figure 3.8: Theoretical XRD patterns of the encountered phases in this thesis ($\text{Cu } K_\alpha$ radiation).

Phase	Pearson symb. Space group	Lattice param.	Atoms	Reduced coordinates
β	$cI2$ $Im\bar{3}m$	$a = 3.266$	Ti	$[0\ 0\ 0]$
ω	$hP3$ $P6/mmm$	$a = 4.63$ $c = 2.84$	Ti_1 Ti_2	$[0\ 0\ 0]$ $[\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2}]$
α''	$oC4$ $Cmcm$	$a = 3.061$ $b = 4.911$ $c = 4.619$	Ti_1 Ti_2 Ti_3 Ti_4	$[0\ \frac{1}{5}\ \frac{1}{4}]$ $[0\ \frac{4}{5}\ \frac{3}{4}]$ $[\frac{1}{2}\ \frac{7}{10}\ \frac{1}{4}]$ $[\frac{1}{2}\ \frac{3}{10}\ \frac{3}{4}]$

Table 3.3: Structural parameters of indexed phases in $Ti - 12Mo$

3.4.2 Microstructural characterisation

The initial grain size has been measured on light and SEM micrographs. The microstructure in Figure 3.9 shows well recrystallised and equiaxed grains. The mean grain size has been measured as $50\ \mu m$.

**Figure 3.9:** Light micrograph of the initial microstructure of $Ti - 12wt.\%Mo$.

An Inverse Pole Figure (IPF) map of the BCC phase of the same specimen as the one analysed by XRD is shown in Figure 3.10. β twins are readily observed with this kind of mapping since it reflects the crystalline orientation of the sample with respect to a particular direction of the sample. It can be seen that the imposed macroscopic plastic strain is accommodated by the formation of a regular pattern composed of mainly two twinning systems, indexed as $\{332\}\langle 113 \rangle_{\beta}$ twins as confirmed by the pole figures in Figure 3.11, and that numerous secondary deformation products are present within the coarse primary twins. The characterisation of these hierarchical features will be performed within the next chapters.

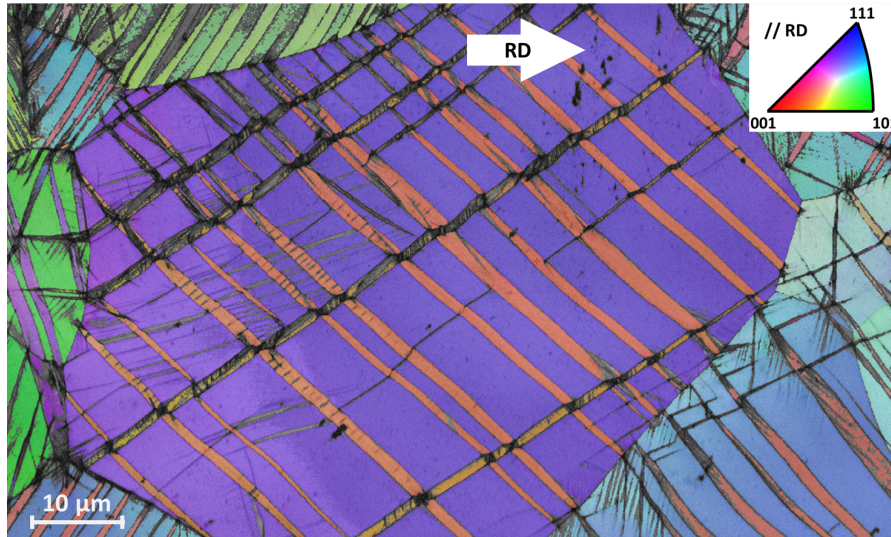


Figure 3.10: β phase inverse pole figure map for the rolling direction after a tensile strain of $\varepsilon = 0.05$ ($E = 15$ kV, step size = 75 nm).

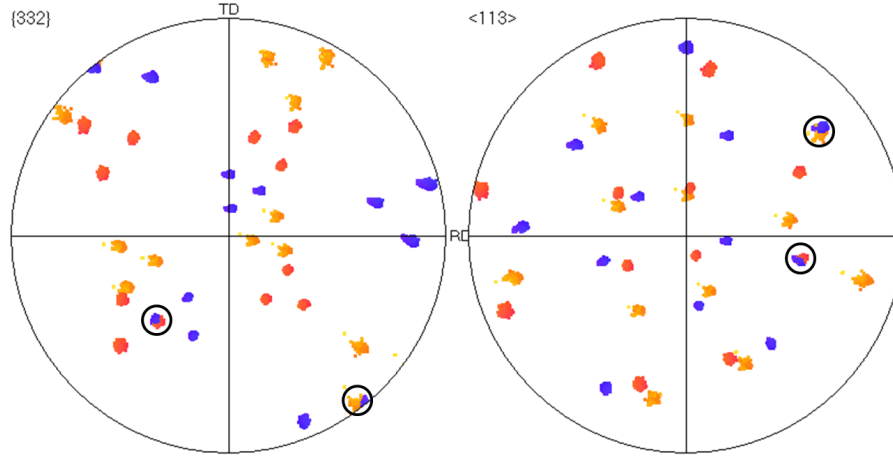


Figure 3.11: $\{332\}$ and $\langle 113 \rangle$ pole figures of the central grain of Figure 3.10, with circles showing the common poles between matrix and twins.

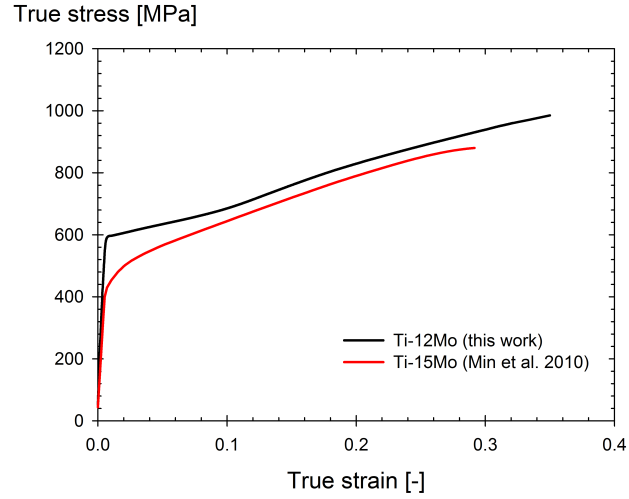
3.4.3 Tensile behaviour

The result of monotonic tensile loading of the as-quenched Ti-12wt.%Mo alloy is shown in Figure 3.12(a). The Young's modulus of this alloy has been evaluated by linear regression in the elastic regime (between 50 and 350 MPa) and has a mean value of 85 ± 5 GPa. However, a non-negligible spread in the results has been observed (ranging from 75 to 95 GPa). This spread is believed to result from 2 main factors. Firstly, the resolution of the mechanical extensometer, and secondly, the initial microstructure. Indeed, both texture of the β matrix and amount of ω_{ath} phase can have a huge influence on the apparent Young's modulus of β titanium alloys [82,97].

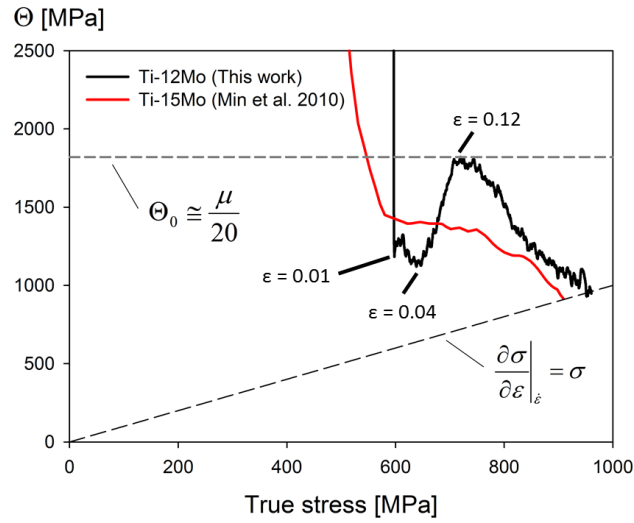
The yield strength is close to 600 MPa, followed by an increase of the true stress up to 1000 MPa combined with an uniform elongation of 0.35. These enhanced mechanical properties arise from the unusual work-hardening rate developed by the alloy, showing non-monotonous

evolution along deformation (see Figure 3.12(b)). Indeed, the complete work-hardening rate process can be divided into 3 different stages : a first slightly decreasing stage from the elastic-plastic transition ($\varepsilon = 0.01$) up to a total strain level of 0.04 (Stage I), then a large monotonic increase is observed between strain levels of 0.04 and 0.12 (Stage II), followed by a smooth decrease (Stage III) down to the plastic localisation phenomenon (*necking*) when the work-hardening rate fulfills the Considere criterion ($\frac{\partial \sigma}{\partial \varepsilon} \big|_{\dot{\varepsilon}} = \sigma$).

It is worth noting that the achieved maximum work-hardening rate is close to the theoretical limit of the Kocks-Mecking formalism, that is the initial dislocation storage rate Θ_0 ($\sim \mu/20$) [62]. It corresponds to the maximum dislocation storage rate when no dynamic recovery is occurring.



(a)



(b)

Figure 3.12: (a) Tensile true stress - true strain curve and (b) evolution of work-hardening rate with true stress of as-quenched Ti-12wt.%Mo. The curves corresponding to Ti-15Mo [64] are given for comparison.

3.5 Discussion

As predicted by the design strategy, the $Bo - Md$ position corresponding to the Ti-12Mo grade results in the activation of both stress-induced martensite (SIM) and mechanical twinning as deformation mechanisms. A complex pattern of deformation products appears within the microstructure during plastic deformation. It is supposed that the periodicity of the observed patterns is a consequence of a stress relaxation mechanism. The formation of a twin relaxes the stress on a given distance, ultimately leading to a regular pattern within the grains. The unusual work-hardening seems to depend on the activation of these phenomena, and the particular role of each mechanism has to be established. A comparison of the mechanical behaviour of Ti-12Mo with the one of Ti-15Mo alloy in the same as-quenched condition is given in Figure 3.12. Since Ti-15Mo also exhibits $\{332\}\langle 113 \rangle$ mechanical twinning, it is believed that the non-monotonous evolution of the strain hardening of Ti-12Mo comes from a synergy between both mechanical twinning and martensitic transformation.

Ti-12Mo and other designed alloys exhibit very interesting mechanical properties compared to stable $\beta - Ti$ alloys as illustrated in Figure 3.13. It is worth noting that the shape of the tensile curves is similar for the three compositions. It is thus reasonable to think that the other alloys exhibit the same mechanisms and deformation sequence as Ti-12Mo.

In other metallic systems exhibiting the same kind of deformation mechanisms, such as advanced austenitic steels, these mechanisms also postpone plastic localisation (necking) and thus enhance their ductility [99]. It was proposed that the hardening observed within these materials is related to a dynamic “Hall-Petch” effect, a refinement of the dislocation mean free path due to the formation of twin and/or phase boundaries [100,101]. It was also suggested that a composite effect could arise due to the mismatch of mechanical properties between the matrix and the twins, the latter being harder than the matrix [102,103]. Finally, it can be supposed that the twin/phase boundaries act as new dislocation sources, thus leading to further hardening of the matrix.

As already mentioned, several authors screened the mechanical

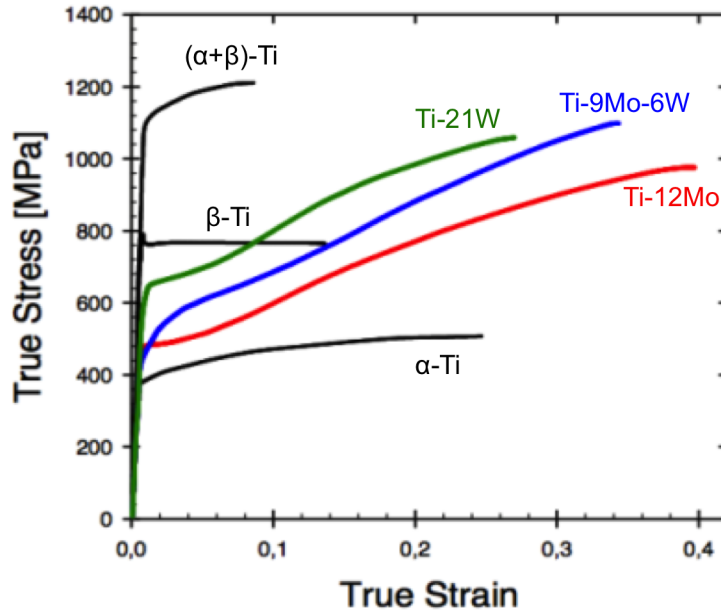


Figure 3.13: Tensile curves of 3 alloys designed with the d-electron design strategy [66, 67]. Typical behavior of classical Ti alloys are shown for comparison [98]. α -Ti is CP-Ti, β -Ti is Ti-15V-3Al-3Cr-3Sn and $(\alpha + \beta)$ -Ti is Ti-6Al-4V (in wt.%).

properties of the $Ti-Mo$ system in the past [58,93], but without any microstructural characterisation. Their results, as well as the one from this study, are summarised in Figure 3.14. The effectiveness of the design strategy in enhancing the mechanical properties is straightforward. This figure also suggests that both mechanisms are needed to reach the best combination of mechanical properties, meaning that these mechanisms act synergistically.

An interesting point is that Ti-12Mo already exhibits outstanding properties without any optimisation of the initial microstructure. It suggests the possibility of further enhancements of these properties.

To highlight the high potential of this new family of titanium alloys, a materials property map containing common structural materials has

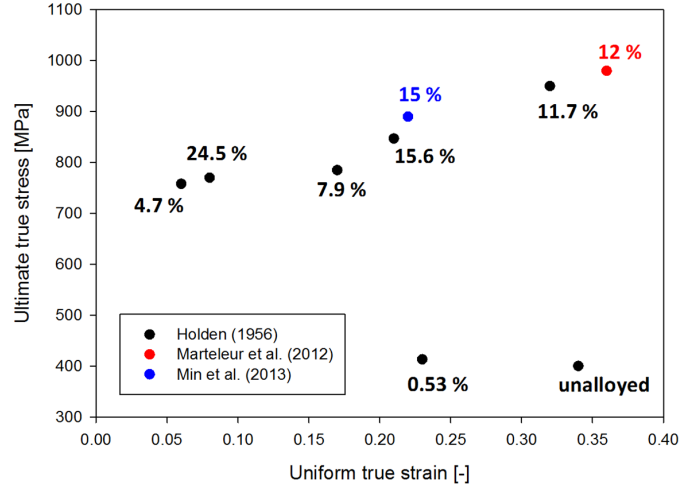


Figure 3.14: Comparison of the mechanical properties of as-quenched $Ti - xMo$ (wt.%) alloys (from [58] and [104]). The outstanding properties of $Ti-12wt.\%Mo$ are straightforward.

been drawn with the database of the CES EduPack software (version 2012). The specific ultimate tensile strength (UTS), *i.e.* normalised with the materials bulk weight², is plotted versus the elongation to fracture in Figure 3.15. This kind of map introduced by Ashby is a powerful tool for material selection [106]. It can be seen that the newly designed alloys reach the level of properties of the best stainless steels currently available. Since there have been no optimisation performed yet, this observation is very promising for further enhancements.

²The density of Ti-15Mo alloy, 4.96 g/cm^3 [105], has been used. Since the typical range of density of β Ti alloys is $4.70 - 4.98$ [13], this value is believed to be very close to real one.

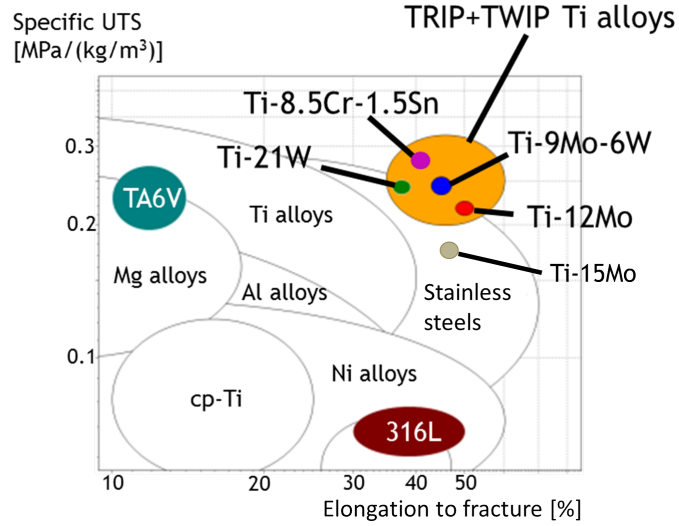


Figure 3.15: *Specific UTS vs. elongation to fracture map of currently used structural materials. Properties of the new family of Ti alloys are highlighted, as well as Ti-15Mo grade for comparison.*

3.6 Conclusion

The **simultaneous activation of different plasticity mechanisms** in the as-quenched Ti-12wt.%Mo grade indicates that the design strategy chosen in this work is suited for the design of a new family of titanium alloys. Indeed, the complex combination of deformation mechanisms results in a **unique combination of tensile strength and uniform elongation**. The characterisation of the microstructure evolution occurring during plastic straining will be covered in the next chapters. The design method works well for the binary model alloy Ti-12Mo, and the strategy has been tested and validated on other multi-elements systems by Pr. Prima and his team (Ti-9Mo-6W [67] and Ti-8.5Cr-1.5Sn [107]). Despite its apparent obsolescence compared to more recent *ab initio* simulations [71], the design tool introduced by Morinaga keeps showing more and more potential, being now extended to plasticity properties. However, the direct link between the *Bo – Md*

couples and the activated plasticity mechanisms has not been explained yet. Since the β phase lattice stability, and thus the tendency to activate a particular deformation mode is correlated to the amount of alloying elements in the material [57, 108], there must exist a **link between the dislocation character in the β phase and the electronic density** in the alloy. Recent investigations by Huang *et al.* on the $Ti - Nb$ binary system support this hypothesis [109]. They used Density Functional Theory (DFT) formalism to calculate the Generalised Stacking Fault Energies (GSFE) of the slip systems of the β phase and concluded that the core structure of the screw dislocations was affected by the electronic density.

Most of the following dissertation focuses on the origins of such an unusual work-hardening behaviour for the purposes of bringing new insights in the understanding of plasticity phenomenon occurring in advanced metallic materials.

Chapter 4

$\beta \rightarrow \alpha''$ transformation versus $\{332\}\langle 113 \rangle$ twinning : competition or transition ?

The design of alloys exhibiting exceptional work hardening owing to both mechanical twinning and stress-induced martensitic transformation has been presented in the previous chapter. The comparison of the work hardening behaviour of these alloys with the one of Ti-15Mo grade, which exhibits only $\{332\}\langle 113 \rangle$ mechanical twinning, suggests that the simultaneous activation of these plasticity mechanisms is a key factor in determining the resulting mechanical behaviour. The present chapter focuses on the morphological evolution of the microstructure with increasing plastic deformation, as well as its potential impact on the work hardening evolution. Finally, the possible scenarios of microstructural evolution are discussed.

4.1 Introduction

Since the beginning of the large-scale industrial use of titanium alloys, researches on this relatively young class of alloys have been mainly driven by aeronautic and biomedical applications. These two fields of applications rely on very strong requirements for materials properties. It is well known that the chemical composition of the β phase has a strong influence on the deformation mechanisms occurring in the material. The martensitic start temperature, as well as the critical resolved shear stress (CRSS) for mechanical twinning, are both dictated by the β lattice instabilities. These instabilities have been suggested to find their origin in the phonon softening mechanism occurring in a particular range of the number of valence electrons over the size of the crystal lattice, e/a [110–112], depending thus mainly on the chemical composition of the alloys. This effect is indeed illustrated in the $Bo - Md$ map shown in the previous chapter.

The stress-induced martensitic transformation from β to α'' phase is mainly involved in superelastic materials, with some alloys designed to achieve relatively large amounts of reversible martensite [113–115]. However, the plasticity properties of the α'' phase have been hardly investigated. Recently, Wang *et al.* investigated the tensile behaviour of a α'' single-phased Ti-11Zr-14Nb-10Sn (*wt.%*) alloy [116]. They found that α'' phase presents low levels of yield strength (300 MPa) and ductility (0.1 of uniform elongation) but exhibits a high work hardening potential since the UTS is larger than 800 MPa.

β -Ti alloys exhibiting mechanical twinning are known for a long time [108, 117]. However, there exists few convincing quantitative study of the relationship between volume fraction of mechanical twins and the evolution of the work hardening rate. Such analysis cannot be performed via diffraction techniques as in the case of stress-induced martensitic transformation where phase quantification by Rietveld refinement on XRD patterns became a routine analysis (except for some particular cases [118]). Recently, Min *et al.* [104] measured the evolution of the volume fraction of twins in a Ti-15Mo grade and attempted to link it qualitatively to the work hardening behaviour.

Furthermore, as detailed in Section 2.2.3, different theories have been proposed to explain the formation of $\{332\}\langle 113 \rangle$ mechanical twins in β -Ti alloys without achieving a global consensus. In this work, some experimental evidences are gathered in order to give new insights about the $\{332\}$ mechanical twinning. This work aims at elucidating the actual sequence of deformation mechanisms occurring in the Ti-12Mo alloy during tensile loading. To do so, a substantial characterisation of the evolution of the microstructure during tensile loading has been performed. The stability of the deformation products is estimated, providing indirect clues for validating the proposed sequence.

4.2 Review of proposed mechanisms for $\{332\}\langle 113 \rangle$ mechanical twinning

4.2.1 The extended Crocker model

Crocker [54] proposed a simple model to explain the formation of $\{332\}$ mechanical twins. An illustration of the model is shown in Figure 4.1. It consists globally in a shear along the $[113]$ twinning shear direction (represented by the red arrows in Figure 4.1) of amplitude equal to $n a/44[113]_{\beta}$, where n represents the position of atomic layer with respect to the twinning plane. Then, half of the atoms undergo a shuffling of $\sqrt{3}/4a$ along another $[113]_{\beta^M}$ direction (represented by the green arrows in Figure 4.1).

This simple model follows the rules of Crocker and Bilby for twinning (see Section 2.2.3) and is thus theoretically possible. However, (i) the large amount of required shuffle and (ii) the position of the atoms at the twin boundaries render this mechanism unlikely in the present state. Indeed, the atoms located on the first (332) layer on each side of the boundary are too close compared to the normal BCC stacking. This results in a huge repulsive energy and is thus unlikely to occur.

To overcome the second issue, Takemoto *et al.* extended the model by adding a local relaxation mechanism consisting in the addition of a displacement of the aforementioned atoms along the $[\bar{1}\bar{1}1]_T$ direction

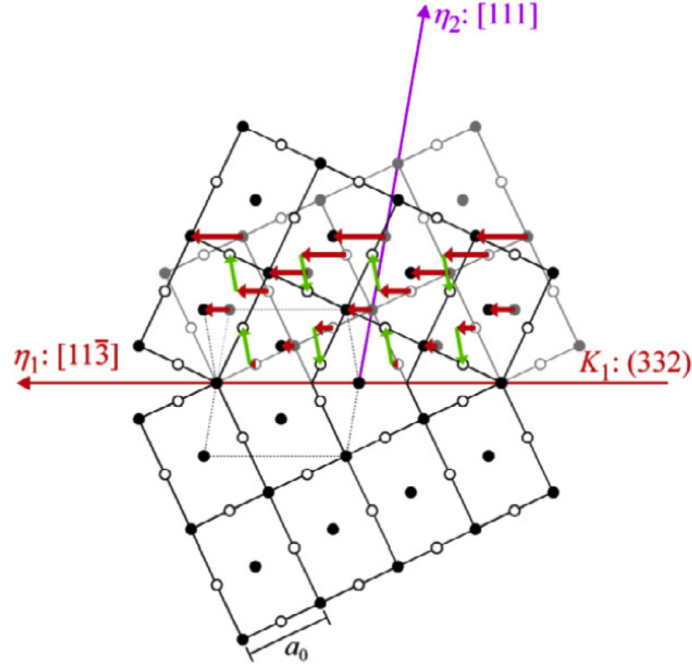


Figure 4.1: $(1\bar{1}0)$ projection of $(332)[11\bar{3}]$ twinning in BCC lattice [61]. Closed circles are atoms in the projection plane while open circles are $\sqrt{2}/2a$ above or below the projection. Red arrows represent shear direction and magnitude, while the green ones represent the shuffling direction and magnitude.

[119]. As a justification, they argue that this additional shuffling results in the formation of a ω layer along the twin boundaries, which is in agreement with experimental observations.

4.2.2 Models based on partial dislocations

Kawabata *et al.* [60] proposed another model for $\{332\}$ twinning in order to take into account the dislocation structure they observed in *TiNbTa* single crystals containing such twins after deformation at 4.2K. They considered a three stages mechanism for twin nucleation :

1. A shear caused by the movement of a $1/22[113]$ partial parallel to a particular $\{332\}$ plane.
2. A shuffling of two third of the atoms (of the initial twin layer) of magnitude $1/11[332]$ in opposite directions.
3. A second partial $1/22[113]$ completes the elementary twin layer.

However, due to the large energy of the interface arising during the first stage, the authors argued that the two partials act at the same time as a pair of stacked twinning dislocations. This introduces numerous ledges at the interface, thus inducing a strain field that has to be relaxed with the formation of dislocations at the interface and within the twin.

Litvinov and Rusakov followed a similar approach by considering the glide of $5/22[113]$ partials on successive $\{332\}$ planes [120]. This approach avoids the need of additional shuffling.

The planes and directions involved here being unusual and not close-packed, energetic calculations should be performed to validate or refute these models.

4.2.3 Martensitic precursor approach

Since similarities between mechanical twinning and martensitic transformation have been established for a long time, some authors suggested that mechanical twinning could result from a stress-induced martensitic transformation. In particular, Wasilewski proposed such a theory, arguing that this approach overcomes some limitations of the traditional shear mechanisms [121]. In this framework, he proposed the following general stress-induced double transformation mechanism :

$$\gamma \xrightarrow{\sigma} M' \xrightarrow{\sigma} \gamma''$$

where γ is the phase stable at high temperature (inaccurately termed “austenite” in the general case of martensitic transformations by many authors), M is the martensitic transition phase, and $'$ denotes the products of a stress-induced transformation. This transformation can

take place at any temperature T in the interval $(M_s, A_f) < T < M_d$, where M_s is the Martensitic Start temperature, A_f is the Austenite Finish temperature, and M_d is the temperature above which no stress-induced martensitic transformation is possible. Since the final product of reaction γ'' is thermodynamically stable, the removal of the stress does not lead to a feedback to the initial γ state. The global deformation associated to this sequence of reaction is the transformation strain due to the change of orientation of the crystal lattice. It should be noted that this theory was initially developed for the $BCC \rightleftharpoons HCP$ twinning cases.

A similar approach has been attempted by Takemoto *et al.* [122]. They proposed a sequence involving a transitory step through the α'' martensite phase before reaching the $\{332\}$ twin stacking, following :

$$\beta \rightarrow \alpha'' \rightarrow \beta_{twin}$$

In this approach, the lattice undergoes a first shear of amplitude 0.2907 along a $\langle 113 \rangle$ direction to form α'' martensite ; then α'' lattice undergoes again a shear of amplitude 0.0628, resulting in the total shear of 0.3535 ($1/2\sqrt{2}$) theoretically calculated by Crocker.

Original sketches of the process are shown in Figures 4.2(a) and (b). Despite some advantages, this sequence of transformation has also one major weakness. Indeed, the orientation relationship between the β matrix and the α'' martensite is not completely satisfied during the first transformation :

$[001]_{\alpha''} // [\bar{1}\bar{1}0]_{\beta}$	OK
$[\bar{1}\bar{1}0]_{\alpha''} // [1\bar{1}\bar{1}]_{\beta}$	OK
$(1\bar{1}0)_{\alpha''} // (1\bar{1}2)_{\beta}$	KO

Very recently, Tobe *et al.* [61] suggested that the low stability of the β phase could be the origin of the change from $\{112\}$ to $\{332\}$ twinning system. They considered the occurrence of lattice instabilities during

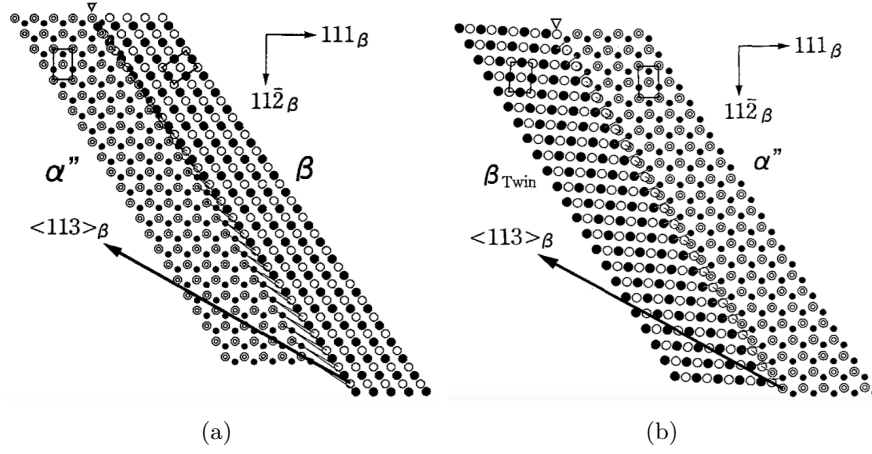


Figure 4.2: Original illustration of the Takemoto model for martensitic $\{332\}$ twinning [122]. (a) $\beta \rightarrow \alpha''$ transformation and (b) $\alpha'' \rightarrow \beta^T$ transformation.

deformation due to the very low shear modulus C'^1 of β -metastable Ti alloys, which suppresses $\{112\}$ twinning while promoting $\{332\}$ one. The lattice instabilities bring small shifts in atomic positions in $\{110\}_\beta$ planes, leading to a pseudo tetragonal structure (t). Then, $(130)_t[\bar{3}10]_t$ twinning occurs in the tetragonal lattice, where the shuffle magnitude is much decreased compared to the initial model of Crocker. This mechanism is illustrated in Figure 4.3.

Currently, no consensus about the mechanism of $\{332\}\langle 113 \rangle$ mechanical twinning has been achieved, since no model has been experimentally validated. The experimental results obtained during the characterisation of strained samples bring some insights in the understanding of this deformation mechanism in the case of the Ti-12Mo alloy.

¹ $C' = \frac{C_{11} - C_{12}}{2}$

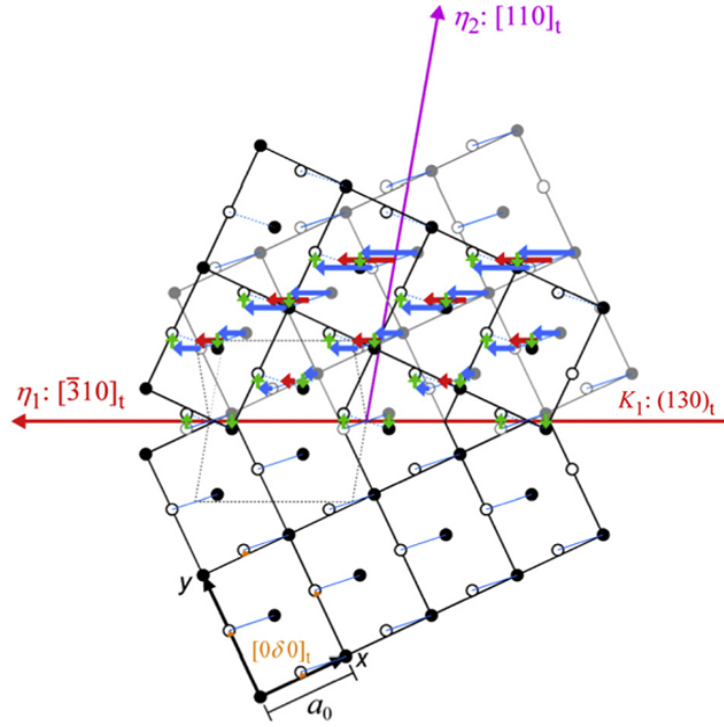


Figure 4.3: (001) projection of the $(130)_t[\bar{3}10]_t$ twinning in the pseudo tetragonal structure (Taken from [61]). Closed circles are atoms in the projection plane, while open circles are $\sqrt{2}/2a$ above or below the projection. Red and blue arrows represent shear direction and magnitude of the motif unit and lattice points, respectively ; blue thin lines represent the motif unit sustaining the shear, while the green arrows represent the shuffling direction and magnitude.

4.3 Results

The evolution of the microstructure of deformed Ti-12wt.%Mo will be analysed keeping in mind the unusual work hardening behaviour of this alloy. The experimental procedure is identical to the one described in Section 3.3.2.

4.3.1 X-ray diffraction

Diffraction patterns of interrupted tensile tests at various strain levels are plotted in Figure 4.4. It is worth noting that the same tensile sample was measured after successive deformation steps to emulate an *in-situ* experiment.

As illustrated in the magnifications of Figures 4.5(a) and (b), some new peaks appear as soon as the specimen is plastically deformed to $\varepsilon = 0.02$. They have been indexed as orthorhombic α'' phase. New peaks of this phase as well as a small increase of their intensities are observed when the sample is more and more deformed. However, the amount of α'' phase remains low in the investigated strain range.

It can also be seen that both the intensities and the full width at half maximum (FWHM) of the β peaks change at each deformation step. The evolution of FWHM is plotted in Figure 4.6, exhibiting a monotonous increase with increasing accumulated strain. Furthermore, the peaks of ω_{ath} phase disappear when the strain level gradually increases.

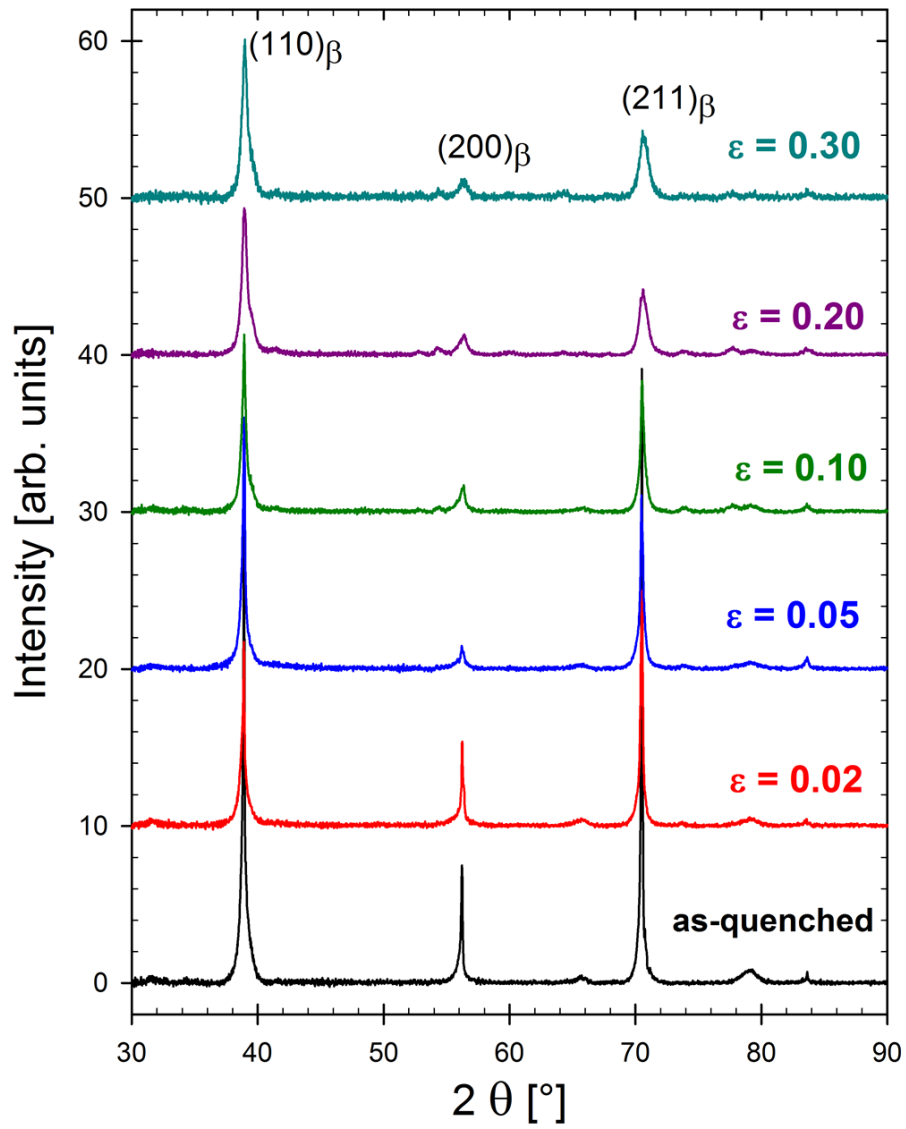
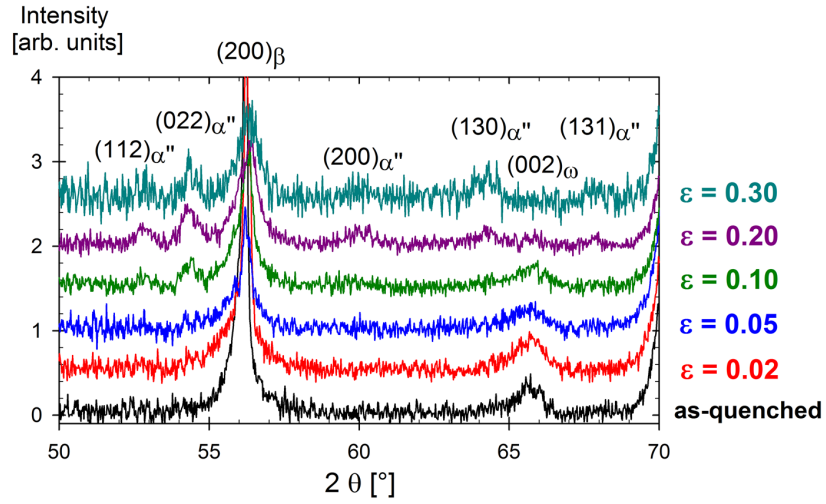
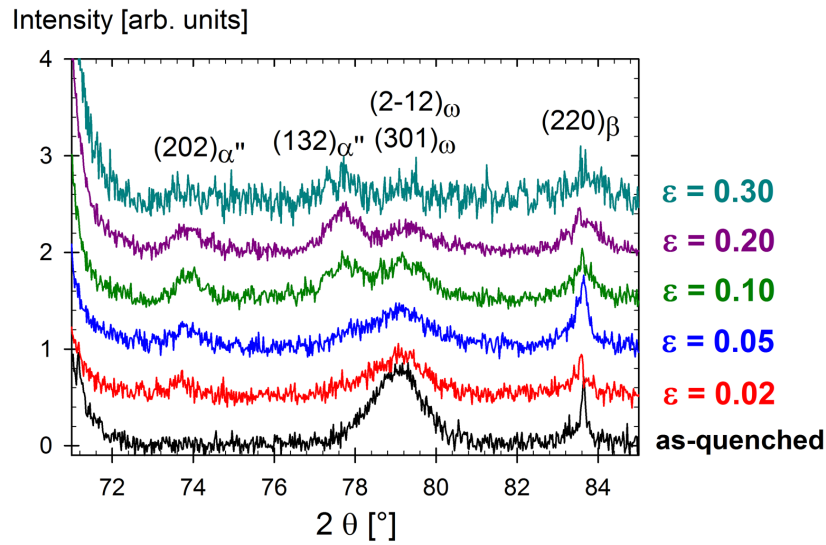


Figure 4.4: XRD patterns of as-quenched Ti-12wt.%Mo and after different levels of tensile plastic deformation.



(a)



(b)

Figure 4.5: Magnification of 2θ ranges of the XRD patterns of Figure 4.4 highlighting some α'' and ω peaks : (a) from 50 to 70° and (b) from 71 to 85°.

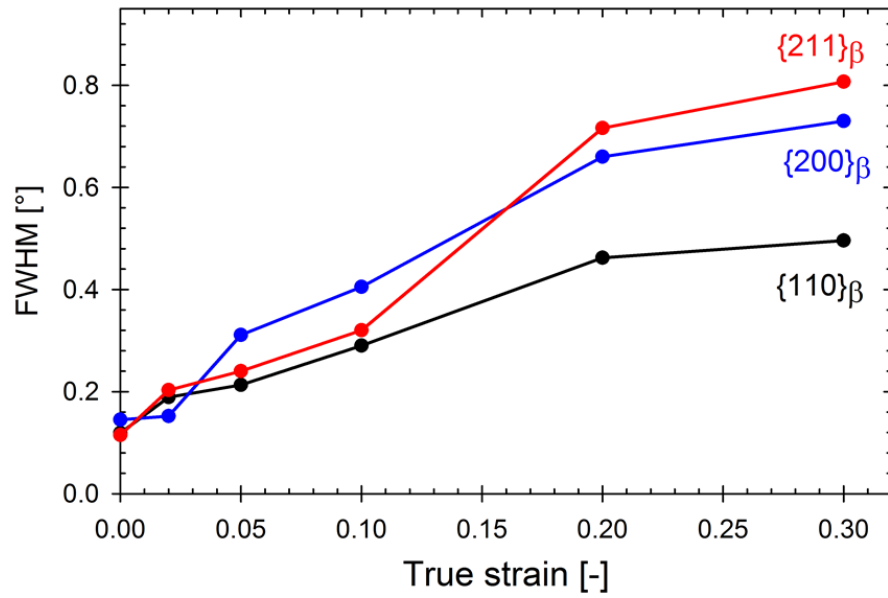


Figure 4.6: Evolution with macroscopic true strain of FWHM of major β peaks.

4.3.2 TEM characterisation².

As-quenched state

TEM observations of the initial as-quenched material provide further informations on the ω_{ath} phase. Figure 4.7 shows the homogeneously dispersed nanoscale ω_{ath} domains in a β grain. The broadening and weak intensity of XRD peaks of this phase is due to the small size of diffracting volumes.

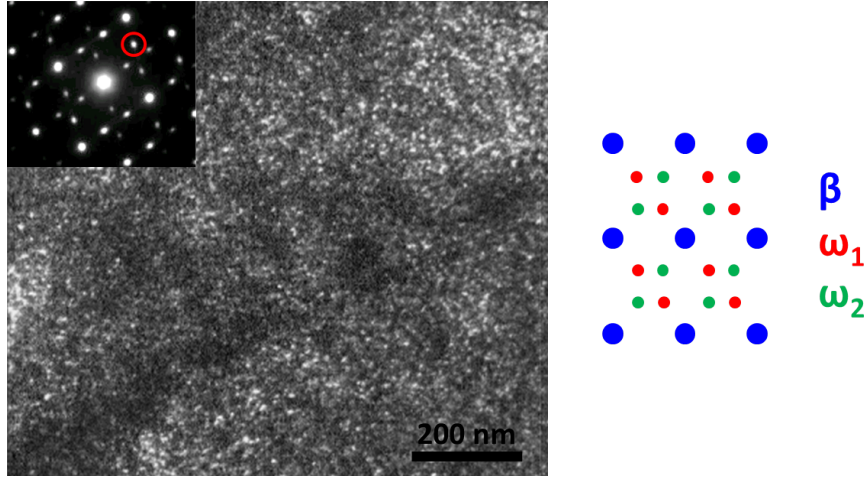


Figure 4.7: Dark field with a ω_{ath} spot in an as-quenched sample. Inset shows the diffraction spot used in the SAD pattern with zone axis parallel to $[110]_{\beta}$. A key diagram is given for pattern interpretation.

Deformed state

TEM reveals intense plastic activity. Indeed, a dense network of nano-sized bands is already present at a strain as low as 0.007 as illustrated in Figure 4.8. SAD pattern analysis along $[110]_{\beta}$ zone axis highlights a

²Parts of this work have been carried out by Dr. Sun from ChimieParisTech and are published in [123].

$\{112\}\langle 111 \rangle_\beta$ twinning orientation relationship³. These mechanical twins present a mean thickness of 40 ± 5 nm while their mean spacing is 180 ± 50 nm.

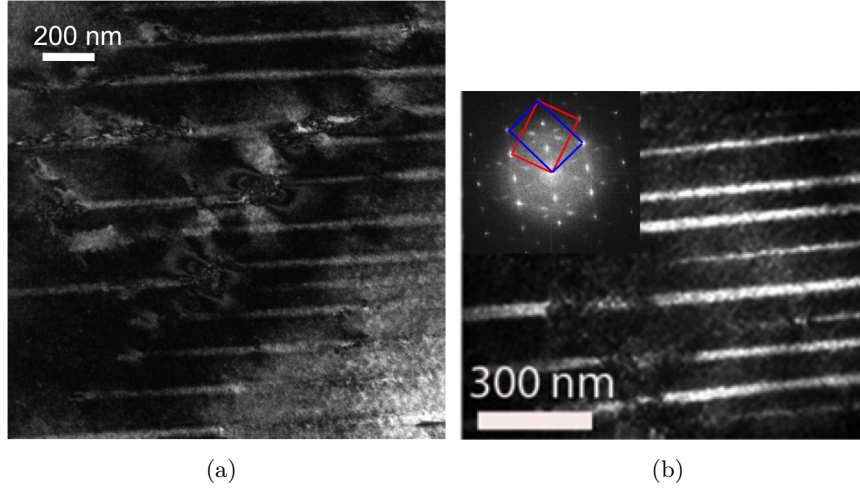


Figure 4.8: (a) Bright field image of Ti-12wt.%Mo after a strain of 0.007. (b) Dark field of the same zone with a $\{112\}_\beta$ twin diffraction spot.

When the imposed strain increases, new features appear in the β grains. Indeed, another twinning system, the $\{332\}\langle 113 \rangle$ system, has been identified at a strain level of 0.015 (see Figures 4.9 (a) and (b)), as already pointed out in Chapter 3. The SAD pattern along the $[110]_\beta$ direction shows this twinning relationship. It can also be seen that ω_{ath} spots also show up in relationship with the twinned β phase. These twins are much thicker than the $\{112\}\langle 111 \rangle$ system. At this strain level, their thickness ranges typically from 600 nm to 1200 nm. It was not possible to measure a mean twin spacing due to limited size of electron transparent zones in TEM samples. Figure 4.9(c) highlights the interesting feature that the

³This analysis differs from the one given in Sun *et al.* [123]. Indeed, some diffraction spots of the twins along the $[110]_\beta$ zone axis coincide with the spots of a variant of ω phase, leading to possible misinterpretation. Chapter 5 will focus on $\{112\}\langle 111 \rangle$ mechanical twinning.

twin seems to be subdivided in smaller lamella. Nano Beam Diffraction (NBD) analysis highlighted a $\{332\}_\beta$ twinning relationship between the primary twin orientation and the secondary products (Figure 4.9(d)). The specimen has been tilted so that the zone axis was parallel to the $[100]_\beta$ direction, which also shows the twin signal, but not the ω phase signal. The double diffraction observed in SAD pattern taken in both primary and secondary twins (red dotted circle) is supposed to come from overlapping interfaces of the two twinning systems. Further explanations of this double diffraction phenomenon can be found in [123].

In the same specimen deformed to $\varepsilon = 0.015$, clusters of mechanically induced α'' martensite have also been observed. Figure 4.10 shows such a cluster containing two variants of α'' phase, like emphasised by the SAD pattern. It has been schematically redrawn for easier discrimination of the diffraction spots (double diffraction spots have been omitted). These acicular needles of martensite have a mean thickness of 250 nm and a length of several micrometers. A better look at the contrast in the α'' needles suggests that they also present an internal structure. This internal structure is in fact due to twinning of the martensite, as illustrated in Figure 4.11. As outlined in Chapter 2 (see Section 2.2.2), the invariant plane for twinning of stress-induced α'' martensite can be of $\{111\}_{\alpha''}$ type *I*, $\langle 211 \rangle_{\alpha''}$ type *II* or $\{011\}_{\alpha''}$ compound type. The intensities of the diffraction spots indicate that the invariant plane is of $\{111\}_{\alpha''}$ type in this case⁴.

⁴This analysis is also different as the one given in [123].

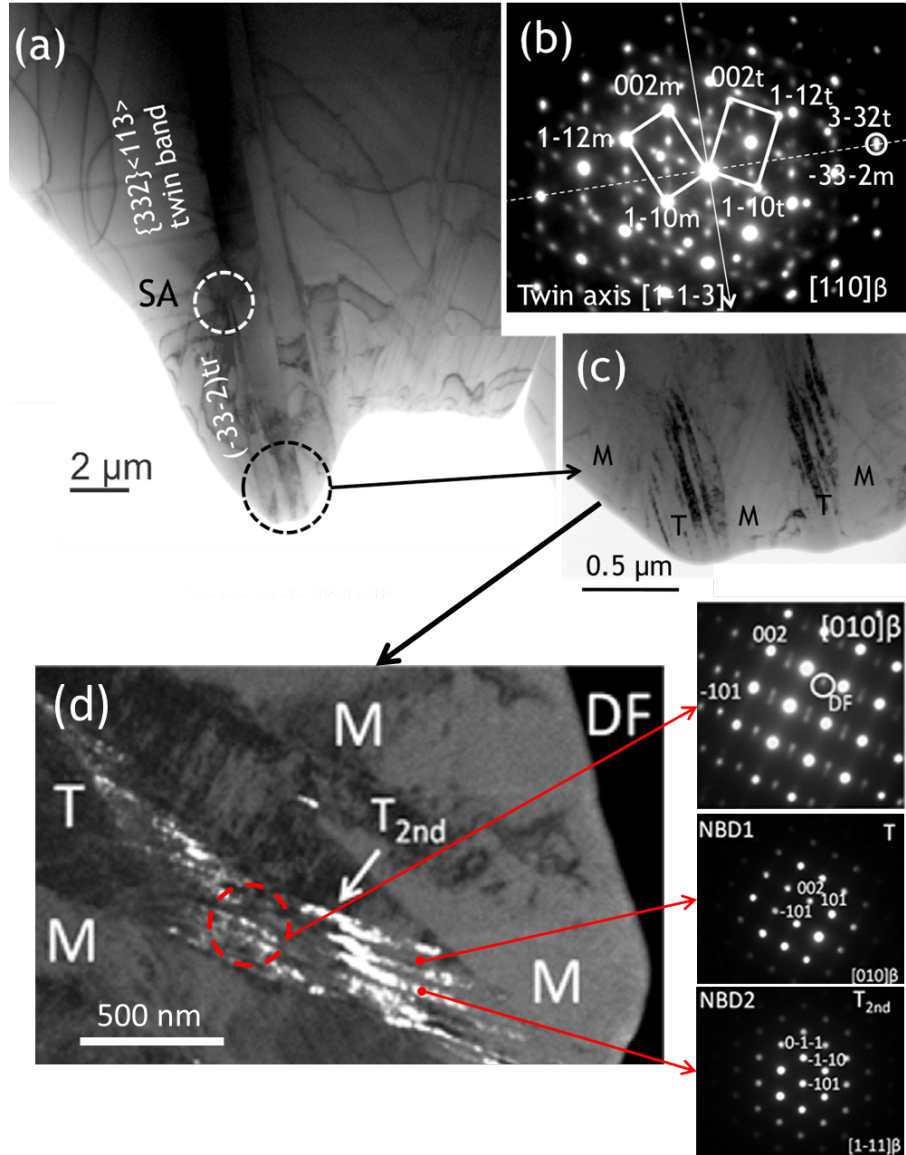


Figure 4.9: (a) TEM bright-field micrographs of a $\{332\}_\beta$ twin at a strain level of 0.015. (b) SAD pattern taken at the twin boundary in (a). The zone axis is parallel to $[110]_\beta$. (c) Magnified view of the twin, illustrating its internal structure. (d) Dark-field image of (c) taken with the diffraction spots of the secondary twins.

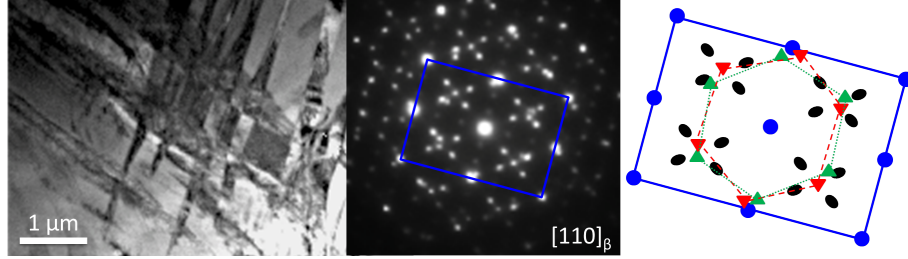


Figure 4.10: TEM bright-field of α'' martensite needles at a strain level of 0.015. Two variants have been identified, as illustrated schematically on the SAD pattern taken along $[110]_\beta/[001]_{\alpha''}$ direction. Blue dots are for the β matrix, black ones for ω_{ath} , red and green ones are for the two variants of α'' phase.

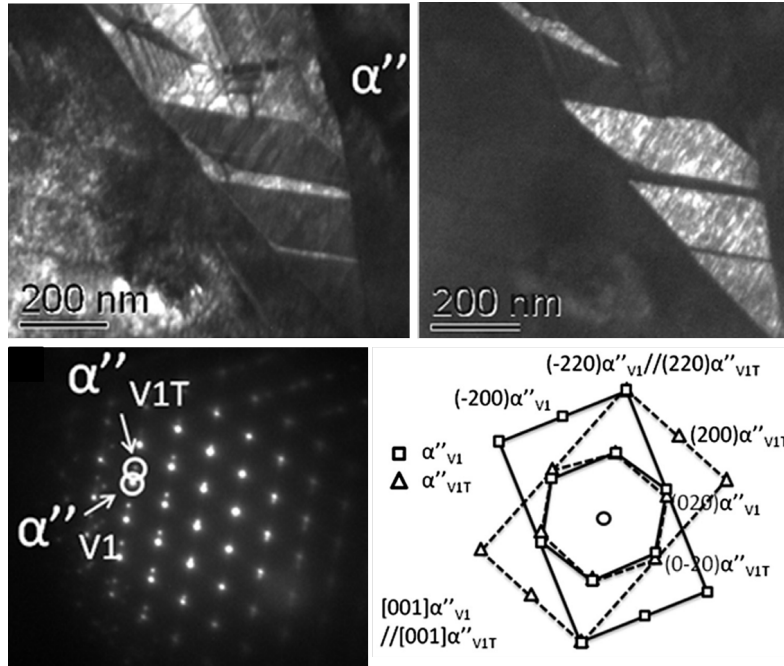


Figure 4.11: TEM dark-field of a α'' martensite needle at a strain level of 0.015. The two orientations are in twinning relationship with the invariant plane being from the $\{111\}_{\alpha''}$ family, as shown on the SAD pattern along the $[001]_{\alpha''}$ direction.

Further investigations of the $\{332\}$ twin boundaries are illustrated in Figure 4.12(a). The internal structure of the twin can be observed as well as a dense ribbon of dislocations on the twin boundary. A magnification of these dislocations is shown in Figure 4.12(b). Dislocations are parallel and have the same length of $\approx 275nm$. Their Burgers vector has been determined in bright-field two-beam condition by the invisibility criterion and is of the $\frac{a}{2}[111]$ type.

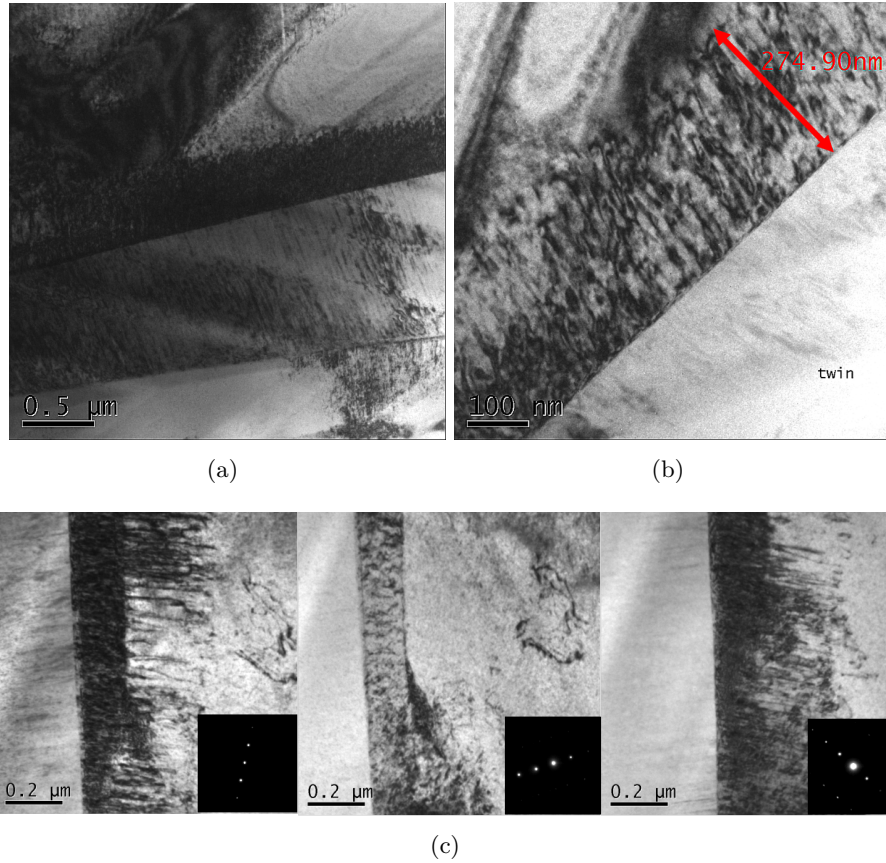
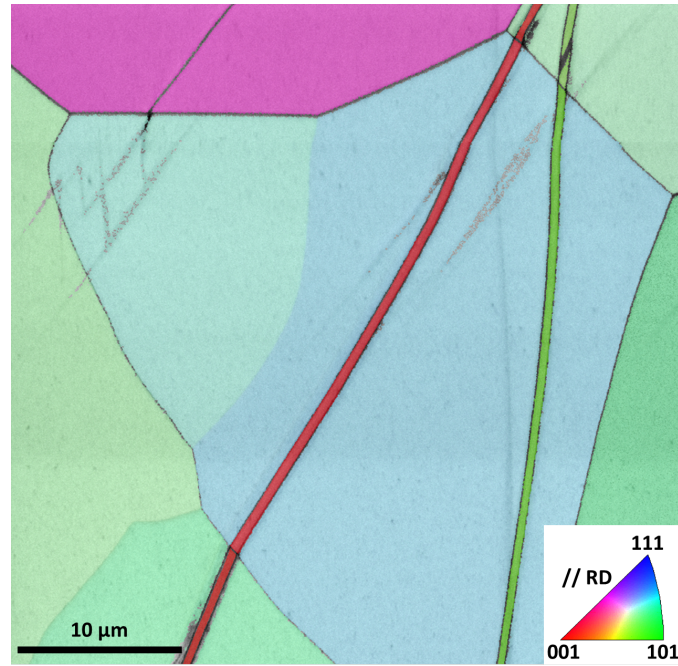


Figure 4.12: (a) TEM bright-field of a $\{332\}\langle 113 \rangle$ mechanical twin. The twin is at the bottom of the image and is shown in edge-on position. (b) Magnification of the twin boundary of (a) showing parallel dislocations nucleating at the interface. (c) Identification of the Burgers vector of the dislocations by the $\vec{g} \cdot \vec{b}$ invisibility criterion in bright-field two-beam condition. Insets show the SAD patterns with respect to the corresponding image.

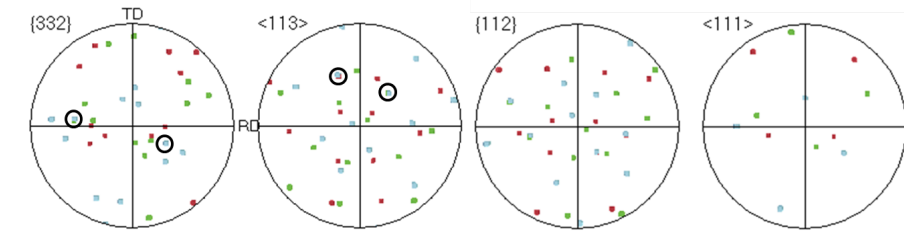
4.3.3 SEM and EBSD characterisation

Microstructure

As soon as a deformation of about 0.01 is reached, new features become visible in SEM and EBSD micrographs. Orientation mapping of the β phase in a grain presenting deformation products is illustrated in Figure 4.13. It can be seen that the bands are indexed as β phase, with a colour different than the matrix. Since TEM characterisation highlighted the activation of two twinning systems, an analysis of the orientation relationship with the matrix has to be performed to confirm their nature. The pole figures of the two twinning systems are plotted in Figure 4.13(b). It can be seen that each twin variants share a common $\{332\}$ plane and a common $\langle 113 \rangle$ direction with the matrix (circled in black), which is not the case for the $\{112\}\langle 111 \rangle$ twinning system. Moreover, the misorientation between the twin and the matrix is about 50.5° , which well corresponds to the $\{332\}$ system [124]. It is also interesting to see that (i) the twins are bent, and (ii) two variants of the $\{332\}$ system have been activated in the same grain. Furthermore, the twins are not confined within one grain as in TWIP steels [125, 126]. Indeed, the twins cross grain boundaries and continue their propagation in neighboring grains, following the misorientation between the parent grains. The thickness of these mechanical twins ranges from 600 to 800 nm at this strain level. Finally, it is worth noting that a thin slightly misoriented layer (~ 0.5 to 1°) of a few hundreds of nm has been found on both sides of the twins within the matrix.



(a)



(b)

Figure 4.13: (a) β phase orientation map of Ti-12wt.%Mo after a strain of 0.01. The accelerating voltage is 20 kV and the step size is 50 nm. (b) Pole figures of the central grain in (a) showing the common planes and directions between the matrix and deformation band.

Other stress-induced features have been observed in the same sample. α'' martensite has been identified in two different configurations. Martensite plates were observed in the β grains with lengths of few micrometers and thicknesses ranging from 250 to 400 nm, as well as in an alternately oriented plates configuration, and related to the $\{332\}_\beta$ twins. Figure 4.14 clearly illustrates the two configurations in which martensite can be found in Ti-12Mo. Two variants of α'' are related to both β matrix and twin. This complex arrangement conducts to a wavy shape of the twin boundaries. Plates of α'' phase also precipitated in the grain at the bottom of the map. Further investigations in samples deformed at a higher level highlighted that this kind of configuration of $\beta - \alpha''$ related deformation products was more and more frequent with increasing macroscopic strain.

The presence of a β^M -oriented⁵ lamella in the deformation band (black arrow in Figure 4.14b) brings some details about the sequence of transformation and will be discussed in the next Section.

The number of features related to plastic deformation (mechanically-induced twins and/or α'' martensite) increases drastically for more deformed samples. Figure 4.15 illustrates the fast developing complexity of the microstructure, already after a strain of 0.05. With the increasing density of deformation products, EBSD is no more able to index all data points due to blurring and distortions of Kikuchi patterns. However, twins and α'' martensite can still be seen at some places, in very complex arrangements. The size of twins at this strain level ranges from 1 μm to 2.5 μm . Even without a correct indexation, the Index Quality map clearly suggests the rapidly increasing density of interfaces in the material. Indeed, low magnification micrographs of Ti-12Mo after tensile strains of 0.1 and 0.2 (Figure 4.16) become hard to discern.

⁵ M exponent is for matrix.

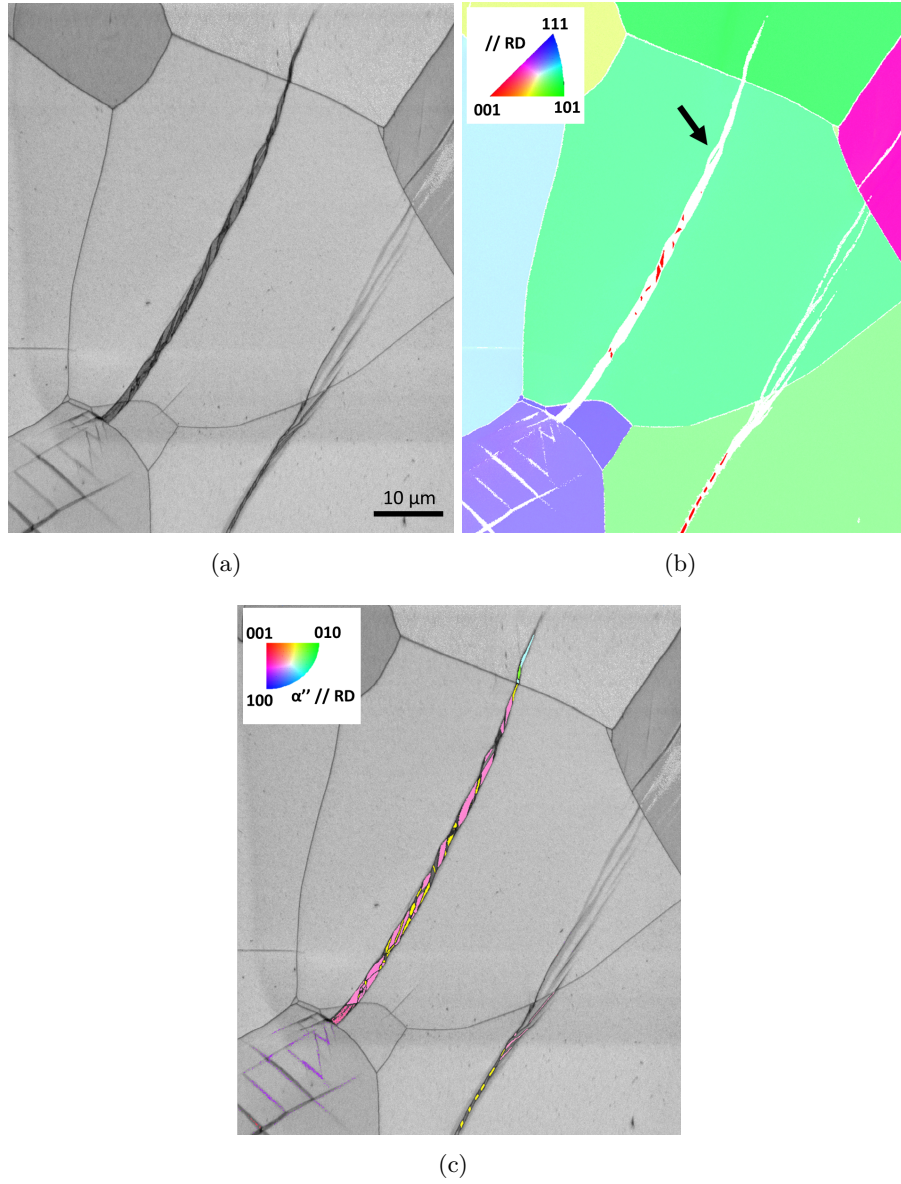


Figure 4.14: (a) Index quality pattern map of a strain-induced deformation product in a sample strained up to 0.01. (b) corresponding β phase orientation map. (c) corresponding α'' phase orientation map.

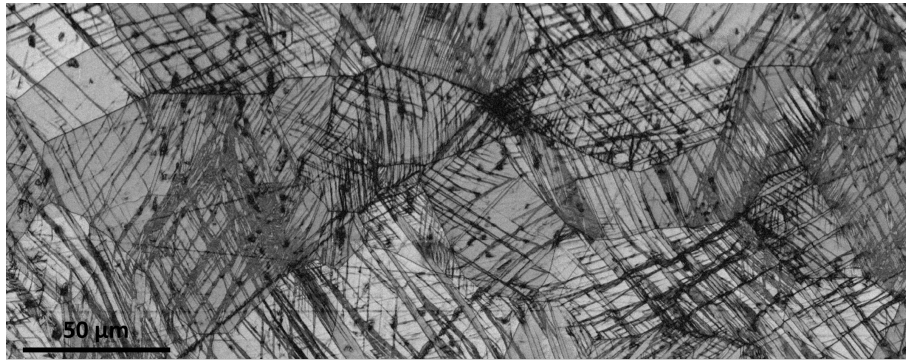
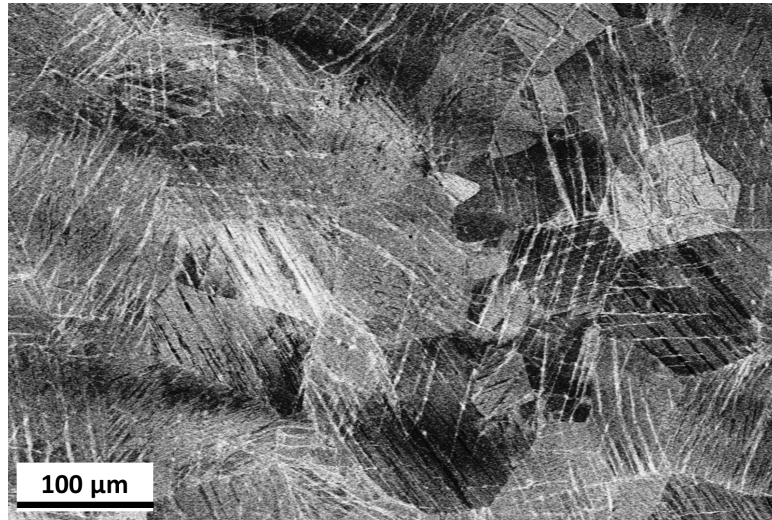
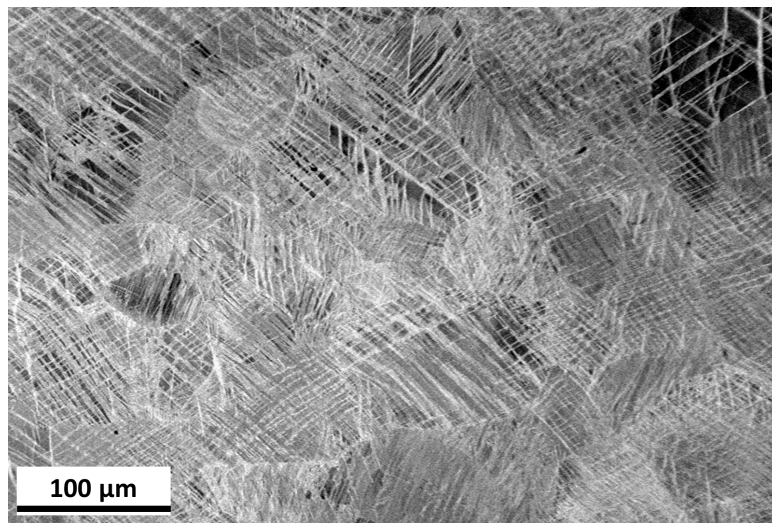


Figure 4.15: *Index Quality Pattern map of a sample deformed to 0.05. All grains are full of deformation band features. The indexation rate fails due to heavy defect concentration.*



(a)



(b)

Figure 4.16: *Back-scattered electron micrographs of Ti-12wt.%Mo after a tensile strain of (a) 0.1 and (b) 0.2.*

Volume fraction of primary twins

The evolution of the volume fraction of deformation bands has been evaluated. For simplicity in the estimation of the volume fraction, it will be assumed that all deformation bands are mechanical twins. The counting method is based on stereology principles, following the method discussed by Renard *et al.* in [125]. The estimation of the volume fraction of a particular feature of the material can be performed by sampling the surface of the material. If the sample area is sufficiently large to statistically fit with the entire microstructure, the following relationships are fulfilled :

$$V_v = A_a = L_l = P_p$$

where V_v is the volume fraction, A_a is the area fraction, L_l is the length fraction and P_p is the point fraction. Both EBSD scans and SEM micrographs were used to perform the analysis. The analysed areas were on average of $600 \mu\text{m} \times 400 \mu\text{m}$. An example of the grid used for point counting is presented in Figure 4.17.

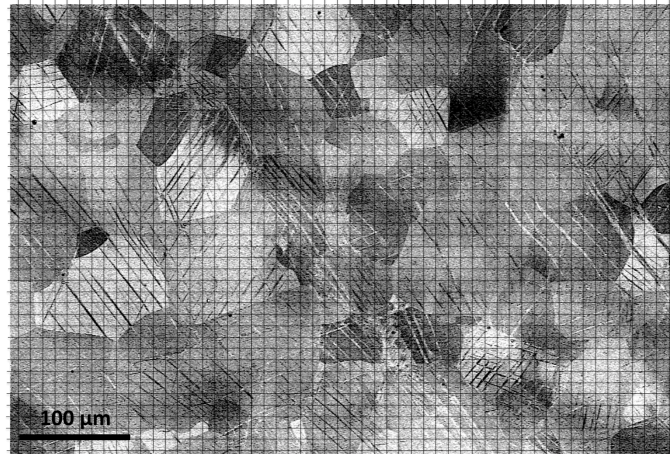


Figure 4.17: Example of grid used for the determination of the twin volume fraction. The sample was deformed to 0.02.

Samples deformed up to 0.01, 0.02, 0.05, 0.08, 0.1, 0.2 and 0.3 were analysed to establish the evolution of twins volume fraction. Results are shown in Figure 4.18.

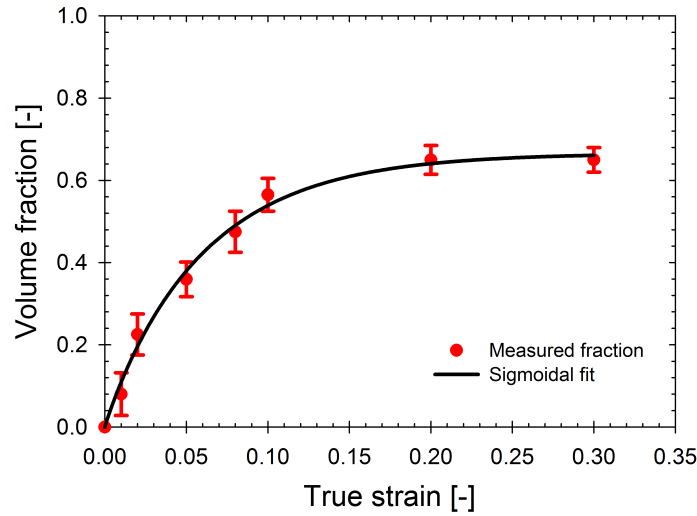


Figure 4.18: *Volume fraction of twins as a function of tensile true strain. The measured values are fitted with a sigmoidal non-linear regression.*

It can be seen that the volume fraction increases steeply as soon as plastic deformation starts, and gradually tends towards a saturation level for a deformation level of 0.1 to 0.2. A correlation between the twin volume fraction and the mechanical behaviour seems to exist, as it has been demonstrated for TWIP steels [125]. The evolution of the volume fraction with true strain has been fitted with a 3 parameters sigmoidal curve :

$$V_{twin} = a \cdot (1 - \exp(-b \cdot \varepsilon))^c \quad (4.1)$$

where the coefficients a , b and c equal 0.666 ± 0.0171 , 16.1061 ± 2.272 and 0.948 ± 0.1078 , respectively. These fitting parameters satisfy statistical

tests such as a normality test of Shapiro-Wilk and a constant variance test.

Interactions of deformation bands with grain boundaries

An interesting feature of the material is “a collective behaviour” of the grains. It means that mechanical twins do not stop lengthening at grain boundaries. The transmission in the neighbouring grain is generally accompanied by a small misorientation, which is supposed to occur to satisfy the orientation relationship. This collective behaviour is observed from very low strain levels and happens during the whole deformation range as illustrated by Figure 4.19.

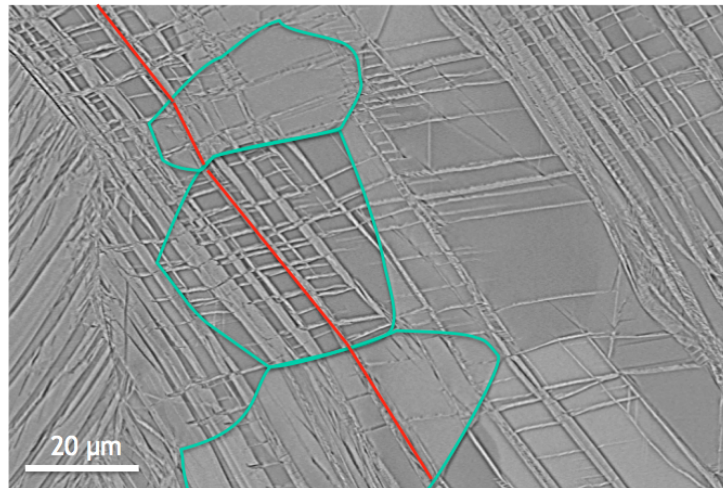


Figure 4.19: *Illustration of the collective behaviour of grains regarding deformation twinning at a strain level of 0.05. The red line is a guide for the eyes.*

4.4 Discussion

4.4.1 Preliminary remarks : $\{112\}$ twinning and ω phase

The very first strain-induced products have been identified as $\{112\}\langle 111 \rangle$ mechanical twins. This deformation mechanism will be thoroughly analysed in Chapter 5. It is worth noting that this plasticity mechanism was not expected in the present case. Indeed, most of authors argue that the selected twinning mechanism depends on the stability of the β phase [124, 127, 128]. The promotion of one system should occur at the expense of the other one. It is clearly not the case here, even if it seems that $\{112\}$ twinning is mostly active during the very beginning of plasticity, as suggested by Christian *et al.* in their review on deformation twinning briefly presented in Section 2.2.3 [41].

The observed disappearance of ω phase diffraction peaks with increasing strain levels is supposed to result from the dislocation activity developing within the material. Indeed, since ω domains result from the collapsing of two successive $\{111\}_\beta$ planes, the consecutive glide of $\langle 111 \rangle$ dislocations in the β matrix results in the progressive “dissolution” of the nano-sized ω domains, hence leading to the vanishing of the diffraction peaks. A potential softening effect could arise from the dissolution of the ω precipitates. However, since the $\beta \rightarrow \alpha''$ transformation also takes place, the signature of a decrease of ω proportion could not properly be quantified.

4.4.2 $\{332\}_\beta$ twinning mechanism

The results presented before suggest a close relationship between the mechanisms of formation of α'' martensite and β twins in the Ti-12wt.%Mo alloy. Determining whether these phenomena are competitive or successive is one of the objectives of this discussion. Blackburn and Feeney already speculated about the possibility of a close relationship between β twinning and BCC to orthorhombic transformation [124].

The following observations will be used to found the analysis :

- The volume fraction of both phenomena ;
- The morphology of deformed microstructure ;
- The stability of the deformation products ;
- The dislocation structure at twin boundaries.

Volume fraction of both phenomena

XRD measurements indicate that the volume fraction of α'' martensite is barely evolving with accumulated plastic strain⁶. Indeed, the intensity of the peaks of α'' phase is very similar between each deformation step, resulting from three possible explanations : (i) a saturation level rapidly reached during straining ; (ii) a reversible martensitic transformation taking place during unloading ; (iii) a transition from α'' phase to $\{332\}_\beta$ twins.

The first suggestion seems unlikely since, to our knowledge, all other systems exhibiting stress-induced martensitic phase transformation show a continuous increase of the martensite volume fraction with increasing stress level. However, the impossibility of reaching a higher volume fraction of martensite could result from a competition between α'' martensitic transformation and another deformation mechanism. In that case, there must exist a criterion leading to the preferential choice of one mechanism, as suggested by Sun *et al.* in [123]. Such a criterion could be a grain size effect or a crystalline orientation effect. It has been suggested recently that the Schmid factor, initially used for slip system selection, could be extended to the selection of twinning system [129]. Min *et al.* [130] also looked at the influence of the Schmid factor in the case of a Ti-15Mo-5Zr (*wt.%*) alloy presenting a TWIP effect. They concluded that some orientations are very efficient in favoring the $\{332\}$ twinning, but that for other ones, the selection criterion is not always fulfilled. Furthermore, the initial β grain size was shown to be of great importance for the initiation of martensitic transformation in the Ti-10V-2Fe-3Al (*wt.%*) alloy [39].

⁶This result will be also considered with more details in Chapter 6.

The second suggestion of reversible martensitic transformation, in spite of being easily conceivable, will be discarded in Chapter 6.

The third possible explanation is similar to the case of several TRIP steels for which ϵ -martensite has been observed as a precursor for α' martensite [131, 132], namely :

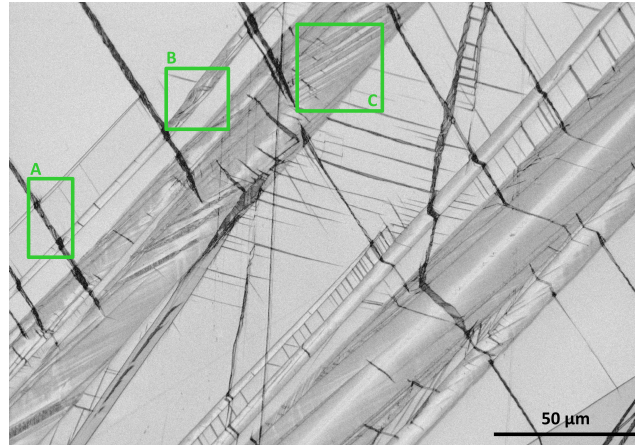
$$\gamma \rightarrow \epsilon \rightarrow \alpha'$$

The authors claim that the stacking fault energy of the austenite, depending on the composition and temperature, dictates the mechanism of formation of the α' martensite. In the case of *Fe – Mn* austenitic steels, it has been shown that, for a fixed composition, the deformation products could change from ϵ martensite to mechanical twins depending on the test temperature [133]. The authors showed that the nature of the stacking fault, depending on the temperature, dictates the deformation products. In their alloy, both mechanisms were observed simultaneously in a particular domain of test temperature, and it is highly probable regarding the present results that the situation could be somewhat similar. The chemical stability of the parent phase is thus the main parameter for occurrence of a particular deformation mechanism, as in the case of β -stabilised titanium alloys.

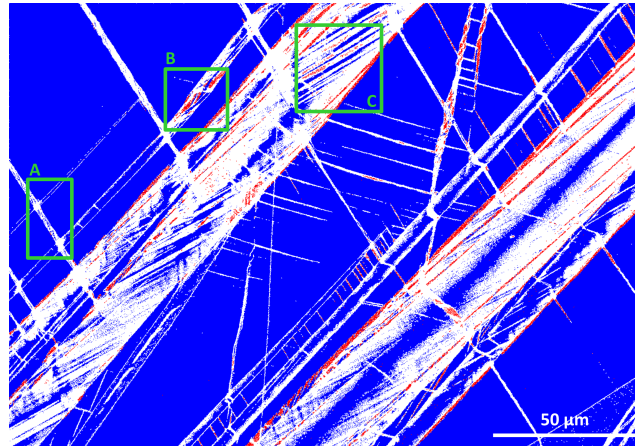
Morphology of deformed microstructures

Even if a precipitation of α'' within $\{332\}$ mechanical twins is possible, careful observation of the EBSD maps suggests that α'' is the first deformation product. The bands containing alternating α'' variants generally present a bent, step-shaped interface. Moreover, the mean trace of the interface is often not on a $\{332\}$ plane. However, if the martensite precipitates first, turning then into β twin, the habit plane should be the one predicted by either the Phenomenological Theory of Martensitic Crystallography (PTMC) or the Topological Model (TM), or at least very close to it. Among β -Ti alloys presenting a martensitic transformation, the observed habit planes coincide generally well with the predictions of these models [134–136].

A coarse grain sample has been analysed by EBSD to obtain a better spatial resolution of the investigated phenomena, since the “size” of the deformation products is related to the initial grain size (see Appendix B). Very interesting features are found within the analysed grain. First, differently oriented deformation products are seen (in terms of habit plane traces). Figure 4.20(a) shows the band contrast map of a coarse grain exhibiting a huge amount of different deformation features after 0.03 plastic strain. The different smaller zones shown in green in this figure will be thoroughly analysed. Figure 4.20(b) is the phase map where blue pixels are β phase and red ones are α'' phase. It is seen that most of the not indexed pixels are located in the deformation bands and in a transient zone between the interfaces and the center of the bands.



(a)



(b)

Figure 4.20: EBSD maps of a coarse grain sample strain up to 0.03. (a) Band contrast map and (b) phase map. Blue pixels refer to β phase while red ones refer to α'' phase.

Zone A is magnified in Figure 4.21(a). The pole figures highlight a $\{112\}\langle 111 \rangle$ twinning relationship between the blue secondary bands and the β matrix, while a $\{332\}\langle 113 \rangle$ relationship exists between the two populations of secondary bands inside the dotted box. These observations lead to the following transformation sequence :

$$\beta^M \rightarrow \beta^{T_{112}} \rightarrow \beta^{T_{332}} \quad (4.2)$$

Furthermore, a small amount of martensite is located on the vicinity of the $\{112\}$ twinned β phase. The orientation relationship between α'' and the β matrix is fulfilled as depicted by the pole figures of Figure 4.21(b). It is worth noting that the $\{112\}$ twin and the martensite present common poles in the $\{112\}\langle 111 \rangle$ system, which suggests that their mechanisms of formation present similarities.

Finally, the following relationships can also be highlighted :

$$[110]_{\beta^M} // [001]_{\alpha''} // [110]_{\beta^{T_{112}}} // [110]_{\beta^{T_{332}}} \quad (4.3)$$

These orientation relationships suggest that the different transformations operating in one deformation band can be depicted on the same $\{110\}$ projection. It is thus highly probable that they are all related to each other.

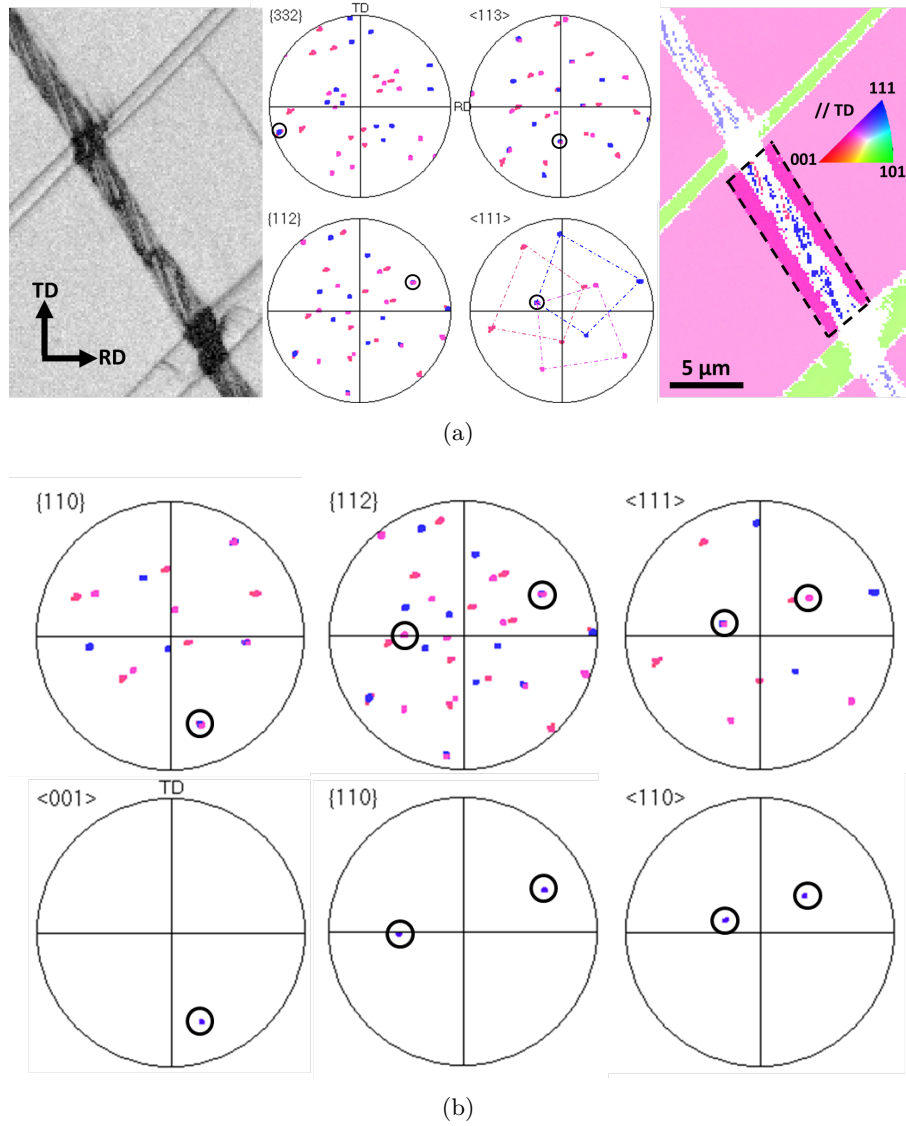
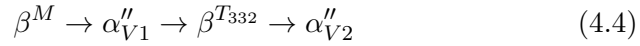


Figure 4.21: (a) Magnification of zone A of Figure 4.20 and β phase pole figures of the surrounded area. The IPF is given with respect to the transverse direction. (b) Pole figures of the orientation relationship between β and α' phases taken in the surrounded area.

Zone B is magnified in Figure 4.22(a). The IPF maps of the β phase show that some bands are indexed as mechanical twins, with a particular disposition. Indeed, it is possible to find matrix-oriented zones between bands of twin or martensite laths. This kind of feature has been often observed and is a clue regarding the transformation sequence. The poles of the blue α'' variant are related to the β matrix, while the poles of the green α'' variant are related to the β twin (Figure 4.22(b)). More importantly, the α'' primary variant (called this way since it is related to the β matrix - the blue one) shares nearly perfectly a $\{113\}_\beta$ direction with the normal to one of its (110) plane. This is consistent with the mechanism proposed by Takemoto *et al.* [122] (Section 4.2.3). It thus suggests that the reaction sequence is the following, each step being an incomplete reaction :



The same orientation relationships are observed between the different strain-induced features present in the larger deformation band of **Zone C**, magnified in Figure 4.23. The global relationship expressed in Equation 4.3 can be written in cases **B** and **C** too.

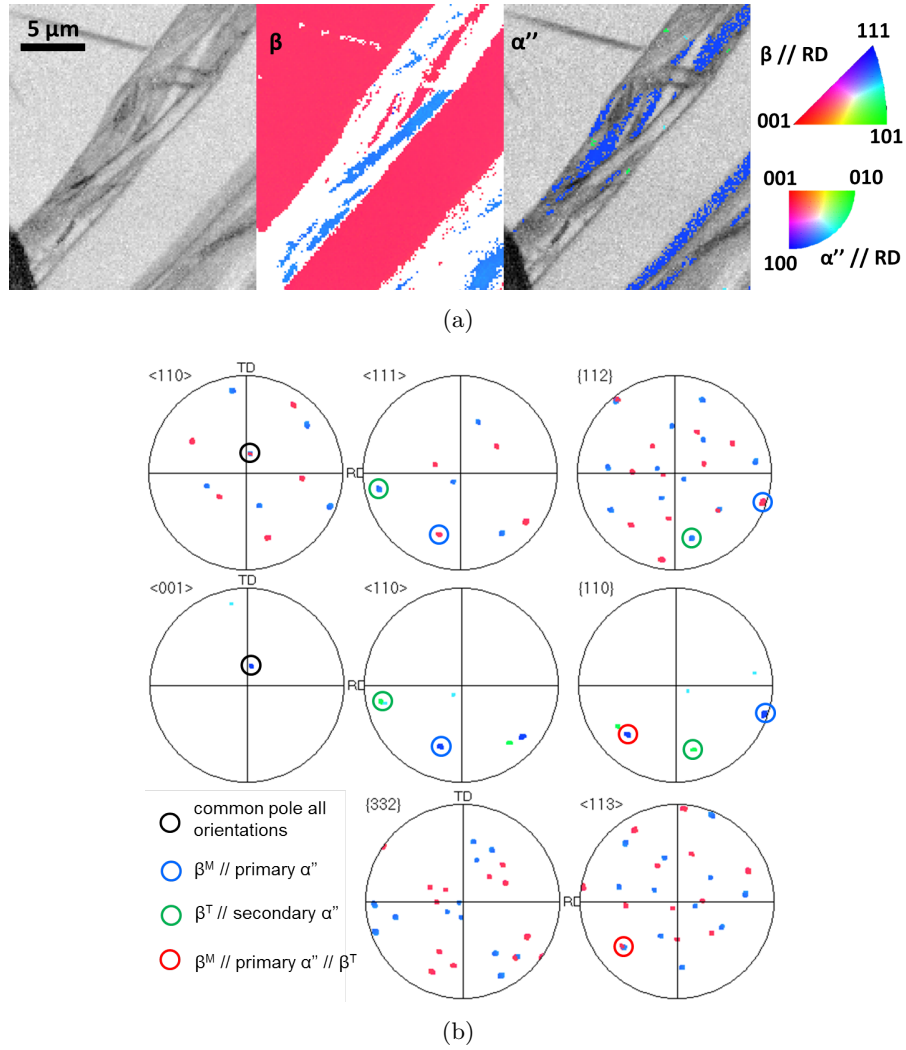


Figure 4.22: (a) Magnification of zone B of Figure 4.20 showing the IPF maps of both phases. (b) Pole figures of the Zone B showing the orientation relationships between all strain-induced features.

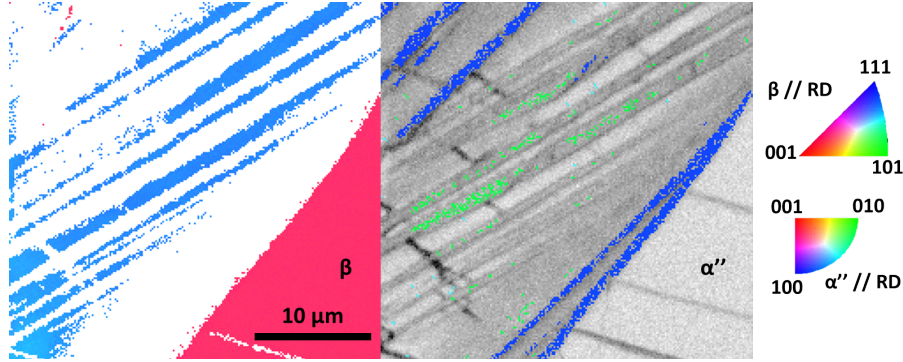


Figure 4.23: Magnification of zone C of Figure 4.20 showing the IPF maps of both phases.

The complex arrangement of deformation features together with the wavy shape of the outer interfaces with the β matrix thus seem to indicate that the first step is the formation of α'' martensite variants. A possible scenario would be that once a large nucleus of $\{332\}$ twin is formed from the transformation of a primary α'' variant, the twin can easily propagate through the grains. If it meets a small misorientation grain boundary, the stress concentration at the twin tip brings enough energy to trigger the transformation in the next grain. This would result in the microstructure illustrated in Figure 4.19. In that case, it means that there is a distinct scenario for the nucleation step, and another one for the propagation step.

A recurrent problem that occurred during EBSD characterisation was the indexation problems between the β and the α'' phase. Indeed, the crystalline structure are very close to each other, and the indexation automated algorithm often gave random results, particularly within the deformation bands as illustrated in Figure 4.24. This suggests that the diffraction patterns of α'' variants and β twins are very close to each other, as supported by the transformation sequence. Figure 4.24 summarises the complete sketch of relationships between the deformation products.

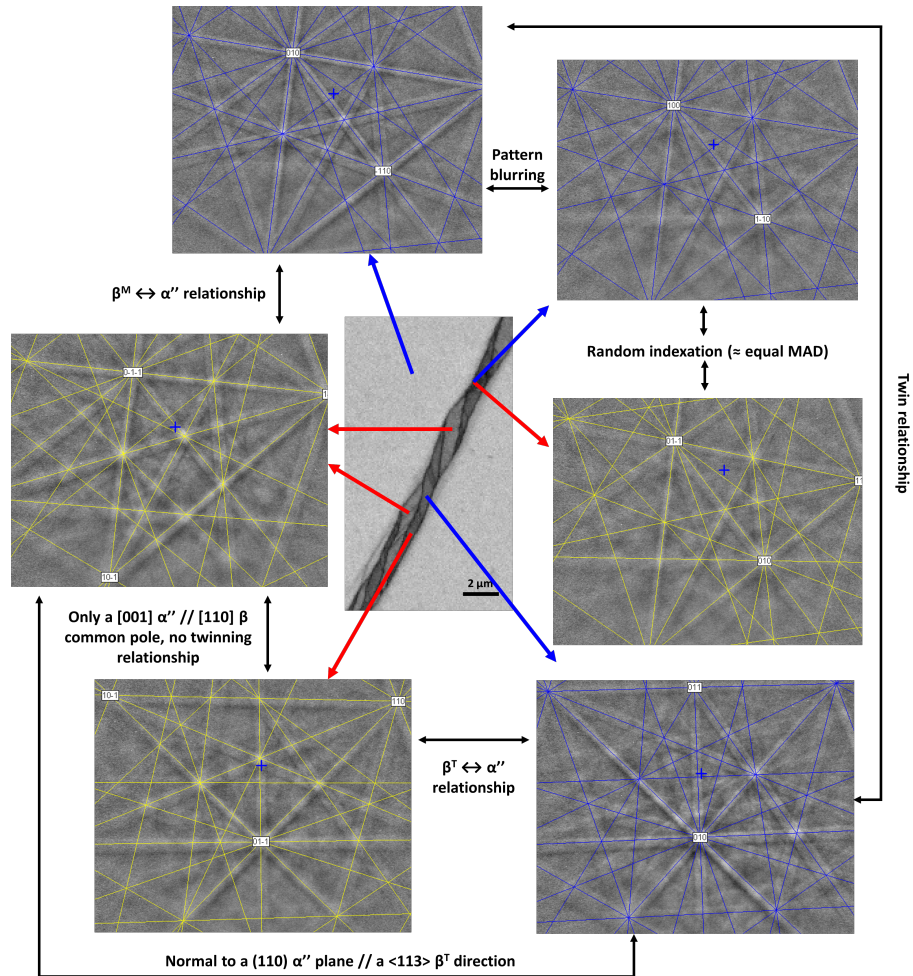


Figure 4.24: Kikuchi patterns coming from different deformation products of a grain illustrated in Figure 4.14. The different relationships are also summarised.

Thermal stability of the deformation products

Deformed samples have been subjected to short heat treatments to study the stability of the deformation products. Indeed, it is known that a sample containing α'' martensite undergoes reverse transformation once reheated at high temperature [114]. Figure 4.25 illustrates the microstructure of a sample strained up to $\varepsilon = 0.05$ and annealed at 800°C for 5 minutes. Two interesting observations can be performed :

- The entire map is indexed as β phase, which was also confirmed by XRD measurement. Interestingly, the α'' precipitates transformed to β phase after annealing. The interior of the β twins is completely indexed with the twins orientation, meaning that the thermal treatment gave enough energy to the system for the $\alpha'' \rightarrow \beta^T$ transformation. The reversion of martensite in the β^T orientation could result from two mechanisms : (i) a “neighbouring” effect, i.e. the crystalline orientation of the transformed product is determined by its environment or (ii) a lower ΔG between the α'' and β^T rather than between α'' and β^M , leading to favoured transformation path. In the latter case, it would suggest that α'' precipitates act as precursors of β twins.
- Twins undergo a “detwinning” process, i.e. a reversion of the twinned regions back to the initial crystallographic orientation of the grain, generally starting from grain boundaries to the interior of the parent grains, with anisotropic detwinning rates. This process starts from the intersection between the twins and the grain boundaries and consumes the twins progressively, mostly towards the direction parallel to the twin boundaries. This phenomenon has recently been observed in another Ti alloy [137]. The authors attributed the different detwinning rates (normal and parallel to the twin boundary velocities) to a combined effect of incoherent interface structure and higher stress concentration at grain boundaries, resulting in a larger free Gibbs energy available for detwinning.

The global reactions occurring during the annealing treatments of plastically strained samples are thus :

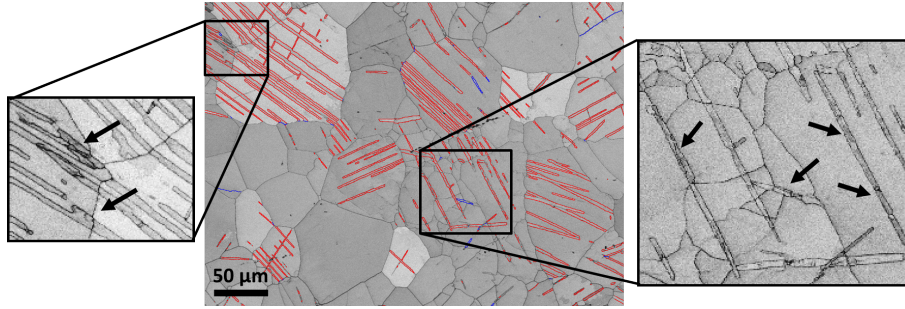


Figure 4.25: Band contrast EBSD map of a sample strained up to $\varepsilon = 0.05$ and annealed at 800°C for 5 minutes. The red and blue lines correspond to $\Sigma 11$ (corresponding to $\{332\}$ twinning) and $\Sigma 3$ CSL boundaries (corresponding to $\{112\}$ twinning), respectively. The black arrows highlight the vestiges of the former deformation products.

Dislocations on the twin boundaries

A large amount of dislocations nucleating on the twin boundaries propagate within the matrix on a few hundreds of nm . The $\vec{g} \cdot \vec{b} = 0$ criterion highlighted a $\frac{a}{2}[111]$ type Burgers vector, consistent with the BCC structure. These defects are supposed to result from the formation mechanism. Indeed, the continuity between the β and α'' phases has to be maintained despite the changes of shape and volume of the lattice. This could be accomplished by the addition of extra half-planes of atoms in the $\langle 111 \rangle$ direction on either a $(110)_\beta$ or a $(112)_\beta$ plane, as suggested by the lattice distortions depicted in the mechanism of Takemoto [122]. Indeed, such elastic distortion can be relaxed by Geometrically Necessary Dislocations. This point will be studied in Chapter 7.

4.4.3 Deformation sequence

The initial activation sequence proposed by Sun *et al.* in [123] is given in Figure 4.26. For a detailed description of the scenario, the reader is invited to read the article. Globally, it describes well most of the observed features of the deformed microstructure and can thus be considered as reliable. However, at the light of the results shown in this Chapter, it is believed that parts of the deformation features result from an alternative sequence that is depicted in Figure 4.27. Firstly, a dense network of $\{112\}\langle 111 \rangle$ mechanical twins forms. Secondly, primary α'' plates precipitate and some of them act as $\{332\}\langle 113 \rangle$ twin precursors, while others remain “stuck” in martensitic state. It is believed that if a twin nucleates this way, it grows up to a point where it interacts with another crystalline defect (such as a martensite plate or a grain boundary). Finally, secondary martensite can form within the $\{332\}\langle 113 \rangle$ twins, which may or may not also transform into secondary twins. Some questions remain in order to validate this alternative scenario, and it has to be kept in mind that the real situation could be a mixture of these two discussed sequences. Indeed, it was suggested in Section 4.4.2 that the nucleation and propagation steps could be different. In that case, the new scenario proposed in this work essentially depicts the nucleation step of the first twins.

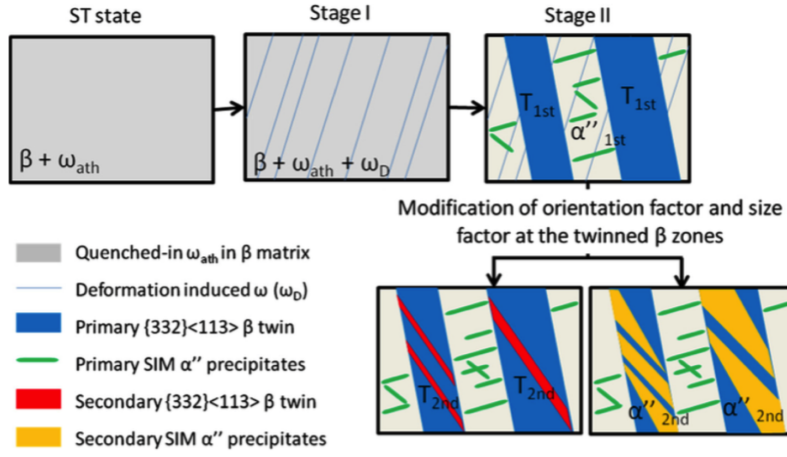


Figure 4.26: Initial activation sequence of deformation products [123].

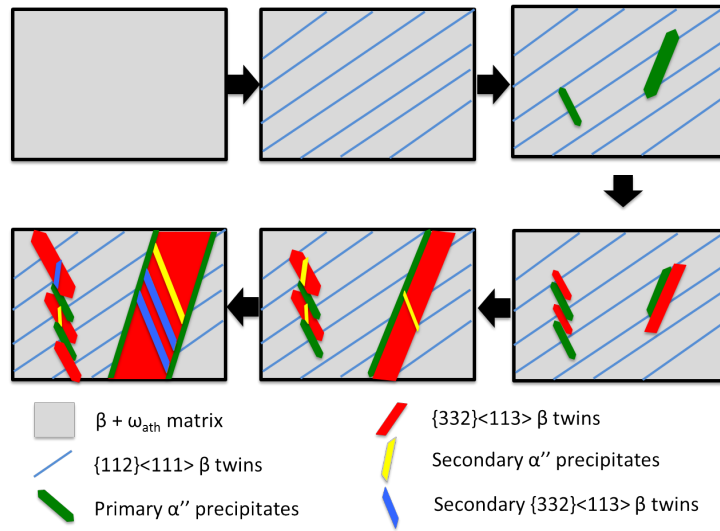


Figure 4.27: Qualitative sketch of the alternative activation sequence proposed in this work.

4.4.4 Relationship with mechanical properties

Figure 4.18 showed that the volume fraction of twins increases steeply at the onset of plasticity. Unlike in TWIP steels or *Co*-based alloys [125,138], an incubation strain for twin formation does not seem to be necessary in the present material, or a very short one only. Metallographic analysis showed that twins and martensite were already present after 0.01 strain level. This is consistent with the proposed mechanism here, since no particular configuration of dislocations have to be produced to incubate a twin. On the other hand, the nucleation of martensitic precursors is probably the relevant parameter in the case of Ti-12Mo. If we consider that the introduction of mechanical twins in the microstructure is a source of hardening, the evolution of the work hardening rate should thus be correlated to the variation of the twinning rate arbitrarily defined as $\partial V/\partial \varepsilon$ in this work⁷. This evolution is shown in Figure 4.28, together with the points calculated from experimental values ($\Delta V/\Delta \varepsilon$). Small discrepancies exist between the derivative of the fit and the calculated points since the choice of the fitting equation fixes the shape of the derivative, but the trend is the same for large strain levels.

Interestingly, a delay exists between the steep increase of volume fraction of deformation-induced features and the increase of the work hardening rate. Indeed, a slightly decreasing rate occurs during the first few percent of plastic strain, followed by a large increase, similarly to the case of TWIP steels [125]. This increase is still a matter of debate, some authors claiming that a dynamic Hall-Petch effect occurs, while others argue that it is due to a composite effect, the twins being harder than the matrix. Comparison of the internal structure of twins highlighted that the work hardening rate differences between austenitic steel grades could be attributed to the twins structure [139].

⁷Obtained by numerical derivation of Equation 4.3.3.

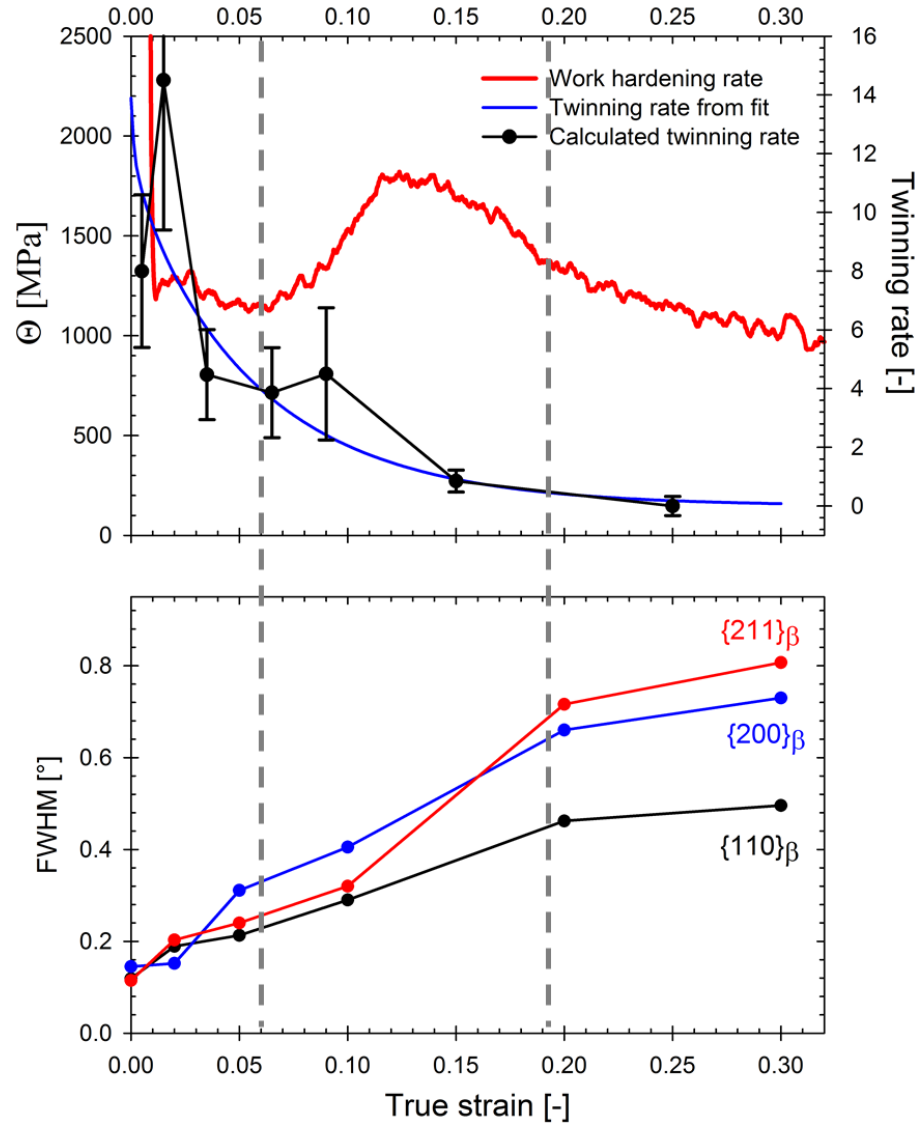


Figure 4.28: Twinning rate, work hardening rate and FWHM of β peaks as functions of tensile true strain.

In Figure 4.28, the evolution of the FWHM of several β peaks is also put in parallel with the twinning rate and work hardening rate evolutions. Peak broadening results from two different origins : a small size of diffracting volumes and the defect concentration. In the present case, the second origin is certainly the main one since the defect concentration becomes very large with increasing strain. It has often been suggested that the FWHM can be view as an indirect evidence of the dislocation density [140]. Under this assumption, the observed evolution of the FWHM can be divided in three steps (separated by grey dotted lines) that could be interpreted as follow : from strain level of 0 to about 0.06, the increase is moderate due to the consumption of the continuously created dislocations involved in the twinning and transformation processes, then a higher increase rate is observed due to forest hardening and massive dislocation pile-up formation on the twin boundaries previously formed, and finally a steady-state where the emission of new dislocations becomes less and less effective. However, the effect of both mechanical twinning and SIM transformation on the FWHM is not known, and must certainly taken into in order to link correctly these two evolutions.

A comparison of our results with the ones of Min *et al.* [104] for the twin volume fraction evolution in Ti-15Mo is given in Figure 4.29, together with the evolution of the work hardening rate of both alloys. No substantial difference exists between both twinning rates, as well as in the morphologies of the deformed samples. The observed difference of work hardening rate evolution cannot thus be attributed to a different dynamic Hall-Petch effect. Either the composite effect and/or the second phase (α'') precipitation must be essential in the case of Ti-12Mo.

The influence of the dynamic Hall-Petch and composite effects can be qualitatively added in the hardening law :

$$\sigma(\varepsilon) = \sigma_0 + \frac{K_{H-P}}{\sqrt{\Lambda(\varepsilon)}} + K_{comp}f_{twin} + K_{forest}\sqrt{\rho(\varepsilon)} \quad (4.6)$$

where K_{H-P} is the constant of the Hall-Petch mechanism, Λ is the dislocation mean free path, K_{comp} is the constant for the composite

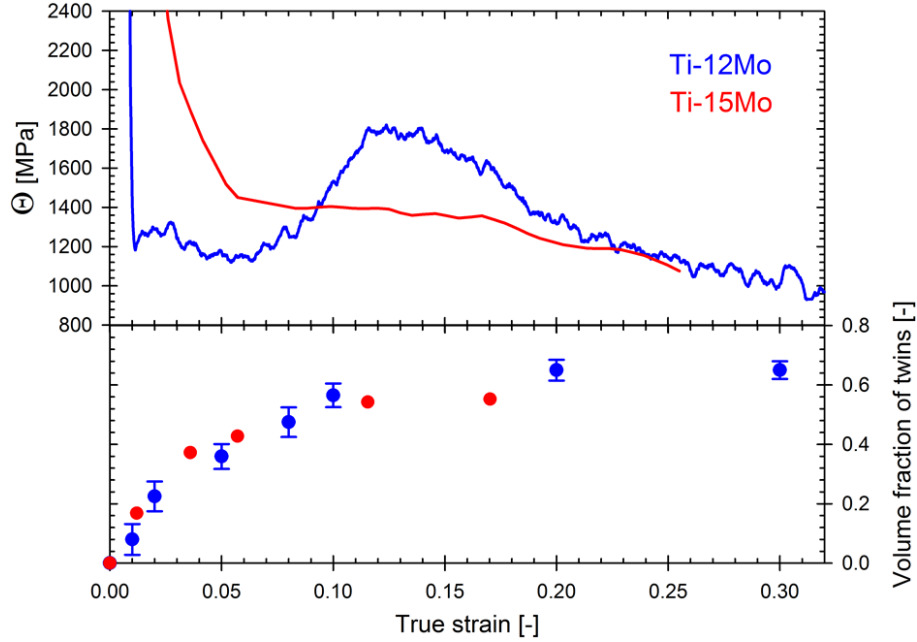


Figure 4.29: Comparison of the evolution of the twin volume fraction between Ti-12Mo and Ti-15Mo grades (taken from [104]) as a function of strain. The work hardening rate evolutions are also reminded.

effect, f_{twin} is the volume fraction of twins, K_{forest} is the constant for forest hardening effect and ρ is the dislocation density. Moreover, it is possible to express the Λ parameter as a function of the grain size and the twin spacing if we consider that the twin boundaries act similar to grain boundaries on dislocation motion. The following harmonic mixing law [141] can be used for the estimation of Λ :

$$\frac{1}{\Lambda} = \frac{1}{D} + \frac{1}{L} \quad (4.7)$$

where D is the grain size and L is inter-twin spacing. Finally, L can be estimated from the twin volume fraction f_{twin} and thickness (t) through Fullman's stereological law [142] :

$$\frac{1}{L} = \frac{f_{twin}}{2t(1 - f_{twin})}. \quad (4.8)$$

All non constant terms in Equation 4.6 are thus dependent on either f_{twin} or ρ , which are both function of the amount of plastic strain accumulated in the material.

It thus seems that both effects should be taken into account for explaining this behaviour. Since the internal structure of twins in Ti-12wt.%Mo is different from the initial β matrix, a composite effect certainly plays a role in the present case. It is supposed that the terms of Equation 4.6 are common (with possible different K_i constant values) to both Ti-12Mo and Ti-15Mo grades. A term similar to the third term of the righthand side of Equation 4.6 can be added in order to take into account the effect of α'' precipitation. Ultimately, the continuous creation of new interfaces in the microstructure introduces strain-gradient plasticity effects, which should also be taken into account for accurate modelling of the global mechanical behaviour. The existence of such effects is indeed suggested by (i) the mechanical contrast between β and α'' phases and (ii) the ribbon of dislocations forming at the twin boundaries.

Finally, the gradual decrease of work hardening rate corresponds to the saturation of the increase of the volume fraction of the deformation-induced bands. It is supposed that a phenomenon of “starvation” of hardening sources is occurring, the microstructure being saturated with primary twins and other defects.

It can be seen that twinning occurs in all the grains. It is different from austenitic TWIP steels where grains oriented along the $\langle 111 \rangle$ parallel to tensile axis develop twins, while grains oriented along the $\langle 100 \rangle$ parallel to tensile axis mainly deform by dislocation slip and stay free of mechanical twins [65]. This difference could result from the fact that the present Ti alloy is initially highly textured, leading to easy twin transmission through grain boundaries. Furthermore, dislocations can easily cross-slip in *BCC* lattices, while they can only glide on $\{111\}$ planes in *FCC* ones. It means that the probability to be in a good configuration for dissociation into partial dislocations is larger in *BCC*

crystals, leading to more twinning possibilities. Finally, if the nucleation of twins in Ti-12Mo is related to martensitic precursors, it can be speculated that the mechanism of formation is probably more restrictive in the case of TWIP steels. Indeed, one crystalline orientation of β gives rise to six different variants of α'' , while particular dislocation reactions are necessary to produce mechanical twin nuclei in *FCC* lattice [100].

4.5 Conclusions

The evolution of the microstructure with applied plastic strain has been characterised and a potential activation sequence of deformation mechanisms was proposed. Two main conclusions can be drawn from the present analysis.

Firstly, different characterisation techniques highlighted that the α'' stress-induced martensitic transformation, as well as $\{112\}\langle 111 \rangle$ and $\{332\}\langle 113 \rangle$ mechanical twinning are active deformation mechanisms. These mechanisms form hierarchical structures. The evolution of the volume fraction of the primary deformation features with macroscopic strain level has been estimated and it seems to saturate when reaching a strain level of ≈ 0.15 . This strain level corresponds to the maximum of the work hardening rate evolution. **A direct correlation between the volume fraction of twins and the work hardening rate evolution** has thus been established. However, other contributions to work hardening must be taken into account to explain the complete work hardening rate evolution since Ti-12Mo and Ti-15Mo present similar twinning rates but very different work hardening rates.

Secondly, a mechanism similar to the one proposed by Takemoto *et al.* [122] seems to be active in the present alloy. A thorough analysis of the orientation relationships between the deformation products highlights **a reaction sequence involving α'' martensite as a transition state to reach the β twin orientation**. A $\langle 113 \rangle_{\beta M}$ direction parallel to the normal of a $(110)_{\alpha''}$ plane is observed. This corresponds to the shear direction suggested by Takemoto. However, a modification of their model is needed to take into account the correct orientation relationship

observed between the β^M and α'' orientation. This can be achieved by reversing their sequence of transformation, for example. Moreover, the addition of periodic half-planes of atoms (edge dislocations) are necessary in the proposed model to keep the continuity at the interface while relaxing the elastic stresses at the interface. The formation of a **dense layer of dislocations**, presumably Geometrically Necessary Dislocations due to their arrangement, results in a semi-coherent interface. An alternative deformation sequence is proposed to take into account the morphology of some deformation features.

As in the case of TRIP steels, the **chemical stability of the β phase** is thus the relevant parameter for determining the active deformation mechanism. It appears that all deformation products share a common pole, namely a $(110)_\beta$ one. It is consistent with the suggestion of numerous authors concerning the tendency of a crystal lattice to transform martensitically when the elastic shear modulus decreases [110,143].

To confirm the proposed model, further investigations are required. *In situ* tensile tests with EBSD characterisation would allow the tracking of the evolution of deformation-induced bands. Also, Electron Channeling Contrast Imaging (ECCI) technique could be used for characterising the dislocation structure forming in and around the deformation products. Indeed, this technique allows the observation of dislocations similarly to the weak-beam technique in a TEM, with the advantage that it can be performed on bulk samples in a SEM. The tracking of the interactions of dislocations with dynamically created interfaces could be of great interest for a deeper understanding of the plasticity phenomena activated in this material.

Chapter 5

On the mechanism of $\{112\}\langle 111\rangle$ twinning in as-quenched Ti-12wt.%Mo alloy

The very first plasticity events occurring in Ti-12wt.%Mo has been found to be the $\{112\}\langle 111\rangle$ mechanical twinning. This mechanism was not expected in the present alloy, and its participation in the global work hardening behaviour is difficult to establish since it only seems to operate at the onset of plasticity. In this chapter, a nucleation mechanism for $\{112\}$ twins is proposed, and its impact on the global behaviour is assessed.

5.1 Introduction

Among the various mechanisms of plastic deformation in crystals, mechanical twinning has gained more and more interest since its discovery. Indeed, twinning has been observed in various crystallographic systems, regardless of the symmetry of the crystal lattice. Among them, the body-centered cubic crystals can exhibit $\{112\}\langle 111 \rangle$ mechanical twinning, $\{112\}$ and $\langle 111 \rangle$ being the twinning plane and direction, respectively. Numerous authors have discussed the mechanism of twin formation in various crystalline systems. A short review of nucleation mechanisms for $\{112\}\langle 111 \rangle$ twinning in *BCC* materials will be presented in the next section.

$\{112\}\langle 111 \rangle$ mechanical twinning has been massively observed in *BCC* metals strained at low temperature. This fact has been attributed to a faster increase of the flow stress for perfect dislocation glide than for twinning with decreasing temperature. Twinning is also of primary importance in the global mechanical response of an alloy. Indeed, twin boundaries (TB) can potentially play the role of barrier to dislocation glide resulting in pile-ups, as well as dislocation sources. Interactions between gliding dislocations and twins in *BCC* materials have been theoretically discussed by Sleeswyk and Verbraak [144] and experimentally observed by Levasseur [145] in $\alpha - Fe$ and by Mahajan [146] in a *Mo - Re* alloy. Depending on the orientation of the Burgers vector with respect to the crossed twins, they concluded that the interactions could lead to growth or shrinkage of twins, while allowing complete transmission of the initial perfect dislocation.

In this work and work of co-workers, metastable $\beta - Ti$ alloys exhibiting high strain-hardening rate have been designed [66, 67, 107]. It was shown that the simultaneous activation of several plastic deformation mechanisms, namely stress-induced martensitic (SIM) transformation and $\{332\}\langle 113 \rangle$ mechanical twinning [66, 123], is responsible for the unusual large work-hardening achieved for titanium alloys. Further investigations in samples deformed at very low levels revealed the ac-

tivation of $\{112\}\langle 111 \rangle$ mechanical twinning, which was not highlighted by our previous investigations. Since these mechanical twins have often been related to initiation mechanisms of microcracks in, for example, cold worked Fe-Si alloys [147], pure Mo [148, 149] and pure Cr [150], a better understanding of this plasticity mechanism is necessary to determine its implications in the deformation sequence of the metastable β -Ti alloys.

The aim of the present chapter is thus to identify the formation mechanism as well as the role of $\{112\}\langle 111 \rangle$ mechanical twins in the global mechanical behavior of TRIP/TWIP titanium alloys. First, TEM foils of slightly plastically strained bulk samples have been characterised to identify the dislocations involved in the process as well as their interactions with the newly formed mechanical twins. Secondly, *in situ* tensile tests on FIB-milled nanobeams have been performed to understand the very first steps of twin nucleation. *in situ* mechanical twinning has recently been observed in low stacking fault energy (SFE) *FCC* metals like *Au* nanowires [151], but such direct observation of mechanical twinning in *BCC* alloys has hardly been reported in the literature.

5.2 Overview of $\{112\}\langle 111 \rangle$ twin formation mechanisms

Different mechanisms of formation of $\{112\}\langle 111 \rangle$ twin have been proposed in the literature since their first observation, but without leading to a complete consensus. Several detailed reviews dedicated to deformation twinning can be found in [41, 152, 153].

Dislocation-based mechanisms

The first model of *BCC* twinning was proposed by Cottrell and Bilby in 1951 [154]. It was based on the pole mechanism, where a sessile portion of a perfect $\frac{a}{2}[111]$ dislocation dissociates in a sessile $\frac{a}{3}[112]$ pure edge segment (the pole) and a glissile $\frac{a}{6}[\bar{1}1\bar{1}]$ partial twinning dislocation. While the glissile part moves away from the pole on a (112) plane, thus

leaving a stacking fault behind it, it will have to cross-slip in order to curl around the pole dislocation, leading to an helicoidal shape. This pole mechanism is illustrated in Figure 5.1. In this model, a twin will thus grow from a monolayer fault nucleus. It can be noticed that the dissociation process is not energetically favorable.

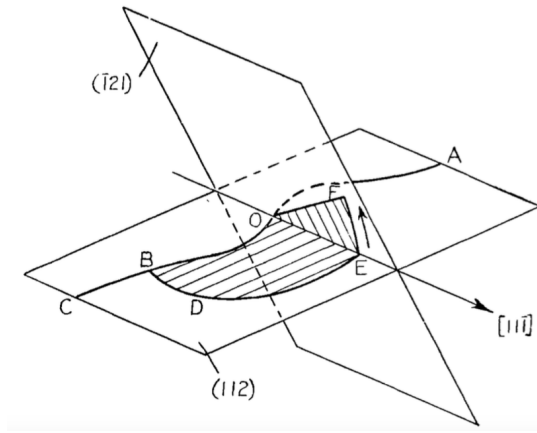


Figure 5.1: *The pole mechanism of mechanical twinning as proposed by Cottrell and Bilby (Taken from [154]). AO and OC represent lattice dislocation with $\vec{b} = \frac{1}{2}[111]$, OB is a sessile partial with $\vec{b} = \frac{1}{3}[112]$ and BDEFO is a glissile twinning partial with $\vec{b} = \frac{1}{6}[11\bar{1}]$*

Later, Sleeswyk [155] adapted the Cottrell-Bilby model in order to allow twinning nucleation with more common dislocation configurations. In this model, a three-layer twin nucleus is formed by dissociation of a perfect $\frac{a}{2}\langle 111 \rangle$ screw dislocation into three partials on three (112) planes with threefold symmetry according to the reaction :

$$\frac{a}{2}\langle 111 \rangle = \frac{a}{6}\langle 111 \rangle + \frac{a}{6}\langle 111 \rangle + \frac{a}{6}\langle 111 \rangle \quad (5.1)$$

This dissociation reaction is energetically favorable, and the author claims that twin growth arises by incorporation of crossing $\frac{a}{2}\langle 111 \rangle$ screw dislocations by the pole mechanism. However, Sleeswyk's initial dissociation reaction proposal has been shown to be unstable, and one of the three partials have to cross-slip on another (112) plane for the global

configuration to be a viable twin nucleus. Also, atomistic calculations performed by Vitek [156] suggest that monolayered stacking faults (both intrinsic and extrinsic) have too large energies to be created, while the author concluded that multilayered intrinsic stacking faults (I_n) on n successive $\{112\}$ planes with $n \geq 3$ could have sufficiently low energy to occur in practice.

In the same time, other authors (Crussard [157] and Cohen *et al.* [158]) suggested that dissociation of dislocations could arise on $\{110\}$ planes instead of $\{112\}$ planes. However, it can be intuitively expected that dissociation on $\{110\}$ planes is always more energy-consuming than on $\{112\}$ planes. Computer calculation of the generalised stacking fault energy (γ) surfaces by Vitek [29] have shown that no stable intrinsic stacking faults could exist on $\{110\}$ planes. Furthermore, no experimental evidence of $\{110\}$ -type stacking fault have been reported so far, while stacking faults on $\{112\}$ have been observed in pure *Nb* [25].

Another mechanism for nucleation of $\{112\}$ twins was proposed by Priestner and Leslie [48]. They suggested that dissociation of dislocations is due to pile-ups against sessile jogs. These jogs form at the intersections of slip planes. The authors analysed the stress concentration required for different kind of slip plane intersections. They also gave some experimental evidences supporting their model in the case of $\alpha - Fe$ alloys.

More recently, Hsiung and Lassila [52] applied the mechanism depicted in [22] to explain their experimental results in the case shock-induced tantalum and tantalum alloys. This mechanism is an extension of the Cottrell-Bilby model based on the same dissociation reaction as Sleeswyk, but with the addition of a zonal dislocation with no net Burgers vector, a concept initially introduced by Kronberg for the *HCP* twinning case [159]. This mechanism is schematically illustrated in Figure 5.2. Hsiung and Lassila argued that the large amount of jogs contained in their crystals could explain the effectiveness of the mechanism in creating numerous twins. They also showed that a

different dissociation reaction could lead to the formation of platelets of ω phase instead of twins when the shock energy is sufficiently large since it requires the activation of a $\frac{a}{3}\langle 111 \rangle$ anti-twinning partial dislocation whose gliding energy is much higher than the one of $\frac{a}{6}\langle 111 \rangle$ twinning dislocations. Other authors have successfully applied the aforementioned mechanism to their observations of mechanical twinning and ω transition in a Ti-23Nb-0.7Ta-2Zr-1.2O at.% alloy (also called Gum metal) deformed in compression [160].

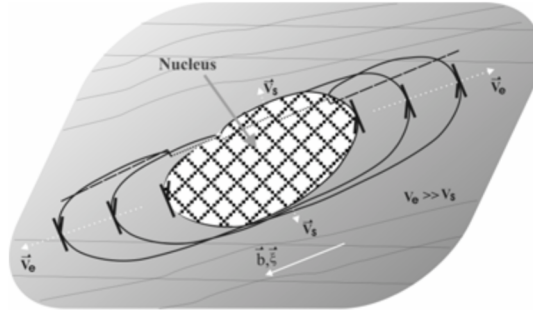


Figure 5.2: *Dislocation agglomerate formation from jogs (Taken from [161]). $\vec{v}_s$, $\vec{v}_e$, $\vec{b}$ and $\vec{\xi}$ denote screw and edge segment velocities, Burgers vector and line vector, respectively.*

Finally, Ojha et al. managed to model the $\{112\}$ twin nucleation stress in *Fe*-based alloys with excellent agreement with experimental values [162]. They used the dissociation mechanism of Sleeswyk and calculated the generalised plane fault energy (*GPFE*) in order to introduce it in the general expression of the energy of the system. Their calculations confirmed the suggestion of Vitek that the stable twin nuclei are made of three layers, while the growth of twins needs the overcoming of a fixed energy quantity, the twin boundary migration energy γ_{TBM} , as illustrated by the *GPFE* evolution with the amount of shear in Figure 5.3. They concluded that the important parameters governing $\{112\}$ mechanical twin nucleation are the stable stacking fault energy (SFE) γ_{sf} , the unstable twinning fault energy γ_{ut} and the stable twin stacking fault energy $2\gamma_{tsf}$. According to them, the *GPFE*

approach is effective in illustrating the importance of these parameters, what previously proposed models could not manage.

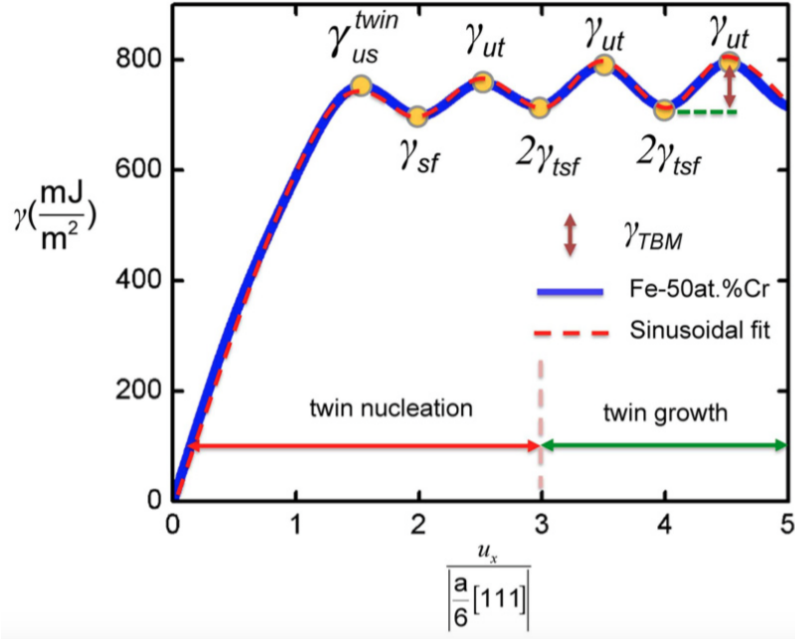


Figure 5.3: GPFE evolution with the amount of normalised shear displacement on successive $\{112\}$ planes (Taken from [162]). It can be seen that a stationary oscillating state is achieved after three $\{112\}$ layers, thus forming a stable nucleus.

Shuffle mechanism

Wasilewski [163] proposed that a shuffle mechanism could lead to the formation of $\{112\}$ twins. He argued that such a mechanism does not require a unique shear stress direction and that it was also favored by compressive straining, both being commonly observed experimentally. He also suggested that the complete mechanism could be a mixture of shear and shuffle to reach the final twin configuration. As already

explained in Section 2.2.3, Bilby and Crocker [44] predicted all possible twinning modes for all crystal types by considering combinations of shear and shuffle, the shear magnitude being the most important parameter to take into account. To our knowledge, no experimental evidence supporting this shuffle mechanism has been reported yet.

Phase transformation assisted mechanism

In a recent study, Wu et al. [164] proposed another model based on the β to ω phase transformation in a *BCC* $Ti - 30Nb - 3Pd$ (wt.%) alloy. They suggested that the reverse transformation, from hexagonal to cubic phase, is the driving force for $\{112\}$ twinning. They argued that the ω phase stability is the key parameter for $\{112\}$ twinning, since they did not observe twins in a $Ti - 30Nb$ (wt.%) grade where ω phase is more stable. Contradictorily, Lai *et al.* demonstrated in a very recent work that the ω phase precipitation on twin boundaries in $\beta - Ti$ alloys is induced by mechanical twinning [165].

5.3 Experimental procedure

TEM samples for post-mortem analysis of the $\{112\}\langle 111 \rangle$ mechanical twins were prepared from macroscopic tensile samples strained up to $\varepsilon = 0.007$ using the procedure described in Section 3.3.2.

Figure 5.4(a) shows the push-to-pull (PTP) device designed for *in situ* TEM uniaxial tensile tests. A single-tilt PI 95 TEM PicoIndenter (Hysitron Inc.) is used to push on the PTP which will induce a displacement between the two parts located in the white square (for more details about the nanomechanical testing, see [166]). Nanobeams of Ti-12Mo were milled from bulk material by FIB. Prior to the FIB preparation, orientation mapping on a wide zone of a bulk sample has been performed in order to choose particular orientations for the nanobeams (a $[110]$ direction aligned with the electron beam in the TEM). Figure 5.4(b) shows the Inverse Pole Figure (IPF) parallel to the rolling

direction of the bulk sample with the location where the beam has been extracted. The beam is made of 2 crystalline orientations with the grain boundary located near the center of the sample. Electron-beam assisted *Pt* deposition was first applied on the surface of the bulk sample with very low energy electrons (5 kV, 0.8 nA) to avoid damaging of the surface, followed by an ion-beam assisted *Pt* layer deposition (30 kV, 0.23 nA), which prevents the penetration of Ga^+ ions in the top surface of the sample. After the thinning steps, a final cleaning of both sides of the thin lamella was performed using a very low energy ion beam of 1 kV and 95 pA to avoid damage or amorphisation. Subsequently, the Ti-Mo thin lamella was cut from both sides using the Ga^+ ion beam to achieve the desired dimensions and transferred to the PTP device using an Omniprobe micromanipulator on the zone located in the white square of Figure 5.4(a), as shown in the magnification in Fig. 5.4(c). The sample was then attached to the PTP device using electron beam deposited *Pt* (Figure 5.4(d)). This layer will act as the jaws of a tensile machine and maintain the sample attached during mechanical testing. The dimensions of the nanobeams are about $4 \times 1 \times 0.2 \mu m$.

Due to the nanometric scale of the mechanical test, the experiment has been performed in load control mode since the response of the small-scale material was unknown. Indeed, the mechanical response will be greatly size dependent at this scale. A preliminary test with a constant displacement rate of $0.5 nm/s$ has been performed in order to identify the time scale range of defect formation. This test highlighted a very short interval between deformation events and failure. It has been chosen to work in load control mode with a stress plateau to observe the plasticity mechanisms. The displacement rate to achieve the stress plateau was of $0.5 nm/s$, and the stress was maintained at a level of $2.25 GPa$ for 240s before unloading.

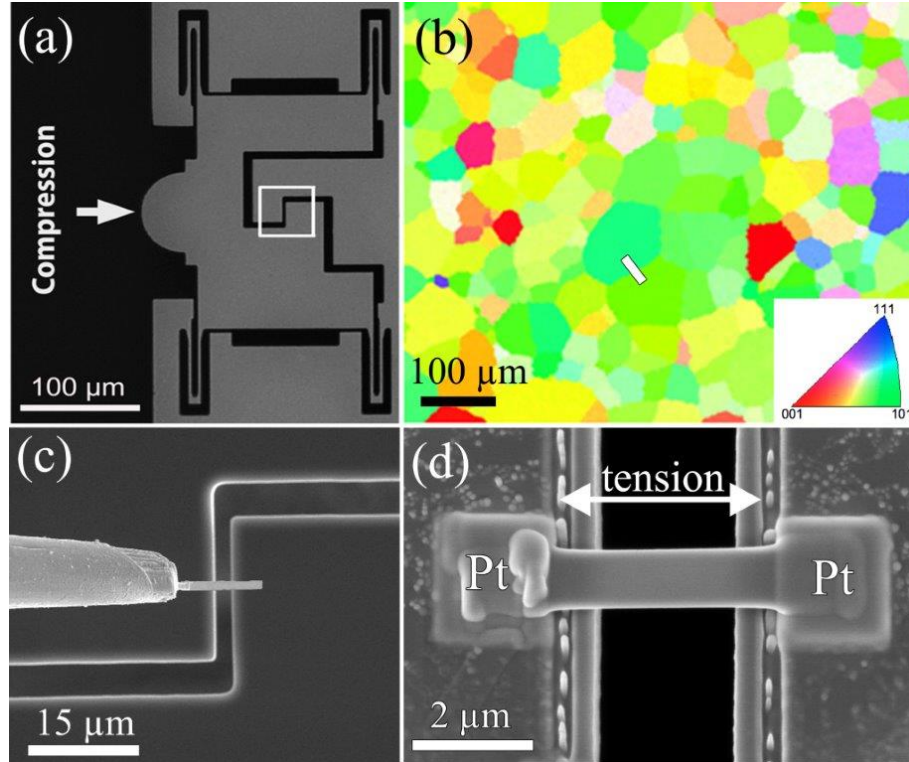


Figure 5.4: (a) SEM picture of the Push-to-Pull MEMS device. (b) IPF map of the as-quenched material along the rolling direction. The white rectangle represents the location from where the FIB-milled sample has been extracted. (c) Positioning of the tensile sample in the PTP with Omniprobe micromanipulator (magnification of the white square in (a)). (d) Illustration of the final setup used for in-situ tensile testing in the TEM.

The strain has been estimated by an in-house modified Correlation-Tracking freeware Toolbox in MatLab. The elongation was measured on snapshots coming from the movie of the experiment. More details about the tracking method are given in Appendix E. The strain is calculated for both grains of the beam using microstructural features as references¹.

5.4 Results and Discussion

5.4.1 Post-mortem $\{112\}\langle 111\rangle$ mechanical twins

Bulk samples strained at a level of 0.007 are very close to the onset of the plasticity regime and corresponds to a macroscopic tensile stress of 600 MPa. The microstructure corresponding to this strain level is shown in Figure 5.5(a). A dense stack of parallel straight-lined features can be observed in Bright-Field (BF) mode. These features can be indexed as $\{112\}\langle 111\rangle$ mechanical twins as shown in the SAD pattern taken along a $[\bar{1}10]_\beta$ zone axis in Figure 5.5(b). These mechanical twins have a mean thickness of 40 ± 5 nm and their mean spacing is 180 ± 50 nm, as already mentioned in Section 4.3.2. The Dark-Field image (Figure 5.5(c)) highlighting the twins corresponds to the $(011)_{\beta^T}$ diffraction spot, which also corresponds to the $(10\bar{1})_\omega$ diffraction spot. It explains the presence of homogeneously dispersed nanoscale ω_{ath} precipitates in the matrix in Figure 5.5(c). However, the indexation cannot be ensured based on the SAD pattern taken along $[110]_\beta$ since all the diffraction spots from the twins coincide with ω phase spots, as shown in the key diagram in Figure 5.5(d). To overcome this ambiguity, HR-TEM has been performed on a deformation-induced band as illustrated in Figure 5.6. It clearly shows that the band possesses the stacking of the BCC phase, with a $\{112\}\langle 111\rangle$ twin relationship as confirmed by the Inverse Fast Fourier Transform (IFFT) in the inset. ω phase precipitation is observed at the twin/matrix interface with a $(2\bar{1}\bar{1})_\beta // (01\bar{1}0)_\omega$ lattice coincidence, consistently with the results of Lai

¹This method has been chosen since the beam was attached far from the visible sides of the PTP device, resulting in a dynamical L_0 length. A correct evaluation of the strain was thus impossible since some elongating parts were not visible.

et al. [165]. This ω phase precipitation is possible owing to the shear process involved in $\{112\}_\beta$ twinning, the shear bringing enough local elastic energy to the system for triggering the transformation.

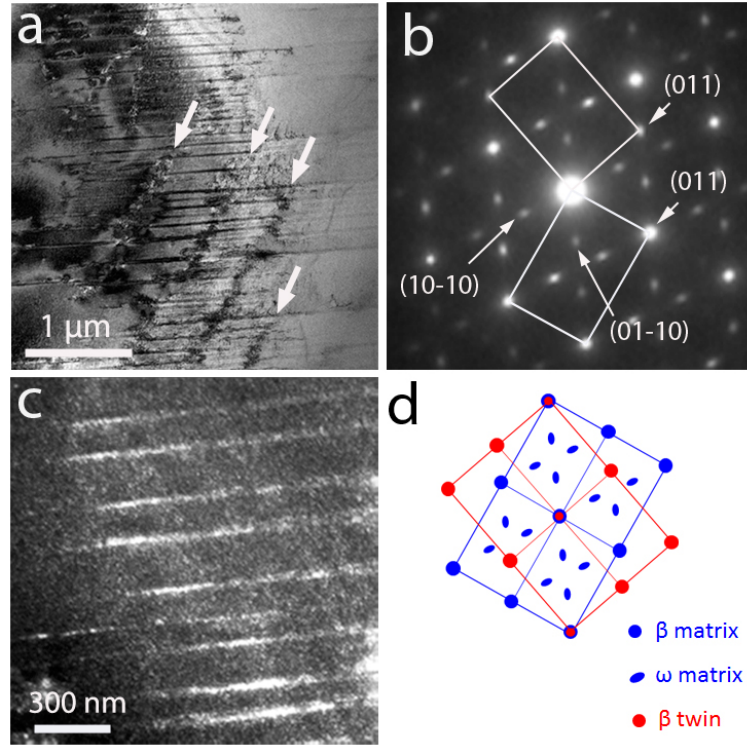


Figure 5.5: (a) Bright-Field image of Ti-12wt.% Mo sample after $\varepsilon = 0.007$. The white arrows highlight the twinning dislocation sources. (b) SAD pattern of the grain shown in (a) taken along a $[\bar{1}10]_\beta$ zone axis. (c) Dark-Field image of a magnified region from (a) obtained from the (011) spot of the β twin. (d) Key diagram showing the correspondence between the matrix and the twin diffraction patterns.

What could be the scenario for $\{112\}\langle 111 \rangle$ mechanical twinning in the case of as-quenched Ti-12wt.%Mo alloy ? As suggested by Hsiung and

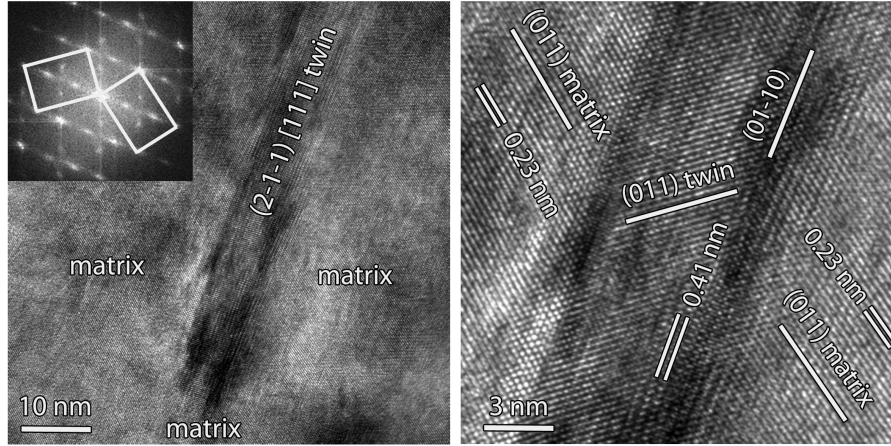


Figure 5.6: HR-TEM images of a $\{112\}$ mechanical twin illustrating the BCC packing within the twin and ω phase precipitation on the twin/matrix interface.

Lassila [52], it requires the existence of numerous thermal jogs within the grains, *i.e.* fragments of dislocations that were not completely annihilated during heat treatments. Such low energy defects can indeed be extremely difficult to remove during thermal processes. The particular arrangement of the jogs observed in this work, shown by white arrows in Figure 5.7(a), can be explained following the scenario schematically represented in Figure 5.8. This scenario is similar to the pure Nb case depicted in the work of Louchet and Kubin [167]. Dislocations will move within the grains during cold-working and long straight screw segments remain due to the velocity difference between edge and screw parts in the BCC structure. Indeed, the strain field associated with the core of the screw segments is spread along various planes containing the Burgers vector direction [21], which increases the frictional forces that need to be overcome compared with non-screw segments. During subsequent heat treatments of the samples, the dislocations reorganise themselves and form a zigzag pattern by climbing to decrease their energy and progressively take the form of an helix, up to the point where only coaxial prismatic loops remain within the grains.

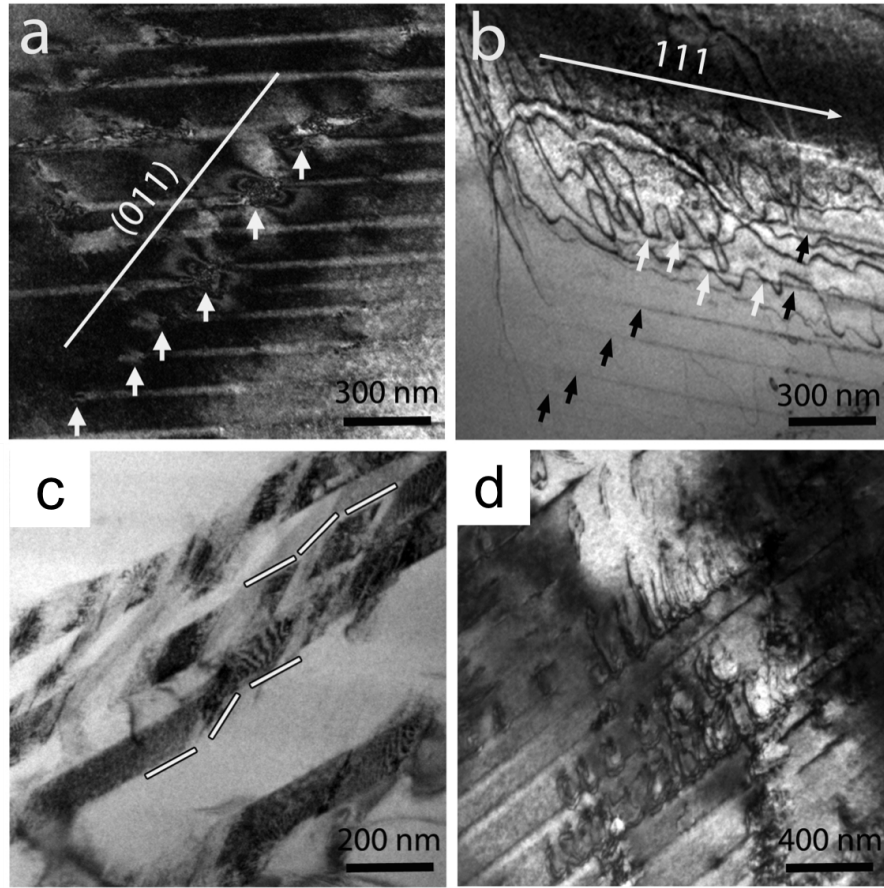


Figure 5.7: (a) Initially present jogs (white arrows) aligned in a $(011)_\beta$ plane. (b) Cross-slip events (white arrows) in a screw dislocation due to jog formation resulting from its interactions with twin/matrix interfaces (black arrows). (c) Discontinuities of the twin boundaries due to super-jogs formation. (d) Emission of dislocations from the jogged twin/matrix interfaces.

These jogs will act as dislocation sources once the critical resolved shear stress (CRSS) is reached, and the mechanism proposed by Hsiung and Lassila will be activated. It is clear from Figure 5.7(a) that mechanical

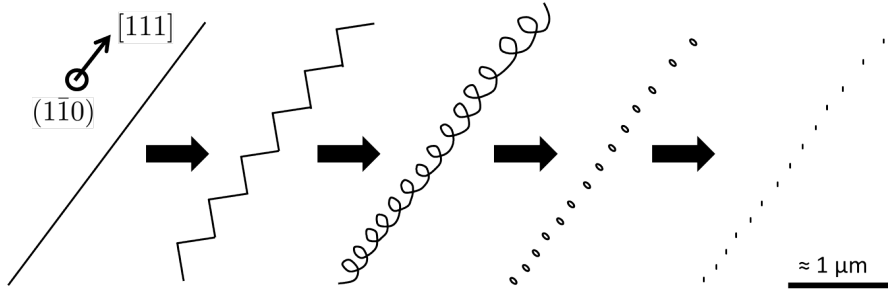


Figure 5.8: Schematic representation of the formation mechanism of thermal jogs during heat treatment of BCC lattice.

twinning is related to the jogs present in the alloy since each twin starts from such a jog. Moreover, they are aligned with a (011) plane, which is coherent with their formation mechanism presented in the previous section. According to Hsiung and Lassila, perfect $\frac{a}{2}[111]$ dislocations will thus be emitted from these jogs, decompose into three $\frac{a}{6}[111]$ partials that will glide on successive $\{211\}$ planes, inducing the same amount of shear on these planes and resulting in a three-layer micro-twin domain. As pointed out in Section 5.2, Ojha *et al.* concluded that three-layer twin domains are stable, and growth of the nucleus happens by incorporation of further dislocations. Since screw segments velocity is much smaller than their edge counterparts, the nucleus will have a straight elongated shape, so that the twins will finally present a very limited thickness. Indeed, the observed twins have a thickness of a few tens of nanometres, while their length is around the grain size (several tens of micrometers). Figure 5.7(b) illustrates the typical interactions between the screw dislocations and the twin/matrix interfaces observed in the strained sample. White arrows depict pinning points of the screw dislocation when encountering a twin/matrix interface (indicated by the black arrows). It can be seen that the dislocations undergo a large amount of cross-slip, which is a typical behaviour in BCC alloys due to the non-uniqueness of the gliding plane possibilities.

As stated before, a growth mechanism by dislocation incorporation can be assumed with further deformation. The incorporation of screw

dislocations has been theoretically discussed in details in [144]. It was shown that incorporation could result in growth or shrinkage of the twins, with the creation of jogs at the twin/dislocation intersections as illustrated in Figure 5.9. These jogs are normally too small to be observable in conventional TEM microscopy since their height is of one or two $\{112\}$ interplanar distances depending on the Burgers vector of the incoming dislocation. However, the accumulation of such incorporation events will progressively bring the formation of “super-jogs”, as illustrated in Figure 5.7(c). The discontinuities observed in the twin boundaries are due to these superjogs. The twins have been tilted far from the edge-on position, and interference fringes characteristic of stacking faults (SF) can be seen within the twins. These SF indicates that the growth mechanism involves the incorporation of twinning partials ($\frac{a}{6}[111]$) gliding on the twin boundaries created after the change of direction of a perfect dislocation crossing the twin boundaries, as theoretically suggested by Sleswyk and Verbraak [144].

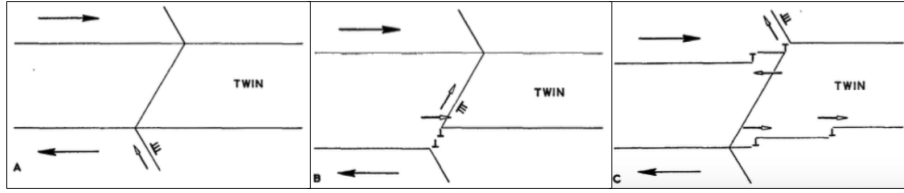


Figure 5.9: *Sequence of the transverse growth process of a twin due to dislocation incorporation mechanism (taken from [144]). Two $\frac{a}{6}[111]$ twinning partials are created when the perfect dislocation crosses the twin boundaries, which will glide on a (211) plane and cause growth of the twin.*

These jogs and superjogs are important features of the microstructure for further plastic behaviour of the material. Indeed, as shown in Figure 5.7(d), the twin boundaries act as very effective dislocation sources. A large amount of dislocation loops are emitted from the TBs. The $\{112\}\langle 111 \rangle$ twins will thus play mostly a role of dislocation sources, since the $\{112\}$ twin boundaries does not seem to be effective obstacles for dislocation motion.

5.4.2 *in situ* tensile test of nanobeam

The tested beam is composed of two crystals of different orientations as shown in Figure (see Figure 5.10(a)). The grain on the left and the one on the right will be labelled $G1$ and $G2$ in the following, respectively.

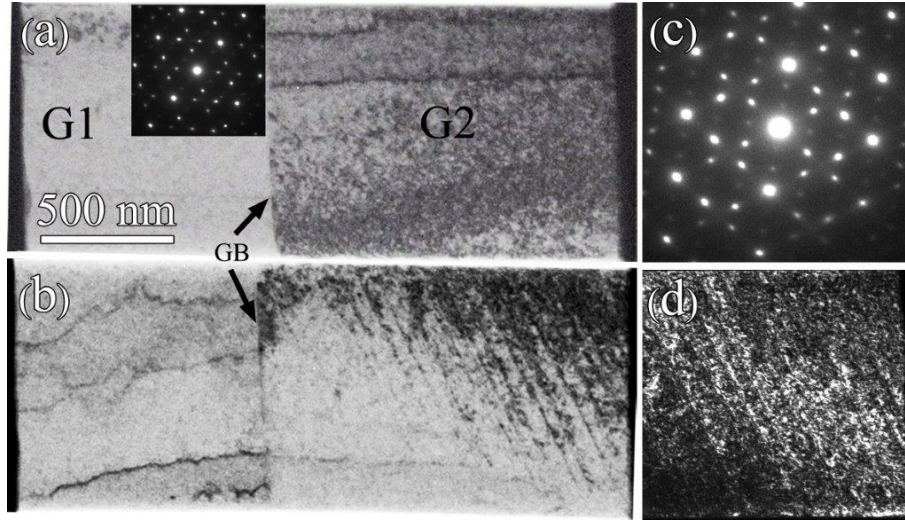


Figure 5.10: (a) Bright-Field image of the sample before loading. Inset : SAD pattern of grain $G1$. (b) Bright-Field image of the sample after the first loading cycle, showing appearance of numerous bands. (c) SAD pattern of grain $G2$ after the first cycle. (d) Dark-field image taken with the $(01\bar{1}0)_\omega / (011)_{\beta T}$ diffraction spot.

The strain evolution with time for grains $G1$ and $G2$ are plotted in Figures 5.11(a) and 5.12(a), respectively. It is worth noting that the results of tracking are much more reliable for $G1$, as explained in Appendix E. However, several methods have been attempted to estimate the strain in $G2$ also, and they all converged to the same value of $\varepsilon \approx 0.025$ just before the first plasticity events were observed in the microstructure, at a stress value of 2.25 GPa . Two different grids have been used in an attempt to take into account the huge changes of contrast appearing in $G2$. The evolution of the “elastic” part of the curve is believed to be wrong, especially in the first percent of strain. Indeed, the results were

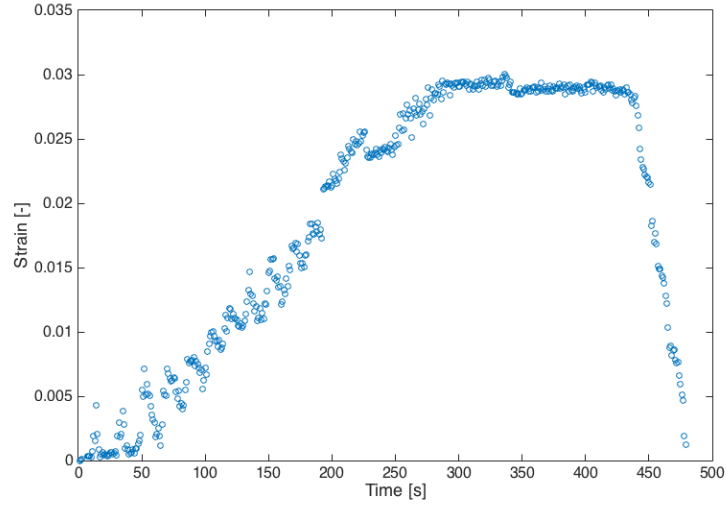
highly dependent on the size of the grid chosen for the tracking, which is a sign of ineffectiveness of a tracking algorithm. The strain evolution is different for the two grains. Indeed, $G1$ remains elastic during the whole cycle up to the plateau stress, while a permanent strain is observed in $G2$, as suggested by Figures E.2(b) and E.3(b). This deviation in $G2$ occurred after the targeted stress was achieved.

The difference of elastic strain observed between the two grains comes from the different crystalline orientation. Indeed, the E_{hkl} for the two crystalline orientations calculated from the theoretical elastic constants (see Chapter 2) are :

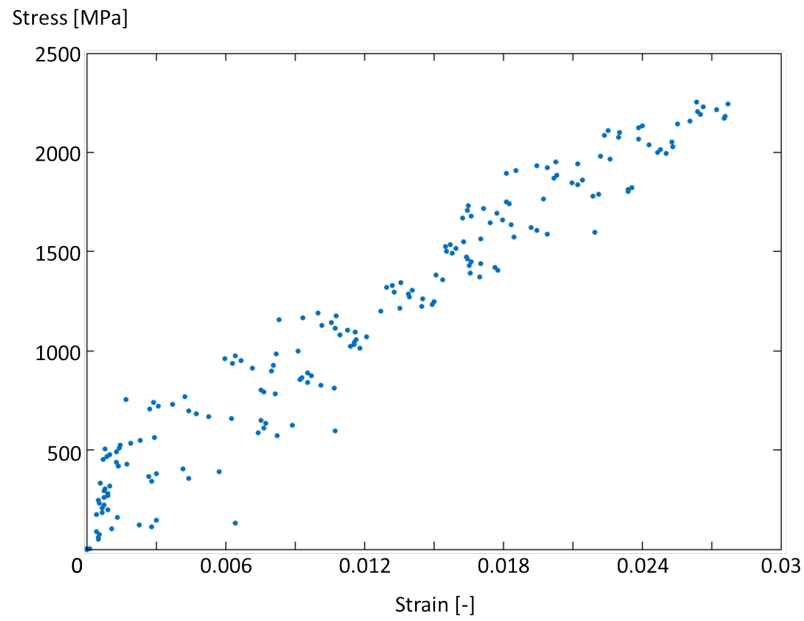
$$E_{118} \approx 40GPa$$

$$E_{111} \approx 110GPa$$

The interpolated value for grain $G1$ is $\approx 115GPa$, which is very close to the theoretical one. In the case of grain $G2$, the calculated value does not match the measurements. However, the part of the curve located between $1.5GPa$ and $2.25GPa$ (just before twinning) has a slope of $\approx 50GPa$, which could correspond to the theoretical value.

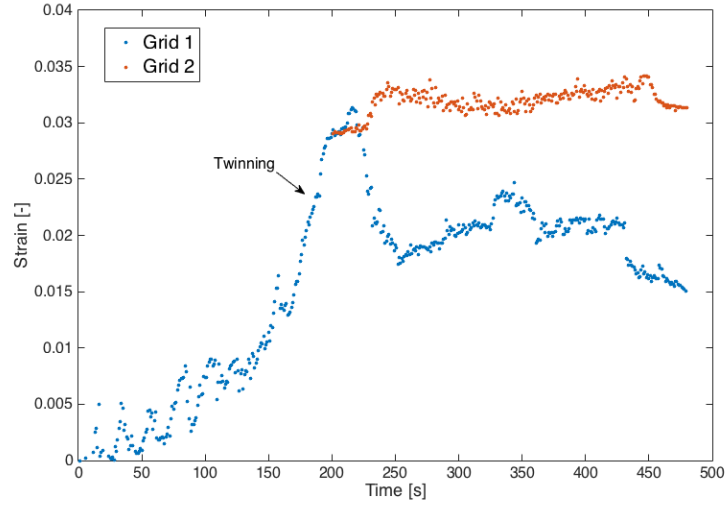


(a)

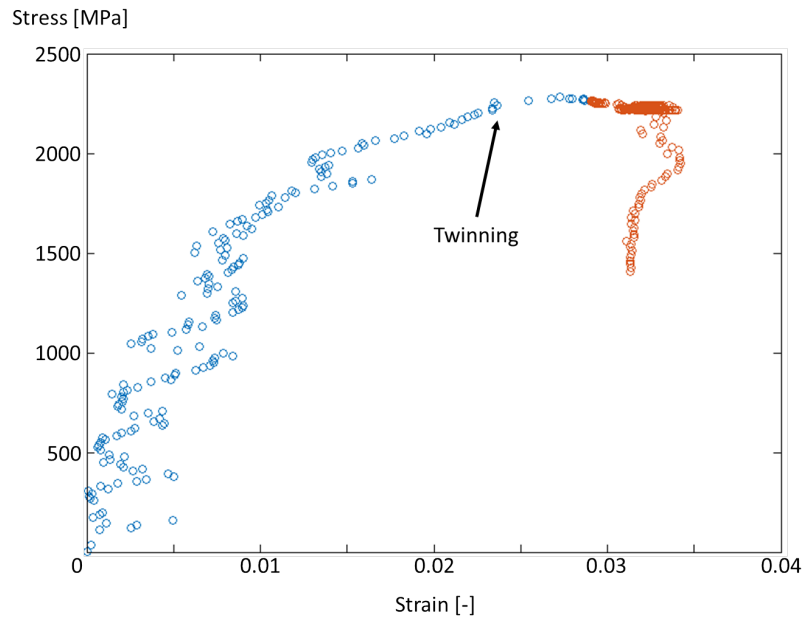


(b)

Figure 5.11: (a) Strain-time and (b) stress-strain curves for grain G1 obtained by automated tracking method. The interpolated Young Modulus is equal to $E \approx 115\text{GPa}$.



(a)



(b)

Figure 5.12: (a) Strain-time and (b) stress-strain curves for grain G2 obtained by automated tracking method.

TEM picture of the sample before loading is shown in Figure 5.10(a). The contrast observed in $G2$ could be attributed to either FIB-induced damages or ω_{ath} . The exact nature of this contrast has not been investigated. Indeed, this information is not necessary to confirm the proposed mechanism, as shown in the following discussion.

Figure 5.10(b) represents a snapshot of the sample unloaded after the first cycle of loading to a stress level of 2.25GPa . It can be seen that numerous bands appeared in grain $G2$, while nothing clearly visible happened in grain $G1$ (except the changes in the bend contours). The inset in Figure 5.10(a) is the SAD pattern of grain $G1$ before straining, while Figure 5.10(c) is the SAD pattern of grain $G2$ after unloading. The SAD pattern of grain $G1$ indicates that this grain has a $\{111\}$ plane nearly normal to the loading direction, while for grain $G2$ the loading direction is normal to a $\{118\}$ plane. The dark-field image in Figure 5.10(d) has been taken on the $(011)_\beta$ spot and suggests that the thin bands are in twinning relationship with the matrix. It is worth noting that some variations were detected within the bend contour in grain $G1$, but the tilt of the sample after unloading could not highlight any defects. The bend contours of both grains evolved during the loading plateau, suggesting thus slight rotations of the crystals with respect to the electron beam.

Figure 5.13 shows the evolution of the beam within a time scale of one second during which most of the events take place. It can be seen that every noticeable events occur within grain $G2$, as already mentioned above. Numerous twin nuclei appear within three frames, *i.e.* in a time interval of 0.4s . This is easier to observe by looking at the differences between successive frames. Beside the variations in the bend contours and the twin nuclei, a straight line crossing the whole grain also appeared within this time interval.

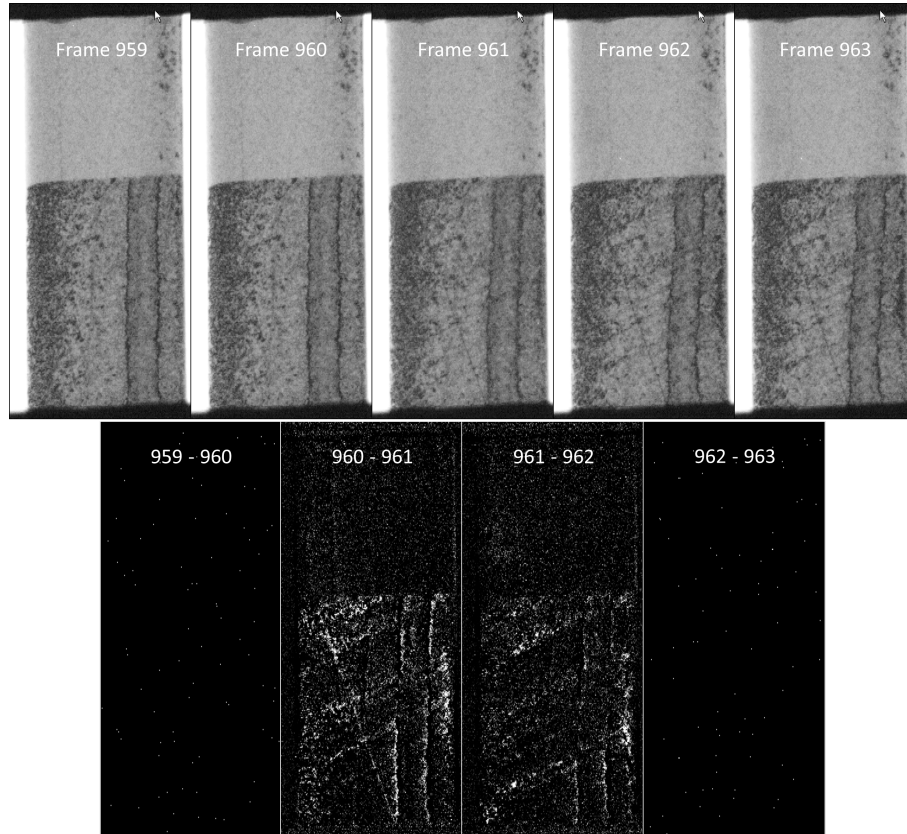


Figure 5.13: *Evolution of the contrast within the beam in the time interval corresponding to nucleation of visible plasticity events. The time interval between two frames is 0.2s. The images below correspond to the difference between two upper frames, with a contrast enhancement for visibility.*

This straight line has been indexed as being a $\{321\}\langle 111 \rangle$ -type screw dislocation, which could have nucleated either at the visible grain boundary, or from another defect located in the hidden part of the beam. A better look at this dislocation suggests that most of the deformation bands nucleate on contrast features interacting with this dislocation (Figure 5.14), even though it has to be confirmed with more spatially resolved microscopy. It can also be seen that the dislocation is not completely straight, the small deviations from linearity seem to happen when the dislocation encounters a dark feature in the contrast. These features could be ω_{ath} precipitates, which would induce cross-slip of the dislocation during its propagation, thus generating kinks or jogs in the dislocation line. The deviations from linearity suggest cross-slip events. The large amount of ω_{ath} precipitates seen in the dark-field image of grain *G2* does not allow us to ensure the nature of these defects (see Figure 5.10). The velocity of twin nuclei formation is extremely fast, which is in good agreement with the experimental attempts of measurement performed by several authors. Indeed, most of them estimated a time formation for twins around about a few μs using different techniques as piezoelectric effect (Mason *et al.* in *Sn* [168]), resistivity changes (Bunshah and Mehl in *Bi*, *Zn* and *Fe* [169]) or strain-gauge measurements (Reid *et al.* in *Mo – Re* [170]).

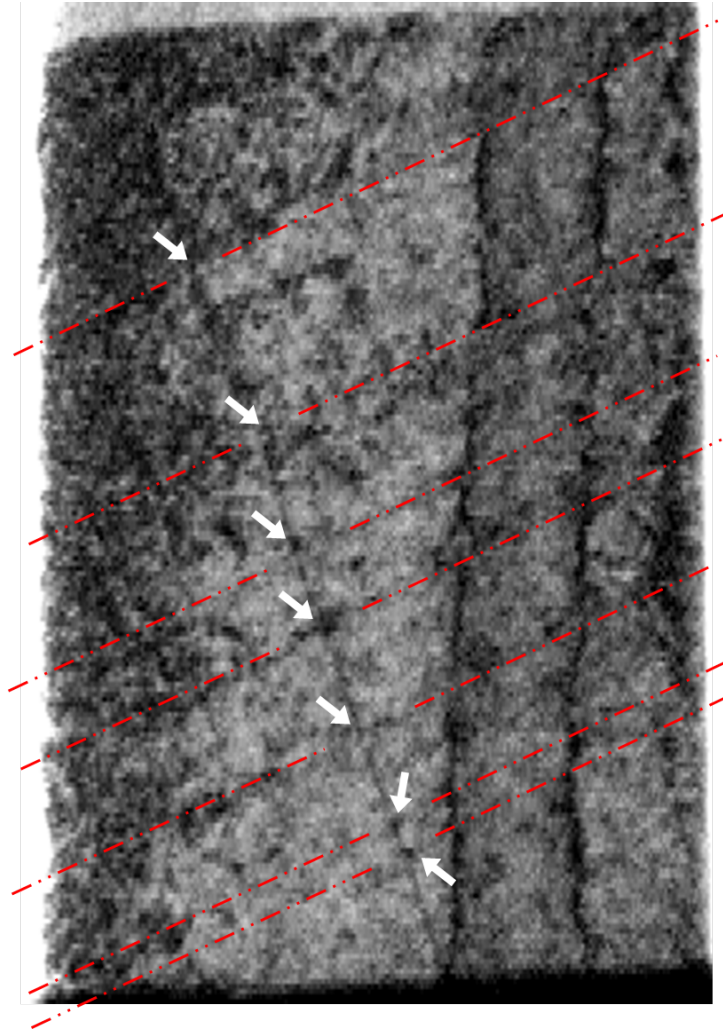


Figure 5.14: *Magnification of grain G2 just after the appearance of a straight screw dislocation and mechanically induced twin nuclei. The red dotted lines show some twin nuclei while the white arrows highlight the features that could act as nucleation sites for these twins.*

The presence of such defects could explain the formation of the twin nuclei, by the partial dislocation mechanism exposed in the previous section and illustrated on the drawing in Figure 5.15. The sample has then been reloaded up to 2.5GPa , where fracture happened relatively quickly.

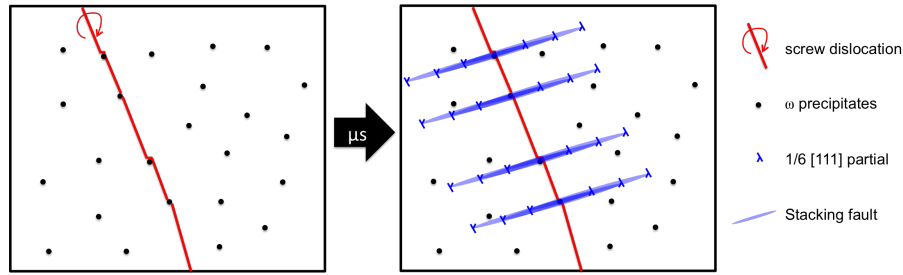


Figure 5.15: Sketch of the twin nuclei formation during the *in situ* tensile test.

Figure 5.16(a) illustrates the sample slightly tilted before the second load cycle to enhance to contrast of the twin nuclei. The black arrows highlight some of the twin nuclei appeared during the first cycle, while the white arrows in Figure 5.16(b) show new nuclei formed just after reaching the second stress plateau (2.5GPa). The former twins does not appear to thicken after reaching a higher stress. The sample after failure, occurring during the second load plateau, is shown in Figure 5.17. Failure of the beam happened quickly within grain $G1$ after reaching this stress level. The angle of fracture is nearly 45° regarding the tensile direction. No sign of necking was detected.

The behaviour of the material in this nanoscale sample is different from the behaviour of bulk samples. Indeed, very high levels of stress are achieved while nearly no dislocation activity was detected. However, it is possible that some dislocation activity happened in grain $G1$ without being observed if they were not in right Bragg conditions. The surface defects created during FIB preparation as well as the presence of nanoscale ω_{ath} precipitates does not seem to act as dislocation sources, but the time resolution of the movie is not sufficient to ensure that the

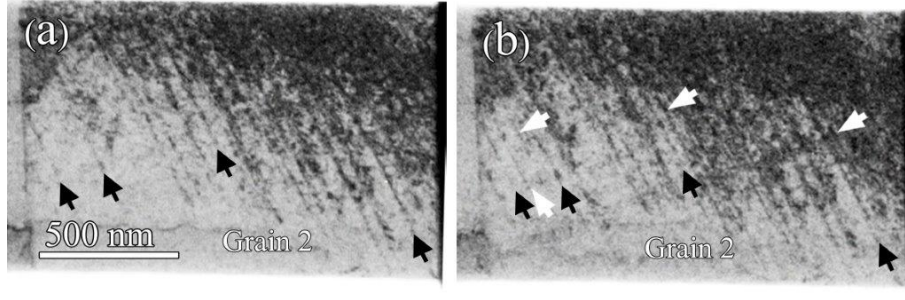


Figure 5.16: (a) Bright-Field image of the strained sample after the first loading cycle and (b) same image taken during the second stress plateau (2.5GPa). Black arrows show some twins formed during the first cycle and white arrows show new twins formed during the second one.

$\{321\}$ -type screw dislocation observed did not nucleate from such ω_{ath} precipitate. The formation of this type of dislocation as first active slip system is rather unusual. Indeed, even if these planes are often cited as possible slip planes in the *BCC* lattice, most of reported data concern $\{110\}$ - and $\{112\}$ -type slip systems [171]. However, Kaun *et al.* reported a nearly simultaneous activation of $\{110\}$ and $\{321\}$ slip systems during tensile loading of *BCC* single crystals when the loading direction is close to a $[110]$ direction of the crystal [172], which is the case here. The Schmid Factor (SF) of both grains for several *BCC* slip systems have been calculated and are listed in Table 5.1. It can be seen that amongst the $\{110\}$ and $\{321\}$ slip systems, the highest Schmid Factor corresponds to the latter type.

When the load is maintained at a certain value, $\{112\}$ twin nuclei with a thickness smaller than $10nm$ form nearly instantaneously within one of the grains. It is worth noting that the twins encountering the grain boundary do not cross it, contrarily to $\{332\}$ twins as pointed out in Chapter 4. It can be seen in Table 5.1 that the $[11\bar{1}](2\bar{1}1)$ slip system in grain *G2* possesses the higher value of Schmid Factor that corresponds to the twin system activated during the experiment. The activation of a $\{112\}$ slip plane instead of a $\{110\}$ one (corresponding to the most dense

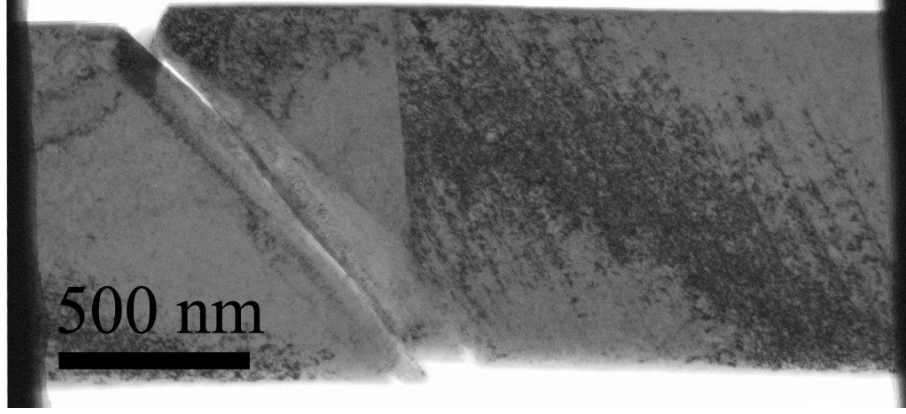


Figure 5.17: Observations of the failure process during the second loading stage. Failure occurred in grain G1.

packing in *BCC* lattice) has been largely observed in pure *BCC* refractory metals and interpreted by Seeger [173] as a consequence of the core structure of the screw dislocations based on its theory of kink-pair formation on screw dislocations [174]. Recently, Kamimura *et al.* proposed a generalized Peierls-Nabarro model and showed that the normalised Peierls stress (τ_p/G) of dislocations was largely dependent on the crystal structure [175]. They showed that the Peierls stress range for *BCC* transition metals was of $2-8 \cdot 10^{-3} G$ for $\frac{1}{2}\{110\}\langle 1\bar{1}1 \rangle$ screw dislocations. This corresponds to values of $70 - 280 \text{ MPa}$ in the case of Ti-12Mo ($G = 35 \text{ GPa}$), which seems consistent with the post-mortem observations since numerous twins as well as dislocations have been found in bulk samples loaded up to a macroscopic stress level around 600 MPa (refer to previous section). In this *in situ* experiment, the resolved shear stress corresponding to the highest Schmid Factor in grain G2 is equal to $\tau_r = 868 \text{ MPa}$. Even if the slip system is not the same as the one taken into account in the work of Kamimura *et al.*, it can be assumed that the activated slip system will be the one with the smallest CRSS, so that the resolved shear stress of the $\{110\}\langle 111 \rangle$ system should be higher than 868 MPa in this experiment.

	Slip system	Schmid Factor
G1	$[\bar{1}11](1\bar{1}2)$	0.351
	$[111](1\bar{2}1)$	0.351
	$[\bar{1}11](\bar{1}10)$	0.322
G2	$[11\bar{1}](2\bar{1}1)$	0.386
	$[\bar{1}\bar{1}1](\bar{1}10)$	0.334
	$[\bar{1}\bar{1}1](101)$	0.334
	$[11\bar{1}](3\bar{1}2)$	0.379
	$[11\bar{1}](3\bar{2}1)$	0.379

Table 5.1: Calculated Schmid Factor for some slip systems in both grains of the beam.

This large difference in stress for the activation of dislocation motion between the bulk and monocrystalline samples is believed to come from a size effect as well as a lack of effective dislocation sources in the nanobeam. Indeed, the first twin nuclei have been observed as soon as one screw dislocation has been formed within the grain. The mechanism of mechanical twinning is intimately linked to the defect structure of the initial crystal. Once the stress concentration is reached for generating a dislocation in the sample, new partials will immediately be emitted and form nanotwins at a sonic velocity to relax the elastic strain imposed to the sample. Also, in contrast to bulk samples, the twins did not thicken after their nucleation. It is supposed that the growth of twins is hindered by the lack of perfect screw dislocations in the beam. During the second loading plateau at a higher stress, new twins will form again as a relaxation mechanism.

These observations suggest that the SFE in the as-quenched Ti-12Mo grade should be very small (or even negative) since, once an effective source of defects is present, it is easier for the system to form partial dislocations (which have to drag a stacking fault behind it) rather than form new perfect dislocations. This conclusion is not consistent with previous calculations of SFE on other *BCC* materials such as *Fe*-based alloy [162] as well as *Ti* – *Nb* alloys [109]. A decrease of the SFE with

decreasing stability of the β phase of Ti has indeed been confirmed by *ab initio* simulations, but the lower values of SFE are still quite large compared to *FCC* alloys (more than $200\text{mJ}/\text{m}^2$ for the less stable *Ti – Nb* alloy).

5.5 Conclusions

In this Chapter, both post-mortem observations of deformed samples and *in situ* tensile test have been performed to investigate the $\{112\}\langle 111\rangle$ twinning mechanism in the as-quenched *Ti – 12Mo* grade. It was shown that this type of mechanical twinning happens at the onset of plasticity, bringing a microstructure fulfilled with such kind of mechanical twins. They seem to essentially play a role of **dislocation source for further deformation mechanisms** such as $\beta \rightarrow \alpha''$ transformation and subsequent $\{332\}\langle 113\rangle$ twinning. Furthermore, a ribbon of ω_{ath} phase precipitates at the twin boundaries to relax the elastic strain field associated to the interface creation.

The TEM observations are consistent with the mechanism proposed by Hsiung and Lassila [52], with the initial presence of defects like thermal jogs acting as nucleation sites. Moreover, the *in situ* tensile test on a nanobeam seems to confirm the **need of such nucleation sites for mechanical twinning** to occur. The defect-free material does not tend to form the partials needed for the formation of twins. In contrast, once a defect such as a screw dislocation appears in the material, the formation of twins is nearly instantaneous in order to relax the elastic strain inside the beam.

A lot of authors considered the possibility of mechanical twins as crack initiation sites in *BCC* alloys. It does not seem to be the case in Ti-12wt.%Mo since **fracture occurred in the untwinned grain** during the *in situ* tensile test.

Some of the aforementioned conclusions need some further analysis to be completely validated. A finer characterisation of the defects in the beams after loading should be performed to ensure their nature. Different crystalline orientations should also be tested to refine the analysis concerning the influence of the Schmid Factor on the trigger stress of twinning. It could also be valuable to test samples containing initial dislocations and/or thermal jogs to emulate the bulk situation and estimate the trigger stress of $1/6[111]$ partial dislocations.

Finally, the experimental setup should also be redesigned for an easier tracking of the deformation in the whole sample (strain mapping). Indeed, the dynamical contrast of the TEM renders it difficult to apply correctly a DIC technique. To do so, some marks could be added to the beam (*Pt* plots on the surface, intentional defects addition, strain gauge machining,...). Nevertheless, the PTP device has a lot of potential for *in situ* characterisation of nanoscale plasticity mechanisms.

Chapter 6

***in situ* cyclic loading of Ti-12wt.%Mo under synchrotron radiation**

*It has been underlined in Chapter 4 that the larger work hardening of Ti-12wt.%Mo compared to a Ti-15wt.%Mo alloy cannot be attributed to a different twinning rate. The other plastic deformation mechanism activated in the Ti-12wt.%Mo grade, i.e. the stress-induced martensitic transformation, should thus also be taken into account to explain correctly the complete work-hardening rate evolution. Furthermore, the monitoring of the elastic response of the β matrix during mechanical loading could help in a better understanding of the work hardening capability of the material. This Chapter aims at exploring *in situ* the elastic response of both β matrix and stress-induced α'' martensite during tensile loading of the Ti-12wt.%Mo alloy.*

6.1 Introduction

The analysis of the deformation of polycrystalline aggregates has been a prolific topic of materials science for decades. The emergence and mastering of powerful characterisation tools like synchrotron radiation and neutron diffraction brings about the accurate determination of lattice strains of well-oriented grains. Analysis of lattice strains becomes a unique way for the determination of residual stresses, which are of primary importance for engineering applications. Indeed, internal stresses build up in the material during loading due to different grain orientation and/or phases, and these internal stresses play an important role in the macroscopic response of the material during further mechanical loading.

Since TRIP effect is associated with phase transformation under the application of a stress, one may expect that some stress-partitioning occurs between the matrix and the transformed martensite, the two phases exhibiting different elastic properties. Indeed, extensive studies on multiphase steels have shown that a high mechanical contrast between the different constitutive phases could appear during loading, whether they were present before loading (DP steels [176]) or stress-induced (TRIP steels [99]). Dual-phase titanium alloys like Ti6Al4V also received a lot of attention related to the appearance of internal stresses during processing and/or loading [177–179]. Similarly, several studies on TWIP effect in austenitic steels highlighted that a mechanical contrast appears between the matrix and the mechanical twins. This contrast was attributed to a composite effect, the twins being harder than the surrounding matrix [102].

The present Chapter aims at exploring the role of strain-induced martensitic α'' phase in Ti-12wt.%Mo alloy with a refined grain size by the analysis of

- the evolution of the phase proportions as well as the reversibility of the α'' phase transformation ;
- the evolution of the elastic stress state in both the β matrix and α'' martensite.

In situ cyclic tensile tests with continuous synchrotron X-ray radiation have been carried out on Ti-12Mo to highlight the role of the martensite in the global evolution of the work hardening rate of the alloy.

6.2 Experimental method

6.2.1 Initial microstructure

Ti-12wt.%Mo alloy has been synthesised in an arc melting furnace from high purity raw materials in Ar atmosphere and remelted several times to ensure chemical homogeneity. The alloy was then heated up to 1223K for 15 minutes in air and water quenched to keep 100% $\beta + \omega_{ath}$ phase microstructure. Cold rolling was applied on the ingots with reduction levels larger than 90%. Dog-bone tensile samples with gauge length of 2.75mm and width of 1.25mm were then machined with the tensile direction parallel to the rolling direction. Since the diffraction experiment requires small grain sizes to achieve statistically meaningful results (typically a few microns), a short thermal treatment consisting of 45 seconds at 1173K in air followed by water quenching was performed on the tensile samples in order to hinder the β grain growth. ω_{ath} phase reappeared during quenching. The resulting samples were then mechanically thinned down to 0.2mm with *SiC* papers and polished with diamond paste to remove the hardened layer and avoid roughness effects in XRD experiments. The complete processing route is schematised in Figure 6.1.

The obtained initial microstructure is shown in the EBSD pattern quality maps of Figure 6.2. The microstructure and local orientation has been analysed in two different zones out of the calibrated zone, as shown in the insets of Figures 6.2(a) and (b). It can be observed that the microstructure is not homogeneous since part of the microstructure is recovered, with the formation of slightly misoriented subgrains like suggested by the yellow lines corresponding to boundaries with 3 to 15° of misorientation. Such a competition between recovery and recrystallisation processes has been reported in refractory metals with *BCC* crystal

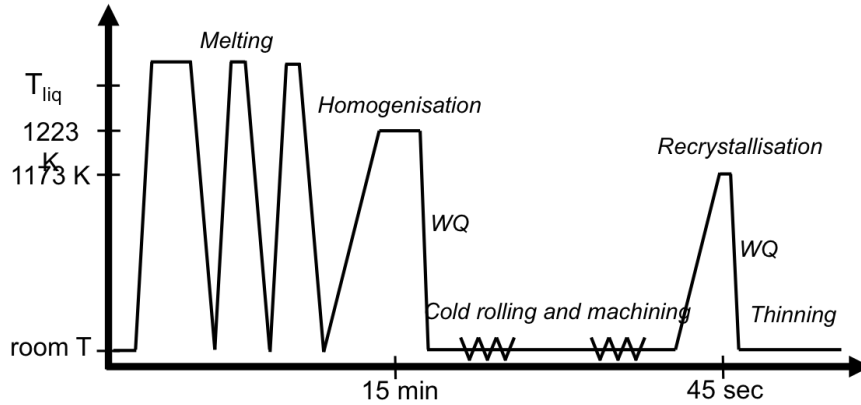
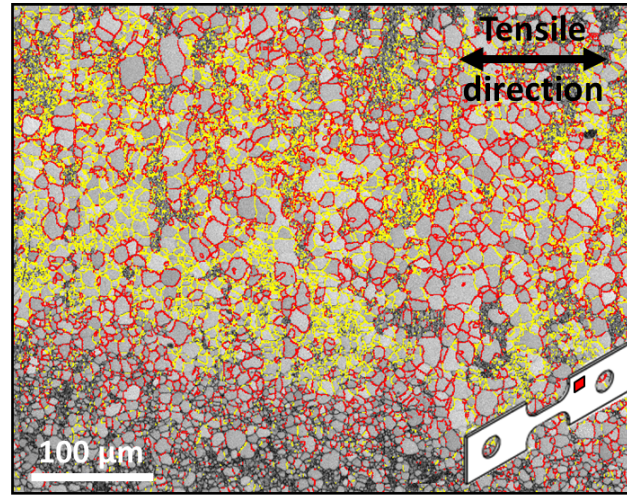
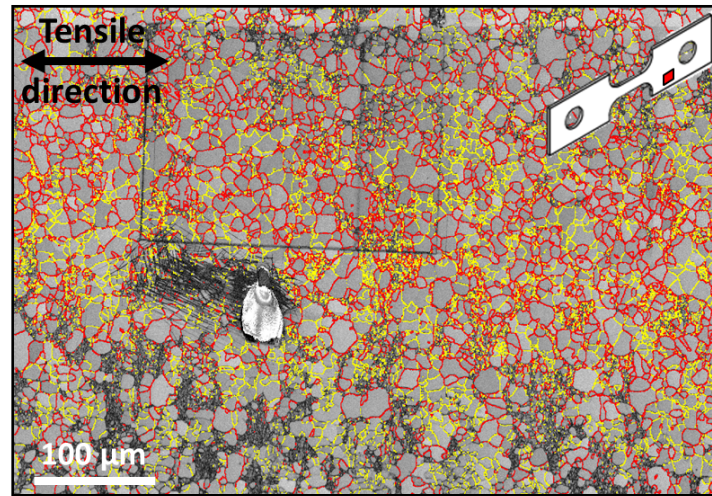


Figure 6.1: *Processing route of samples used for tensile testing under synchrotron radiation.*

structure such as W, Mo or Nb due to the easy cross-slip ability of their dislocations [180]. Raabe and Lücke also observed both recrystallised and recovered structures in cold-rolled Fe and heat treated for a short time [181]. They attributed this phenomenon to a lack of orientation gradients between subgrains after cold working, leading to insufficient kinetic instabilities necessary for triggering the recrystallisation process. Nevertheless, since the dislocation content within the cells is greatly reduced, the cell size can reasonably be assumed as the grain size for the recovered fraction of material. The grain size distribution will thus be considered as a bimodal one. This distribution is presented in Figure 6.3 with a fit consisting of a sum of 2 log-normal distributions. The higher mean grain size is 7.1 micrometers and the smaller one is 1.2 micrometers. The rather continuous grain size distribution with some grains reaching a size of 30 micrometers is very difficult to avoid in β titanium alloys because of the fast grain growth rate achieved above the β transus [182]. As already stated, reaching a small grain size is a primary requirement for a quantitative analysis of the results obtained during such diffraction experiment in the used particular configuration (see Section 6.2.2) [183].



(a)



(b)

Figure 6.2: *Kikuchi Pattern Quality (KPQ) index maps of unstrained tensile sample for in situ diffraction experiment (red lines correspond to misorientations larger than 15° while yellow lines correspond to misorientations between 3° and 15°). Insets show the locations where EBSD measurements have been performed.*

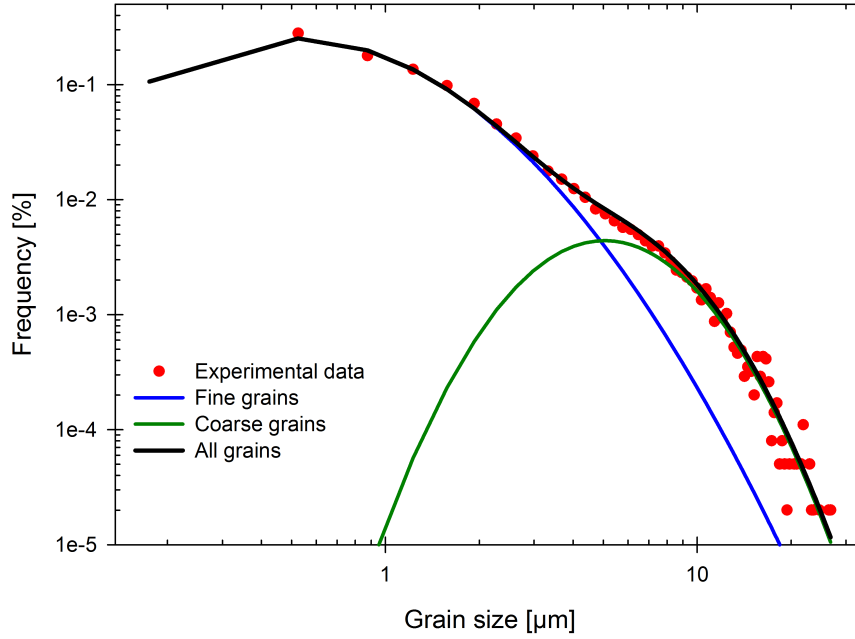
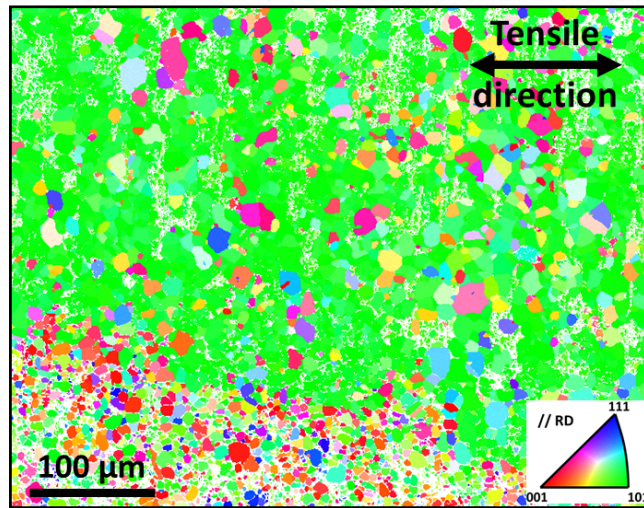


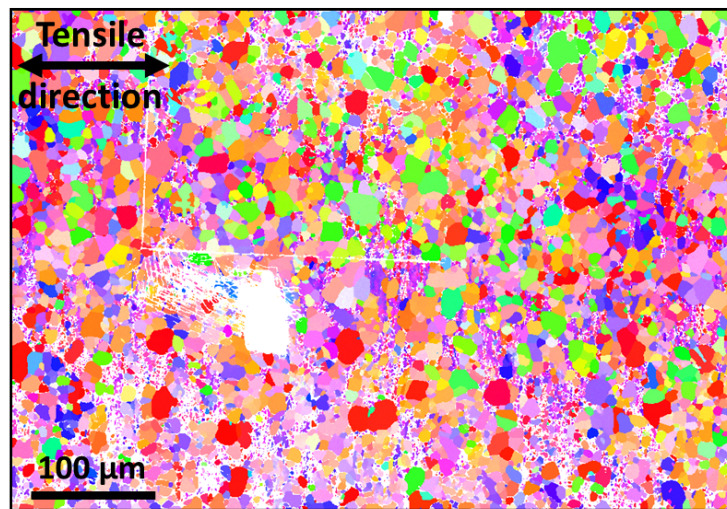
Figure 6.3: Grain size distribution of the initial microstructure shown in Figure 6.2 fitted with a bimodal lognormal function.

Inverse pole figure maps along the tensile direction of both zones shown in Figure 6.2 are given in Figure 6.4. It shows that the material is highly textured, which is typically observed in annealed β -Ti alloys after heavy cold working [184, 185]. More importantly, it also suggests that the microstructure is composed of macrozones of texture, i.e. large areas with mostly one component of texture. This is confirmed by the inverse pole figure (IPF) along the three principal directions given in Figures 6.5 and 6.6 for the upper and lower maps, respectively. The IPFs are given for the recrystallised zones (6.5(a) and 6.6(a)) as well as for the recovered zones (6.5(b) and 6.6(b)). It is observed that the texture of the recrystallised and recovered zones are nearly the same, particularly for the upper map. Another interesting feature is the alignment of a $\{112\}$ crystallographic direction with the normal direction (ND) of the sample in both cases. The presence of macrozones may be an indicator of the

influence of initial β (deformed) grain orientation on the recrystallisation and grain growth kinetics. Indeed, the grain size of the as-cast ingot was of several hundreds of microns to some millimetres, which could correspond to the observed size of these macrozones. In the upper map of Figure 6.4, the material exhibits a very pronounced recrystallisation texture close to $\{112\}\langle 110 \rangle$ (component of the α_{bcc} -fiber), which is a commonly observed recrystallisation texture observed in cold-rolled β -Ti alloys heat treated above the β transus [184–186].



(a)



(b)

Figure 6.4: Inverse pole figure maps corresponding to Figure 6.2 taken along tensile direction.

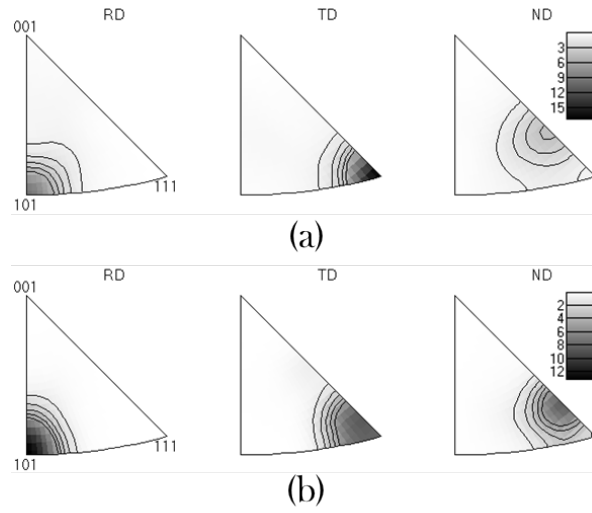


Figure 6.5: Inverse pole figures corresponding to Figure 6.4(a) for the recrystallised zones (a) and the recovered zones (b).

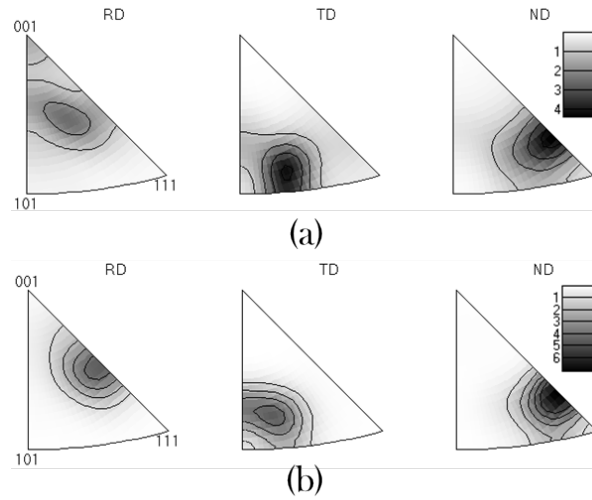


Figure 6.6: Inverse pole figures corresponding to Figure 6.4(b) for the recrystallised zones (a) and the recovered zones (b).

6.2.2 Mechanical testing and X-ray diffraction

Tensile tests with in-situ SXRD measurements were carried out at the Swiss Light Source on MS-Powder beamline with wavelength of $0.6598\text{\AA}$. Measurement of macroscopic strain has been performed by Digital Image Correlation. Flat zones on the shoulders of the tensile specimens were used as extensometer (red squares in Fig. 6.7(a)) Acquisition of diffraction patterns was done by a fast scanning 1D detector in a reflection configuration. Each scan took about 10 seconds and the strain rate was of $5.5 \cdot 10^{-5} [\text{s}^{-1}]$, so that no interruption during tensile loading had to be applied for XRD measurements. The normal to the diffracting planes was perpendicular to the applied stress. The tensile direction was parallel to the rolling direction. The experimental setup is described in details in [187] and is schematically shown in Figure 6.7(b).

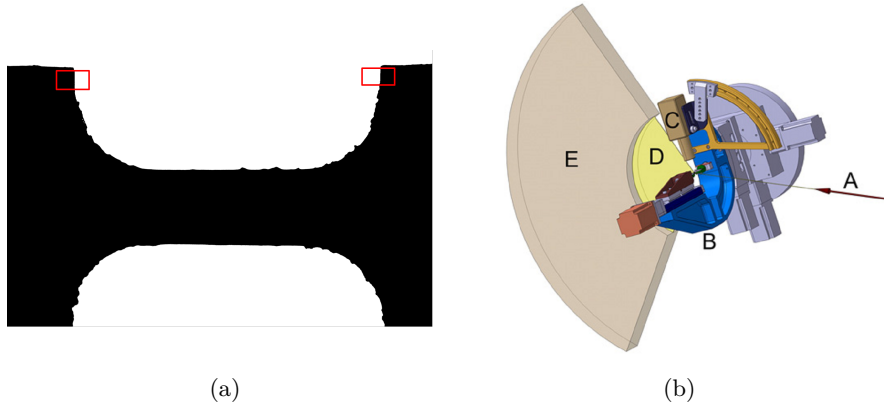


Figure 6.7: (a) *Macrograph of the tensile samples used for DIC measurement of elongation.* (b) *Illustration of in-situ mechanical device used in this experiment, taken from [187]. A : incoming X-ray beam, B : tensile machine on goniometer, C : CCD camera, D : diffracted beam and E : 1D high-resolution detector.*

Abaqus simulations with the sample geometry have been performed to estimate the Young's modulus of the material, since the displacement was measured between the shoulders of the tensile specimen. The calcu-

lated modulus is 80 *GPa*, which is a typical value for this composition.

It has to be noted that the maximum macroscopic strain achieved during the experiment could not be calculated. Indeed, one of the flat zones used as tracking feature for the DIC calculation went out of the video screen, rendering the tracking no more possible. For this reason, the results implying the macroscopic strain are plotted up to the maximum measured strain level.

The monitoring of the peak profile evolution with applied tensile stress has been performed by a Matlab fitting routine¹ using a sum of constrained Pearson VII profile functions. The code of this routine is given in Appendix A. This evolution is an average for each grain illuminated by the X-ray beam. Due to the complexity of the XRD patterns and the progressive appearance of new diffraction peaks corresponding to the SIM phase, the following fitting procedure has been adopted :

- The background was fitted with a Chebychev polynomial of the fourth order in the unstrained specimen pattern, and was kept constant during the whole fitting routine.
- The evolution of fitting parameters is constrained by boundary values to avoid divergence of results.
- The boundary values are updated between each patterns. For example, the intensity of the *hkl* peak of *i*th pattern I_i must be comprised between $0.5 \times I_{i-1}$ and $2 \times I_{i+1}$.
- The batch calculation has been reloaded several times with different initial parameters and constraints to ensure the observed tendencies.
- The error bars represent the standard deviation of the values obtained in the previous step. Only the sets of parameters with a mean value of the residuals ($\bar{R}$) below a value of 1 and a standard deviation below a value of 5 are chosen for data representation.

¹Core written by Dr. Steven Van Petegem (private communication) and modified by the author for the present analysis.

Lattice strains are calculated using the Bragg's law to convert the diffracted beam angles into lattice spacing d_{hkl} , and then using these calculated d_{hkl} in the following equation :

$$\varepsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0} \quad (6.1)$$

where d_{hkl}^0 is the lattice spacing of the hkl family of planes in the unstrained crystal.

Finally, Rietveld refinement has been performed using the TOPAS 4 suite of Bruker AXS. Instrumental parameters have been predetermined by refining a pure *Si* NIST standard in the same experimental setup. Convergence was considered satisfactory when the R-Factors reached a value lower than 2. The error bars on the Rietveld refinement correspond to the uncertainties given by the software for this convergence criterion.

6.3 Results

6.3.1 Statistical analysis

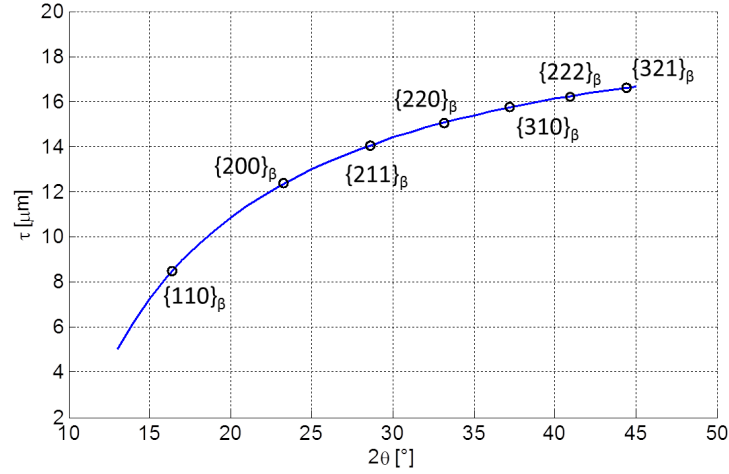
The estimation of diffracting grains is done following the method depicted in [183]. The illuminated volume equals $V = \tau \times 300 \times 500 \mu m$, the penetration depth τ times the beam size. The penetration depth is given by :

$$\tau = \frac{1}{\mu(E)k}, \text{ with } k = \frac{\sin\alpha + \sin(2\theta - \alpha)}{\sin\alpha \sin(2\theta - \alpha)} \quad (6.2)$$

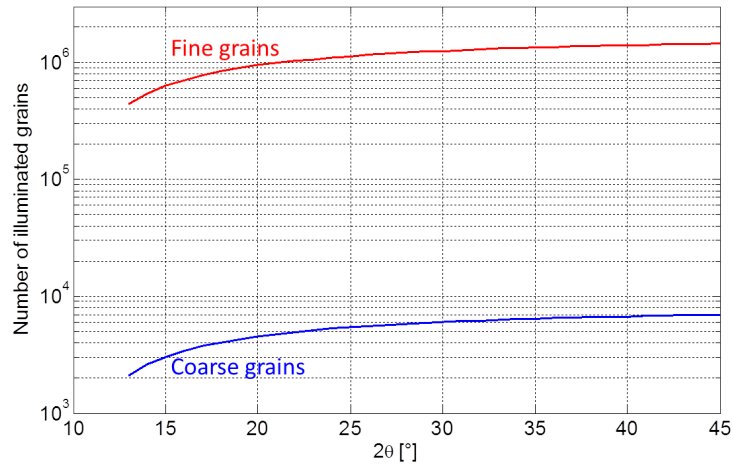
where $\mu(E)$ is the absorption coefficient for X-rays of energy E and k is a geometrical factor depending on 2θ , the diffraction angle and α , the angle between the incoming X-ray beam and the sample. In this experiment, α has a value of 10° , and μ is estimated around 80 cm^{-1} at 18.8 keV [188]. The variation of the penetration depth, and thus of the illuminated volume, is shown in Figure 6.8(a). It can be seen that there is a factor 2 between the $\{110\}_\beta$ reflections ($2\theta \sim 16.4^\circ$)

and the $\{321\}_\beta$ reflections ($2\theta \sim 44.4^\circ$). The corresponding number of illuminated grains is given in Figure 6.8(b) for the grain sizes calculated before. If we consider that a fraction of $\sim 1/1000$ grains is currently in diffraction condition and thus contribute to the diffraction profile as suggested in [183], it can be seen that the the number of fine grains contributing is significant (about 10^3) while the number of coarse grains is very low (a few ones). On the other hand, the large texture of the material can be seen as a “buffer” with respect to the actual fraction of diffracting grains. Indeed, the IPF of Figures 6.5 and 6.6 suggest that in a particular zone of the sample, a majority of the grains share the same mean orientation. A measured diffraction signal could then be viewed as belonging to a larger amount of grains compared to a completely randomly oriented sample.

In any case, the results of these calculations have to be kept in mind during the analysis of the diffraction peaks, particularly concerning the coarse grain components of the peaks (see Section 6.3.2).



(a)



(b)

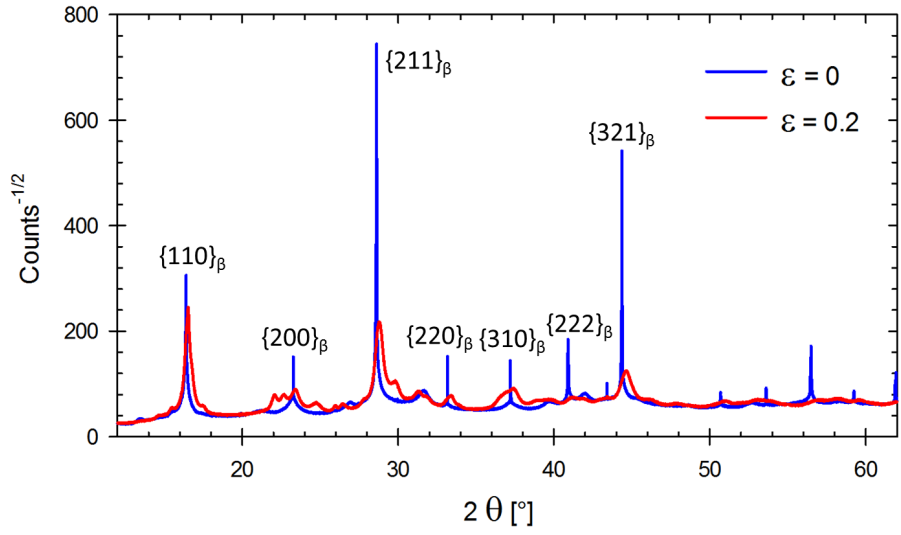
Figure 6.8: (a) Penetration depth in Ti-12wt.%Mo as a function of diffraction angle for $\alpha = 10^\circ$ with the mean position of the diffraction peaks of β phase indicated with black circles and (b) corresponding number of illuminated grains for a fine grains microstructure (red curve) and coarse grains microstructure (blue curve).

6.3.2 Multiple peaks tracking

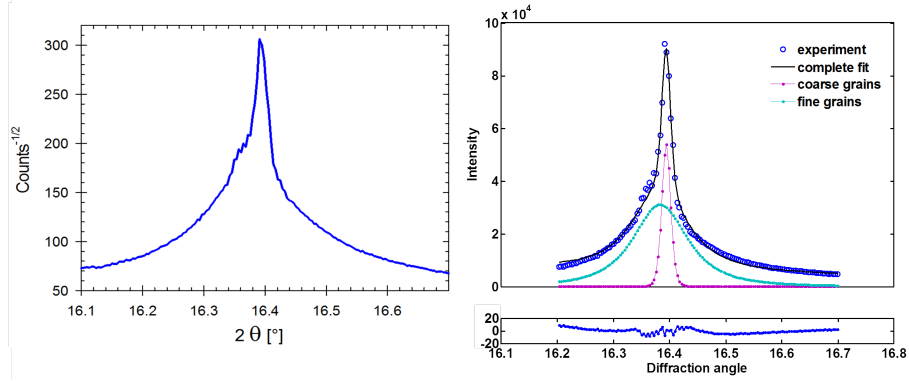
X-ray diffraction pattern of the as-quenched material is shown in blue in Figure 6.9(a). For convenience, the y -axis represents the square root of the intensity. As expected, high intensity β peaks are present, as well as very low intensity ω_{ath} ones. The weak intensity of ω_{ath} diffraction peaks is due to a low volume fraction of the precipitates arising upon quenching from temperatures above β transus [17]. It can be seen that the β highest intensity diffraction peak is the $\{211\}$ reflection. This is consistent with the $\{112\}\langle 110\rangle$ texture derived from EBSD measurement. A closer look at β peaks suggests the presence of 2 components in the shape of the β grain peaks (Figure 6.9(b)). These two components are supposed to come from the inhomogeneous microstructure observed in EBSD. Indeed, XRD peak shape is highly dependent on the diffracting volume size, which is proportional to the grain size, as well as on the defect concentration [189]. The mean lattice parameter in the as-quenched state for the two families of β grains have been calculated by the least square method applied on all β phase diffraction peaks. They are 3.268 Å and 3.27 Å for the coarser (recrystallised) and finer (recovered) grains, respectively.

Figure 6.9(a) presents the diffraction patterns of the as-quenched material and after a strain of 0.2. Extra peaks due to martensitic transformation are clearly seen in the strained material, as well as the peak displacements due to elastic loading of the lattices. The evolution of the integrated intensities of β and α'' diffraction peaks with applied macroscopic strain is presented in Figure 6.10. Once α'' martensite starts to form, its maximum of diffracted intensity is quickly reached (at about $\varepsilon = 0.08$) and stays rather constant up to the failure of the sample.

Due to the two distinct families of grains, the tracking of β peaks has been performed using two fitting peaks, the sharper one corresponding to coarse grains, the broader one to small grains. As already mentioned in Section 6.3.1, the heterogeneous nature of the microstructure could give rise to statistical problems in the case of coarser grains and this point



(a)



(b)

(c)

Figure 6.9: (a) Synchrotron X-ray diffraction patterns of Ti-12wt.%Mo before tensile loading (blue) and at a strain of 0.2 (red) – (b) illustration of splitting of the $\{110\}_\beta$ peak (unstrained pattern) and (c) example of peak fitting with 2 constrained Pearson VII functions.

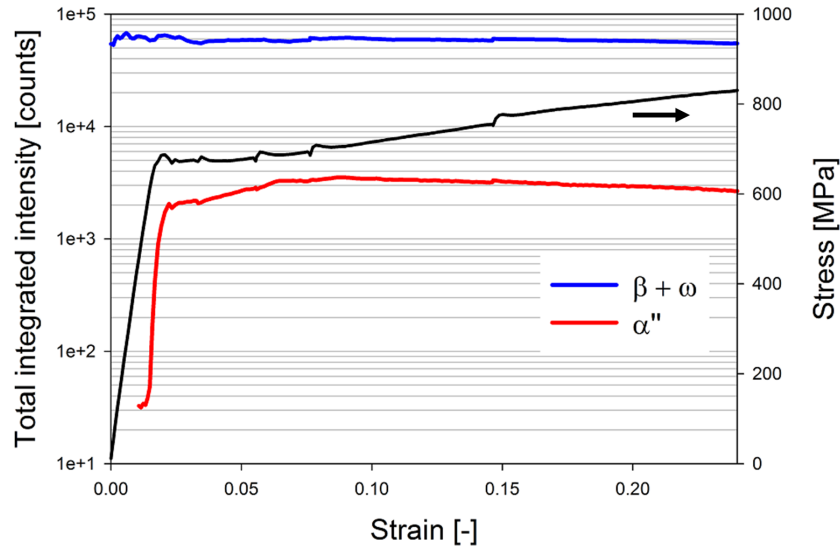


Figure 6.10: Evolution of the sum of diffraction peak integrated intensities with applied strain for the β matrix and α'' martensite.

will be discussed later. Nevertheless, the peak profile analysis allows to obtain parameters of interest such as integrated intensity, full width at half maximum (FWHM) values and peak position for lattice strain calculation. Some examples of multiple peaks fitting results centered on the $\{110\}_{\beta}$ reflection are given in Figure 6.11. Despite the number of peaks, it is seen that the residuals remain in a relatively short interval.

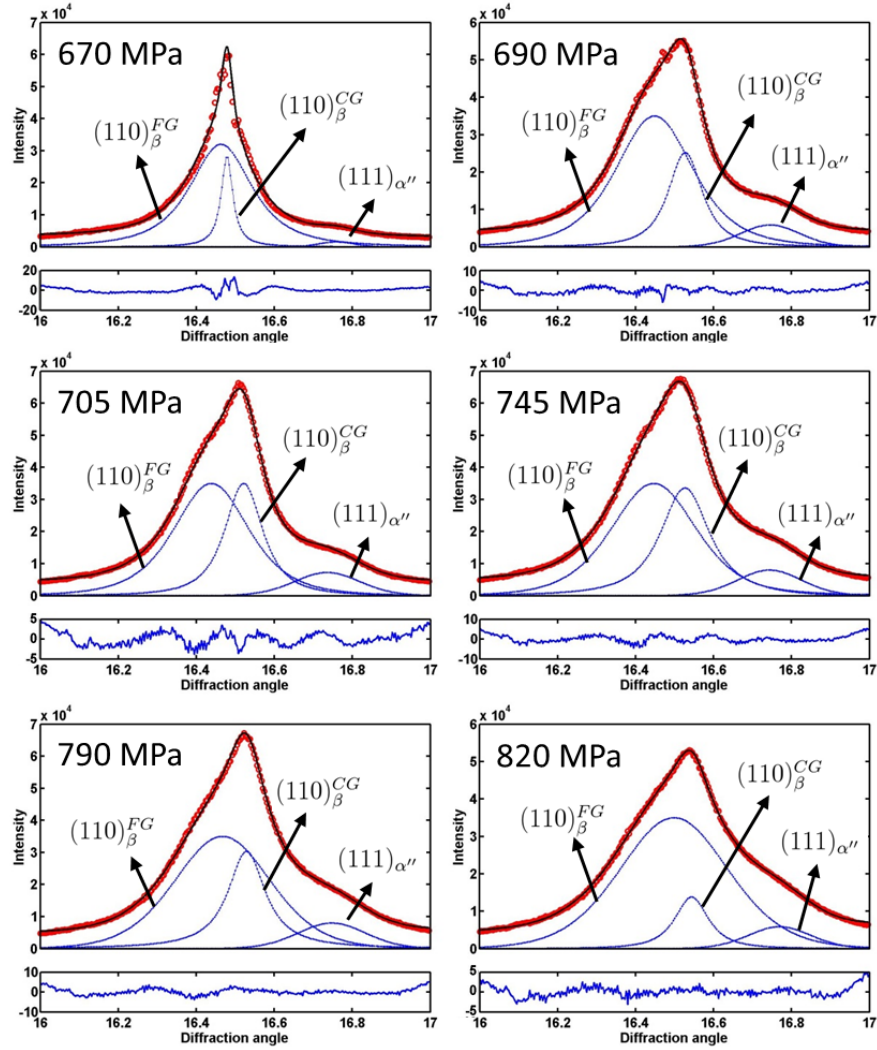


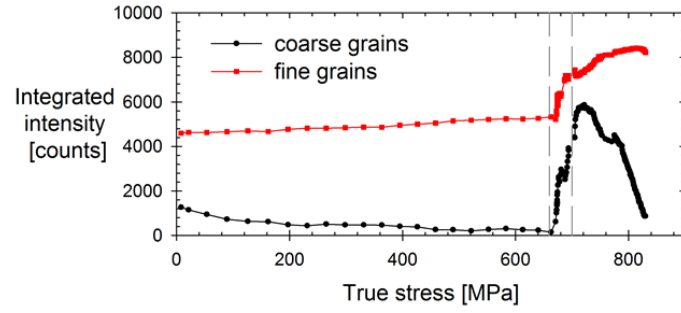
Figure 6.11: Examples of the multiple peaks fitting results centered on the $\{110\}_\beta$ reflection with increasing level of stress.

Evolution of the intensity of the peaks of the β matrix

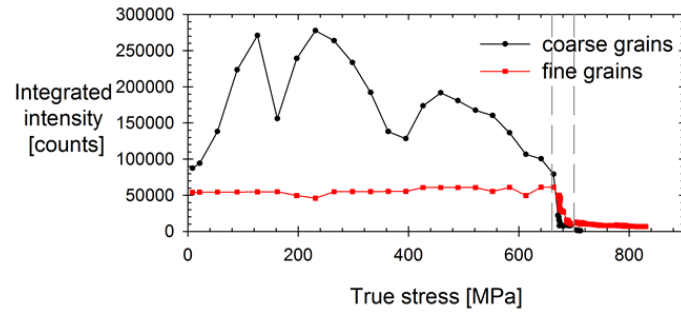
Figure 6.12 presents the evolution of the integrated intensities of the three most intense β reflections, namely the $\{110\}_\beta$, the $\{211\}_\beta$ and the $\{321\}_\beta$ ones. These evolution can be divided into three parts : (i) the elastic regime up to the macroscopic yield stress of 660 MPa, followed by sharp changes between stress levels of 660 and 700 MPa and finally (iii) a monotonous evolution tending to a steady-state in the case of fine grains components. The $\{110\}_\beta$ coarser grain component decreases sharply with increasing stress in this third regime.

Evolution of the FWHM of the peaks of the β matrix

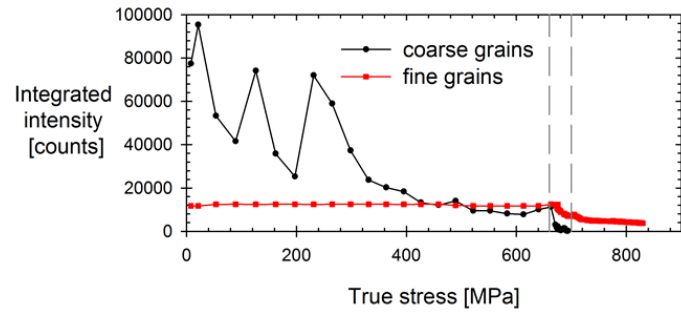
Figure 6.13 shows the evolution of the full width at half maximum of the same reflections as shown in the previous point. Again, these evolutions can be divided into three main parts : (i) the elastic regime with a nearly constant value of FWHM up to the macroscopic yield stress of 660 MPa, followed by (ii) a very sharp increase of the FWHM between stress levels of 660 and 700 MPa and finally (iii) a smoother increase of the FWHM for the fine grains component. The decrease of the FWHM for the $\{110\}_\beta$ coarser grain component is due to the sharp decrease of the peak intensity, as observed in Figure 6.12(a).



(a)

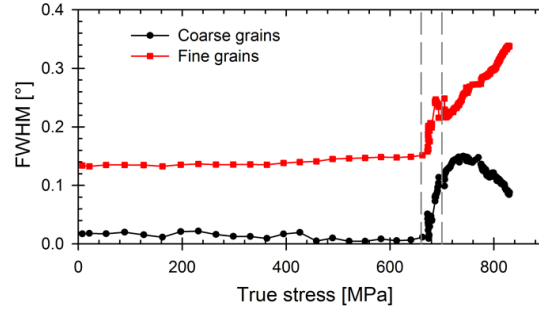


(b)

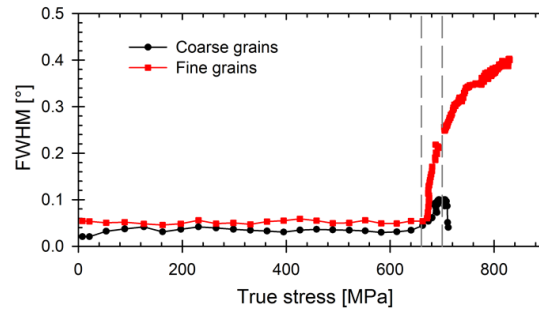


(c)

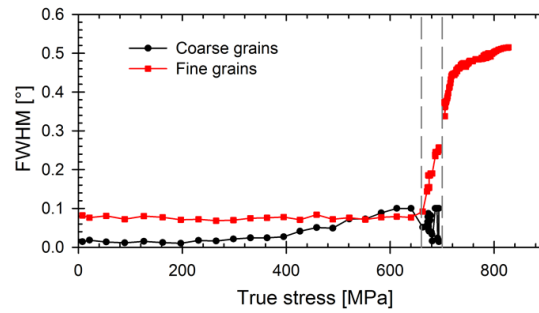
Figure 6.12: Evolution of the integrated intensities with applied tensile stress for (a) the $\{110\}$, (b) the $\{211\}$ and (c) the $\{321\}$ reflections of the β matrix for both families of grains.



(a)



(b)



(c)

Figure 6.13: Evolution of the full width at half maximum with applied tensile stress for (a) the $\{110\}$, (b) the $\{211\}$ and (c) the $\{321\}$ reflections of the β matrix for both families of grains.

Evolution of the lattice strains

The results for the $\{110\}$, $\{211\}$ and $\{321\}$ β reflections are plotted in Figures 6.14, 6.15(a) and 6.15(b), respectively. Again, the lattice strain evolutions can be divided into three main parts : the elastic regime characterised by a linear dependence between ε_{hkl} and the imposed stress, followed by a transition zone with abrupt changes between about 660 and 700 MPa, and finally a monotonic increase of compressive lattice strains up to fracture.

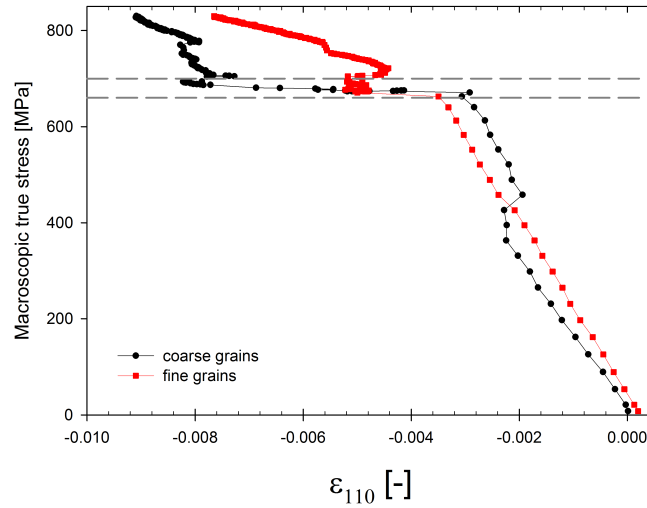
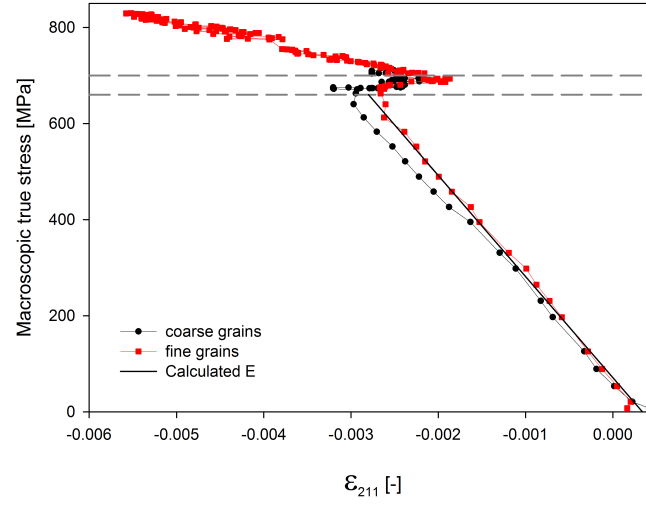
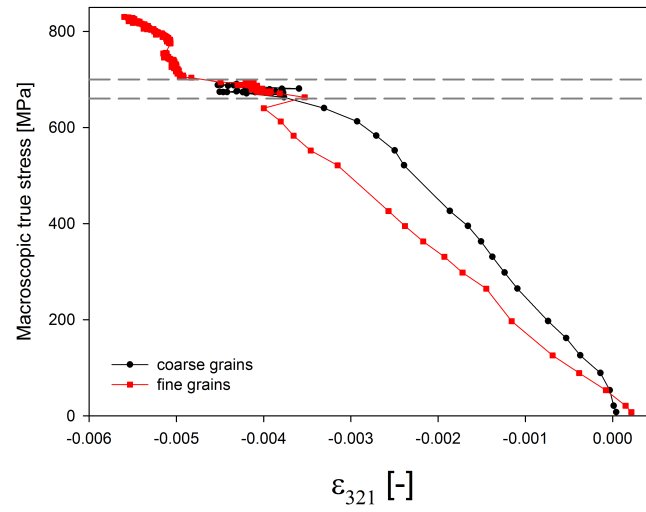


Figure 6.14: *Evolution of the lattice strains of the β matrix with applied tensile stress for the $\{110\}$ family of planes.*



(a)



(b)

Figure 6.15: Evolution of the lattice strains of the β matrix with applied tensile stress for (a) the $\{211\}$ and (b) the $\{321\}$ families of planes.

Finally, the tracking of the integrated intensities and peak positions for several α'' martensite peaks has also been performed during cyclic uniaxial loading/unloading. An example of these evolutions is illustrated in Figure 6.16 for the $(112)_{\alpha''}$ reflection. It can be seen that the diffracted intensity increases during the first few percent of accumulated plastic strain, and then saturates at a rather constant level. Moreover, the peak intensity decreases during the unloading stages, indicating some reversibility of the stress-induced martensitic transformation. Concerning the lattice strains of the α'' phase, it is observed that the lattice strains after unloading of the sample show a departure from the zero level with accumulated plastic strain, meaning that internal stresses build up within the material. It is also worth noting that the lattice strain levels during macroscopic plastic deformation is nearly constant in contrast with the evolution of the β matrix lattice strain.

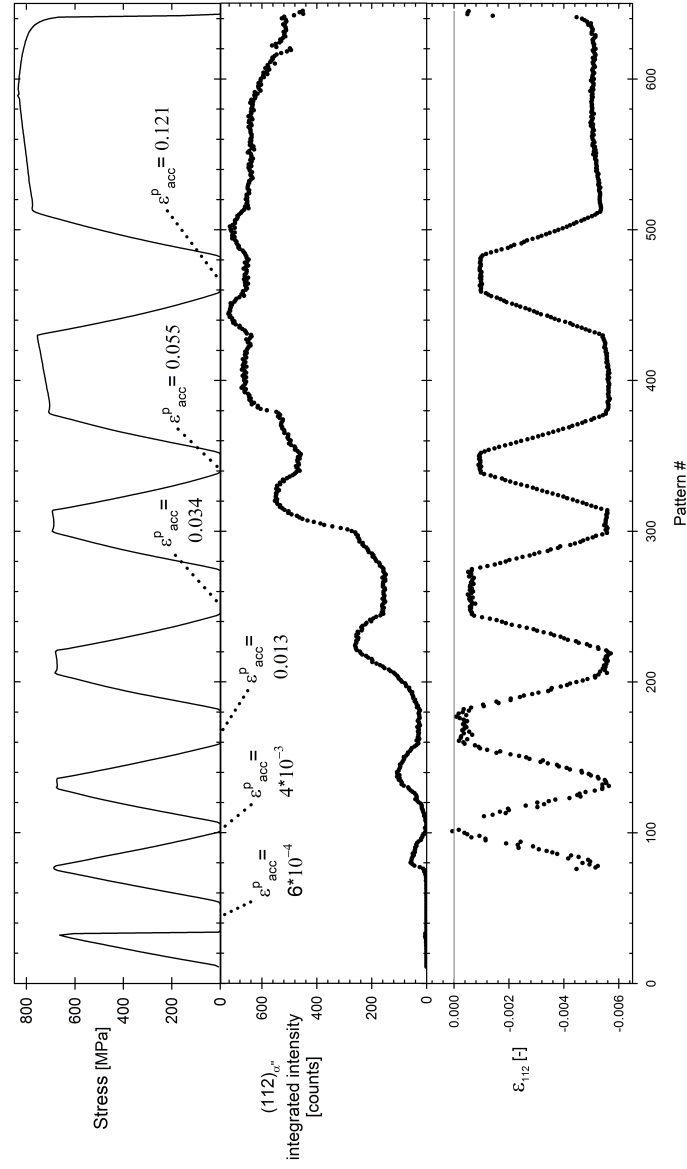


Figure 6.16: Evolution of the integrated intensity and of the lattice strain of the martensite peak (112) during cyclic tensile loading. The accumulated plastic strain is indicated for each unloading plateau.

6.4 Discussion

It was shown in previous chapters that coarse-grained Ti-12 *wt.%*Mo alloy deforms up to 0.35 with high strain hardening due to activation of $\{332\}\langle 113 \rangle$ twinning and martensitic transformation. The appearance and the increase of the proportion of α'' martensite in a bimodal Ti-12Mo grade has been studied during cyclic tensile testing with *in situ* X-ray diffraction, as well as the evolution of lattice strains for both β matrix and α'' martensite. Quantitative tracking of mechanical twinning in the present geometry (transverse 1D diffraction) was considered unachievable and will not be considered in the present chapter. As already mentioned, the XRD setup used in this work does not present a conventional geometry since the sample position is fixed with respect to the incident beam. This intrinsic limitation of the setup can significantly affect the interpretation of the results presented in the previous section. Indeed, illuminated grains in the unstrained configuration can escape the illuminated volume during the tensile test due to Poisson contraction of the sample as explained in details in [183]. If the number of grains participating in a reflection is low and if this number drastically changes between successive diffraction patterns, the observed evolutions of intensities, positions, *etc* cannot be attributed to the global behaviour of the material, but rather to local events.

6.4.1 Evolution of phase proportions and microstructure

Rietveld refinement on several diffraction patterns has been performed in order to estimate the evolution of the phase proportion during tensile loading. Figure 6.17 presents this evolution as a function of the macroscopic true strain. The first appearance of α'' peaks is around 0.01 strain and its proportion seems to quickly reach a saturation value of about 6%. The relatively large error bars on the phase quantification have several origins, the main ones being that the β phase is highly textured (see Section 6.2.1), and that the microstructure is under stress, both leading to difficulties in proper quantitative evaluation [118]. However, the shape of this evolution is similar to the one of the cumu-

lated integrated intensities of the α'' phase, as illustrated on Figure 6.10. It can thus be assumed that the calculation is rather correct. Moreover, previous studies on Ti-12Mo alloy seem to suggest that α'' volume fraction saturates after a few percent of strain [190]. At a strain level of 0.24, about 6% of martensite has formed. Figure 6.18 shows a backscattered electron (BSE) image of the microstructure after fracture. It can be seen that the microstructure is full of deformation bands. The crystallographic contrast given by BSE imaging highlights hierarchical deformation events, as illustrated and discussed in Chapter 4. Due to the high volume fraction of such bands (larger than 50%), it is highly probable that mechanical twinning also occurred in the material in addition to martensitic transformation, since it is a major deformation mechanism in coarse-grained Ti-12Mo alloy. Another interesting feature is the fact that the bands cross the entire microstructure without being stopped at grain boundaries, even when crossing domains of small recovered grains like highlighted by the white arrows. It is supposed that the strong texture, together with a high density of small angle grain boundaries, allows the mechanical twins to develop in neighboring grains. This observation is in agreement with the suggestion of Min et al. that non-favorably oriented grains can still form mechanical $\{332\}\langle 113 \rangle$ twins due to local stress concentration at grain boundaries where twins from neighbouring grains stop [130].

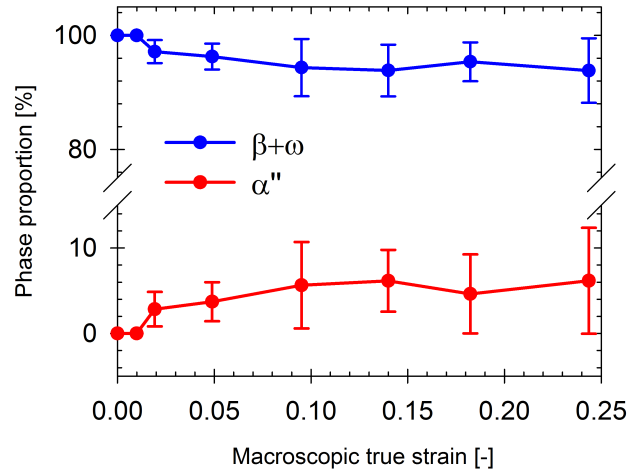


Figure 6.17: *Evolution of phase proportions with applied strain obtained by Rietveld refinement of diffraction patterns ranging from $2\theta = 12^\circ$ to 60° .*

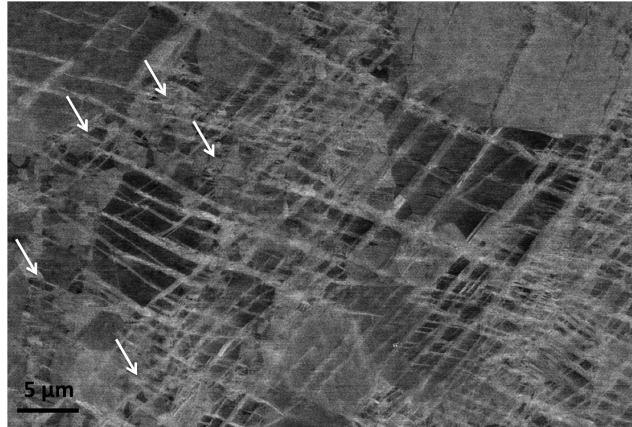


Figure 6.18: *Back-scattered electron micrograph of the sample after fracture. White arrows highlight zones of initial sub-micron recovered grains crossed by deformation features.*

6.4.2 Intensities of the β reflections

As mentioned in Section 6.3.1, the actual number of illuminated grains defines if the observed tendencies can be related to the global behaviour of the material or if it is rather related to a local behaviour (for example, the behaviour of a few grains). The most efficient way to determine in which case we are in is to look at the evolution of the intensity of the diffraction peaks. Indeed, the addition or loss of contributions of diffracting grains should be marked if the number of grains is low. The evolution of the integrated intensities for both families of grains are given as a function of the applied true stress for the $\{110\}_\beta$, $\{211\}_\beta$ and $\{321\}_\beta$ reflections in Figures 6.19, 6.20 and 6.21, respectively. The evolutions are divided into three regimes : (i) the elastic regime, (ii) a transient regime and (iii) a monotonous one up to necking.

In elasticity, the intensities of the finer grains components are more or less constant, so that it can be considered that the number of illuminated grains remains more or less constant. On the other hand, larger variations are observed for the coarse grains component of the $\{211\}_\beta$ and $\{321\}_\beta$ reflections. This is a sign that new grains enter or leave the illuminated volume with a contribution to the entire peak profile which is significant. As a consequence, great care has to be taken during the analysis of their behaviour. However, it is seen that these contributions quickly decrease once the yield stress of the material (660MPa) is reached. Interestingly, the same observation can be done in the case of the fine grains component of these two reflections, as illustrated in the magnifications in Figures 6.20 and 6.21. It is thus reasonable to think that this evolution is a global tendency of the material. Moreover, the evolution is different for the $\{110\}_\beta$ reflection (Figure 6.19). Both fine and coarse components exhibit an increase of the diffracted intensities. This increase can have two origins : either new well oriented grains enter the illuminated volume or new well oriented crystallites appear within the volume. This second origin could be explained by mechanical twinning. Indeed, a change of the ratio of diffracted intensities has been reported in austenitic TWIP steels subjected to high levels of strain [65]. It is thus reasonable to think that changes of β peak intensities can be,

at least partially, attributed to the twinning phenomenon, particularly in the regime where the twinning rate is the highest (see Section 4.4.4). Finally, the evolution of the intensities reaches a steady-state regime, corresponding to true stress higher than 700MPa . This is also coherent with the aforementioned twinning rate evolution. In the case of the $\{110\}_\beta$ reflection, the decrease of the coarse grain component is believed to result from the continuous accumulation of defects in the matrix, leading to the scattering of the X-rays.

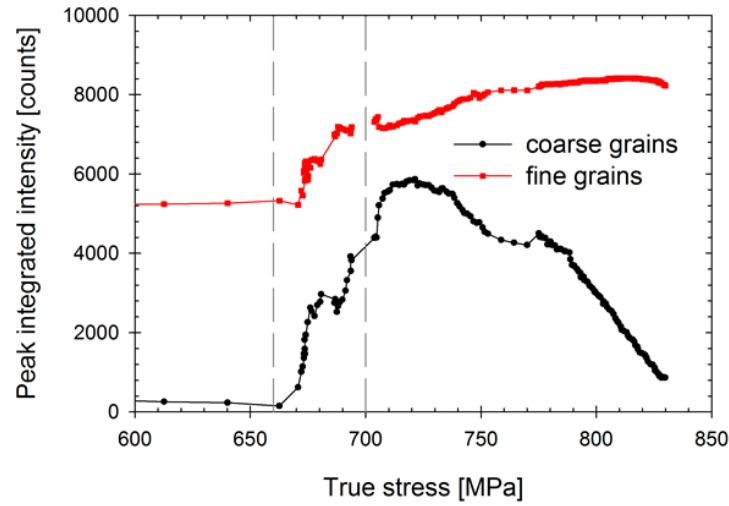


Figure 6.19: *Magnification of the high stress regime of the evolution of the integrated intensity of the $\{110\}_\beta$ reflection.*

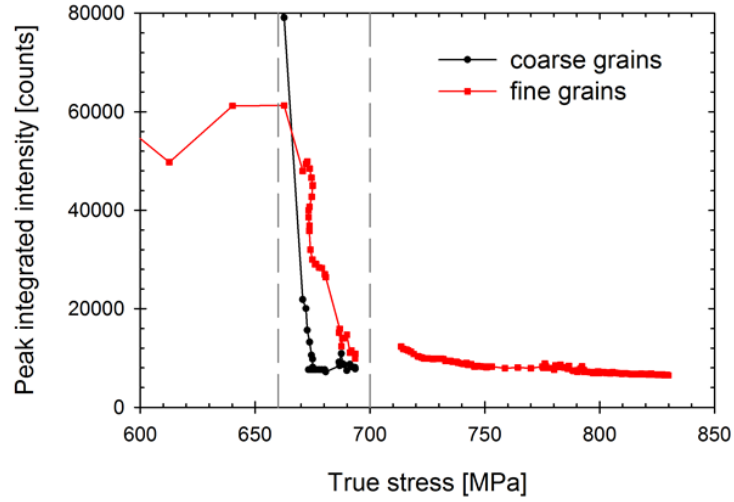


Figure 6.20: *Magnification of the high stress regime of the evolution of the integrated intensity of the $\{211\}_\beta$ reflection.*

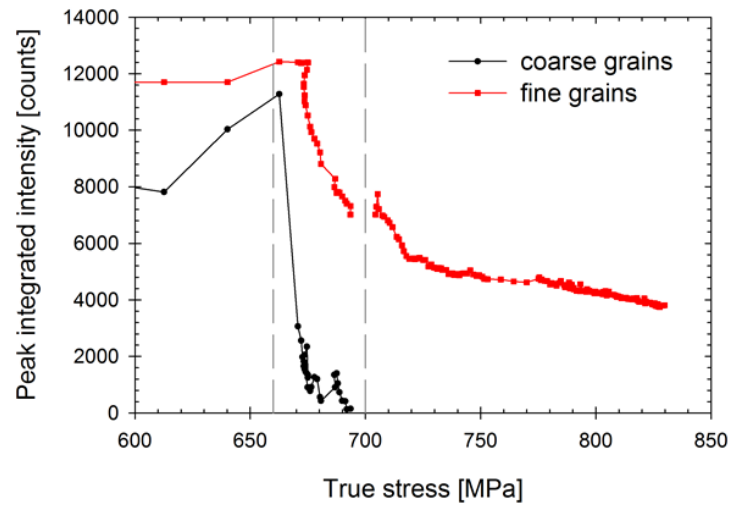


Figure 6.21: *Magnification of the high stress regime of the evolution of the integrated intensity of the $\{321\}_\beta$ reflection.*

6.4.3 FWHM of the β reflections

As already discussed in Chapter 4, the evolution of the full width at half maximum can bring informations regarding the defect density in the material. Indeed, the peak width is essentially the convolution of the resolution function, which depends on the geometry of the setup and on the diffraction angle (see Ref. [183] for more details), with the broadening arising from the defect density in the microstructure. Since the width resolution is fixed for a given 2θ value, the peak broadening is thus directly related to the defect density.

Figure 6.13 gives this evolution for the $\{110\}_\beta$, $\{211\}_\beta$ and $\{321\}_\beta$ reflections as a function of the applied stress. Here again, the three same zones as for the intensity evolution can be separated. In the elastic regime, the FWHM are more or less constant, which is the expected behaviour since there is no new defects. The small changes observed in the case of the coarse grains are attributed to the variations of intensity discussed in the previous point. Once the yield stress is reached, a sharp increase of the FWHM is observed for both families of grains and for the three investigated reflections, except for the coarse grain component of the $\{321\}_\beta$ reflection. This exception is easily explained when looking at the vanishing intensity of this peak in the transient regime (refer to Figure 6.21). This sharp increase is attributed to the fast increase of the dislocation density within the β matrix together with the multiplication of interfaces inherent to the mechanical twinning and SIM transformation phenomena. Finally, the slower peak broadening observed in the third regime is attributed mostly to the further accumulation of dislocations, even though secondary twinning and/or martensitic transformation cannot be completely discarded.

6.4.4 Lattice strains of the β phase

Since only transverse information is available, it is not possible to directly compare the theoretical values of E_{hkl} with the elastic part of the curves. However, since mostly one component is present in the texture, it can be performed for the $\{211\}$ planes. Indeed, most grains have a

$\langle 110 \rangle$ direction parallel to the loading direction, meaning that one of the $\{110\}$ planes is perpendicular to the loading direction. Since $E_{110} = E_{211}$ in a cubic lattice, the observed elastic modulus should be close to the theoretical one. Extrapolated elastic stiffness values from [191] for the Ti-12Mo alloy are the following : $C_{11} = 125 \text{ GPa}$, $C_{12} = 100 \text{ GPa}$ and $C_{44} = 41 \text{ GPa}$. Crystal plasticity simulations² based on Taylor assumption (all grains undergo the same deformation) have been performed on a non-textured polycrystalline aggregate of 10000 grains and resulted in Young's modulus of 82 GPa, which is very close to the value obtained from experimental data. In comparison, the same simulations with the ALAMEL model [192] resulted in a value of 78 GPa. It is worth noting that the Taylor value is a upper boundary for the mean Young's modulus. Since the calculated values are very close to the experimentally observed ones, the extrapolation of the components of the elastic stiffness tensor can thus be reasonably validated. Moreover, it has been proposed that a small value of C'^3 , which is the case here, could be the origin of martensitic transformation in several systems [110]. The calculated value of E_{211} is 72 GPa with these elastic constants, and is plotted in Figure 6.15(a) for comparison with experiment. It can be seen that theoretical values match very well the experiment for that orientation.

Once the yield point is overcome, a transition zone with an unusual behaviour seems to arise in the three investigated families of planes. The stress interval delimiting this zone corresponds to the stress/strain levels where three deformation mechanisms act synergistically, dislocation glide, mechanical twinning and SIM transformation. In the present experiment, this transient zone corresponds to true stress levels ranging from 660 to 700 MPa. Magnifications of this zone for the three investigated β reflections are presented in Figures 6.22, 6.23 and 6.24, respectively.

²with help of Ir. Gueric Lemoine

³ $C' = \frac{C_{11}-C_{12}}{2}$

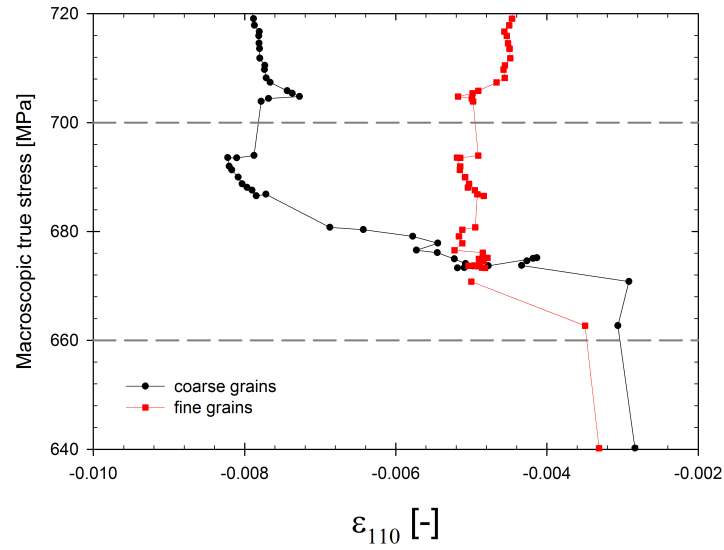


Figure 6.22: *Magnification of the transient zone of Figure 6.14.*

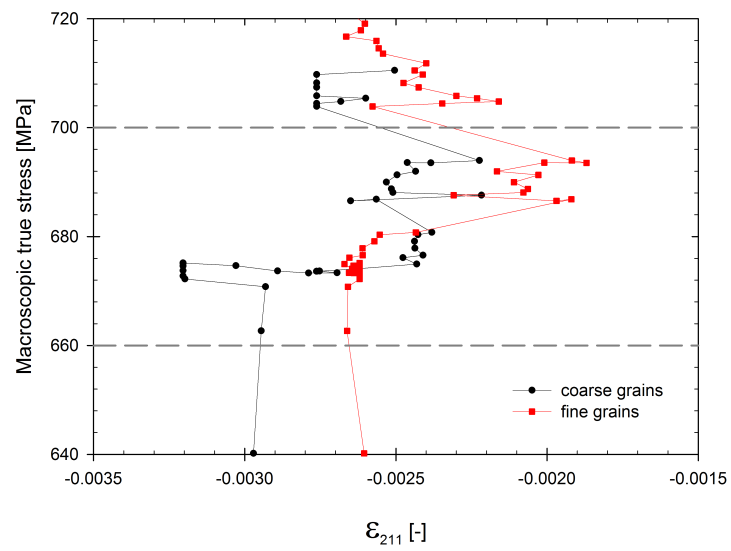


Figure 6.23: *Magnification of the transient zone of Figure 6.15(a).*

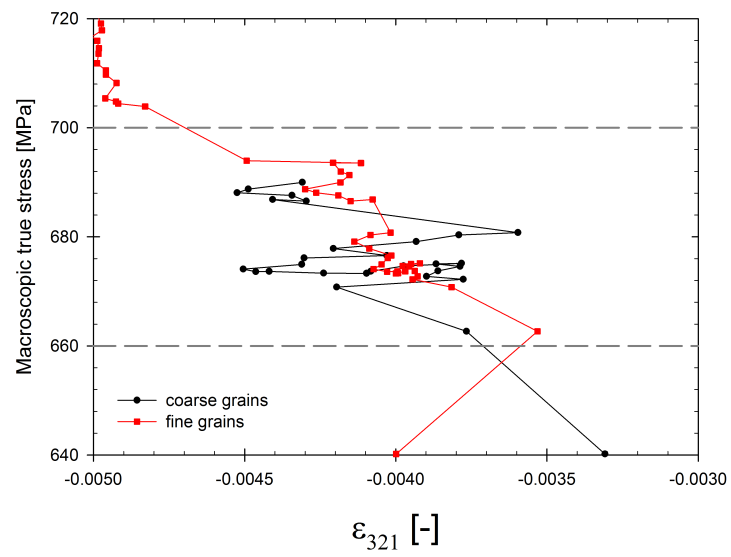


Figure 6.24: *Magnification of the transient zone of Figure 6.15(b).*

For the $\{110\}$ planes, the behaviour of the two families of grains is rather different. An increase of the imposed stress is not accompanied by an increase of the lattice strain of the finer (recovered) grains. These grains thus seem to show no or few strain hardening in this stress interval, while a large increase of lattice strain is observed in the case of the larger (recrystallised) grains. This difference in behaviour is believed to come from the triggering of mechanical twinning in the coarser grains first due to a lower CRSS for twinning (proportional to the inverse of the square root of the grain size). This is coherent with the observed increases of both intensity and FWHM of this reflection, as shown in Figures 6.19 and 6.13(a), respectively. The increasing density of interfaces, together with large amount of dislocations observed at the twin/matrix boundaries (Chapter 4) would induce significant strain gradients in the microstructure whose signature would be seen during SXRD measurements.

For the $\{211\}$ planes, the evolutions are qualitatively similar. Indeed, both families of grains exhibit steps of roughly constant lattice strains compared to the $\{110\}$ case. An hypothesis for explaining this behaviour could be the progressive activation of SIM transformation, each step representing the crossing of the energy barrier depending on the orientation of the parent grain. Indeed, the orientation relationship between β and α'' phases includes a $(110)_{\alpha''}/(112)_{\beta}$ correspondence, so that the transformation from one lattice to the other could induce instantaneous lattice tension/compression depending on the α'' variant activated. However, no significant changes in the diffracted intensity (see Figure 6.20) have been observed to support this hypothesis. Another explanation would be that the number of diffracting grains is too small to be statistically accurate, and that the behaviour of only a few grains is probed in this case.

Finally, concerning the $\{321\}$ planes, the finer grains exhibit a slightly monotonic hardening, while the evolution for coarser ones is more erratic. This erratic evolution is attributed to the vanishing of the diffraction peak of the coarse grains, as suggested by the intensity evolution in Figure 6.21. The monotonic evolution of the fine grains lattice strain is coherent with the large hardening capacity of the *BCC* matrix of the

studied alloy.

Once the transition zone is overcome, it was not possible to distinguish the two diffraction peaks after some plastic strain in the case of the $\{211\}$ and $\{321\}$ families, and only one peak was used for the fitting from these points. This choice has a straightforward explanation : as it can be seen on the BSE image of the microstructure after failure, the grains are full of deformation bands (mostly mechanical twins and α'' martensite plates). It is reasonable to think that a dynamic grain refinement occurs in the material, leading to peak broadening. This is also clearly supported by the evolution of the diffracted intensities. It has been shown in Chapter 4 that the volume fraction of primary events (massive $\{332\}\langle 113 \rangle$ twinning) reaches a saturation value after about $\varepsilon = 0.1$, which corresponds approximately to a true stress level of 700 MPa. After a stress level of 720 MPa, a monotonic increase of the lattice strain is observed. The hardening rate above this stress level is very high compared to what is usually reported in similar studies on more conventional materials with plasticity driven by dislocation glide only [193, 194]. Since the amount of martensite already reached its saturation level, the monotonic hardening of the β phase is supposed to result mainly from an intense dislocation activity as well as from secondary twinning, *i.e.* formation of twins inside the primary twins. Very recently, Gauss *et al.* [195] studied the appearance and evolution of strain-induced martensite in an austenitic steel. The evolution of the lattice strain in austenitic phase is similar to the one reported here for the β matrix. Since the amount of martensite is quite different between the two materials, it is supposed that the effect of both martensitic transformation and mechanical twinning on the lattice strains within the matrix is similar. This observation is logical when considering these two phenomena as sources of new interfaces that act as dislocation barriers. This will result in large amount of dislocation pile-ups throughout the entire microstructure, responsible for the observed increase of lattice strains in the matrix. Moreover, the possibility that both phenomena are intimately linked goes also in that sense (see Chapter 4). Figure 6.25 finally highlights the development of residual stresses after unloading in the three families of β planes investigated during cyclic loading. The evolu-

tion shows two main parts : the first one, up to about 0.05 accumulated macroscopic strain, shows erratic evolution while the second is monotonic up to fracture of the specimen. The first part is attributed to the fast increase of both mechanical twin volume fraction and phase transformation, which can both induce variations of internal elastic stresses (this point will also be discussed in Chapter 7). In the second part, all the investigated peaks develop compressive residual stresses. Since the mechanical balance must be zero in the unloaded state, there must exist families of grains that are in a tensile state. Also, mechanical twinning could be responsible for this observation, since the change of orientation in the twins implies that part of the previously well-oriented grains does not satisfy Bragg's law anymore and will thus not participate to the diffracted signal. Finally, the anisotropy of the cubic lattice has to be taken into account as well. Indeed, the elastic anisotropy is quantified by the elastic anisotropy factor A , defined by :

$$A = \frac{C_{44}}{C'} \quad (6.3)$$

In unstable β titanium alloys, the term C' , representing the elastic shear modulus, can show abrupt changes in a very narrow composition range [196]. It has been proposed that the decrease of C' , widely observed in various systems presenting a martensitic transformation, originated from a phonon softening mechanism that induces lattice modulations [110, 143]. With the elastic constant used previously, the A parameter reaches a value of 3.28. This high value of anisotropy could result in a non-negligible stress-partitioning between the β grains during tensile loading. Indeed, large difference in stiffness between neighbouring grains will bring stress accommodation between them in order to reach mechanical equilibrium once the external load is removed. Finally, the aforementioned formation of dislocation pile-ups on continuously created interfaces is also a source of residual strains in the unloaded material.

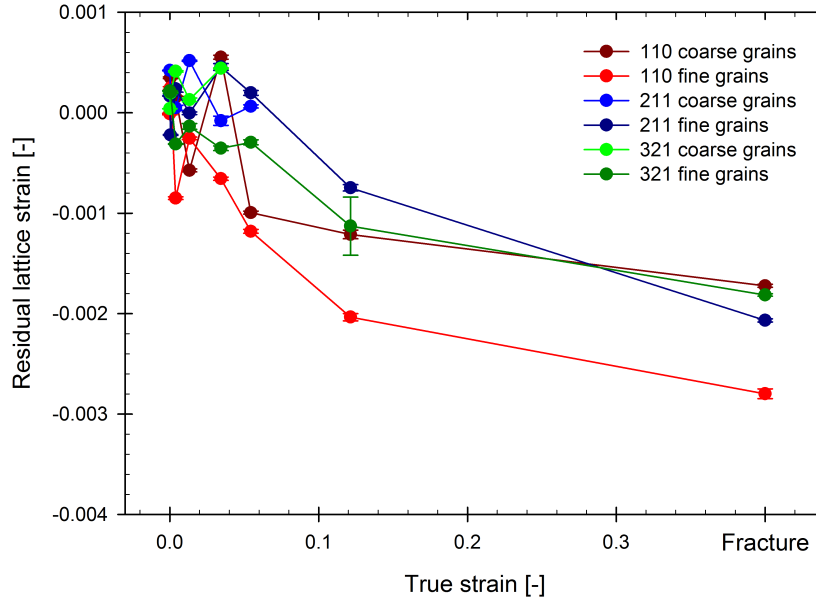


Figure 6.25: Evolution of the residual strains after unloading in the β matrix for both families of grains with accumulated plastic true strain.

6.4.5 Stress-induced martensite

The sample was tested upon cyclic tensile loading. The evolution of the integrated intensities of several α'' peaks has been monitored *in situ* during the experiment⁴. An important observation was that some amount of martensite was reversible when the sample was unloaded, and the proportion of reversibility decreases with accumulated plastic strain, as illustrated in Figure 6.26. At the onset of plasticity, about 90% of the martensite underwent reverse transformation, and this amount quickly decreases as the material accumulates plastic deformation. At a strain level of 0.12, the reversible fraction is barely 15%.

⁴The errors bars correspond to the standard deviation of the integrated intensities of the martensite peaks after unloading, since the sample was kept unloaded during a given time between two loading cycles.

This decrease of reversibility is attributed to the pinning of β/α'' interfaces by dislocations which hinder the reverse transformation when the stress is removed. This phenomenon is well known in the case of superelastic materials and shape memory alloys [197]. Since the density of dislocations increases with plastic deformation, the amount of dislocations at the interfaces matrix-martensite becomes critical for the reverse transformation to happen.

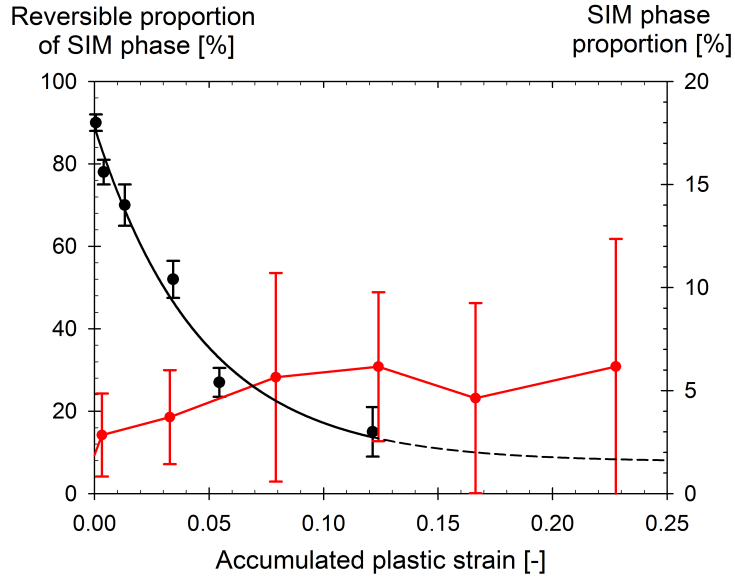


Figure 6.26: *Evolution of the fraction of reversible martensite with accumulated plastic strain during cyclic tensile loading. The evolution of the SIM phase proportion is also given for comparison.*

Since the α'' phase cannot be stabilised at room temperature without the application of an external stress in the present chemical composition, the estimation of the unstrained α'' lattice parameters is needed in order to calculate the lattice strain evolution. The following method has been used.

Once α'' diffraction peaks remain after unloading, the residual strains in the two β phase components have been evaluated based on d_{hkl} . It

was also supposed that the $\{211\}$ planes are representative of the mean behaviour of the BCC lattice [198]. Based on these calculated residual strains in the β matrix, a mixing law has been applied with Hooke's law of elasticity following Equation (6.4) in order to estimate the residual strains in the α'' phase after unloading :

$$\sigma^{macro} = 0 = \frac{E_{\beta}}{\nu_{\beta}} [f(\beta_{CG})\varepsilon_{\beta_{CG}}^{res} + f(\beta_{FG})\varepsilon_{\beta_{FG}}^{res}] + f(\alpha'')\sigma_{\alpha''}^{res} \quad (6.4)$$

with :

- $E_{\beta} = 80GPa$
- $\nu_{\beta} = 0.34$
- $f(\beta_{CG}) = 0.54$
- $f(\beta_{FG}) = 0.45$
- $f(\alpha'') = 0.01$
- $\varepsilon_{\beta_{CG}}^{res} = 1.84 \cdot 10^{-4}$
- $\varepsilon_{\beta_{FG}}^{res} = -2.2 \cdot 10^{-4}$

The fractions of each β phase components are based on the ratio of the integrated intensities of the two $\{211\}$ peaks, and the fraction of martensite is based on a Rietveld fitting after unloading. It follows that the level of residual stresses in the α'' martensite in the second cycle of loading-unloading did not lead to a significant level ($\approx 10 MPa$), and so the $d_{hkl}^{\alpha''}$ stabilised during the first unloading plateau where α'' peaks are observed are used to fit the lattice parameters of unloaded martensite. It corresponds to the second cycle, since some peaks were slightly remnant after this cycle, like in the example of Figure 6.16 where the results for the (112) reflection are presented. The residual strains in the different hkl planes of α'' are relatively small after the third cycle, which validate the methodology for estimating the unstrained lattice

parameters. The least square calculation results in the following lattice parameters for α'' martensite : $a = 3.087$, $b = 4.912$ and $c = 4.642$ (Å), which are of the order of what is found in other metastable $\beta - Ti$ alloys [199].

With the estimation of the unstrained lattice parameters, the evolution of lattice strains can be calculated. Figure 6.27(a) illustrates these evolutions for several planes of α'' phase. For all reflections, the evolution of the martensite lattice strains shows a rather constant value with increasing macroscopic load from the end of martensitic transformation (after 700 MPa) up to the failure of the material. An hypothesis explaining this observation would be that the martensitic phase presents no or nearly zero work hardening during further tensile loading, hence it has a nearly perfect plastic behaviour. This does not seem to be consistent with the results of Wang *et al.* on a Ti-11Zr-14Nb-10Sn (wt.%) alloy [116], where a high strengthening of the material was observed during loading. However, in their case, the material was already 100% martensitic in the unstrained condition so that the nature of α'' martensite was not exactly the same. This could explain the different behaviour upon mechanical loading. Moreover, the α'' phase has been considered as a transition state during the $\{332\}\langle 113 \rangle$ mechanical twinning in Chapter 4. The lack of hardening could derive from the further transformation to the final β^T orientation. It is thus believed that, besides its role in the mechanical twinning process, the α'' martensite plays mainly a role of dislocation sources, as well as barriers for further motion in the β matrix, causing its hardening and explaining part of the lattice strain evolution observed. The evolution of the FWHM of the α'' peaks is shown in Figure 6.27(b). It can be seen that all reflections exhibit a large initial increase in the transient regime (660-700 MPa), followed by a small increase with applied stress compared to the evolutions observed in the case of the β matrix (see Figure 6.13). The initial large values are thought to come from both a small diffracting domain size as well as a broad distribution of stress states within the different precipitates. Another possible explanation would be the inheritance of the defect concentration of the matrix coming from the phase transforma-

tion mechanism. The evolution of FWHM can be divided into 2 parts : between 660 MPa (the appearance of α'' phase) and about 700 MPa, corresponding to the maximum value of the strain hardening rate (see Chapter 3), and from 700 MPa up to necking of the sample. The first regime is characterised by a higher broadening rate than the second regime. There may be different reasons explaining the quick broadening in the first regime, for instance the continuous nucleation of new martensite domains with different stress states or the formation and accumulation of new defects in α'' martensite (dislocations and/or twins). Indeed, the evolution of lattice strains in this range of applied stress also shows variations with stress (see Figure 6.27(a)). Beyond 700 MPa, the FWHM evolution becomes really smooth. Since a very high plastic activity occurs in the β matrix, it is believed that this broadening comes mostly from continuously developing strain gradients between the two phases.

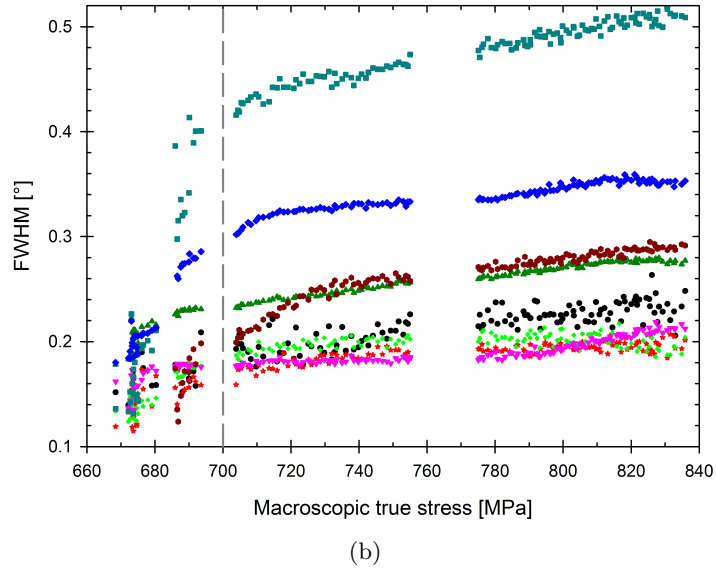
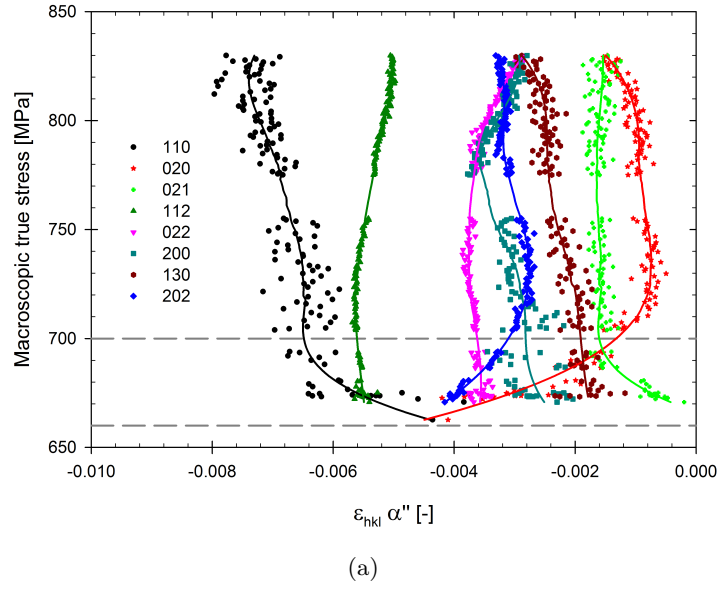


Figure 6.27: Evolution of (a) lattice strains and (b) FWHM of various peaks of α'' martensite with applied tensile stress.

A final remark concerning the SIM α'' phase is that the shape of the precipitates is not known a priori. If the precipitates are elongated, their mechanical response will be highly dependent on their orientation regarding the imposed stress direction. Many authors focused on homogenisation models for predicting the mechanical response of inclusions in a deforming matrix [200–202] since the seminal work of Eshelby [203]. However, most of them focussed on hard elastic inclusions within an elasto-plastic matrix, and the predictions are mostly aimed at the fracture initiation mechanism (debonding and/or inclusion cleavage). However, some results of these theories can qualitatively be taken into account for the discussion of the present case. Lee and Mear studied the effect of several parameters on the stress concentration around an elastic spheroidal particle in a plastically deforming matrix [204]. Among these parameters, some of their conclusions are of particular interest here :

- The interface stress concentration factor is independent on the Young's modulus ratio of the two phases at large effective strain, which seems to be a reasonable hypothesis in this experiment. Moreover, the Young's modulus of β and α'' phases should not be as different as the cases they used in their modelling.
- The aspect ratio of the particle (w^p) as well as its orientation regarding the loading state is of primary importance. The effect of the particle shape on the interfacial normal tension for uniaxial loading along the particle length is illustrated in Figure 6.28.

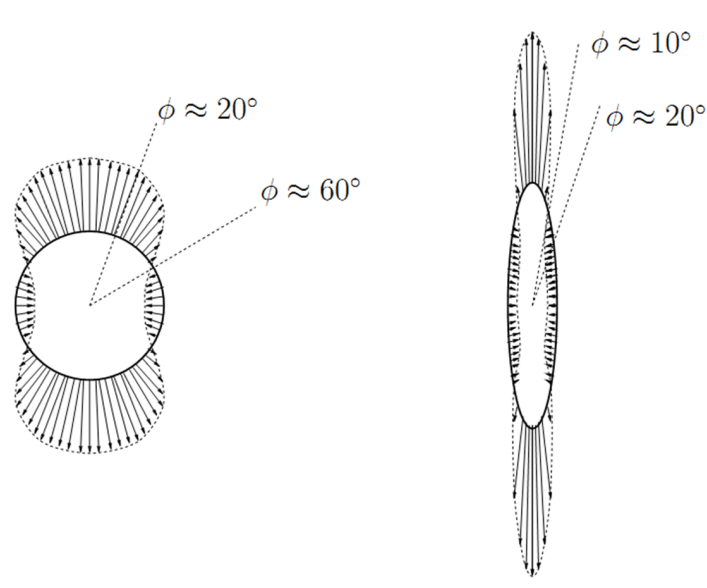


Figure 6.28: *Distribution of interfacial normal tension around a particle (left : $w^p = 1$ and right : $w^p = 7$) in an elasto-plastic matrix under macroscopic uniaxial tension [205].*

If the results may extend to plastic inclusions, at least qualitatively, one can see that the compressive state in the direction parallel to the X-ray beam in a particle aligned with the tensile direction is decreased. Hence, a more detailed analysis of the shape and orientation distribution of the α'' precipitates has to be performed to ensure the other conclusions concerning the plastic behavior of the martensite in Ti-12wt.%Mo.

6.5 Conclusion

The stress-induced martensitic transformation as well as the hardening behavior of both the β matrix and α'' martensite have been monitored during *in situ* tensile testing using synchrotron X-Ray radiation. The following conclusions arise from this investigation :

- SIM transformation occurs in as-quenched Ti-12wt.%Mo at the onset of plasticity and quickly reaches a **saturation value of about 6%**. However, due to the high texture of the sample together with a low statistics concerning the coarser grains, this amount of martensite could be underestimated and other characterisation tools should be used to ensure this results. A large amount of martensite seems reversible as long as the accumulated plastic strain remains small, and reversibility is hindered with increasing plastic deformation. **Mechanical twinning does not seem to be affected by the heterogeneity of the initial microstructure.**
- β matrix sustains a large amount of hardening during the whole plastic deformation stage. It is believed that the simultaneous occurrence of dislocation glide, mechanical twinning and SIM transformation is responsible for the abrupt changes of lattice strains observed between 620 and 700 MPa. After this point the evolution becomes monotonic, while having an unusual hardening rate. This high hardening rate has been attributed to the **dislocation pile-ups forming on the continuously created interfaces** (both β twin/matrix and α''/β ones).
- Martensite precipitates seem to exhibit a **behaviour close to the one of a perfectly plastic material**. However, more informations are needed to confirm this hypothesis. Particularly, the same experiment with a 2-dimensional detector could provide the axial lattice strains that are necessary to validate these conclusions. It is believed that the martensite mainly plays a role of dislocation sources and barriers in the global work-hardening of the material, the ductility of the material being way too large compared to the transformation strain. Moreover, the peak broadening of the martensite reflections is clearly low compared to β matrix ones. The involvement of α'' in the twinning process could also be the cause of this lack of hardening.
- The TRIP effect in titanium alloys has a different nature compared to TRIP steels. Indeed, α' martensite in steels acts as a reinforcing

phase which will sustain a high load nearly elastically, while in the case of titanium, martensite seems to have a **plasticity enhancer role** instead of bringing additional load carrying capacity. A more detailed analysis of the α'' particles has to be performed to validate these two last conclusions.

Chapter 7

High Angular Resolution - EBSD characterisation of strain-induced interfaces

The work of the present chapter has been carried out in close collaboration with Dr. Jon Alkorta from CEIT, University of Navarra.

In the previous chapters, the different contributions to work hardening of Ti-12wt.%Mo that have been considered are mostly the amount of mechanical twins, the amount of martensite and the intrinsic hardening of both β and α'' phases along plastic deformation. Besides the increasing density of defects leading to dislocation creation and anchoring, the continuous formation of new interfaces in the material is also associated with the formation of strain gradients. These strain gradients are thought to be of great influence in the global work hardening behaviour of nanostructured materials. It is thus of great importance to quantify the magnitude of the strain gradients that appear within Ti-12Mo. In order to achieve this goal, a tool able to probe the stress field at the nanoscale has to be designed. The first insights in the mapping of the absolute stress field in the vicinity of stress-induced interfaces are achieved in this chapter.

7.1 Introduction

Determination of inter- and intragranular elastic strains, and thus stresses, in crystalline materials has always been of great importance for understanding their mechanical behaviour. However, it remains an issue due to the lack of accurate technique. Indeed, a resolution of the order of 10^{-4} radians is required for elastic strain measurement to be of practical use [206]. The origin of these strains/stresses can arise from several phenomena : mismatch of thermal expansion coefficient in multiphase materials or composites, stress partitioning between phases and/or crystalline orientations during mechanical loading, strain gradients during processing, etc. An interesting review of the role of residual stress in the behaviour of materials has recently been published by Withers [207].

Experimental measurement of internal strains by X-ray diffraction is known for nearly a century since the pioneer work of Lester and Aborn in 1925 [208], and it remains nowadays the most widely used technique. However, it consists in a mean measurement on several well-oriented grains, meaning that both differences of behaviour of the different grains and strain gradients inside them are hidden in the global diffraction peak displacement. The emergence of other more angularly resolved techniques in the last decades allows now the determination of strains inside one grain of the polycrystal. Among these techniques, one can cite CBED (Convergent beam electron diffraction) in TEM with the problems linked to thin foils ; Laue microdiffraction with synchrotron facilities, so hard to access on a regular basis ; Kossel microdiffraction with a limited spatial resolution of several microns [209] ; and finally Electron Back-Scattered Diffraction (EBSD). Since the beginning of its commercial availability, EBSD has been largely improved, allowing now the mapping of wide regions in a relatively short time. The spatial resolution of this technique has reached a few tens of nanometers depending on the electron source, the accelerating voltage and the investigated material. However, the angular resolution of the classical indexation through Hough transform is limited to $1 - 0.5^\circ$ [210]. This resolution is not high enough for determining elastic strains and crystal rotations since it is of the same order of magnitude as the investigated

phenomena. Recently, Wilkinson proposed a method based on digital image correlation (DIC) technique on Electron Back-Scattered Patterns (EBSP) to improve the angular resolution of the technique down to 10^{-4} radians [206], allowing accurate determination of microstrains and small lattice rotations [211]. However, this approach suffers from several limitations :

- each orientation needs a reference pattern that is assumed to be “stress-free”, meaning that the stress states calculated are only relative ones ;
- only small shifts in EBSPs can lead to solutions through DIC analysis.

To overcome the first drawback, some authors proposed to use simulated Kikuchi patterns [212–214]. In this case, absolute stress states can be measured theoretically. Alkorta [215] studied the effects of a wrong pattern center (PC) calibration with the use of simulated patterns and showed that different combination of strain states and PC locations can lead to the same phantom stresses, rendering the calculation of internal stresses wrong. Simulation-based HR-EBSD must thus be performed with great caution in a very finely calibrated system.

The second point is trickier to manage. Indeed, it means on the one hand that only small displacement gradients can be obtained, and on the other hand, that the measurement has to be intragranular. This second issue, added to the uncertainty on the actual state of the reference point, brings large difficulty in the estimation of the absolute stress/strain state in a polycrystal, as well as the densities of Geometrically Necessary Dislocations (GND).

Since a few years, several materials have been investigated by EBSD-based methods to retrieve GND densities at a microscopic scale. Kysar *et al.* studied wedge-indented *FCC* single crystals [216, 217] with conventional EBSD and recently applied Nye-Kröner-Bilby dislocation theory to decompose the total GND density in individual dislocation types [218]. Wilkinson *et al.* performed the same kind of analysis

on coarse grained *Fe* with HR-EBSD [219]. They reached a noise level of $\pm 10^{12} \text{ m}^{-2}$ for GND density compared to $\pm 10^{14} \text{ m}^{-2}$ for standard Hough-based analysis, illustrating well the efficiency of this new technique. Karamched *et al.* analysed thermally and mechanically induced strains and rotations near a carbide inclusion in a *Ni* superalloy [220]. They showed that the content of GND is much larger in the neighborhood of the hard inclusions compared to the rest of the *Ni* matrix. A similar study has been carried on by Littlewood *et al.* on a polycrystalline *Ti - 6Al - 4V* alloy and they found high density zones of GND located in the vicinity of the retained β grains due to accommodation of transformation strain [221]. In a recent investigation, Jiang *et al.* showed that large (mesoscopic) GND density maps can be acquired by changing some parameters like the EBSD binning or step size without reducing too much the accuracy of the measurements [222, 223]. It should be noted that most of these studies are related to the same team of A. Wilkinson.

In this work, a new hybrid approach of DIC applied to EBSD has been implemented and tested on a slightly plastically deformed Ti-12Mo alloy. The interfaces between the β matrix and plates of α'' martensite or $\{332\}\langle 113 \rangle$ twins were investigated. With assumptions based on the determination of the habit planes of these interfaces, the components of the elastic strain tensor components were calculated and mapped around the interfaces, allowing the calculation of residual elastic stress state in the material. The densities of Geometrically Necessary Dislocation (GND) were extrapolated from lattice rotations owing to Nye tensor.

7.2 Experimental procedure

EBSD scans were performed with a field emission gun scanning electron microscope (FEG-SEM) Jeol JSM-7100F equipped with Oxford Nordlyss II camera with acquisition software HKL Channel 5. The accelerating tension was 15kV with a step size of 100nm. The Kikuchi patterns were recorded with highest resolution, longest acquisition time without CCD saturation and no binning for cross-correlation calculation.

The present approach is an hybrid method combining both simulated EBSP and experimental ones, which allows the absolute measurement of lattice rotations and elastic strains in both intra- and intergranular scenarios. It is the result of a collaboration with Alkorta from CEIT.

7.2.1 Simulation-based DIC

There exist two kinds of simulation for EBSP. The first one are Bragg (or kinematic) simulations which can be computed efficiently, but where intensities are quite different from actual experimental EBSP. The second kind of simulation is based on the dynamic theory of electron diffraction (taken into account, for example, the effects of multiple scattering within a crystal) [224]. Dynamic EBSP are much closer to experimentally observed ones, but their generation requires powerful computational resources.

In this approach, kinematic EBSP are used, and the fitting is not performed on the patterns themselves, but on a gradient image of the patterns. This approach was initially suggested by Tzimiropoulos *et al.* for estimation of translations, arbitrary rotations and scale factors on two different images of the same object [225]. New patterns are created by deriving the intensity of each pixel along x and y of both experimental (G_{real}) and simulated (G_{simu}) patterns. An example of the gradient images obtained by this method is shown in Figure 7.1. If the initial patterns clearly show large differences, it can be seen that it is not the case anymore for gradient ones, particularly concerning the background intensities.

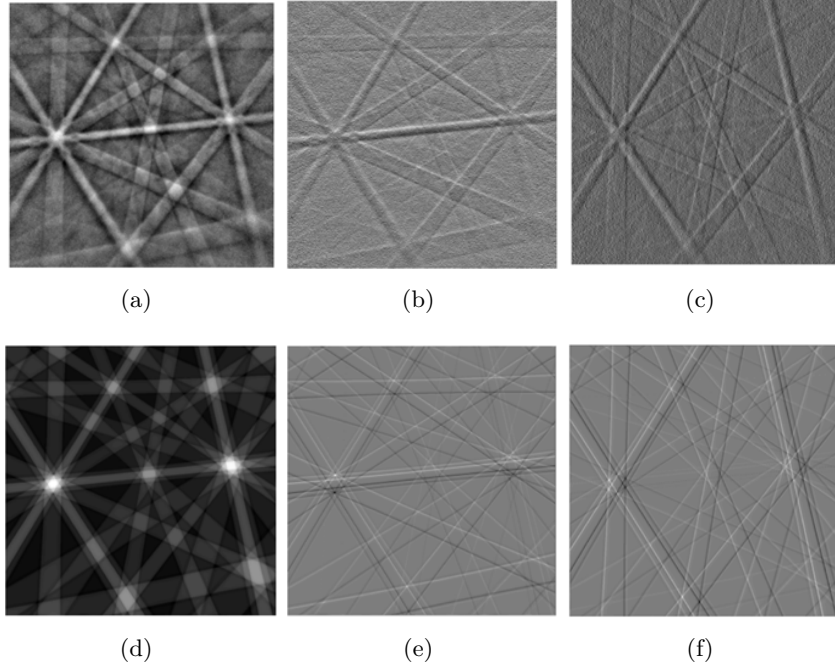


Figure 7.1: (a) Experimental and (d) kinematically simulated EBSD of β phase in Ti-12wt.%Mo. (b) and (e) are corresponding image gradients along the x direction, while (c) and (f) are image gradients along the y direction.

Fast Fourier Transform (FFT) is then applied on the gradient images ($\hat{G}_{real}$ and $\hat{G}_{simu}$), and the cross-correlated image is finally obtained following the equation :

$$C_{ij} = F^{-1}(\hat{G}_{real}\hat{G}_{simu}^*) \quad (7.1)$$

where F^{-1} is the inverse FFT and $\hat{G}_{simu}^*$ is the complex conjugate of $\hat{G}_{simu}$. The peak position of C_{ij} corresponds to the shift between the initial images. Figure 7.2 shows the result of the gradient approach compared to the normal approach. It can be seen that the peak height-to-background ratio is improved with the gradient approach, allowing a

better fitting of kinematically simulated EBSP.

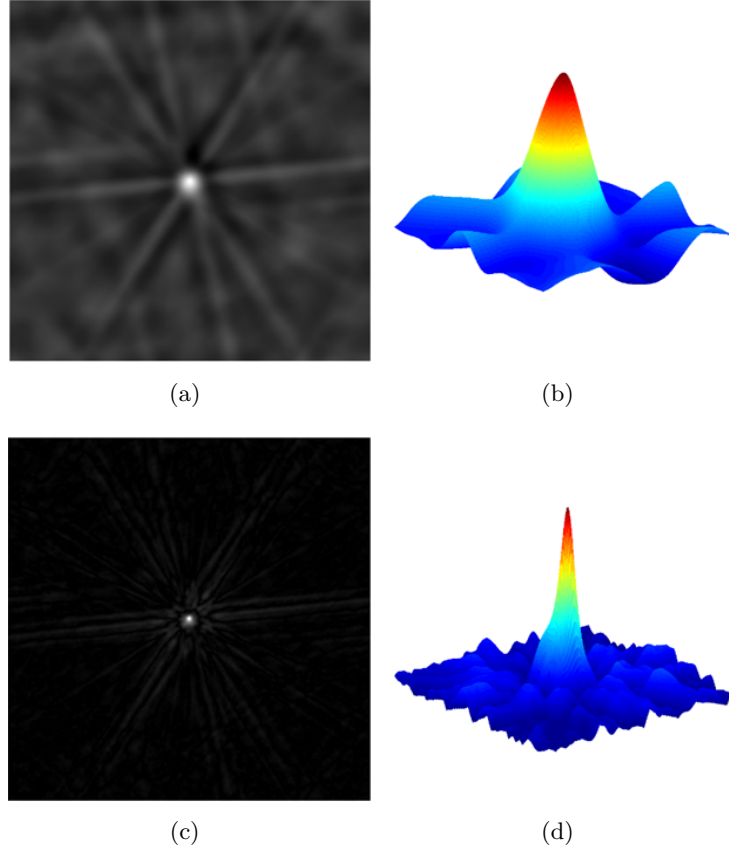


Figure 7.2: (a) and (b) : Cross-correlation between experimental and simulated initial EBSP shown in Figure 7.1. (c) and (d) : Cross-correlation between gradient images of EBSP.

Finally, in order to extract accurate values of deformation gradient between the experimental and simulated patterns, the cross-correlation is performed on different subregions (regions of interest - ROI) of the patterns, and the mean value of the shifts obtained for each ROI is used for further calculations. In this work, 32 ROI of 256×256 pixels were used to achieve reliability, as stated by Wilkinson [211].

7.2.2 Pattern center location

In order to get rid of phantom stresses mentioned in the introduction, an accurate estimation of the PC location has to be performed. Since any point (X_1^D, X_2^D) in the 2D EBSD is uniquely associated to a 3D direction of the crystal, it follows that :

$$X_i^D = \frac{u_i}{u_3} D ; i \in \{1, 2\} \quad (7.2)$$

where D is the distance between the detector and the sample and u_i are the coordinates of the crystal direction. If the sample location is shifted by a vector $(\Delta_1, \Delta_2, \Delta_3)$ (uncertainty of exact sample location), the new corresponding point on the EBSD becomes :

$$T_{\vec{\Delta}}[X_i^D] = X_i^D (1 + \frac{\Delta_3}{D}) + \Delta_i ; i \in \{1, 2\} \quad (7.3)$$

which means that the pattern will be either expanded or contracted by a factor $(1 + \Delta_3/D)$ and then shifted by (Δ_1, Δ_2) .

Also, if the crystal is distorted (by any kind of stress field), corresponding to $\bar{u}_i = F_{ij}u_j$, the new point becomes :

$$X_i^D = \frac{\bar{u}_i}{\bar{u}_3} D = \frac{F_{ij}u_j}{F_{3k}u_k} D ; i \in \{1, 2\} \text{ and } j, k \in \{1, 2, 3\} \quad (7.4)$$

Combining (7.2) with (7.4) and considering small strain approximation (elastic strains) $F_{ij} = \delta_{ij} + U_{ij}$ with $U_{ij} \ll 1$, it follows that :

$$\bar{X}_i^D \simeq (1 - U_{33})X_i^D + U_{ij}X_j^D + U_{i3}D - U_{3k}X_k^D ; i, j, k \in \{1, 2\} \quad (7.5)$$

In the case of hydrostatic lattice distortion, the EBSD is thus an invariant. It was also shown in Equation (7.3) that only the third component of the shift will expand or contract the EBSD. Considering only the F_{i3} components, Equation (7.5) becomes :

$$\bar{X}_i^D = \frac{1}{F_{33}}[X_i^D + F_{i3}D] ; i, j \in \{1, 2\} \quad (7.6)$$

which acts similarly to Equation (7.3) on the EBSP. Finally, if both lattice distortions and sample shifts are taken into account, we obtain :

$$T_{\bar{\Delta}}[\bar{X}_i^D] = \frac{1 + \Delta_3/D}{F_{33}}[X_i^D + F_{i3}D] + \Delta_i ; i \in \{1, 2\} \quad (7.7)$$

It is clear from Equation (7.7) that particular combinations of distortions and shifts will maintain the EBSP invariant. It follows that the calculation of the PC location in a real sample (i.e. containing defects) is an underdetermined problem and further assumptions are necessary to solve it. Three of the four hypotheses come from the fact that EBSD is a free surface measurement, meaning that the σ_{i3} components in the sample can be set to zero. The last assumption must be evaluated depending on the history of the analysed sample.

In the case of the sample analysed here, the sample was slightly plastically strained ($\varepsilon \simeq 1\%$) after complete recrystallisation. A reasonable assumption is thus that the mean surface biaxial stress is equal to zero, i.e. $(\sigma_{22} + \sigma_{33}) = 0$.

To summarise, the complete procedure to calibrate the PC location is the following iterative scheme :

1. Obtention of approximate PC location and crystal orientation by conventional Hough transform ;
2. Simulation of a kinematical EBSP with inputs of step 1 ;
3. Calculation of strain gradient tensor in the detector's coordinate system by gradient-based DIC procedure (see Section 7.2.1) ;
4. Calculation of a sample shift that fulfills the constraints, as well as corresponding deformation gradient tensor ;
5. Refinement of the PC location with the calculated shift $\bar{\Delta}$;

6. Simulation of a new EBSD with the new PC location and corresponding strain gradient ;
7. Repetition of steps 3 to 6 until the correction to apply to PC calculation falls below a fixed threshold.

In order to validate the method of PC calibration, the algorithm has been tested on six orientations of a Si wafer (supposed stress-free). The results are very satisfactory, as illustrated by the measurements of the misorientation angle in Figure 7.3 for both methods (gradient-based (a) and direct DIC (b)).

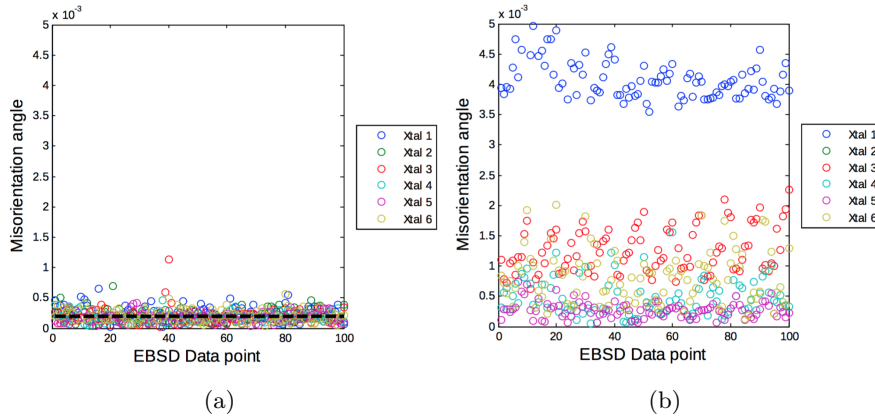


Figure 7.3: *Misorientation angle with respect to the mean crystal orientation for each of the analysed crystals as calculated using the gradient-based approach (a) and the direct approach (b). Dotted line corresponds to the average misorientation value ($< 2 \cdot 10^{-4}$).*

7.2.3 Hybrid HR-EBSD

Once the PC is well calibrated, the simulation-based procedure can be applied. In order to approach the same accuracy as relative measurements, another iterative procedure is applied :

1. Selection of n_0 points in each grain of the initial Hough transform-based map ;
2. For each point k , the deformation gradient tensor is computed in two ways : $\Delta \mathbf{F}_{ij}^{k,real}$ (relative to the reference point and following the gradient-based or conventional approach) and $\mathbf{F}_{ij}^{k,simu}$ (in an absolute manner with simulated EBSPs) ;
3. Averaging of $\Delta \mathbf{F}_{ij}^{k,real}$ and $\mathbf{F}_{ij}^{k,simu}$;
4. Computation of the absolute $\mathbf{F}_{ij}^1$ of reference point : $\mathbf{F}_{ij}^1 = (\Delta \bar{\mathbf{F}}_{ij})^{-1} \cdot \bar{\mathbf{F}}_{ij}$;
5. Computation of $\Delta \mathbf{F}_{ij}^{k,real}$ for all points of the grain ;
6. Computation of the absolute $\mathbf{F}_{ij}^k$ of each point ;
7. Simulation of a new EBSP with the new PC location and corresponding strain gradient ;
8. Repetition of steps 1 to 6 for each grain in the map.

Since twinning corresponds to an abrupt change of orientation and phase transformation to other kind of crystal lattice, this approach seems particularly well suited for TRIP and/or TWIP materials.

In this work, since the orientation of both twins and martensite are related to the matrix with an ideal orientation relationship, their reference EBSPs have been calculated from the parent grain reference patterns instead of being taken randomly from points in the deformation bands.

7.2.4 Estimation of densities of Geometrically Necessary Dislocations

The assessment of the GND content is based on Nye's analysis [226]. First, the distortion gradient tensor ($\beta_{ij} = \frac{du_i}{dx_j}$) is calculated from DIC analysis. Indeed, assuming small angle approximation, $\mathbf{F} \approx \mathbf{I} + \boldsymbol{\beta}$ where $\mathbf{F}$ is the measured shifts matrix and $\mathbf{I}$ is the identity matrix. The integration of the displacement field around a closed loop C must equal

zero to ensure continuity. Considering that the tensor β_{ij} is made of an elastic and a plastic part (ε and ω), and using Stokes theorem, it follows that :

$$\oint_C \beta d\mathbf{x} = \iint_S \nabla \times (\beta^e + \beta^p) ds = 0 \iff \nabla \times \beta^e = -\nabla \times \beta^p \quad (7.8)$$

Also, since the net Burgers vector $\mathbf{b}$ of dislocations piercing the loop C equals :

$$\mathbf{b} = -\oint_C \beta^p d\mathbf{x} = -\iint_S \nabla \times \beta^p ds \quad (7.9)$$

and remembering the definition of the Nye's tensor α [226] :

$$\mathbf{b} = \iint_S \alpha ds \quad (7.10)$$

it finally gives :

$$\alpha = \nabla \times \beta^e \quad (7.11)$$

The elements of the α tensor are related to the different types of dislocations by the following relation :

$$\alpha_{ij} = \sum_{s=1}^{s_{max}} \rho_s b_i^s t_j^s \quad (7.12)$$

where ρ_s is the density, b_i^s the components of the Burgers vector and t_j^s the unit line direction components of the s th dislocation type.

Considering simultaneously Equations (7.11) and (7.12), one can see that the displacement gradient can indeed be related to the dislocation density within the crystal. In the strictest sense, the calculation of GND is related to both the elastic strain field and the lattice curvature. However, Wilkinson stated that among all the HREBSD experiments carried out by his group, the rotation gradients are generally considerably larger than the elastic strain gradients [219]. Relative HREBSD

measurements can thus still lead to an analysis of the GND content since it will only require the knowledge of the rotation gradients. Nevertheless, since the new hybrid method allows absolute measurements, all components of β^e can be used for a more accurate determination of the total geometrically necessary dislocations density ρ^{GND} .

Furthermore, since in a 2D EBSD map only derivatives in the surface directions can be calculated, the terms related to derivatives in the out-of-plane direction are not measurable. This means that unless further assumptions are made, only some components of the Nye's tensor are accessible from a single 2D EBSD map. Hopefully, further assumptions can be made in the neighbourhood of special boundaries if the habit plane can be guessed or estimated.

7.3 Results

Small scans of β/α'' interfaces and $\{332\}\langle 113 \rangle_\beta$ twin boundaries have been performed, and the EBSP of each analysed point was acquired. The analysis of the distortions of the Kikuchi patterns compared to the reference pattern brings about the calculation of the elastic distortions gradients, and thus of the lattice deformations and rotations in the vicinity of interfaces. The reference patterns were taken at a few micrometers away from the regions of interest.

7.3.1 Confidence index of the DIC

The confidence index of the DIC calculation is a relevant parameter for interpretation of the results. It is roughly an indicator of the peak height of the cross-correlation result (see Figure 7.2). The peak heights are compared to the result of an auto-correlation (reference pattern), which is normalised to unity. Generally, a value of 0.3 is chosen as the minimum threshold value for validation of the cross-correlation in the literature [219]. This value is arbitrary and should be adapted depending on the studied phenomenon. The confidence index maps are shown in Figure 7.4. The remarkable quality of the cross-correlation is well

illustrated, since the smallest values are located just below 0.65. It is thus reasonable to think that the results presented below are robust and may be valuable for determining the internal elastic stress state as well as a compatible set of GND density in the material.

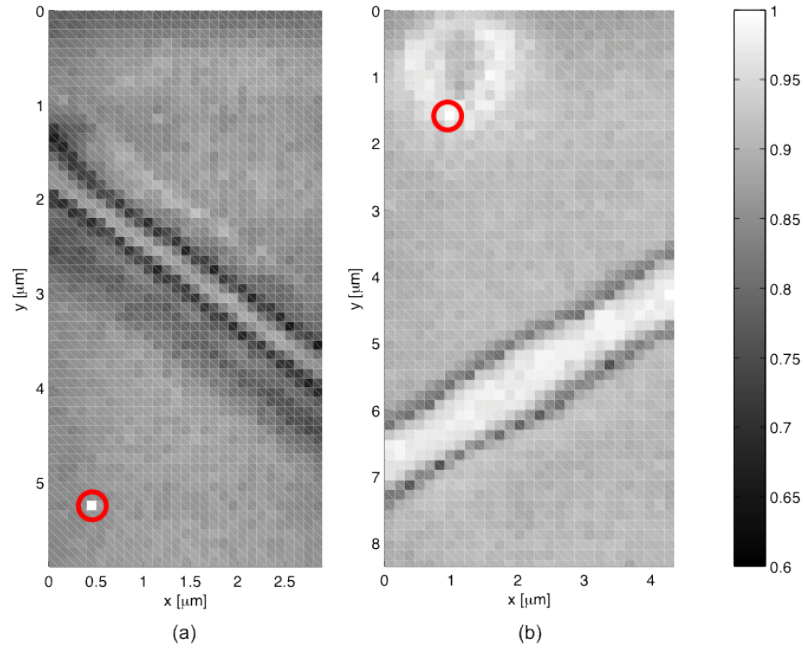


Figure 7.4: *Confidence index of the cross-correlation in the case of (a) a $\{332\}\langle 113 \rangle$ mechanical twin and (b) a α'' martensite plate. Red circles correspond to reference pixels.*

7.3.2 Local misorientations

$\beta - \alpha''$ interface

For the α'' plate, misorientations are calculated with respect to the theoretical ideal orientation relationship (OR), in this case :

$$\begin{array}{lll} [001]_{\alpha''} & // & [\bar{1}\bar{1}0]_{\beta} \\ [\bar{1}\bar{1}0]_{\alpha''} & // & [1\bar{1}\bar{1}]_{\beta} \\ (1\bar{1}0)_{\alpha''} & // & (1\bar{1}2)_{\beta} \end{array} \quad (7.13)$$

Figure 7.5 shows the misorientation angle for the last 3 elements of the quaternion (q_i) representing the rotation axis with respect to a reference point in the matrix :

$$(q_x, q_y, q_z) = (r_x, r_y, r_z) \cdot \sin\theta \quad (7.14)$$

where (r_x, r_y, r_z) is the unit vector corresponding to the rotation axis and θ is the misorientation angle.

In the misorientation profiles, 3 different regions can be distinguished : the interior of the β phase (red boxes), the interior of the α'' phase (blue box) and the misfit at the interfaces (black dash lines). It is observed that the rotation axis at the two sides of the interphase boundary present opposite signs, especially for the upper grain boundary (left side in Figure 7.5). This means that OR is not maintained in the neighborhood of the interphase boundary.

$\{332\}\langle 113 \rangle$ mechanical twin

Here, misorientations are calculated with respect to the activated variant of the $\{332\}\langle 113 \rangle_{\beta}$ orientation relationship (determined by conventional EBSD) :

$$\begin{array}{lll} [01\bar{1}]_M & // & [1\bar{1}0]_T \\ [\bar{3}\bar{1}\bar{1}]_M & // & [11\bar{3}]_T \\ (\bar{2}33)_M & // & (332)_T \end{array} \quad (7.15)$$

where M and T indicate the matrix and twin, respectively. Figure 7.6 shows the misorientation angle for the last 3 elements of the quaternion (q_i) representing the rotation axis with respect to a reference point in the matrix by means of the last 3 elements of the corresponding quaternion (same procedure as above).

Again, three different regions can be distinguished : the interior of the matrix (red boxes), the interior of the twin (blue box) and the misfit at the two twin boundaries (black dash lines). In this case, the misorientation profiles are more continuous across the twin boundaries. This could indicate a more coherent interface than in the martensite plate case. Also, the profiles show variations at the vicinity of the twin boundaries (about one micrometer in the β matrix).

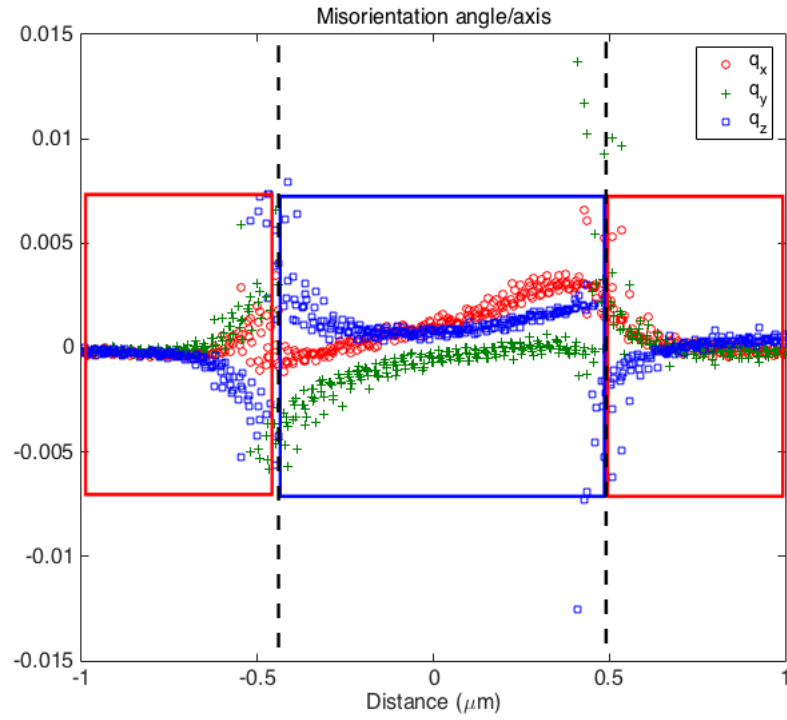


Figure 7.5: Misorientation angle for each components of the quaternion (q_i) representing the rotation axis with respect to the β phase grain interior across the martensite plate. Red boxes correspond to the β phase, the blue box corresponds to the interior of the α'' martensite and the black dotted lines correspond to the interface between both phases.

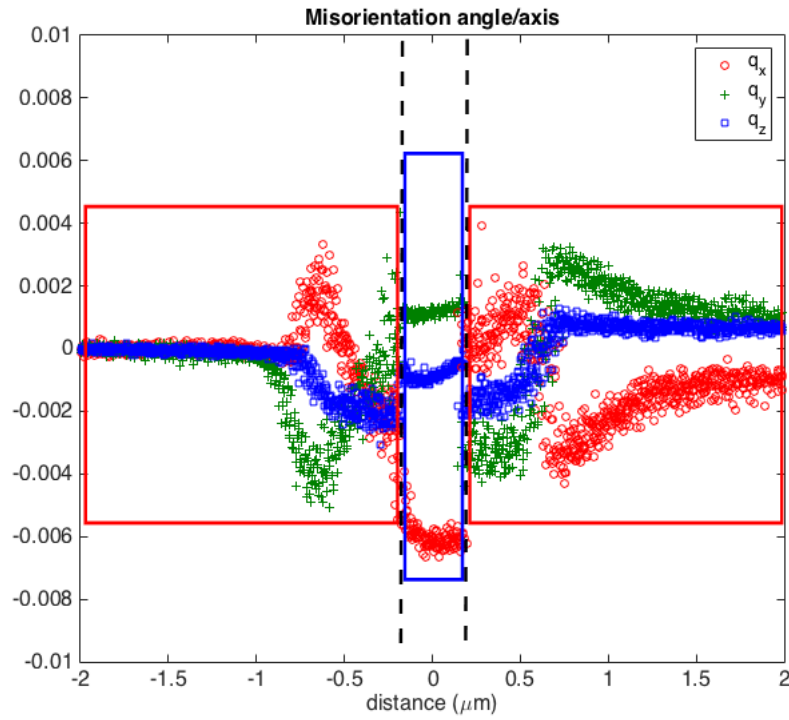


Figure 7.6: *Misorientation angle for each components of the quaternion (q_i) representing the rotation axis with respect to the β phase matrix across the mechanical twin. Red boxes correspond to the matrix, the blue box corresponds to the interior of the twin and the black dotted lines correspond to the twin boundaries.*

7.3.3 Elastic distortion gradient and Nye's tensor

In the analysed samples, the habit planes are known or can be derived from EBSD measurements (see previous point). The misorientation maps indicate that all the gradients are perpendicular to the trace of the habit plane in both cases. Thus, if we could reconstruct the Nye tensor in a new reference system where direction 3 corresponds to the normal of the habit plane, then $\beta_{ij,1} = \beta_{ij,2} = 0$ and the full Nye's tensor can be calculated as follows:

$$\alpha_{ij} = \begin{pmatrix} \beta_{12,3} & -\beta_{11,3} & 0 \\ \beta_{22,3} & -\beta_{21,3} & 0 \\ \beta_{32,3} & -\beta_{31,3} & 0 \end{pmatrix} \quad (7.16)$$

The results of the analysis for the three regions defined above will be depicted separately for clarity, since most features are expected to be located near the interfaces. The $\beta_{ij,3}$ elastic distortion gradients are given in Appendix D. The Nye's tensor components for the $\beta - \alpha''$ interfaces are shown in Figures 7.7(a) and 7.7(b), while the components for $\{332\}\langle 113 \rangle$ mechanical twin boundaries are shown in Figures 7.8(a) and 7.8(b).

In the case of the martensite plate, the results show that the distortions around each phase boundaries exhibit opposite sign. This suggests that it will be the same for the calculated dislocation structure. The decomposition of the α_{ij} components in their elastic strain and lattice curvature (leading to GND estimation) parts is done in the next section.

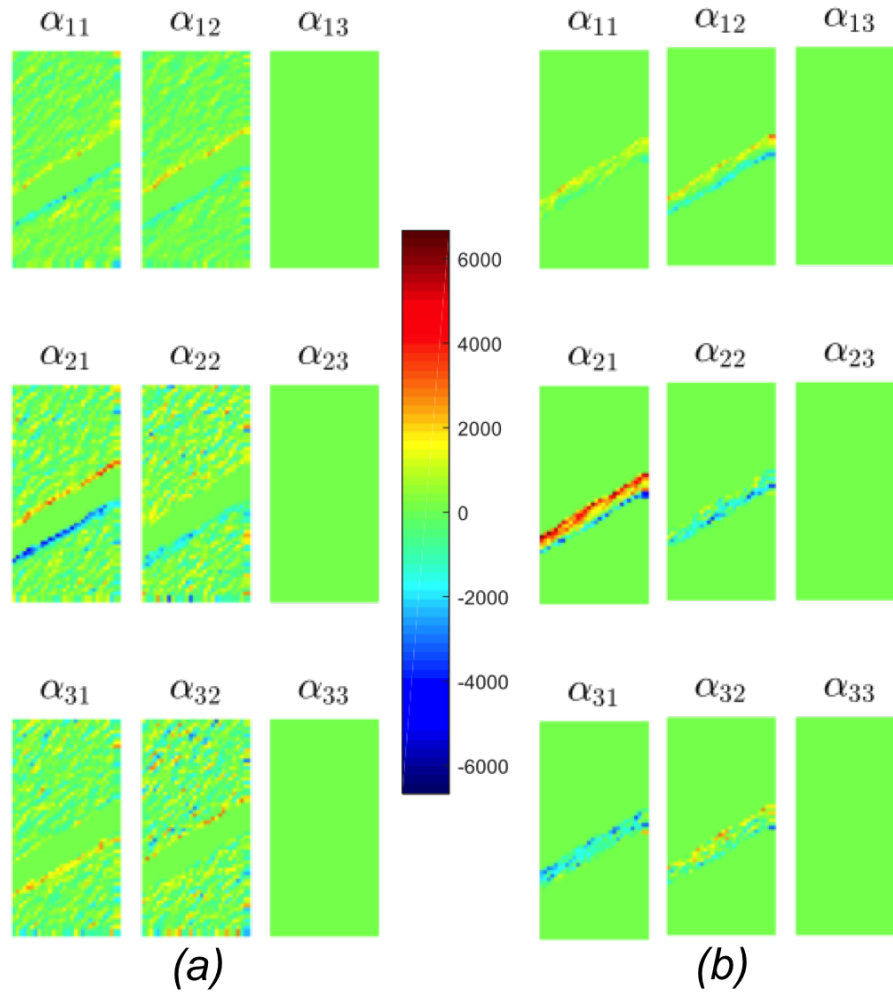


Figure 7.7: Nye's tensor mapping of (a) the β matrix and (b) the α'' plate.

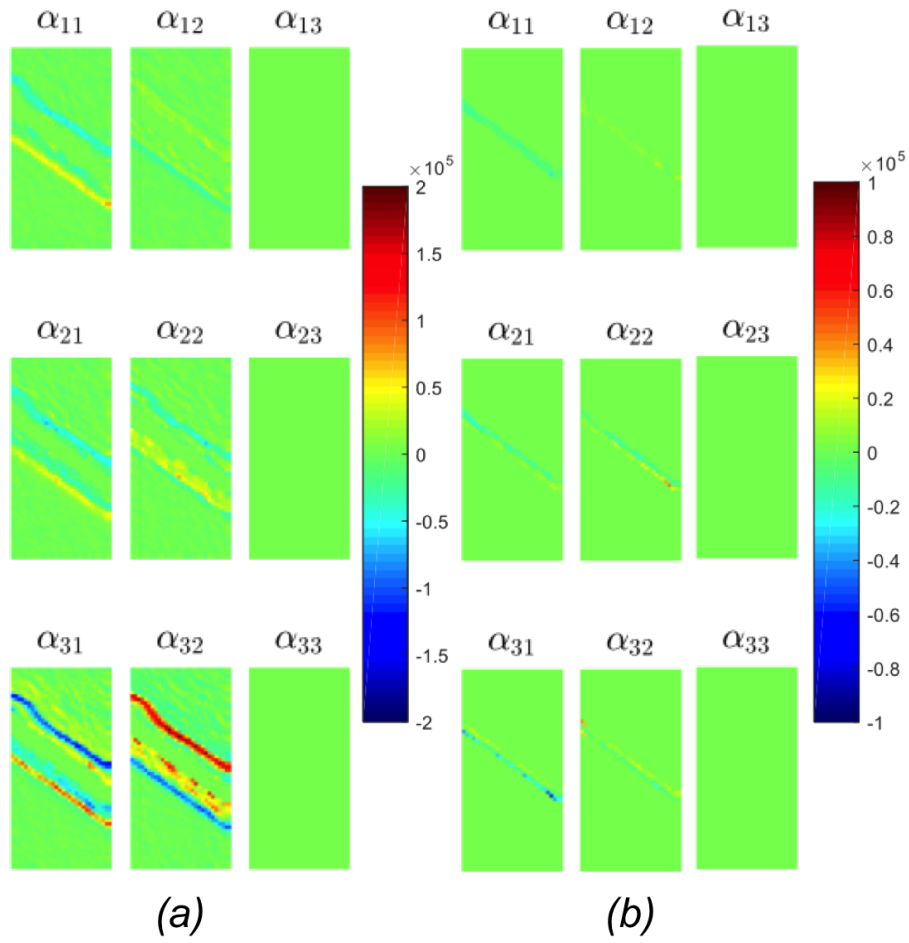


Figure 7.8: Nye tensor mapping of (a) the β matrix and (b) the mechanical twin.

7.4 Discussion

As explained in the introduction, the DIC-based High-Resolution EBSD technique introduced by Wilkinson is a promising technique for mapping elastic stresses and densities of GND. The hybrid method proposed by Alkorta has been applied on a slightly plastically strained Ti-12wt.%Mo sample. It allows the determination of the absolute elastic stress state compared to the initial method, reaching thus one step further in polycrystalline sample characterisation.

7.4.1 Habit plane determination

As explained in Section 7.2.4, assumptions are necessary in order to calculate the full Nye tensor. The determination of the habit plane of the strain-induced interfaces brings about further informations that help in determining such assumptions.

$\beta - \alpha''$ interface

Recently, Chai *et al.* [136] have shown that the mean habit plane observed in the case of α'' martensite precipitation in β -Ti alloys is in fact made of terraces and steps, as illustrated in Figure 7.9. Depending on the misfit between the two phases, the habit plane can range from nearly pure $\{211\}_\beta // \{110\}_{\alpha''}$ (fully coherent interface) up to $\{433\}_\beta$ planes for some metastable Ti alloys, which will result in shorter terrace length λ .

It is known that $\langle 0\bar{1}\bar{1} \rangle_\beta$ must lay on the habit plane since it is the direction of the transformation shear. Moreover, the 2D EBSD map brings the trace of this habit plane. Assuming these two conditions, the habit plane has been estimated to be around $(3\bar{3}5)_\beta$. A scheme of the situation is shown in Figure 7.10.

The calculated habit plane is well in the interval defined by Chai *et al.*. In the defect configuration of Figure 7.9, it can be seen that the addition of edge dislocations b_y and b_x can relieve a part of the transformation strains ε_{yy} and ε_{xx} induced by the martensitic transformation,

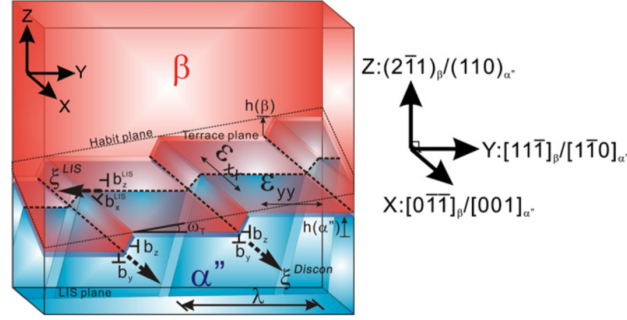


Figure 7.9: Schematic diagram illustrating the β/α'' interface. (Taken from [136])

respectively. Owing to the knowledge of the lattice parameters of the α'' martensite (see Chapter 6), it is possible to calculate the transformation strain components ε_{xx} and ε_{yy} using the equations [136]:

$$\varepsilon_{xx} = \frac{c_{\alpha''} - \sqrt{2} \cdot a_{\beta}}{\frac{1}{2}(\sqrt{2} \cdot a_{\beta} + c_{\alpha''})} \quad (7.17)$$

$$\varepsilon_{yy} = \frac{(\sqrt{a_{\alpha''}^2 + b_{\alpha''}^2}) - \sqrt{3} \cdot a_{\beta}}{\frac{1}{2}(\sqrt{3} \cdot a_{\beta} + (\sqrt{a_{\alpha''}^2 + b_{\alpha''}^2}))} \quad (7.18)$$

which give $\varepsilon_{xx} = 0.0053$ and $\varepsilon_{yy} = 0.0255$. Since $\varepsilon_{yy} \gg \varepsilon_{xx}$, the mechanism activated for the relief of the transformation strain component ε_{yy} will be dominant and will be the only one considered here.

Since ε_{yy} is positive, the β matrix will be in tension in the vicinity of the β/α'' interface, along a $(211)_{\beta}$ plane (depending on the activated α'' variant) and $[111]$ edge dislocations should form to relieve the strain. Moreover, the observed misorientations in opposite directions observed (see Figure 7.5) between the two crystals seem to indicate a strong dislocation activity of opposite signs on both sides of the interphase boundary. These two points will be discussed in Section 7.4.3.

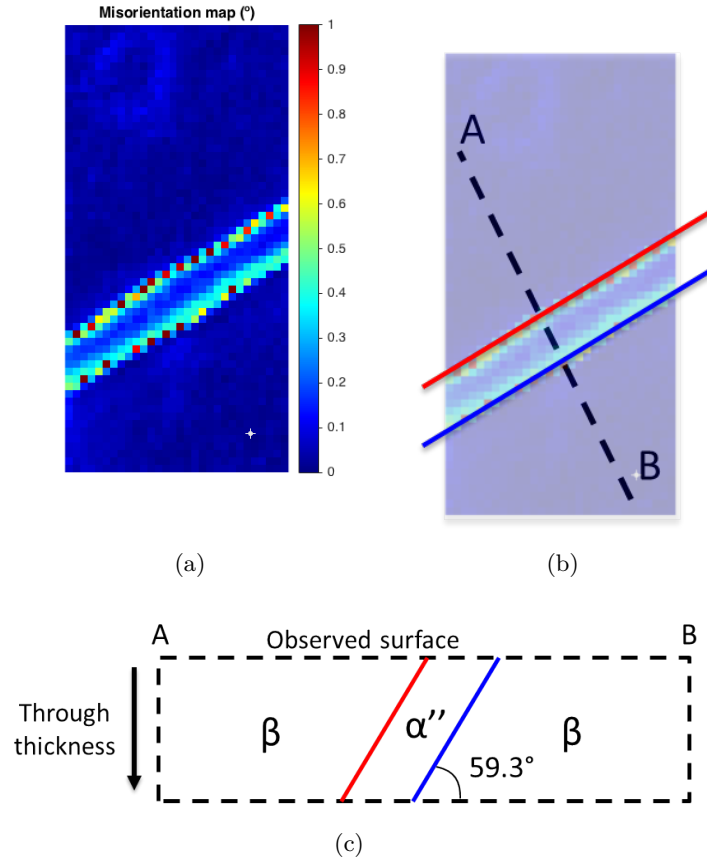


Figure 7.10: (a) Misorientation map with respect to the pixel highlighted in grey. For the martensitic phase, a misorientation equal to 0 corresponds to an ideal orientation relationship as described in Equation (7.13). (b) and (c) Schematic representation of the orientation of the habit plane of the analysed $\beta - \alpha''$ interface. (c) is the AB cut shown in (b) in the depth of the sample.

$\{332\}\langle 113 \rangle$ twin boundaries

It is assumed that the habit plane of the twin boundary corresponds to the symmetry plane between the matrix and the twin. The orientation of the trace of the boundary in the 2D EBSD map suits rather perfectly with this assumption. The orientation of this plane is shown in Figure 7.11.

The measured misorientation profiles show large variations in the vicinity of the boundaries. This indicates large gradients of elastic distortions (as shown in Appendix D), and thus probably large strains and dislocation activity.

It is seen that the orientation of the analysed twin is far from the edge-on situation and it should be kept in mind during the analysis of the other results. Indeed, in EBSD measurements, the interaction depth can reach a few hundred *nm* [227]. A part of the analysed volume could then come from both the matrix and the twin, which would thus bias the results.

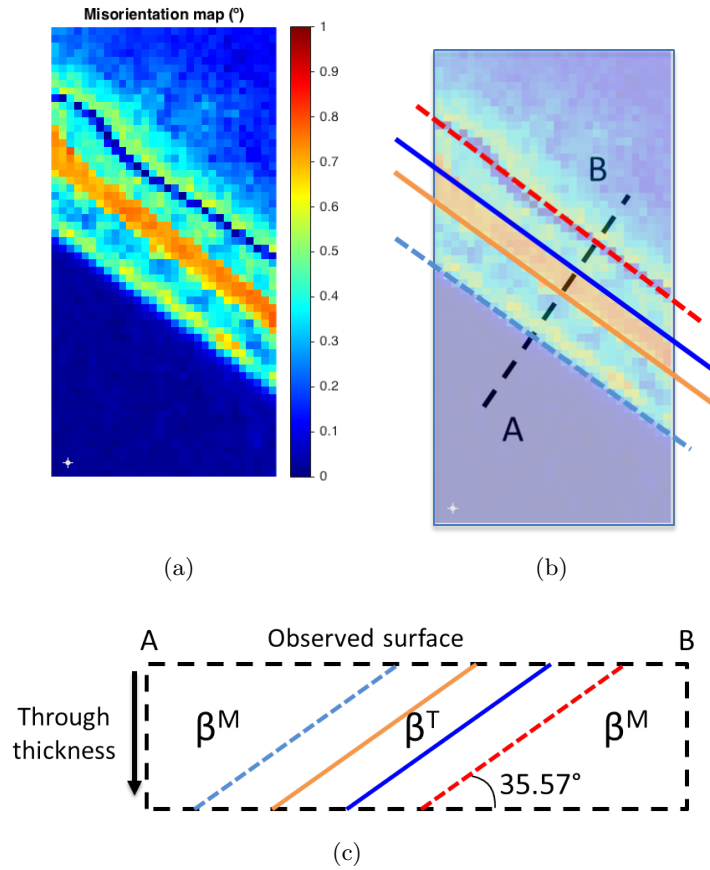


Figure 7.11: (a) Misorientation map with respect to the pixel highlighted in grey. For the twin, a misorientation equal to 0 corresponds to an ideal orientation relationship as described in Equation (7.15). (b) and (c) Schematic representation of the orientation of the analysed twin boundaries. (c) is the AB cut shown in (b) in the depth of the sample.

7.4.2 Analysis of the residual stress fields

The measurement of the displacement gradients allows the calculation of local lattice strains and distortions with the spatial resolution of EBSD. The mapping of these strain fields, convertible in stress fields via the generalised Hooke's law, is shown in Figures 7.12 and 7.13 for the α'' plate and mechanical twin, respectively. Clearly, differences exist between the two cases.

In the case of the martensite plate, the transition zone between the matrix and strain-induced product is very thin (one or two pixels), as already suggested by the misorientation profile (Figure 7.10(a)). Indeed, there does not seem to exist a transition zone of high elastic strains in the matrix. On the contrary, large elastic strains are clearly visible in the martensite plate. The plate is in compressive state along the x direction and in tension along both y and z directions. The shear components are nearly null, except at the interfaces.

The elastic strain components ε_{11} have values between ≈ 0.002 and ≈ 0.005 at the interface, i.e. up to one order of magnitude smaller than the theoretical ε_{yy} calculated in Section 7.4.1. This thus suggests that a relaxation mechanism occurred at the interface. It could be the formation of GND or even phase precipitation. As already pointed out, ω phase precipitation is commonly cited as a relaxation mechanism in metastable β -Ti alloys and has been observed in the present alloy (see Chapter 5).

In the case of the mechanical twin, all components of the strain field are close to zero below the twin up to the transition zone where they take large values of elastic strains, particularly for the normal components. This was already suggested by the misorientation profiles. It is worth noting that two components of the strain field (ε_{22} and ε_{13}) show a different state between the two sides of the twin, after the transition zone. This could be due to the fact that the twin is far from the edge-on configuration, thus introducing local disturbance. Also, only the ε_{22} has a non-negligible component in the twin (under the assumption that the ideal orientation relationship is respected).

The elastic constants used for the estimation of the stress field are the

same as the one used in Chapter 6. As a reminder, their values are (in *GPa*) :

$$C_{ij} = \begin{pmatrix} 125 & 100 & 100 & 0 & 0 & 0 \\ 100 & 125 & 100 & 0 & 0 & 0 \\ 100 & 100 & 125 & 0 & 0 & 0 \\ 0 & 0 & 0 & 41 & 0 & 0 \\ 0 & 0 & 0 & 0 & 41 & 0 \\ 0 & 0 & 0 & 0 & 0 & 41 \end{pmatrix} \quad (7.19)$$

It is worth noting that, since the elastic constants of the α'' phase are not known, the same elastic tensor has been used for the evaluation of the stress state in the martensite. This approximation will obviously lead to a wrong estimation of the stress field within the martensite, but should at least give a clue about the real state.

With these values, the absolute residual stress fields are calculated and plotted in Figures 7.14 and 7.15 for both cases. After transformation in stress fields, the trends remain more or less the same. The martensite plate is mostly in a compressive stress state, while the matrix is slightly in tension in the y direction. The phase boundaries show a huge stress concentration. Since the martensitic transformation from β to α'' lattices implies a volume expansion ($\approx 0.8\%$), the compressive state observed in the α'' plate is logical.

In the case of the twin, its surrounding is strongly in a compressive state, while the twin and part of the matrix are slightly in tension. This is a necessary condition due to the mechanical state imposed as supplementary hypothesis for the calculations (null surface biaxial stresses). The fact that the surrounding of the twins is in compression could possibly have interesting consequences regarding the fatigue life of the material. Indeed, mechanical twins are often viewed as favourable sites for cracks initiation due to stress concentration. However, if their surrounding is in compressive state, it could hinder the crack propagation and delay the failure of the material.

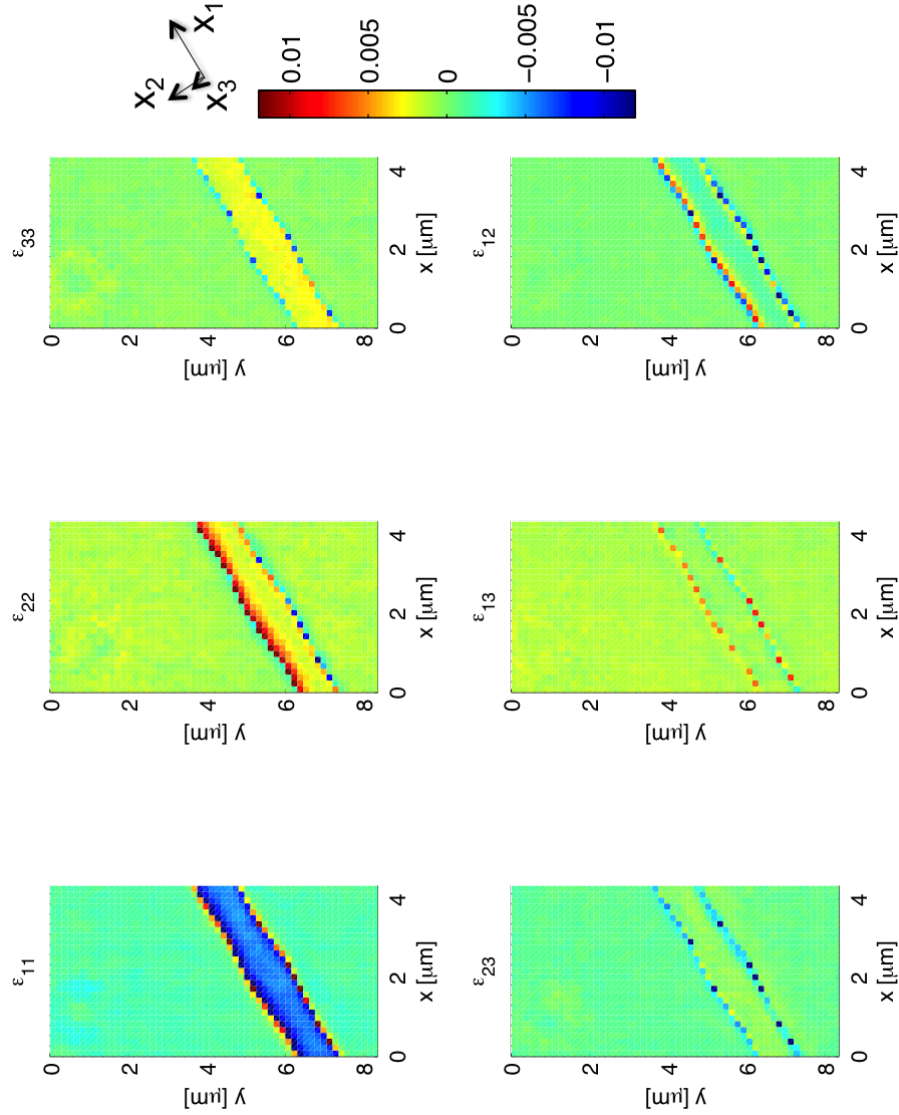


Figure 7.12: Calculated absolute elastic strain field components around a α'' martensite plate. The orthonormal reference system is attached to the habit plane, with x_2 slightly getting out of the plane (normal to the habit plane) and x_3 entering the plane of the sheet (parallel to the habit plane).

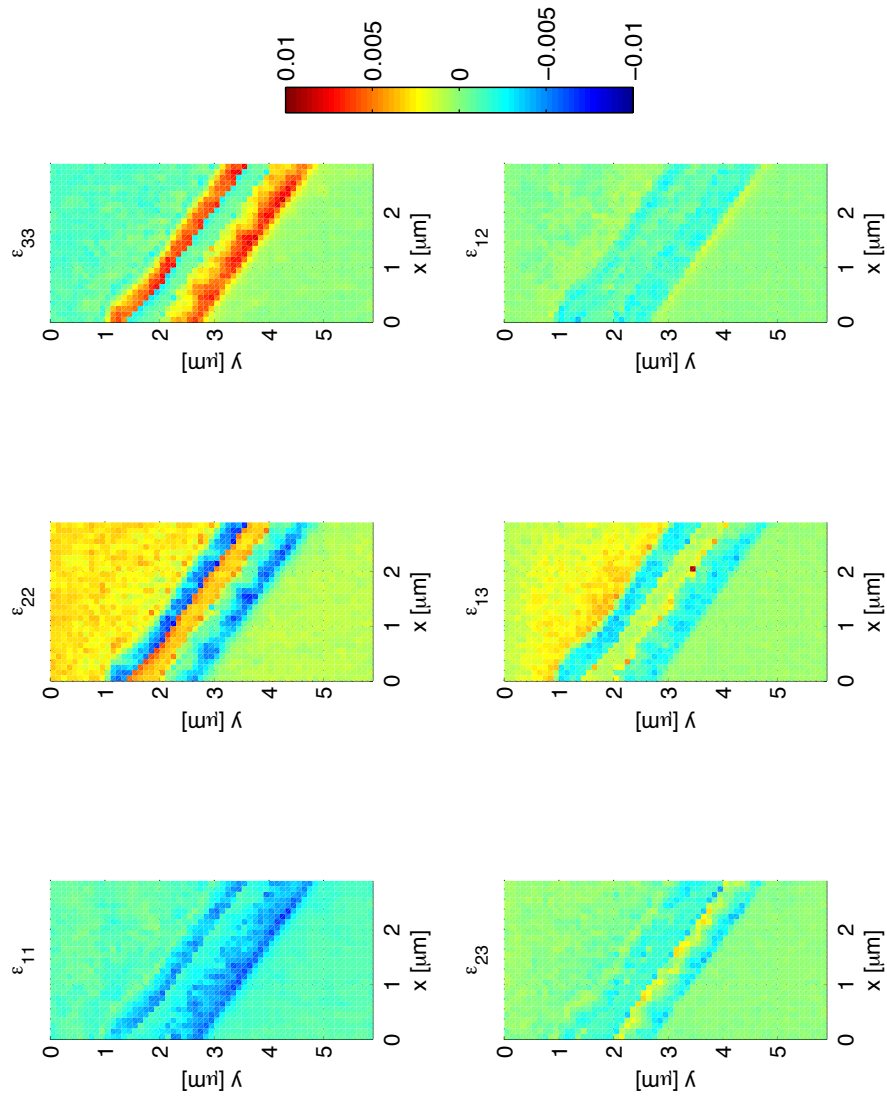


Figure 7.13: *Calculated absolute elastic strain field components around a $\{332\}\langle 113 \rangle$ mechanical twin.*

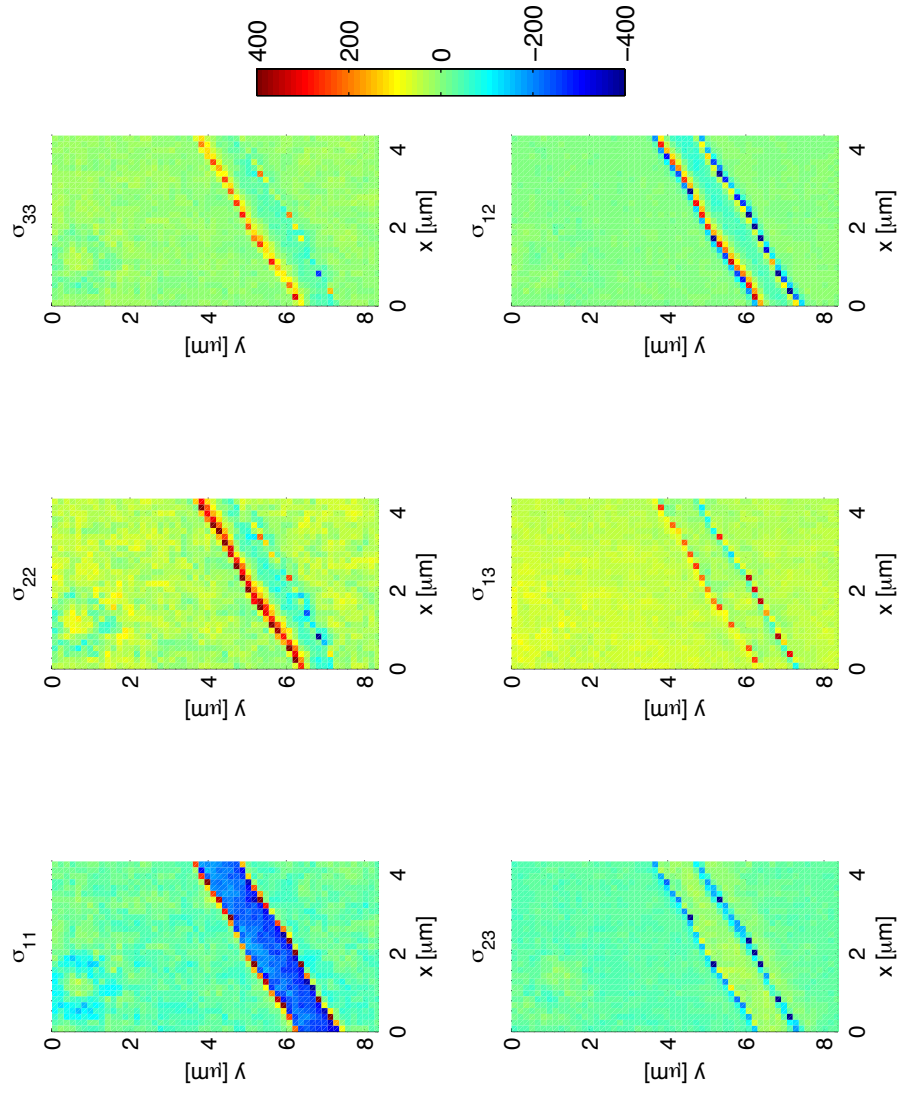


Figure 7.14: *Calculated absolute stress field components around a α'' martensite plate.*

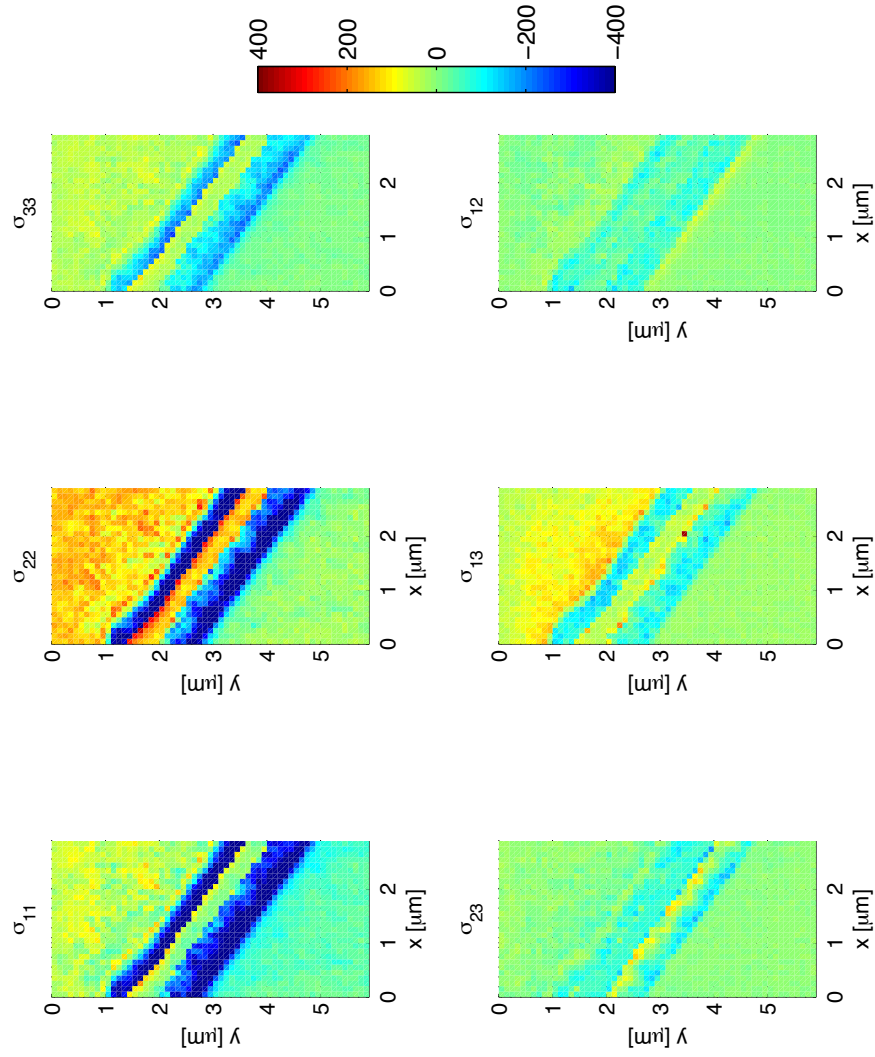


Figure 7.15: *Calculated absolute stress field components around a $\{332\}\langle 113 \rangle$ mechanical twin.*

7.4.3 Densities of GND

The densities of Geometrically Necessary Dislocation are computed from the rotations tensors in each pixel of the EBSD measurements. It is worth noting that if lattice curvatures can uniquely be calculated from a given set of GNDs, the reciprocal is not true and the estimated densities are lower boundaries of the real amount of GNDs. Indeed, there exists potentially an infinite number of solutions leading to the measured lattice rotations. However, the calculations can be considered relatively reliable since there is no particular reason for the material to create a large excess of dislocations for accommodating the deformation features and grain rotations corresponding to a given amount of plastic strain.

The assessment that will be performed in the following discussion is thus one of the possible solutions of the system of equations, obtained by the minimisation of the total dislocation line energy. The number of allowed slip systems will influence the calculation results. Here, the 12 $\{110\}\langle 111 \rangle$ and 12 $\{112\}\langle 111 \rangle$ systems as well as 4 *screw* – $\langle 111 \rangle$ systems will be used unless otherwise expressed.

$\beta - \alpha''$ interface

The estimated values of densities of GNDs for the matrix away from the interfaces are of the order of 10^{11} m^{-2} (for each components), as depicted in Figure 7.16. This level seems adequate for a recrystallised sample which underwent only a small amount of plastic deformation. Indeed, an order of magnitude of $\rho^{tot} = 10^{12} \text{ m}^{-2}$ was reported for recrystallised *Fe-Si* alloys [228] and for pure *Cu* and *Al* annealed crystals [229]. The values calculated in the vicinity of the β/α'' interfaces are at least one order of magnitude higher than far from them.

The results in Figure 7.16 show that the dislocation structures around each interphase boundary show opposite sign. Moreover, the dislocation structure can be almost fully described by $(1\bar{1}2)[\bar{1}11]$ edge dislocations (apart from a second order term corresponding to $[111]$ screw dislocations). These dislocations correspond to the $[\bar{1}\bar{1}0]_{\beta}$ direction that corresponds to the edge of the terrace planes suggested by Chai

et al (see Figure 7.9). This suggests the need of this kind of dislocations to accommodate such interface architecture, as already pointed out by the strain mismatch between the two phases.

The slip systems associated to orthorhombic α'' phase are not known and GND density in the plate cannot be readily extracted. However, the Nye tensor indicates a similar behavior at the two sides of the interphase boundary (see Figures 7.7(a) and (b)). The resulting density of GND in α'' derived in terms of active slip system of β phase is shown in Figure 7.17. If we assume that the slip systems of BCC phase can be translated in α'' slip systems by the ideal orientation relationship, the $(1\bar{1}2)[\bar{1}11]_{\beta}$ edge dislocations would correspond to $(1\bar{1}0)[110]_{\alpha''}$ edge dislocations. If such dislocations exist in the orthorhombic phase, these results suggest that the mismatch between β and α'' lattices is partially accommodated by edge dislocation formation, and with a fewer importance, by screw dislocations.

Considering the misfit observed at the interphase boundaries with respect to ideal orientation relationship, it is possible to estimate a GND structure for the interface (in terms of BCC slip systems), as shown in Figure 7.18. Presumably, this cannot be directly translated to the real defect structure of the interface. Anyway, it could help in interpreting a further TEM characterisation of the β/α'' interface. An interesting point is that the corresponding “GND density” is more than one order of magnitude higher than the GND densities in the interior of the β grain and α'' plate.

Twin boundary

The dislocation activity in the neighbourhood of the twin boundary is notably superior (by more than one order of magnitude) than the one observed around the α'' martensite plate, as illustrated in Figure 7.19. Moreover, the results show the presence of two $[\bar{1}11]$ tilt boundaries of opposite sign on both sides of the twin boundary at a distance of a few hundreds of nm . Considering only $\{110\}\langle 111 \rangle$ and $\{112\}\langle 111 \rangle$ slip systems, the tilt boundary is mainly constituted by a similar amount of $(1\bar{1}2)[\bar{1}11]$ and $(101)[\bar{1}11]$ dislocations, which geometrically coincides

with pure $(2\bar{1}3)[\bar{1}11]$ dislocations. In order to confirm this, the GND density has been recalculated with the addition of the 24 $\{321\}\langle 111\rangle$ slip systems, and the results are plotted in Figure 7.20. The presence of $(2\bar{1}3)[\bar{1}11]$ is confirmed but the other dislocations with identical Burgers vector cannot be discarded.

This last observation can *a priori* be related to the easiness of cross-slip observed in *BCC* materials due to the core structure of the dislocations.

Figure 7.21 illustrates the GND density within the twin. As emphasised by the scale, it is clearly negligible with respect to the matrix at the neighborhood of the twin boundaries since it is one order of magnitude smaller.

Finally, considering the misfit observed at the twin boundary with respect to ideal orientation relationship, we can also calculate a corresponding GND structure (in terms of matrix slip systems), as shown in Figure 7.22. Here again, this cannot presumably be directly translated to the real defect structure of the interface, and HR-TEM observations of the twin boundaries should be performed. The results show that in this case, the two twin boundaries do not have the same character in contrast with what was observed in the case of β/α'' interfaces. This difference could come from the high inclination of the twin boundary.

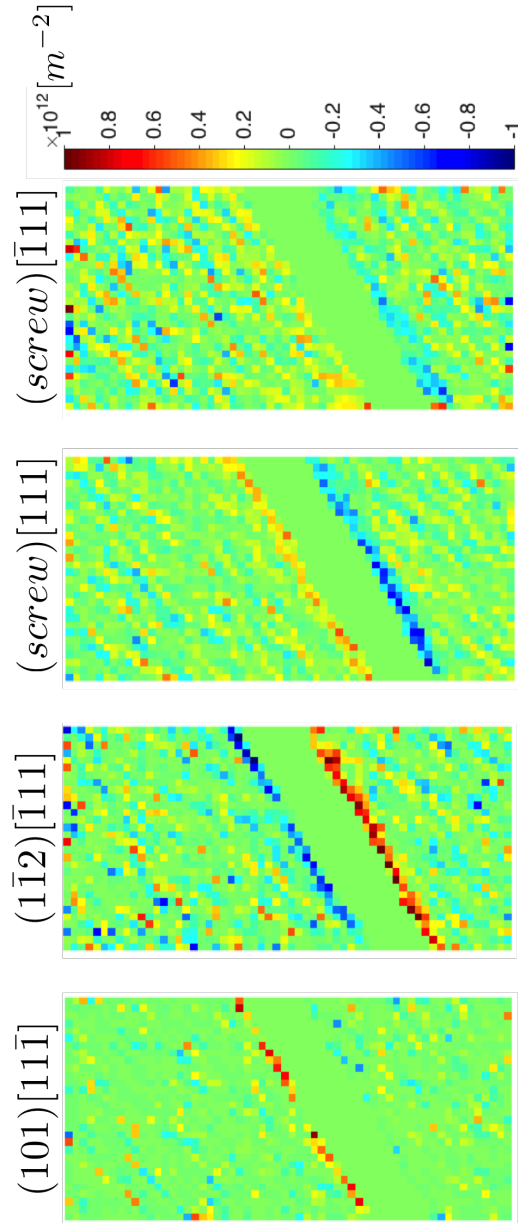


Figure 7.16: Estimated GND density (in m^{-2} - meters of dislocation line per cubic meter of material) from Nye tensor for β matrix around an α'' plate. Only the significant components are shown (the complete map is given in Appendix D).

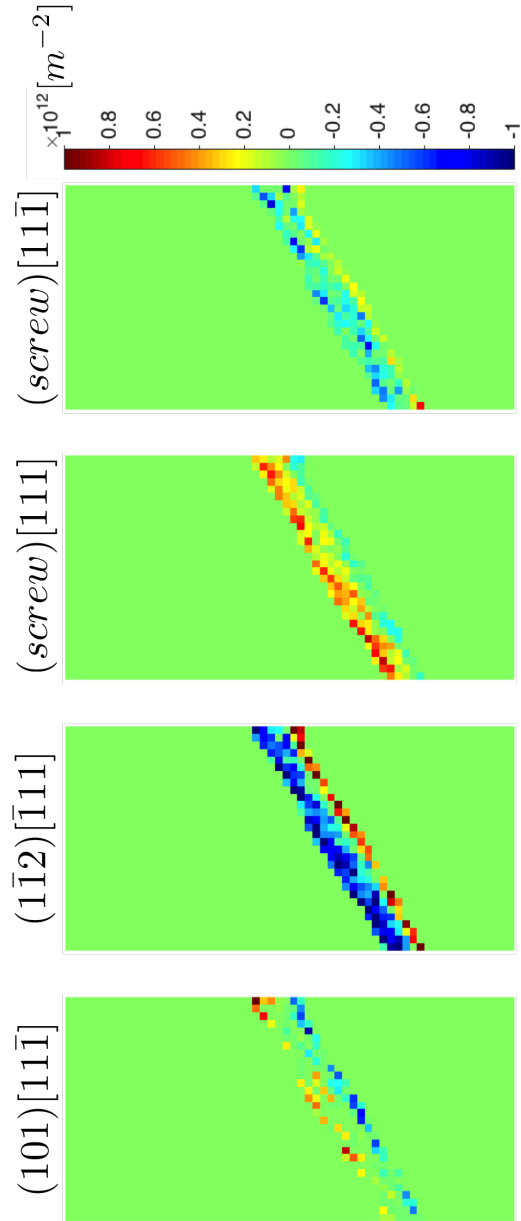


Figure 7.17: Estimated GND density (in m^{-2}) from Nye tensor for the α'' plate (in terms of BCC slip systems). Only the significant components are shown (the complete map is given in Appendix D).

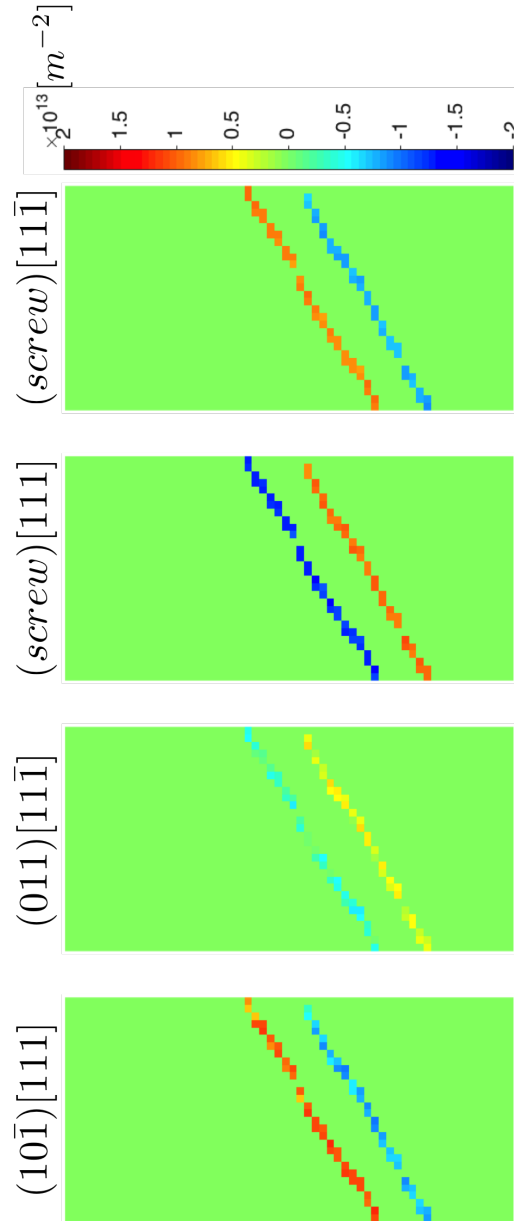


Figure 7.18: Estimated GND density (in m^{-2}) from Nye tensor for the β/α'' interface. Only the significant components are shown (the complete map is given in Appendix D).

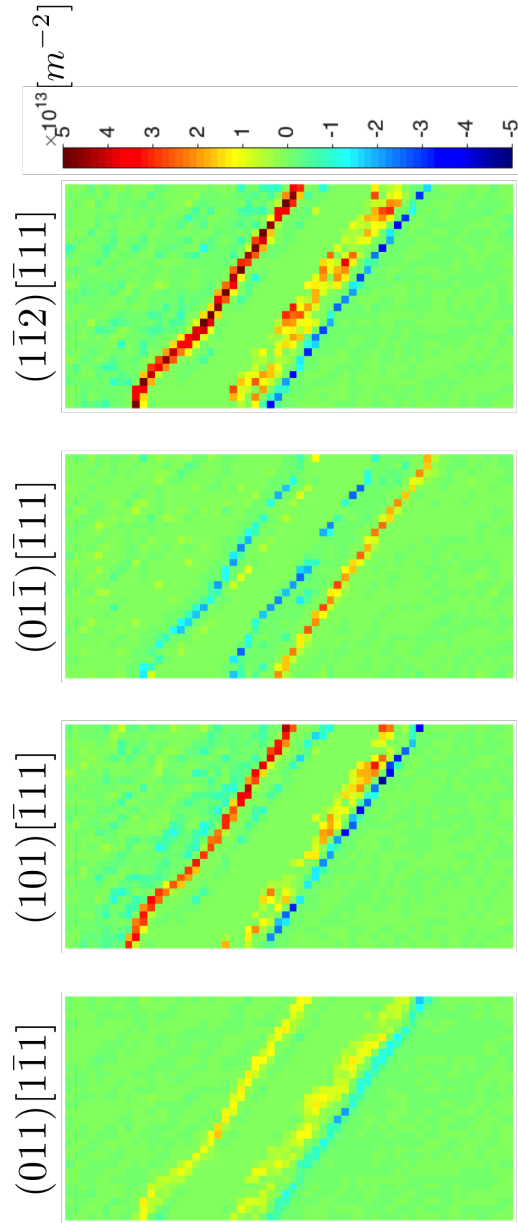


Figure 7.19: *Estimated GND density (in m^{-2}) from Nye tensor for β matrix around a mechanical twin. Only the significant components are shown (the complete map is given in Appendix D).*

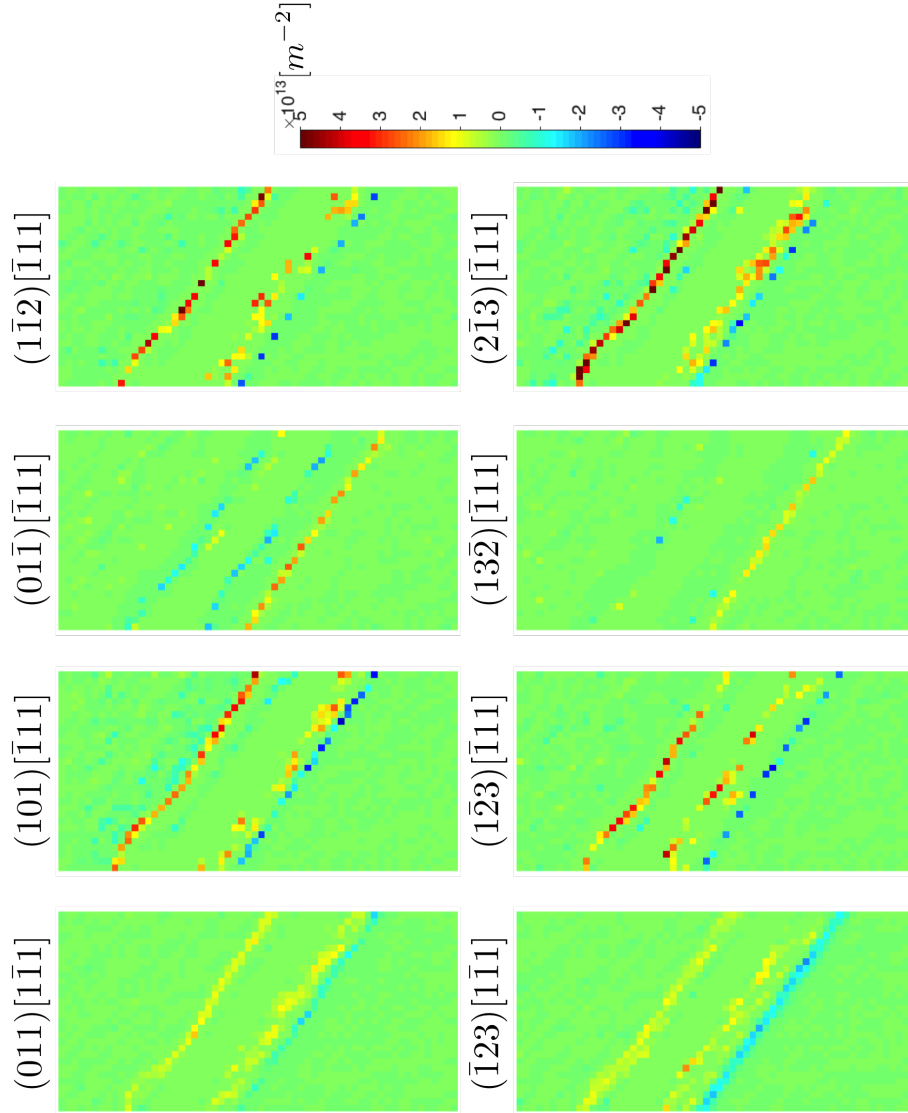


Figure 7.20: Estimated GND density (in m^{-2}) from Nye tensor for β matrix around a mechanical twin with additional 24 equivalent $\{321\}\langle 111 \rangle$ slip systems. Only the significant components are shown (the complete map is given in Appendix D).

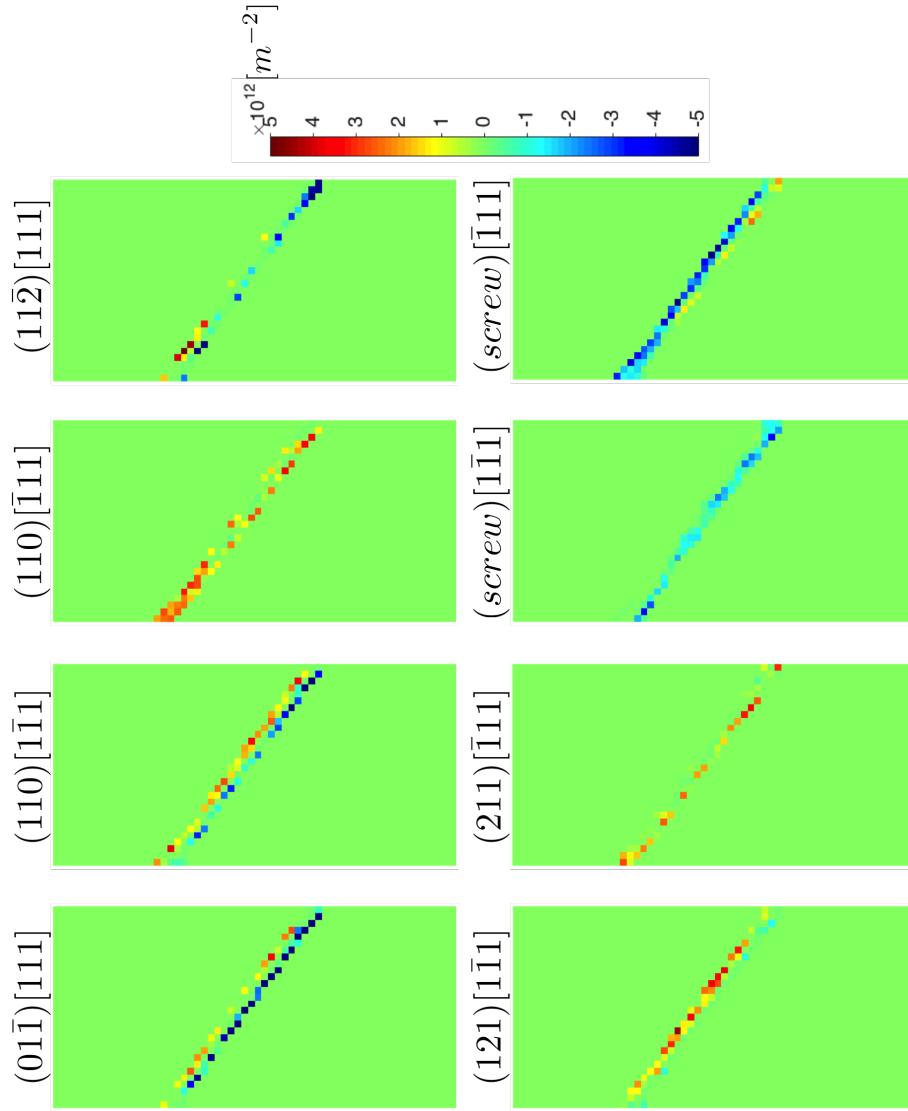


Figure 7.21: Estimated GND density (in m^{-2}) from Nye tensor inside the β twin. Only the non-zero components are shown (the complete map is given in Appendix D).

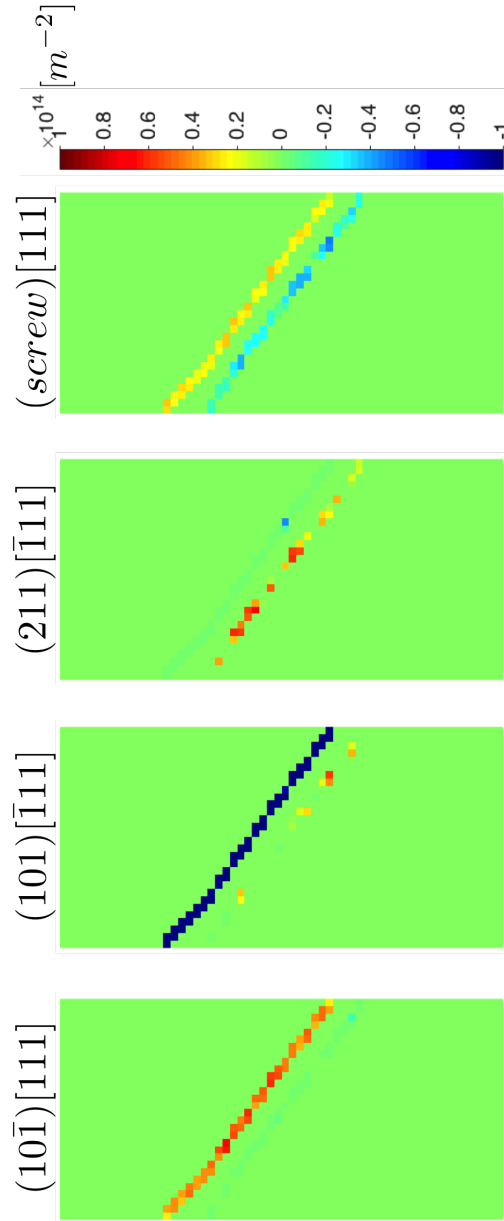


Figure 7.22: Estimated GND density (in m^{-2}) from Nye tensor at the twin boundaries. Only the significant components are shown (the complete map is given in Appendix D).

A gradient of density of GNDs can be observed at the twin and phase boundaries. This result is not unexpected since the formation of both mechanical twins and martensite plates is related to a shear of the matrix. Indeed, continuity must be maintained between the matrix and the deformation products. The GND calculated in the case of mechanical twins seems also coherent with the TEM observations shown in Chapter 4, at least qualitatively (see Figures 4.12(a) and (b)).

In the system of reference attached to the interface (x and y axis are parallel and normal to the twin boundary, respectively), one can see that the shear stress vanishes. Since screw dislocations are associated with shear stresses only, the compressive stress field in the transition zone may be related to mainly edge dislocations, for which compression arises around the extra half-plane in both x and y directions.

Starting with the expression of the stress field around an edge dislocation,

$$\sigma_{yy} = \frac{-\mu b}{2\pi(1-\nu)} \frac{y(x^2 - y^2)}{(x^2 + y^2)^2} \quad (7.20)$$

simple assumptions based on the shape of the stress field can be proposed :

- the stress field is constant along x direction ;
- the stress field is constant along y direction up to a value of $\lambda \sim 800nm$;
- the edge dislocations are aligned and their Burgers vector are parallel, so that their associated normal stress field are additive (as a first approximation), while their shear stress field are anti-parallel.

The measured stress field can thus be related to a dislocation density :

$$\langle \sigma_{yy}^{measured} \rangle = \sum^{\rho^{edge}} \sigma_{yy} = \rho^{edge} \cdot \frac{-\mu b}{2\pi(1-\nu)} \cdot \lambda_y \quad (7.21)$$

with $\langle \sigma_{yy}^{measured} \rangle = -400 MPa$, $\nu = 0.33$, $\mu = 35 GPa$, $b = 2.5 \cdot 10^{-10} m$ and $\lambda_y = 800 nm$ which is the distance corresponding to the transition zone length along y direction.

The calculated edge dislocation density is about $2.4 \cdot 10^{14} m^{-2}$. This value is of the order of the total dislocation density calculated from the lattice curvature of the matrix. This could mean that most of the internal stresses at twin boundaries are due to this ribbon of dislocations.

This analysis should be extended to the complete deformation features by including the twin/martensite tips. Indeed, these features are often mentioned as stress concentration zones within the material [230]. The present improved EBSD technique could give new insights in the quantification of stress levels and sizes of these zones, as well as their evolution during mechanical solicitation during *in situ* testing for example. Such kind of experiments on Ti-12wt.%Mo will be performed in the future.

Furthermore, an estimation of the elastic constants of the orthorhombic α'' phase should be performed to improve the interpretation of the results obtained in this Chapter. Several methods could be used to achieve this goal : *ab initio* calculations if metastable phase can be modeled, bulk 2D synchrotron/neutron diffraction measurements with unloading steps, nanoindentation in sufficiently large plates to avoid substrate effect with the matrix and with different crystalline orientations.

7.5 Conclusion

High-Resolution EBSD is a promising technique for the investigation of internal stresses and content of GND within crystalline materials. The method proposed here allows the determination of the **absolute stress state** around non-punctual defects like twins and stress-induced phases if some assumptions can be evaluated.

It has been showed that residual stresses are not similar in the both analysed cases. On the one hand, **the martensite plate is in a compressive state** along the direction parallel to the interface, with a magnitude up to about $-200 MPa$ calculated with the elastic constants

of β phase. Also, the interfaces seem to support a huge stress concentration while the matrix is globally free of residual stresses after unloading. On the other hand, the interior of the twin is in a tensile state along the normal of the twinning plane, while the surroundings of the twin boundaries sustain a large compressive state along the three principal directions. This indicates that **large strain gradients** appear in the microstructure as soon as mechanical twins form.

The technique also allowed the **assessment of the geometrically necessary dislocations densities** around the interfaces. The type of dislocations at the interfaces are compatible with the results of the literature in the case of the α''/β semi-coherent interface, i.e. edge dislocations of the $\{112\}\langle 111\rangle$ slip system. Finally, the dislocation arrangement around the mechanical twin is compatible with the one observed in Chapter 4, i.e. a ribbon of parallel $\{111\}$ type dislocations on both sides of the twin.

This technique can be extended for GND and stress mapping between neighboring grains. However, the results obtained here should be confirmed via another characterisation technique and/or simulations to fully insure the validity of the method. Finite Element Crystal Plasticity Modeling of $\{332\}$ mechanical twinning and $\beta \rightarrow \alpha''$ SIM phase transformation will be performed for this purpose. Nevertheless, the results of these HREBSD investigations are consistent with the results obtained by XRD under synchrotron radiation in Chapter 6. **Large internal stresses are present in the material after unloading**, particularly around mechanical twins. Since the volume fraction of primary twins quickly increases with applied macroscopic strain, it can be supposed that the strain gradient calculated in this chapter will be more and more present within the entire microstructure, hence having a marked and permanent signature in mesoscopic measurements such as XRD.

A precise calculation of the internal stress field arising in a plastically strained material can be a valuable input parameter for advanced plasticity modeling of the TRIP and TWIP phenomena, for example in models accounting for strain gradient plasticity. They could lead to better predictions of the internal state of a material after metal forming processes, for example.

Chapter 8

Influence of the deformation path on the plasticity of the Ti-12wt.%Mo alloy

Up to this point, the Ti-12wt.%Mo alloy has only been tested in uniaxial tension. However, a material will be subjected to various loading conditions during its life cycle, either during its forming processes or during its use as structural piece. It is thus of primary importance to study the mechanical behaviour of Ti-12wt.%Mo under other loading paths. This last chapter aims at exploring the mechanical response of Ti-12wt.%Mo alloy during strain path changes, performed by incremental oligo-cyclic shear tests. A first attempt in explaining the observed behaviour will be discussed, taking into account the different contributions to work-hardening highlighted in the previous chapters.

8.1 Introduction

During processes of metal shaping, material generally sustains strain path changes. They are often associated with changes in the flow stress, depending on the shape of the yield surface. Indeed, the mechanical response of the material is dictated by this yield surface, and its response may vary largely between a monotonic loading and a loading with strain path changes for an equivalent strain level [231].

Like in monotonic loading, different microstructural parameters influence the response of a material under a strain path change. These parameters are, for example, the crystallographic texture, the size and morphology of the grains, the nature of the constitutive phases...

Schmitt *et al.* proposed a parameter (α) for measuring the magnitude of a change of strain path after an initial prestrain [232]. This parameter equals :

$$\alpha = \frac{\varepsilon_p : \varepsilon}{\sqrt{\varepsilon_p : \varepsilon_p} \sqrt{\varepsilon : \varepsilon}} \quad (8.1)$$

where ε_p and ε correspond to the tensor of the plastic prestrain and of the subsequent deformation, respectively. Among all possibilities, one can consider the following particular cases :

- $\alpha = 1$ corresponds to no or slight change in the strain path. Previously active slip systems continue to be active during further loading. It is for example the case for the cyclic loading performed in Chapter 6.
- $\alpha = 0$ means that the strain path is abruptly changed. In this case, the active slip systems stop to be active and new slip systems have to be activated.
- $\alpha = -1$ means the reversion of the strain path. During initial plastic loading, stress concentrations build up in the material, and generally lead to a decrease of the yield strength after inversion of the loading direction [233]. This anisotropic effect is called the

“Bauschinger effect”. Here, the same slip systems are active as before, but with an opposite direction.

The Bauschinger effect is observable in most polycrystalline metallic materials. Its magnitude depends on several parameters like the nature of the phases in the material, the crystallographic texture, the grain size, the number of active slip systems, etc. Indeed, while the material is strained, dislocations accumulate and form particular structures like pile-ups or tangles. Once the load is removed, these structures can evolve to reach a mechanical equilibrium. When the load is applied in the reverse direction, the so-called back-stresses help the dislocations to overcome the critical stress needed for their motion, which generally results in a macroscopic lower yield strength in the opposite direction. This phenomenon is the expression of the kinematic hardening, corresponding to a translation of the von Mises yield surface.

All obstacles to dislocation motion can have an effect on the response of the microstructure to a strain path change. Differences in the elastic constants of the constitutive phases can lead to significant levels of back-stresses in the material due to the accommodation of the elastic mismatch. This is for example observed in cold-worked $Ti - 6Al - 4V$ grade as illustrated by the lower curve of Figure 8.1. Indeed, one can see that the compressive yield strength decreases when a tensile prestrain is applied on the alloy. Similar trends (high back-stress values) are also observed in Dual-Phase steels [176, 234, 235].

Different parameters have been proposed to quantify the Bauschinger effect. Some of them are schematically represented on Figure 8.2. The evolution of the back-stress will be investigated here.

The back-stress (σ_{bs}) values are calculated with the following formulae :

$$\sigma_{bs} = \frac{|\sigma_P| - |\sigma_R|}{2} \quad (8.2)$$

where σ_P is the stress just before the load reversal and σ_R is the yield stress of the Bauschinger effect (in the opposite loading direction), as defined on Figure 8.2.

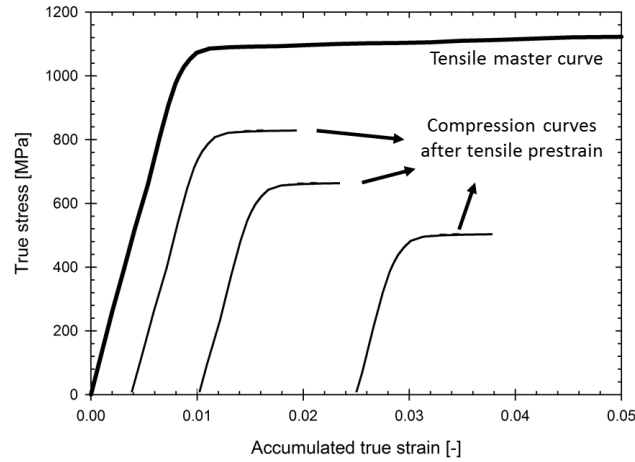


Figure 8.1: *Illustration of the Bauschinger effect in a Ti–6Al–4V grade. The curves are reconstructed with datas coming from [2].*

The goal of the tests carried out in the present chapter is to investigate the mechanical behaviour of the Ti-12wt.%Mo alloy under load reversal with increasing imposed strain. A quantification of the evolution of internal stresses with accumulated plastic strain is performed. Indeed, the complexity of the deformed microstructure (see Chapter 4) should have a significant effect on the mechanical response of the material. These tests were performed via shear-reverse shear experiments. A preliminary monotonic simple shear test has been performed to calibrate the parameters for subsequent cyclic tests.

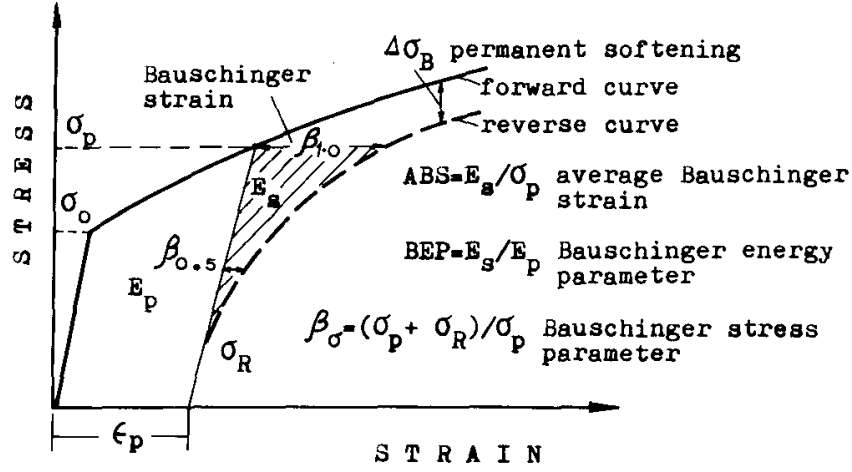


Figure 8.2: Schematic diagram with definition of the parameters characterising the Bauschinger effect [234].

8.2 Experimental Procedure

The tests were performed at room temperature on a home-made bi-axial machine at Université de Liège (Laboratoire de Mécanique des Matériaux et Structures). The setup is schematically drawn in Figure 8.3(a). Prior to experiments, the calibrated zone of the shear samples (illustrated in Figure 8.3(b)) was covered with white painting, followed by a random black speckle pattern necessary for Digital Image Correlation (DIC) analysis. The tests were driven in displacement control mode with an horizontal displacement rate of 0.075 mm/min. The displacement of the lower jaw was measured with a LVDT. Images for DIC analysis were acquired with two ABTPike cameras with a resolution of 640 * 480 pixels. The acquisition frequency was 2.5 Hz. The recorded images were then post-treated with the software Vic3D (version 2010) developed by the LIMESS company. Two sets of images were taken independently in order to ensure the results of the correlation.

The notches on the sides of the calibrated zone help in limiting the edge-effects and reaching a nearly perfect simple shear state in the center of the sample. DIC was performed on different size-decreasing Regions Of

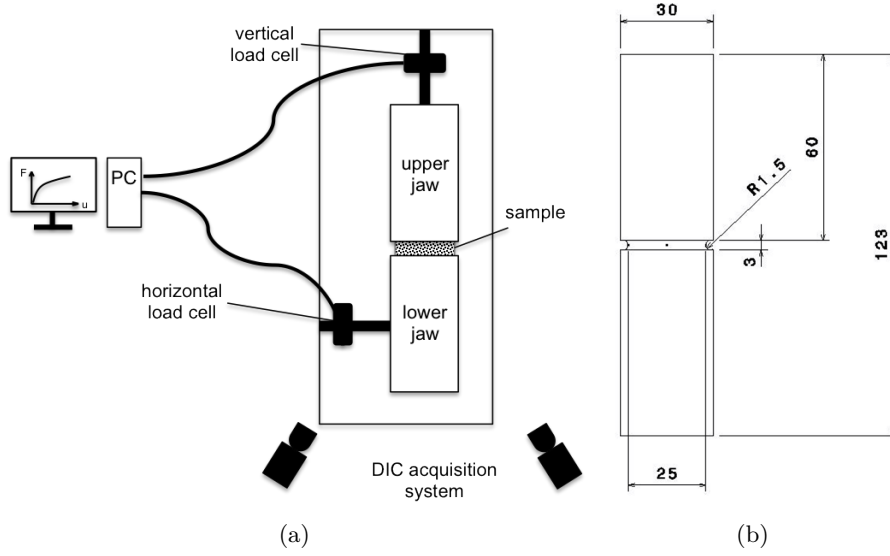


Figure 8.3: (a) Schematic illustration of the (cyclic) simple shear experiments with image acquisition system. (b) Shape and dimensions of the simple shear samples.

Interest (ROI) in order to determine the threshold size where edge effects were no more observable in the simple shear curve. Due to small number of tested samples, the back-stress evolution with prestrain has been characterised by the following procedure. Incremental reverse displacement steps have been imposed to the sample up to $|1|$, $|1.7|$, $|3.3|$, $|5.5|$, $|8|$ mm and up to fracture for sample 1, and up to $|1|$, $|1.25|$, $|1.7|$, $|2.5|$, $|3.3|$, $|4.4|$, $|5.5|$, $|6.6|$, $|8|$ mm and up to fracture for sample 2. The time-displacement curves of the two tests are given in Figure 8.4. The black curves correspond to the imposed horizontal displacement of the jaw and the red curves give the horizontal displacement of the measurement points after post-treatment.

The true shear strain (γ) evolution was then calculated by DIC. For a meaningful comparison with tensile properties, the results can be expressed in terms of von Mises equivalent strain and stress. The shear stress τ and the shear strain γ are converted using the follow-

ing equations :

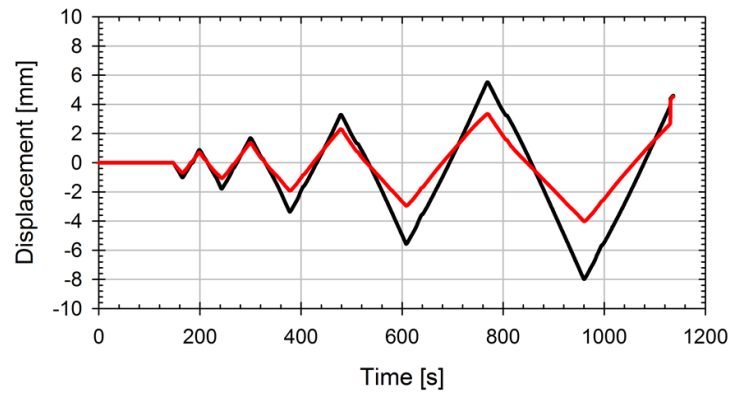
$$\sigma_{VM} = \sqrt{3}\tau \quad (8.3)$$

$$\varepsilon_{VM} = \frac{\gamma}{\sqrt{3}} \quad (8.4)$$

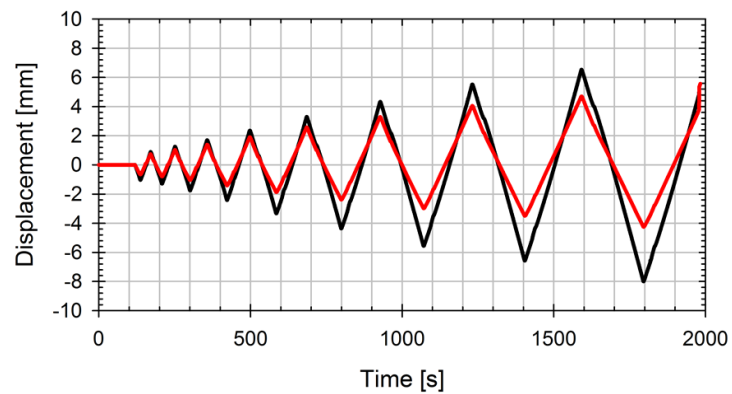
The J_2 plasticity constitutive model has been used to represent the evolution of the equivalent stress with the total accumulated plastic strain with each reversal of the displacement direction. In this formalism, the general expression of the accumulated plastic strain is [236]:

$$\varepsilon_{acc}^p = \int_0^t \dot{\varepsilon}_e^p dt = \int_0^t \sqrt{\frac{2}{3} \dot{\varepsilon}_{ij}^p \dot{\varepsilon}_{ij}^p} dt \quad (8.5)$$

where $\dot{\varepsilon}_e^p$ is the instantaneous effective plastic strain. Since all other ε_{ij} components of the strain tensor are negligible compared to ε_{xy} , Equation (8.5) can be reduced to a sum of the absolute values of the shear components.



(a)



(b)

Figure 8.4: Displacement-time curves for (a) cyclic test 1 and (b) cyclic test 2. The black curves are the imposed displacement on the jaw and the red curves are the measured displacement on the sample.

8.3 Results

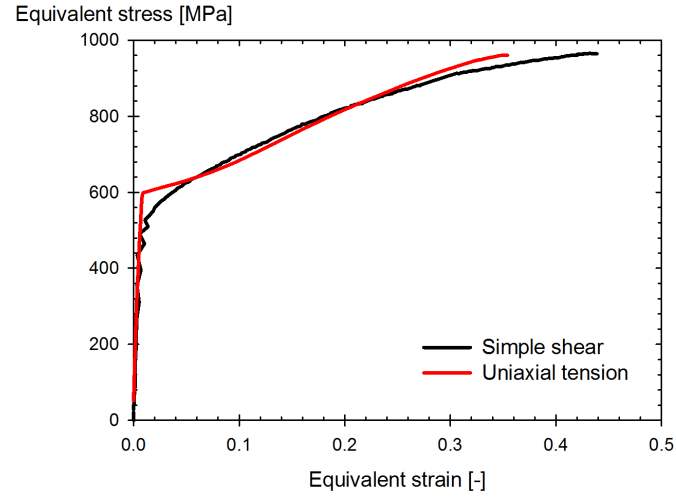
8.3.1 Monotonic simple shear test

Figure 8.5(a) shows the von Mises equivalent strain-stress curve in the case of simple shear loading together with the uniaxial tensile curve (presented in Chapter 3). It can be observed that the global shapes of the curves are not totally the same. Indeed, the simple shear curve has a much more monotonic evolution compared to the tensile curve. The transition between elastic and plastic regimes is less marked and no inflection point is observed during the plastic regime. The yield strength is lower than in the case of the uniaxial tensile test (about 100 MPa). About the same level of maximum equivalent stress is achieved in both modes before failure.

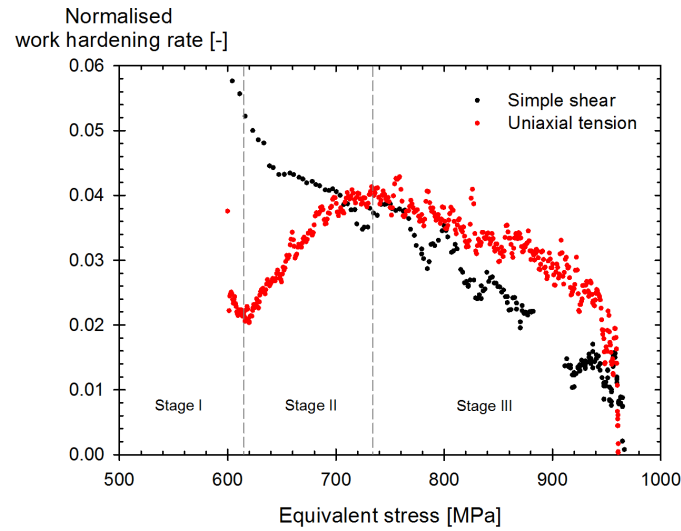
Figure 8.5(b) illustrates the evolution of the work hardening rate for both simple shear and uniaxial tension. It confirms the difference observed on Figure 8.5(a). From the onset of plasticity, the work hardening rate decreases gradually and smoothly in the case of the simple shear test. It does not exhibit an increase of the work hardening rate as observed for the uniaxial tension (Stage II on the figure). In stage III, both rates decrease nearly linearly with increasing stress up to a stress level of 940 MPa where the work hardening rate quickly drops to zero.

Figure 8.6 shows an XRD pattern recorded in the calibrated zone of the simple shear sample after fracture. α'' martensite peaks are present as illustrated by the red arrows. However, their intensities remain very small¹, meaning that the volume fraction of α'' should be relatively small within the material.

¹The y -scale is in square root of counts.



(a)



(b)

Figure 8.5: (a) Stress-strain curve of the monotonic simple shear test on as-quenched Ti-12wt.%Mo (black line), together with the uniaxial tension (red line) for comparison. (b) Work hardening rate evolution of the two loading conditions in (a).

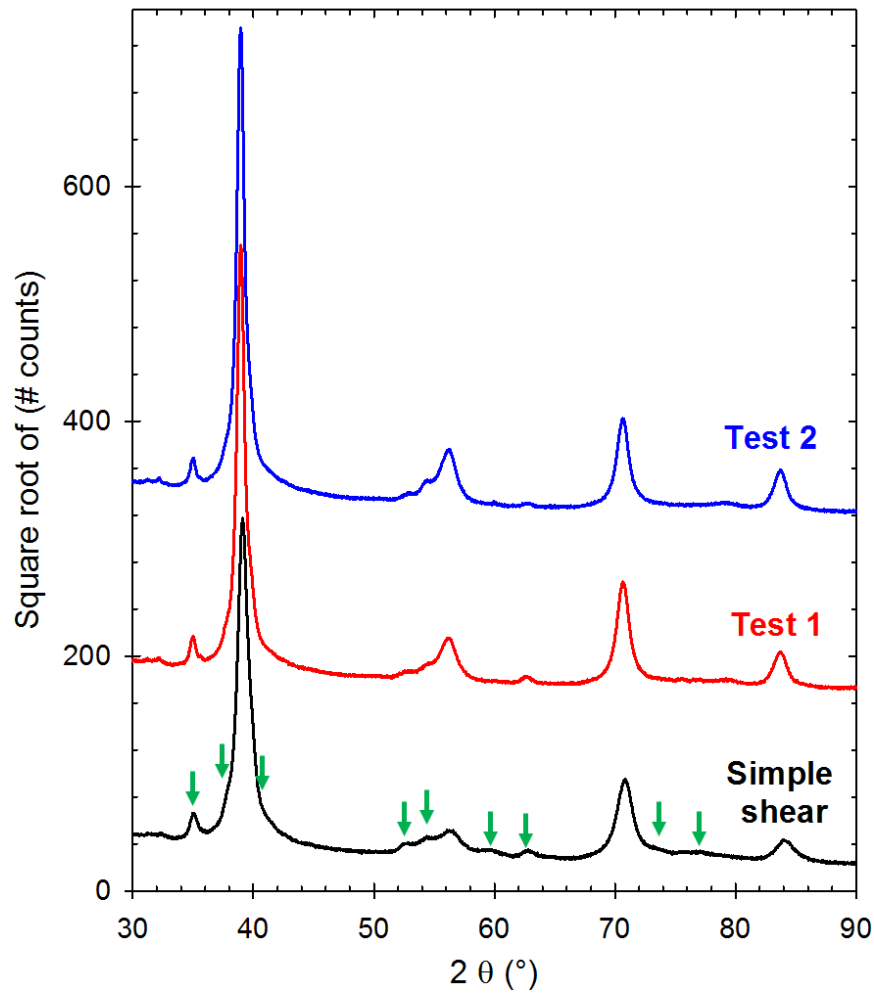


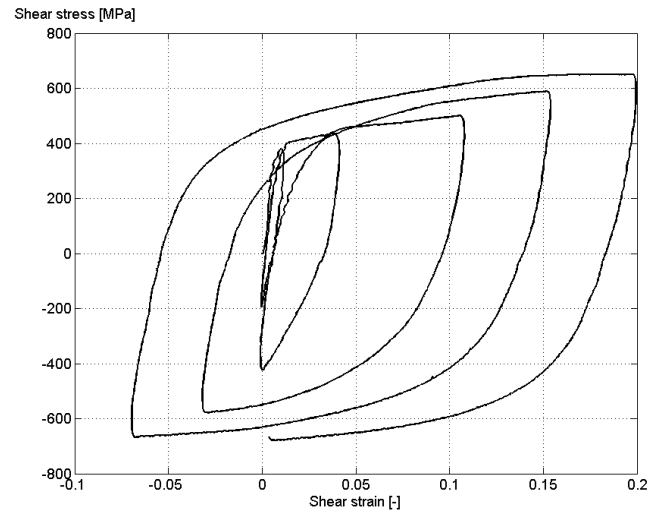
Figure 8.6: XRD patterns of Ti-12wt.%Mo for the monotonic simple shear test (black line) and the two shear-reverse shear tests up to fracture. The green arrows highlight the α'' martensite peaks (refer to Figure 3.8 for indexation).

8.3.2 Cyclic tests

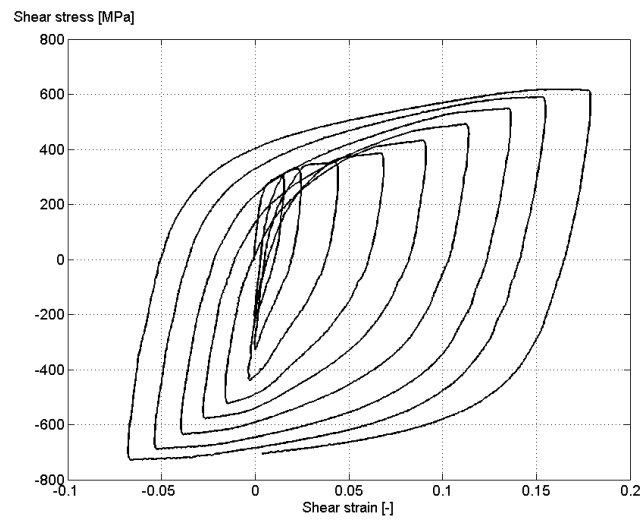
The initial stress-strain curves of the cyclic shear-reverse shear tests are given in Figures 8.7(a) and 8.7(b). For easier interpretation of the results, the evolution of the shear stress have been redrawn as a function of the accumulated shear strain for both tests in Figures 8.8 and 8.9, respectively. The initial yield strengths differ by about 100 MPa.

A large transient inelastic response is observed after each load reversal, either in forward or reverse loading steps. Rather surprisingly, a permanent hardening, *i.e.* a higher flow stress in the reverse direction, is observed in the case of this grade. Furthermore, the strain hardening rate seems larger (at equivalent absolute stress) in the case of reverse direction loading. In the subsequent text, the loading steps in the initial loading direction will be called the *odd* loadings, while the loading steps in the reverse direction will be called the *even* ones.

As for the simple shear sample, XRD measurements have been performed in the calibrated zone of each sample. The diffraction patterns are shown in Figure 8.6 together with the simple shear one. Again, α'' phase peaks of weak intensity are visible for both cases.



(a)



(b)

Figure 8.7: Initial stress-strain curves of the cyclic shear-reverse shear experiments for (a) sample 1 and (b) sample 2.

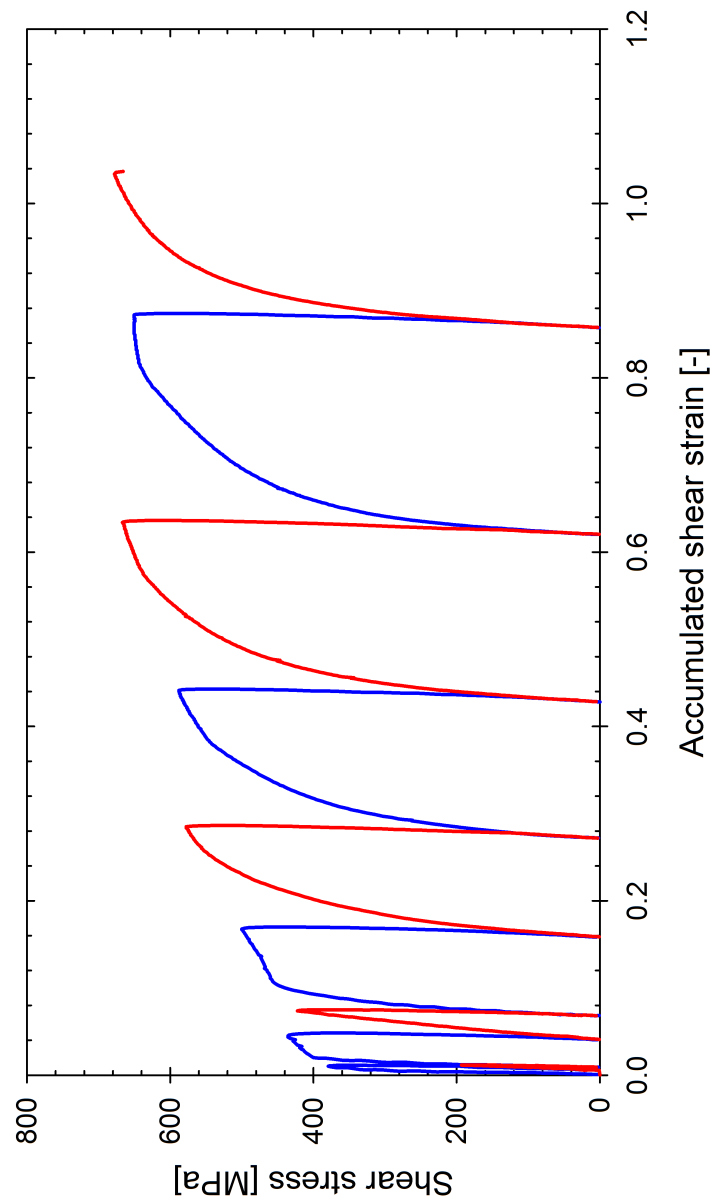


Figure 8.8: Absolute value of shear stress vs. accumulated shear strain for test 1. The blue curves are the odd loadings and the red curves the even ones.

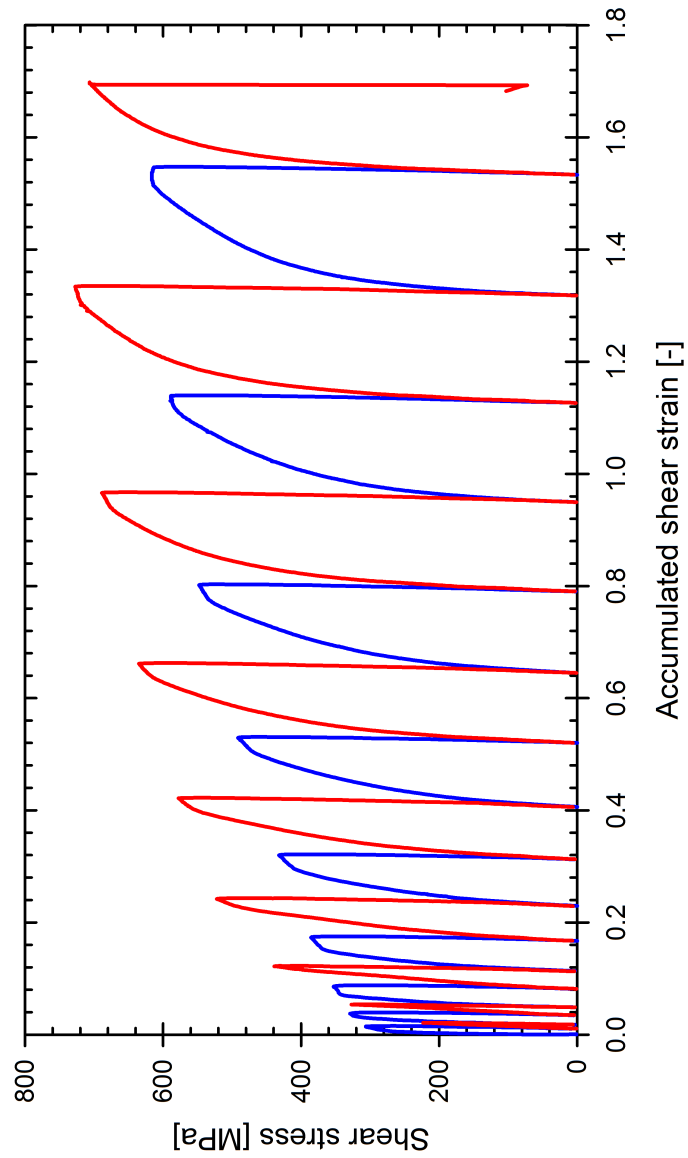
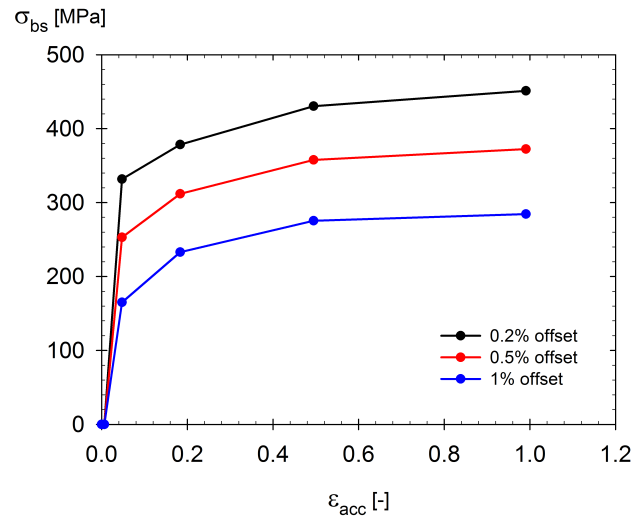


Figure 8.9: Absolute value of shear stress vs. accumulated shear strain for test 2. The blue curves are the odd loadings and the red curves the even ones.

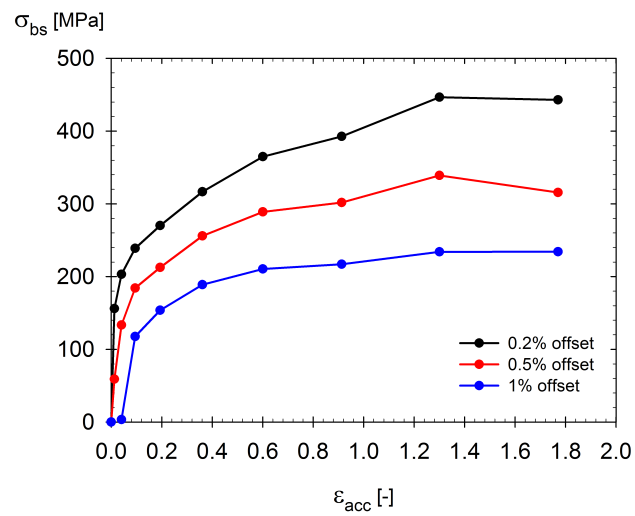
Back-stress evolution

Due to the very marked transient elasto-plastic transition observed during load reversion, the exact determination of σ_{bs} value is not straightforward. To eliminate any ambiguities and to ensure the real trends of the back-stresses evolution in as-quenched Ti-12wt.%Mo, three offset values of strain have been chosen, similarly to the work of Renard et al. for a TWIP steel [65]. These offset values are 0.2%, 0.5% and 1%, corresponding to the most used values in the literature for this kind of experiments. The resulting calculated back-stresses as a function of the accumulated prestrain are plotted in Figure 8.10.

The back-stress as calculated by Equation (8.2) can be seen as an image of the mean level of internal stresses building up in the sample. Figure 8.10 suggests that the level of internal stresses quickly increases in the material, then tends to saturate towards a constant value at high accumulated plastic strain. A non-negligible difference in amplitude is observed between the two tests. The calculated values clearly depend on the choice of the offset value, but the trends are the same for the three offset values. As an example, for a cumulated plastic strain $\varepsilon^{acc} \approx 1$ and offset value of 1%, the back-stress equals 280 MPa for test 1 and 225 MPa for test 2. Whatever which is the most representative between the two tested samples in this experiment, the reached values are very large compared to the absolute strength of the material.



(a)



(b)

Figure 8.10: Evolution of the von Mises equivalent back-stress as a function of the accumulated prestrain for three different offsets. (a) test 1 and (b) test 2.

Permanent hardening

Figures 8.8 and 8.9 clearly highlight a permanent hardening effect in the material. Indeed, the level of stress achieved during an even loading is higher than its odd counterpart. This effect is particularly marked in test 2. The differences between the maximum load points in odd and even loadings are gathered in Figure 8.11. The hardening tends to a constant value after a few cycles. The hardening tends to a constant value after a few cycles.

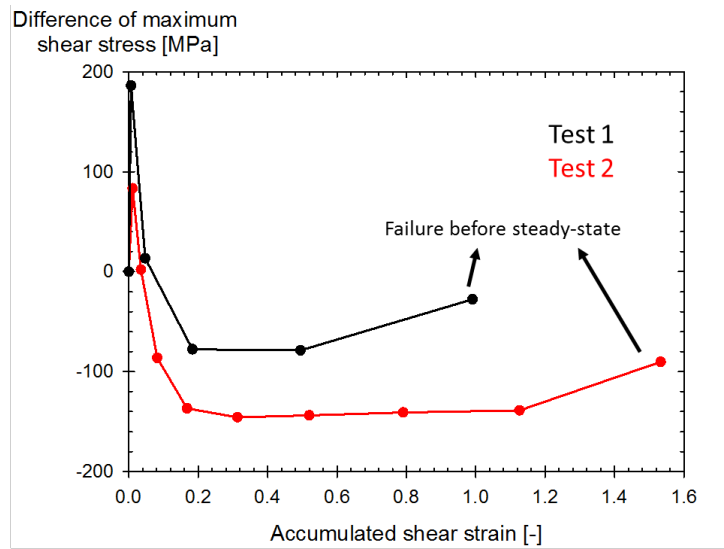


Figure 8.11: *Evolution of the permanent hardening as a function of the accumulated shear strain for the two tests.*

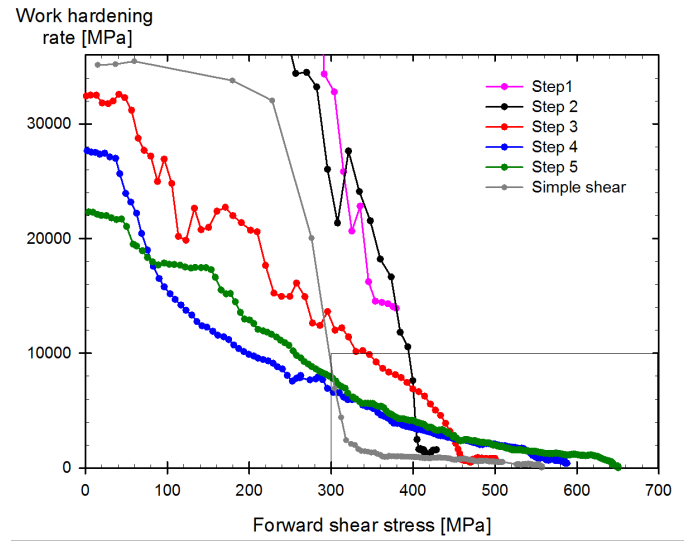
Evolution of the work hardening rate

The evolution of the work hardening rate with imposed shear stress is shown for both odd and even loading steps in Figures 8.12 and 8.13 for test 1 and in Figures 8.14 and 8.15 for test 2, respectively. For the sake of comparison, they are presented together with the work hardening of the monotonic simple shear test.

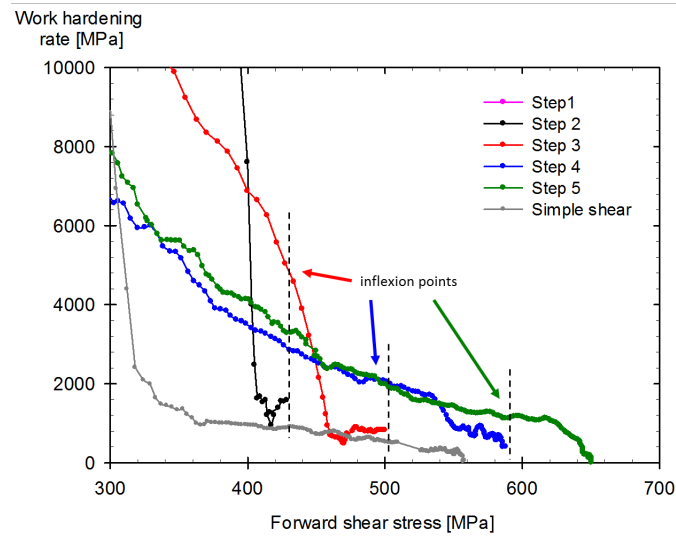
Odd loading steps Firstly, the work hardening rate is larger in the cyclic tests than in the monotonic one, either in odd or in even directions. It is interesting to note that the trends of the monotonic loading seem to be kept during cyclic loading, since the curve of each steps catches up the monotonic one after the transient part. This is particularly clear if the monotonic curve is shifted to match the elasticity limit of the cycled one, mostly for the first test which exhibit a much higher yield point.

It can also be seen that the decrease of the work hardening rate is less and less steep at each stage of the odd loadings. On the magnified views, special points highlighted by arrows correspond to inflection points. It is worth noting that these changes in the shape of the work hardening evolution occur around the maximum stress level achieved during the previous load cycle. The work hardening evolution can be divided into three steps : (i) a smooth decrease corresponding to the transient elasto-plastic part ; (ii) an abrupt decrease and (iii) a nearly constant level up to the reversal of the load direction.

Even loading steps The same trends as in the forward direction are observed. However, for a given level of stress, the instantaneous work hardening rate is nearly two times larger in the case of the even loadings.

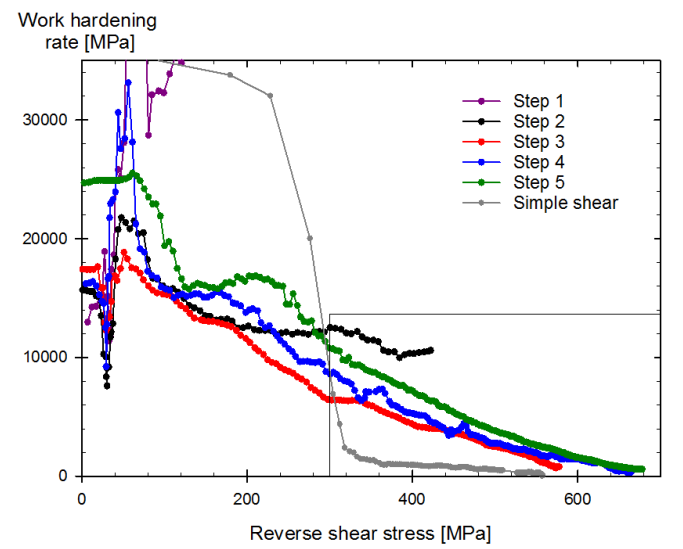


(a)

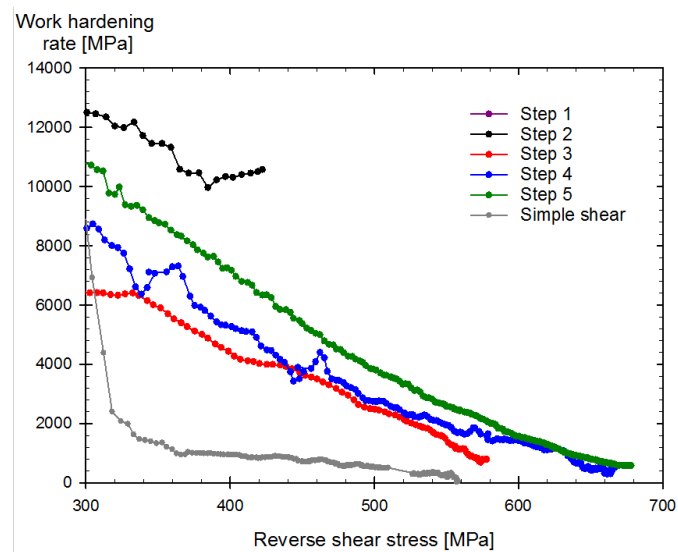


(b)

Figure 8.12: (a) Work hardening rate vs. applied shear stress for odd steps of test 1. (b) Zoom corresponding to the frame in (a). The arrows highlight the slope concavity changes.

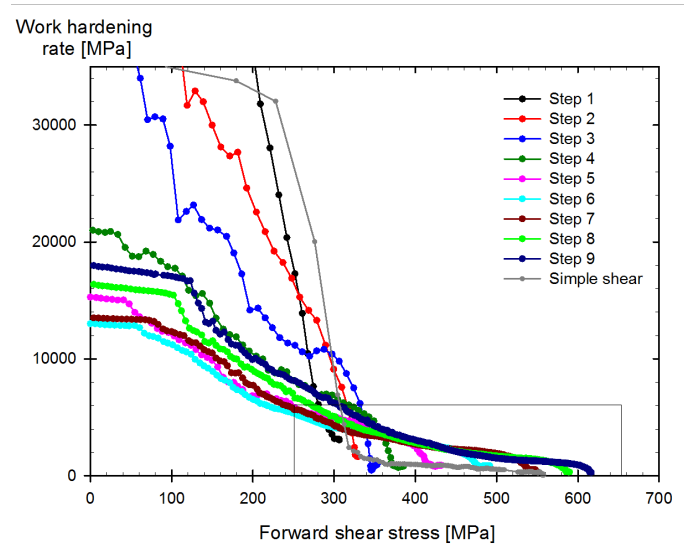


(a)

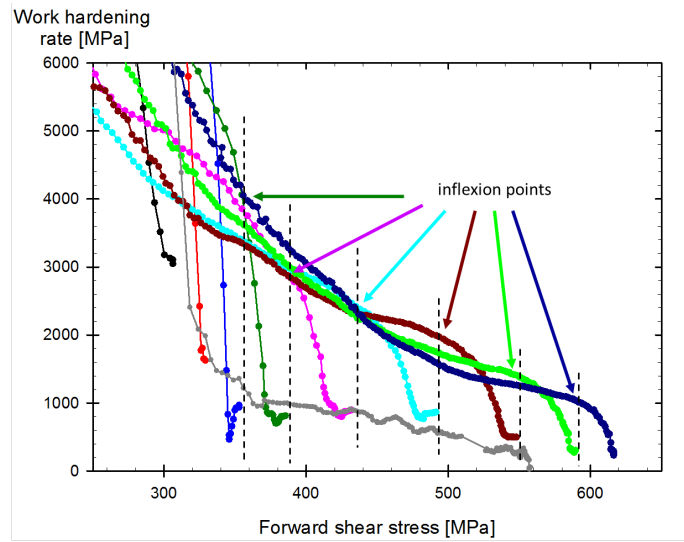


(b)

Figure 8.13: (a) Work hardening rate vs. applied shear stress for even steps of test 1. (b) Zoom corresponding to the frame in (a).

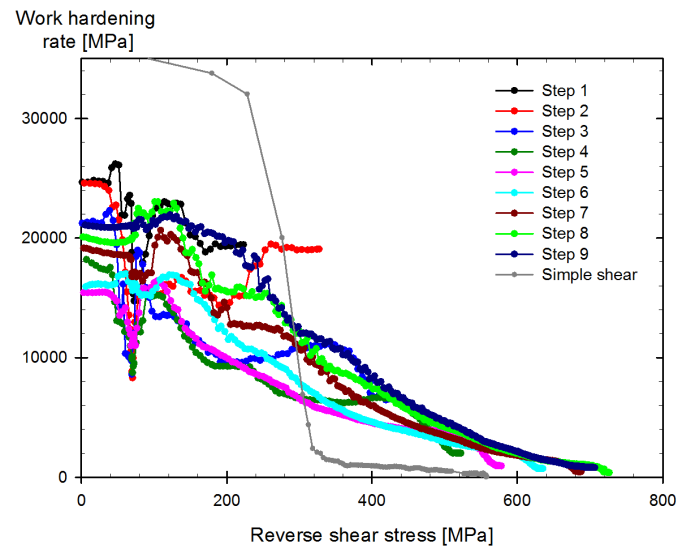


(a)

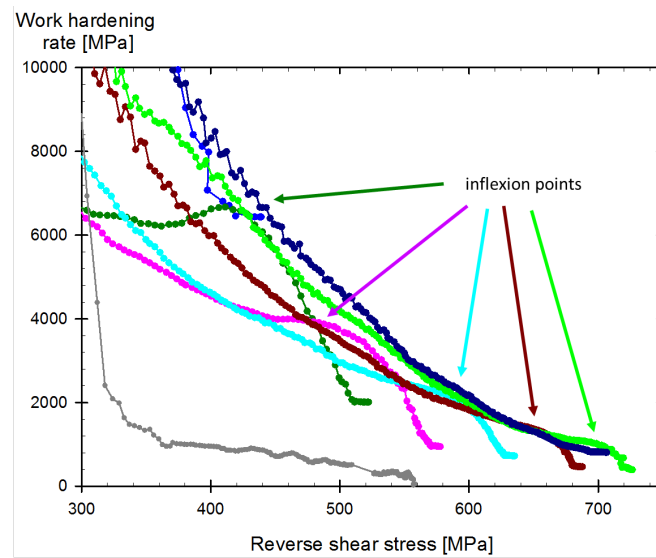


(b)

Figure 8.14: (a) Work hardening rate vs. applied shear stress for odd steps of test 2. (b) Zoom corresponding to the frame in (a). The arrows highlight the slope concavity changes.



(a)



(b)

Figure 8.15: (a) Work hardening rate vs. applied shear stress for even steps of test 2. (b) Zoom corresponding to the frame in (a).

8.4 Discussion

The shear-reverse shear test has been chosen to characterise the kinematic hardening in Ti-12wt.%Mo due to its easiness and the absence of necking or buckling compared to tension-compression tests. The drawback of this approach could be some difficulties in the comparison of the results with the previous chapters where uniaxial tension was the dedicated mode of mechanical testing. However, as a first approximation, we assume that all the active plastic deformation mechanisms in tension are also activated in the case of simple shear. The activation of stress-induced martensitic α'' phase in simple shear has been shown owing to X-ray diffraction (see Figure 8.6), while the observation of mechanical twins after various solicitation modes during the whole experimental work of this thesis (cold rolling, indentation, bending, vibrations during preparation, etc.) strongly suggests that this mechanism is unavoidable in the present material. No plausible explanation concerning the difference of yield strength has been found. Indeed, the grain size measured in the heads of both samples are $60 \pm 4\mu m$ and $72 \pm 8\mu m$ for test 1 and test 2, respectively. This difference is not large enough to explain such a difference of yield strength. Another possibility could be a texture effect. Since the three samples come from the same cold-rolled sheet, it is believed that the global recrystallisation texture is the same in the three samples and this possibility seems unlikely. However, the presence of macrozones of texture has been observed in Chapter 6, and a similar situation could have arisen here too. Whatever the cause, the results are all quantitatively impacted by this initial difference, but the trends are qualitatively the same. This fact highlights an important influence of the initial microstructure on the response during a strain path change. It should be noted that the mechanical tests conducted in this chapter are not usual ones, rendering the comparison with well-known materials difficult. However, the observed behaviour is certainly very usual. A possible scenario will be exposed in Section 8.4.2.

8.4.1 Simple shear behaviour

When tested in simple shear, the present Ti-12wt.%Mo grade seems to exhibit a work hardening slightly different from the one observed in uniaxial tension. Indeed, the decrease of the work hardening rate is more continuous and does not show the 3 characteristic stages exhibited in tension. By contrast, yielding is not as well marked as in tension, corresponding more to an elasto-plastic transition. This different behaviour could be an artifact coming from the experimental setup. After this transition, the decrease of the work hardening is slow and nearly linear with the applied stress down to about 900 MPa, followed by the regime dominated by the starvation of the hardening sources. It is possible that the twinning rate is different in this loading configuration, or that less twinning systems are activated. These two considerations have indeed been observed in a TWIP steel grade [65]. An analysis of the twinning rate similar to the one done in Chapter 4 should be performed in order to validate these hypotheses.

8.4.2 Non-monotonous plasticity

Most of the published results dealing with the Bauschinger effect in titanium alloys focus on the Ti-6Al-4V grade. Some studies in the 1970s dealt with some β -stabilized Ti alloys. In a $Ti - V$ alloy, asymmetry between tensile and compressive flow stresses have been reported in monocrystalline samples when the dominant gliding planes are of the $\{112\}$ family [237]. As already highlighted in the previous chapters, the activated gliding planes in BCC crystals depend on the core structure of the dislocations, itself being dependent on the chemistry of the alloy. Although this asymmetry was clearly observed in monocrystalline samples, polycrystals did not show any asymmetry between tensile and compressive loading. Margolin and co-workers carried out reverse loading experiments on $Ti - Mn$ alloys [238, 239]. They suggested that the difference in behaviour results from the strain gradients appearing in the surroundings between the grain boundaries and the grain interiors during reverse loading. They proposed that the activation of new

slip systems during reverse loading is due to vacancy binding of the dislocations appeared during forward loading.

In order to explain the complete observed behaviour after reversion of the strain path, all possible microstructural mechanisms affecting the work hardening should be taken into account, and their relevance evaluated in the present case. These mechanisms are based on the effectiveness of the dislocation motion.

The first contribution defines the back-stresses : when a load is applied in a particular direction, lattice friction oppose to dislocation motion. Among the dislocation population, a given fraction of them stops their motion because these internal stresses equal the external applied load (with opposite direction). Once the applied load is decreased and reversed, both the applied load and internal stresses add together, so that the glide of the previously non-mobile dislocations is activated at macroscopic stresses lower than in the initial loading direction. It has to be mentioned that all crystalline heterogeneities like dislocation cells, grain boundaries, solute atoms, etc, can be a source of back-stress [240], each one having a more or less strong potential in developing back-stresses. Also, a screening effect of the long-range stress field can arise depending on the dislocation arrangements [176].

The second contribution involves the dislocations that have been pinned during forward loading. Two distinct cases can arise concerning these dislocations. On the one hand, if the trap is not stable upon load reversal, the dislocation can be released from it once a sufficient stress is reached and contribute to the reverse plastic flow. This contribution is thus highly correlated with the obstacle to dislocation motion content. On the other hand, some particular obstacles can lead to stable locks which will deeply anchor the dislocations and prevent them from moving upon load reversal. These effects can be incorporated in the Kocks-Mecking model for the evolution of dislocation density with imposed strain [62].

A last important contribution is the GND content. Indeed, during macroscopic plastic straining, compatibility of deformation at the grain boundaries between each grains of the polycrystal has to be

fulfilled. Strain gradients appear within the grains as a consequence of this compatibility criterion, and GNDs form in the material to accommodate them. These dislocations obviously play a role during strain path changes.

In Ti-12wt.%Mo, the possible dislocation sources are various as highlighted in previous chapters. Initially, grain boundaries and thermal jogs are the effective dislocation sources, rapidly outperformed by the numerous interfaces that form during the increase of work hardening (see Chapter 4). Moreover, the mean free path of dislocations (whatever their type) is rapidly decreasing, conducting to a fast increase of the dislocation density compared to classical dislocation-only driven plasticity.

As shown in Chapter 7, the generation of $\{332\}$ twins is accompanied by the creation of a dense ribbon of GND in the matrix nucleated at the twin boundaries, as well as relatively large accommodating stresses. Permanent stresses after unloading were also highlighted by *in situ* cyclic tensile loading under synchrotron radiation (see Chapter 6). These two characteristics must play an important role, both in the inelastic transient flow stress evolution after reversal of the load and the subsequent evolution of the work hardening rate. These local stress fields will interfere with the glide of the dislocations. Very recently, this effect has also been observed by Paul *et al.* in multiphased TiAl alloys [241]. They observed an increasing elasto-plastic transient response after load reversal with increasing pre-strain (which they call transient softening), as well as some permanent hardening in some cases. However, the low ductility of TiAl alloys renders it difficult to compare the magnitude of this hardening. As an interesting point, the microstructures of TiAl alloys are both multiphased and lamellar. The authors attributed the transient softening effect to the different yield strength of the various components of the alloy which lead to the formation of internal stresses during prestrain, with a magnitude of $\sigma_i = 0.8\sigma_y$. During reverse loading, the sandwich microstructure will deform very heterogeneously, depending on the distribution of the soft grains (favored orientation) and hard grains (not favored orientation). This concept could be extended to the case of the twins networks forming in Ti-12Mo. Indeed, a first network of twins

could form during forward loading. This initial network polarises thus the microstructure. Once the loading direction is changed, the initially formed twins could be seen as hard (undeformable) zones, or at least as heterogeneous structures compared to the rest of the initial grains. Another twinning variant has to be activated, at a higher stress level than the previous one (due to dynamic Hall-Petch effect). This hardening effect would be more and more pronounced between each load direction reversal. An illustration of the process is depicted in Figure 8.16.

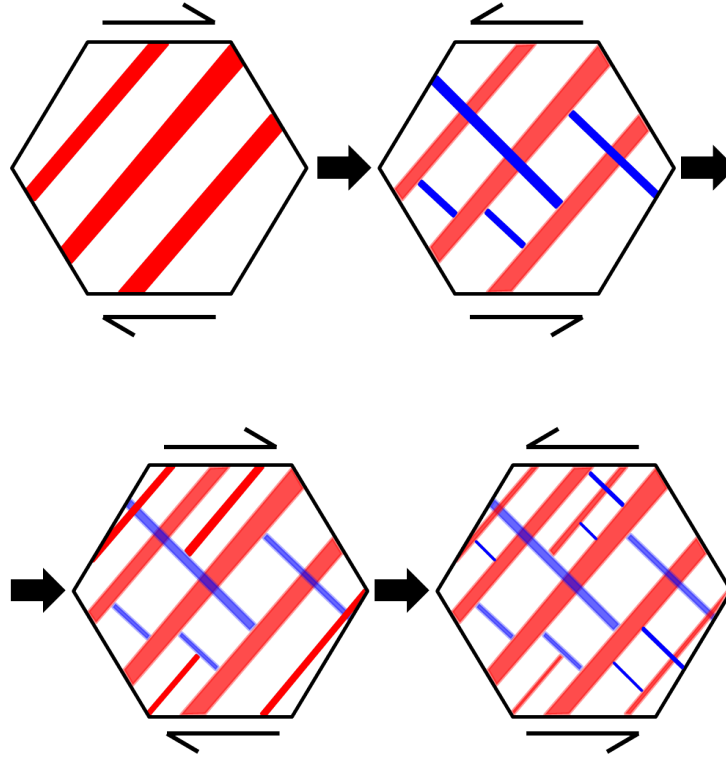


Figure 8.16: *Illustration of the polarisation process of the microstructure, and its consequence on the response after strain path changes.*

The occurrence of a SIM transformation in the material, confirmed by XRD analysis, has also to be taken into account as a potential source of back-stresses. Indeed, it is well-known that dual-phase materials

generally present high levels of back-stresses. In their study of fatigue behaviour of Ti-6Al-4V alloy which shows permanent softening, Steele and McEvily highlighted a pronounced Bauschinger effect in this dual-phase alloy. Recently, a study of Peirs et al. demonstrated the strain rate dependence of the Bauschinger effect in the Ti-6Al-4V alloy [242], showing that the Bauschinger effect was increasing with increasing strain rate. Yet, this results was foreseeable by considering that the dynamic recovery term in the Kocks-Mecking model is temperature and strain rate dependent [243]. Dual-phase steels are also well-known examples of material exhibiting high level of back-stresses during strain path changes. The actual effect of martensite precipitates on the back-stress depends on the degree of coherency between β and α'' phases, as well as the morphology and orientation of these precipitates, as already discussed in Chapter 6. Moreover, the martensitic transformation brings about a lot of new interfaces within the microstructure, which certainly contribute to the increasing heterogeneity distribution in the microstructure (similarly to the twins case illustrated in Figure 8.16).

The saturation value of the back-stresses at high accumulated strain levels must be related to the fact that the density of defects in the microstructure has reached a saturation value. Indeed, it can be seen in Figure 8.10 that a large fraction of the back-stress level is achieved before 0.2 accumulated strain, thus once the saturation level of primary deformation-induced bands is achieved if the results obtained for uniaxial tension can be extended to this solicitation mode (see Chapter 4). It could be an indicator that a large fraction of the back-stress is due to primary twins, either due to a composite effect and/or to dislocation pinning at the interfaces.

Another important point to discuss is the permanent hardening observed in all reverse loading steps. This phenomenon is quite unusual. Indeed, most of investigations on strain path changes have highlighted a permanent softening effect during Bauschinger experiments. Since the experiment performed in this study does not correspond to a true Bauschinger test, the same experiment should be performed on a material of known behaviour. However, as already pointed out, recent investigations on TiAl have reported some permanent hardening, even

if the authors were not able to explain its origin.

Permanent hardening during load reversal has also been scarcely observed in a few austenitic stainless steel grades [244]. Steele and McEvily suggested that the hardening in stainless steels could come from the large number of slip systems, which could promote interaction hardening [245]. In *BCC* alloys, the number of slip systems is even higher, but the easiness of cross-slip in *BCC* compared to *FCC* alloys is not in favor of this hypothesis. Moreover, in their study on various kinds of materials, Smith et al. [244] did not observe any permanent hardening in low alloyed α -steels like AISI 4130 and 4340 grades.

A last possible cause of this difference in behaviour between forward and reverse shear straining is the dependence of yield stress on the loading condition frequently observed in *BCC* metals. Indeed, several authors have reported such dependence in the case of single crystals of pure metals (Argon et al. [246], Sherwood et al. [247], Keh et al. [248], etc.). This deviation from Schmid law (which is correct for *FCC* and *HCP* metals) has been attributed to the threefold symmetry of the screw dislocation core around the dislocation line (Bowman et al. [249], see Chapter 2). Many anomalous slip behaviours in pure *BCC* metals have been explained by computer simulations of the complex 3-dimensional structure of the cores [250–252]. The main effect in the present case implies the twinning-antitwinning asymmetry (this concept has been introduced in Chapter 5). It has been shown that the activation of screw dislocation motion in the twinning sense was always easier than in the antitwinning one due to the asymmetry of their respective critical resolved shear stress (*crss*) [252]. Therefore, if a dislocation is activated in the twinning sense during forward loading, it means that the stress to be applied to move it in the opposite sense (antitwinning one) is higher, hence the work hardening rate is impacted. The flow stress required to reach the “steady-state” regime is thus higher in the reverse sense than in the forward one.

Finally, it was pointed out in Section 8.3.2 that the work hardening rates exhibit three distinct steps. The first decrease corresponds to the non-linear elasto-plastic region where the back-stresses are supposed to be

the most influent, as suggested by Paul *et al.* [241]. Then, an abrupt decrease is observed, at a stress level closely related to the maximum level achieved during the previous cycle. This suggests some kind of memory effect in the mechanical response of the material. It is worth noting that this effect is observed during both forward and reverse loadings. After this decrease, the work hardening rate is rather constant with increasing applied stress up to the following load reversal.

8.5 Conclusions

Shear - reverse shear experiments have been applied on Ti-12wt.%Mo alloy. These mechanical tests highlighted interesting features which are summarised hereunder :

- The **work hardening rate evolution in monotonic loading is mode-dependent**. The elasto-plastic transition in simple shear is more gradual than in uniaxial tension, and no increase was observed in this case. These differences must come from either a different twinning rate and/or different twin variant selection. An effect of the experimental setup may also be important.
- A **large amount of back-stress** arises in the material with increasing accumulated plastic strain, and it reaches a saturation value at high strain levels. The magnitude of the back-stress is strongly offset dependent due to the large transient elasto-plastic response of the material. The main source of back-stress is believed to be the increasing amount of mechanical twins which, by a composite effect, will induce more and more long-range elastic stresses in the material. α'' martensite could also play a role in the development of back-stresses due to differences in elastic behaviour.
- A **permanent hardening** is observed after load reversal. This phenomenon was barely reported and no plausible explanation was found in literature. Its origin is thought to come from the **initial polarisation of the microstructure** during the first loading

step. This permanent hardening also suggests that the yield surface evolution with work hardening is much more complicated than what is observed in conventional materials, and that new models will have to be implemented to take this effect into account. At last, such a behaviour, if properly mastered, could be used during cold working operation to maximise the strength and hardening capacity of the piece regarding its final application.

In order to answer to the open questions remaining at this point, intensive microstructural characterisation during interrupted tests in both forward and reverse steps should be performed. Characterisation should be performed at different scales to highlight the suggested critical role of the screw dislocations as well as the role of twin/martensite volume fractions. Classical Bauschinger tests should also be performed to confirm the back-stress evolution measured in this work, as well as the origin of the permanent hardening.

General conclusions

The aim of this study is to provide answers concerning the origin of the unusual work hardening capability of β metastable titanium alloys. Alloy compositions exhibiting both mechanical twinning and strain-induced martensitic transformation were designed *via* the “d-electron design method” proposed by Morinaga *et al.* The Ti-12wt.%Mo grade and other alloys designed in **Chapter 3** with this strategy exhibit an outstanding combination of mechanical properties with a large improvement of the work hardening. An ultimate tensile strength of 1000 MPa combined with a uniform elongation of 0.35 has been recorded for the as-quenched Ti-12wt.%Mo alloy.

The activation of multiple plastic deformation mechanisms has been confirmed by several characterisation techniques, such as XRD and electron microscopy. These mechanisms are $\{112\}\langle 111 \rangle$ and $\{332\}\langle 113 \rangle$ mechanical twinning, strain-induced martensitic $\beta \rightarrow \alpha''$ phase transformation and dislocation glide.

Though $\{332\}\langle 113 \rangle$ mechanical twinning is considered as an important deformation mechanism in β -Ti alloys, no consensus concerning its formation mechanism exists at present. New insights about this mechanism are given in **Chapter 4**. It is proposed that the nucleation step of mechanical twinning is martensite-assisted. The complex arrangement of deformation products was thoroughly characterised by EBSD and the orientation relationships between them analysed. The results are consistent with a modified version of the model previously proposed by Takemoto. Furthermore, a link between the volume fraction of deformation-induced products and the evolution of the work hardening with imposed strain has been established. The observed increase of work

hardening is related to the fast increase of volume fraction of deformation products, while the beginning of the decrease is concurrent to the saturation level of the volume fraction.

TEM observations of slightly strained samples revealed the activation of the $\{112\}\langle 111 \rangle$ twinning system. Even though this twinning system is the commonly observed one in *BCC* alloys, its activation was not expected in Ti-12wt.%Mo. The mechanism of twin formation has thus been investigated in **Chapter 5**. The characterisation of bulk samples highlighted the initial defect configuration needed to induce the formation of such thin mechanical twins, following the mechanism proposed by Hsiung and Lassila. The growth of the twins is believed to occur by dislocation incorporation, resulting in the formation of “super-jogs”. *In situ* tensile test in the TEM confirmed the need of initial defects to initiate the formation of the twin nuclei.

The main difference between the Ti-12wt.%Mo and the Ti-15wt.%Mo grades is the observation of α'' martensite in the Ti-12wt.%Mo. **Chapter 6** focused on the role of this martensitic phase in the global mechanical behaviour. *In situ* cyclic tensile test has been performed with synchrotron XRD in order to follow (i) the evolution of the phase proportion in the material and (ii) the elastic strain state within both β and α'' phases. It appears that the reversibility of the strain-induced martensitic phase is rapidly decreasing with the accumulation of defects and that the volume fraction of martensite remains fairly low during the whole strain frame of the experiment. Also, the elastic strains within the β phase achieve much higher values than in dislocation glide driven plasticity materials, suggesting a high hardening of the *BCC* lattice. By contrast, nearly no hardening has been recorded in the α'' martensite.

An emerging characterisation technique is the High Resolution EBSD which allows the determination of elastic stress state and density of Geometrically Necessary Dislocations at the grain scale. Currently, only relative measurements can be performed in a confident manner. In **Chapter 7**, an innovative procedure based on image gradients is proposed to allow the absolute measurement of such quantities under a limited amount of assumptions. The technique has been applied to characterise the interfaces of a strain-induced martensitic plate and of

a $\{332\}\langle 113 \rangle$ mechanical twin. The results are significantly different between both deformation-induced products. Indeed, the martensitic plate is in a mean compressive state while the twin is slightly in a tensile state. The α''/β interface does not show long-range stress field while in the case of the twin, a large compressive stress field is observed at the vicinity of the interfaces on a length of several hundreds of nanometers. The estimation of the densities of GNDs in both cases highlighted a much larger amount of dislocations in the twin case. Furthermore, the character of the dislocations obtained by the minimisation of dislocation energy line calculation is compatible with the semi-coherent interface model of the α''/β interface and the structure of dislocations observed by TEM at the twin boundaries.

Finally, first insights in the influence of the deformation path on the mechanical response of Ti-12wt.%Mo are the topic of **Chapter 8**. The behaviour of the alloy under monotonic simple shear has been investigated. At the onset of plasticity, the material does not exhibit an increase of the work hardening rate as in tension, but is monotonously decreasing. Also, cycles of shear-reverse shear has been imposed to the alloy. Firstly, a large Bauschinger effect is observed in the first cycles of the experiment. It is suggested that the Bauschinger effect is due to the large elastic strain gradients built in the grains during mechanical twinning. A composite effect between the matrix and the twins is believed to occur in the material. Secondly, it is shown that the material exhibits a larger hardening in the reverse loading sense compared to the forward sense after a few number of shear-reverse shear cycles. The origin of this hardening is thought to be the polarisation of the microstructure during the first loading cycle. The characterisation of the microstructure should provide some answers to this open question.

In conclusion to this thesis, we can say that we provided an extensive characterisation of the as-quenched Ti-12wt.%Mo alloy designed through an adapted electronic approach. A lot of conflicting results of the literature about the deformation products in this kind of β -metastable titanium alloys can be explained by the present approach. A modification of the model of Takemoto is able to conciliate the orientation relationship between the α'' martensite and the β matrix while

validating the martensitic origin of the $\{332\}\langle 113 \rangle$ mechanical twins. For the first time, the nucleation of $\{112\}\langle 111 \rangle$ mechanical twins has been observed *in situ* in a titanium alloy. This emphasises the need of crystalline defects in order to trigger such kind of deformation mechanism at low stresses achieved in bulk samples. Unlike in TRIP steels where the α' martensite has a role of strengthening precipitates, the α'' martensite barely show hardening during load increase while the β matrix exhibits a huge hardening. This result is coherent with the precursor role attributed to the α'' precipitates for twin nucleation. The new HREBSD method proposed here highlighted large stress fields in the vicinity of the mechanical twins, as well as a higher dislocation density compared to the matrix, as observed by TEM characterisation. Bauschinger tests also suggest that high internal stresses are induced by the formation of twins in the alloy. The anisotropy of the material is ultimately emphasised by the permanent hardening observed during shear-reverse shear experiments.

Further characterisation is necessary to strengthen some of the results obtained in this work. It was shown that the work hardening behaviour in tension is directly linked to the amount of deformation products forming during straining. Now, the impact of the loading mode on the mechanical response and, by extension, on the work hardening behaviour of the Ti-12wt.%Mo grade should be performed and thoroughly characterised. Indeed, a different work hardening behaviour has been observed between tension and simple shear without founded explanation. The permanent hardening appearing in the material during load path reversal seems a promising effect that needs to be further investigated. Also, the impact of the grain size on the activation of the different plasticity mechanisms should be investigated. Indeed, it was observed that the size of the deformation products was directly linked to the grain size. It is thus probable that the mechanical performances will be impacted by this difference. Another interesting parameter to study is the influence of the initial texture on the activation of plasticity mechanisms and thus on the mechanical behaviour. Indeed, the material studied in this work is highly textured, which is believed to have a large impact on twin transmission through grain boundaries. Finally, the results obtained

by HR-EBSD could provide valuable experimental results for validating crystal plasticity models of $\{332\}\langle 113 \rangle$ twinning and $\beta \rightarrow \alpha''$ transformation. The extension of the elastic stress field measurements around the twin tips would also be of great interest. *In situ* tensile tests in the TEM on grains containing a $\{332\}$ twin boundary would give a better understanding of the dislocations interactions with such boundaries.

Appendix A

Matlab code for batch SXRD peak fitting

```
% Routine to fit diffraction peaks with PVII functions
% Written by S. Van Petegem, Paul Scherrer Institut, Switzerland
% November 22nd, 2013
% Modified by M. Marteleur, IMAP, Belgium
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

clc
close all
clear all
global neval modelPrevious

%% Provide general parameters:
filename = 'Ti12Mo2_load_';
first_file_number = 645;
last_file_number = 1;
step_size = -1;

lower_angle = 16;
upper_angle = 17;

number_of_peaks = 3;
peak_names = ['110'; '011'; '111'];
% two 110 beta peak components and the 111 alpha'' peak
```

```

initial_peak_position = [16.5 16.5 16.8];
initial_peak_width    = [0.15 0.25 0.2];
    % fitting starting from highly deformed sample level
initial_peak_intensity = [15000 35000 5000];

for i = 1 : number_of_peaks
    initial_m (i) = 1;
    initial_alpha (i) = 0;
end

% Definition of lower and upper bonds for each variables
% needed in the fminsearchbnd function

% values chosen from previous iterations

peak_LB = [16.37 16.37 16.6];
peak_UB = [16.6 16.6 16.85];
initial_m_LB = 0.01*initial_m;
initial_alpha_LB = initial_alpha;
initial_m_UB = 10*initial_m;
initial_alpha_UB = 0.5*ones(1,number_of_peaks);

correction_background = 0;
    % to be turn off when no influence from out of range data
show_peaks_during_fit = 0;
show_peaks_after_fit  = 1;
save_peaks_after_fit  = 1;
number_of_fitting_trials = 5;

%% Initialization
counter = 1;

fit_res = [];
fit_err = [];
%% Start with fit routine

for i = first_file_number : step_size : last_file_number,
    modelPrevious = [];
    disp(['Fitting spectrum number ' num2str(i)]);
    %%Load data
    name = [filename num2str(i) '.dat'];
    if exist(name, 'file')==2
        A=load(name);
    end
end

```

```
angular_range =  
find(and((A(:,1) > lower_angle), (A(:,1) < upper_angle)));  
x=A(angular_range,1);  
  
y=A(angular_range,2);  
  
% Chebychev function for background fitting  
% of unstrained specimen  
% The background fit is calibrated on angular ranges  
% empty from diffraction peaks  
  
bkgd = ['Ti12Mo2_load_1.dat'];  
B=load(bkgd);  
angular_range_cheb1 =  
find(and((B(:,1) >12.23), (B(:,1) < 13.12))));  
angular_range_cheb2 =  
find(and((B(:,1) >18.5), (B(:,1) < 20))));  
angular_range_cheb3 =  
find(and((B(:,1) >24.5), (B(:,1) < 25.5))));  
angular_range_cheb4 =  
find(and((B(:,1) >34), (B(:,1) < 36))));  
angular_range_cheb5 =  
find(and((B(:,1) >38), (B(:,1) < 38.75))));  
angular_range_cheb6 =  
find(and((B(:,1) >49.5), (B(:,1) < 50))));  
angular_range_cheb7 =  
find(and((B(:,1) >51.4), (B(:,1) < 51.8))));  
angular_range_cheb8 =  
find(and((B(:,1) >64), (B(:,1) < 66))));  
x_cheb1=B(angular_range_cheb1,1);  
y_cheb1=B(angular_range_cheb1,2);  
x_cheb2=B(angular_range_cheb2,1);  
y_cheb2=B(angular_range_cheb2,2);  
x_cheb3=B(angular_range_cheb3,1);  
y_cheb3=B(angular_range_cheb3,2);  
x_cheb4=B(angular_range_cheb4,1);  
y_cheb4=B(angular_range_cheb4,2);  
x_cheb5=B(angular_range_cheb5,1);  
y_cheb5=B(angular_range_cheb5,2);  
x_cheb6=B(angular_range_cheb6,1);  
y_cheb6=B(angular_range_cheb6,2);  
x_cheb7=B(angular_range_cheb7,1);  
y_cheb7=B(angular_range_cheb7,2);
```

```

x_cheb8=B(angular_range_cheb8,1);
y_cheb8=B(angular_range_cheb8,2);

x_cheb=[x_cheb1 ; x_cheb2 ; x_cheb3 ; x_cheb4 ;
x_cheb5 ; x_cheb6 ; x_cheb7 ; x_cheb8];
y_cheb=[y_cheb1 ; y_cheb2 ; y_cheb3 ; y_cheb4 ;
y_cheb5 ; y_cheb6 ; y_cheb7 ; y_cheb8];

C=ones(1,5);
Cheb_tot = @(C,xx) C(1)*cosd(0*(xx-C(5))) +
(C(2))*cosd(1*(xx-C(5))) +
(C(3))*cosd(2*(xx-C(5))) +
(C(4))*cosd(3*(xx-C(5)));
xfit = [x_cheb;x_cheb];
yfit = [y_cheb;y_cheb];
C_guess = ones(1,5);
C_fit = nlinfit(xfit,yfit,Cheb_tot,C_guess);

% additionnal correction due to out of range peaks
% if NECESSARY (in addition to Chebychev polynomial)

if correction_background
    yb1=y(1);
    yb2=y(end);
    ya1=C_fit(1)*cosd(0*(x(1)-C_fit(5))) +
        C_fit(2)*cosd(1*(x(1)-C_fit(5))) +
        C_fit(3)*cosd(2*(x(1)-C_fit(5))) +
        C_fit(4)*cosd(3*(x(1)-C_fit(5)));
    ya2=C_fit(1)*cosd(0*(x(end)-C_fit(5))) +
        C_fit(2)*cosd(1*(x(end)-C_fit(5))) +
        C_fit(3)*cosd(2*(x(end)-C_fit(5))) +
        C_fit(4)*cosd(3*(x(end)-C_fit(5)));
    p=polyfit([x(1);x(end)],[(yb1-ya1);(yb2-ya2)],1);

else
    p=[0 0];
end

%%Initial guess

if i == first_file_number
    pfix = [number_of_peaks];
    pfit = [initial_peak_intensity ...
            initial_peak_position ...

```



```

        initial_peak_width ...
            initial_m initial_alpha ...
        C_fit(1) C_fit(2) C_fit(3) ...
        C_fit(4) C_fit(5) p(1) p(2)];

%% Initial constraints

pfit_LB = [initial_peak_intensity*0 ...
            peak_LB ...
            initial_peak_width*0.01 ...
            initial_m_LB initial_alpha_LB ...
            C_fit(1) C_fit(2) C_fit(3) ...
            C_fit(4) C_fit(5) p(1) p(2)];
pfit_UB = [initial_peak_intensity*inf ...
            peak_UB...
            initial_peak_width*10 ...
            initial_m_UB initial_alpha_UB ...
            C_fit(1) C_fit(2) C_fit(3) ...
            C_fit(4) C_fit(5) p(1) p(2)];
end

%%Fit
optnew = optimset('TolX',1e-5,'TolFun',1e-6,'Display',
    'none','MaxFunEvals',1000000);
neval = 0;
n=number_of_peaks;
pfit = [pfit(1 : n) pfit(n + 1 : 2*n) ...
        pfit(2*n + 1 : 3*n) pfit(3*n + 1 : 4*n) ...
        pfit(4*n + 1 : 5*n) C_fit(1) C_fit(2) ...
        C_fit(3) C_fit(4) C_fit(5) p(1) p(2)];
for j = 1 : number_of_fitting_trials,

%% Constraints update (intensity and width)

pfit_LB = [pfit(1)*0.1 pfit(2)*0.5 pfit(3)*0.01 ...
            peak_LB ...
            pfit(2*n + 1)*0.0001 pfit(2*n + 2)*0.5 pfit(3*n)*0.0001 ...
            initial_m_LB ...
            pfit(4*n + 1 : 5*n)*0 ...
            C_fit(1) C_fit(2) C_fit(3) ...
            C_fit(4) C_fit(5) p(1) p(2)];
pfit_UB = [pfit(1)*100 pfit(2)*3 pfit(3)*100...
            peak_UB ...
            pfit(2*n + 1 : 3*n)*2 ...

```

```

        initial_m_UB ...
        pfit(4*n + 1 : 5*n)*125 ...
        C_fit(1) C_fit(2) C_fit(3) ...
        C_fit(4) C_fit(5) p(1) p(2)];

[pfit,chi,nfeval,output] =
fminsearchbnd('efit_pearson_sym',pfit,pfit_LB,
    pfit_UB,optnew,pfix,x,y,show_peaks_during_fit);

end

[sum_chi,model,integrated] =
    efit_pearson_sym2(pfit,pfix,x,y,
        show_peaks_after_fit,modelPrevious,nfeval);
parsigma=fitterror('efit_pearson_sym',pfit,pfix,x,y,0);

%%Postprocess
if save_peaks_after_fit
    ext = [];
    for j = 1 : number_of_peaks
        ext = [ext '_' peak_names(j,:)];
    end
    figure_name = [filename num2str(i) ext '.jpg'];
    saveas(gcf,figure_name);
    figure_name = [filename num2str(i) ext '.fig'];
    saveas(gcf,figure_name);
end

fit_name = [filename num2str(i) '_fit' ext '.dat'];
Q = [x y model];
eval(['save ' fit_name ' Q -ascii']);

fit_res=[fit_res; [i pfit integrated]];
fit_err=[fit_err; [i parsigma]];
end

end

%% Generate output file
ext = [];
for j = 1 : number_of_peaks
    ext = [ext '_' peak_names(j,:)];
end
file_name_out = ['history' ext '.dat'];
file_name_out_err = ['history_err' ext '.dat'];

```

```
eval(['save ' file_name_out ' fit_res -ascii']);  
eval(['save ' file_name_out_err ' fit_err -ascii']);
```


Appendix B

Comparative grain-scale characterisation of mechanical twinning in austenitic steel and β -Ti

B.1 Introduction

Since its discovery by Sir Hadfield in the late 1800s and the first experimental evidences by TEM characterisation in the 1960s, the TWIP effect in $Fe - Mn - C$ steels has drawn more and more attention due to the outstanding mechanical properties exhibited by these steels. TWIP effect has also been observed in β titanium alloys from the 1970s, and those alloys also show improvement of the work hardening with the activation of mechanical twinning.

During our investigations on the mechanical properties of the as-quenched Ti-12wt.%Mo alloy, a grain-size dependence of the characteristic lengths of twinning (twin thickness and inter-twin distance) has been observed. Interestingly, this dependence had been observed in previous investigations on TWIP steels (Renard et al., unpublished results). Illustrations of these observations are presented in Figure B.1 for a TWIP steel sample after plastic straining up to 0.05 and 0.2. However, the existence of proportionality between the grain size and the two characteristic lengths has not been successfully explained yet. It is proposed

that the patterning observed along plastic deformation accumulation influences in a large way the mechanical response of these materials.

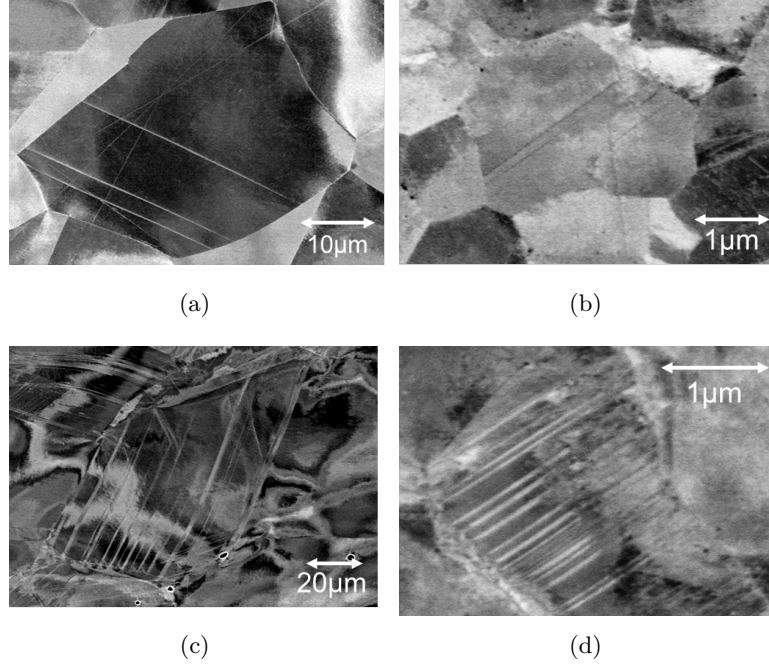


Figure B.1: Example of the grain-size dependence of characteristic lengths of mechanical twinning in a Fe-Mn-C TWIP steel. (a) and (b) : $\varepsilon = 0.05$; (c) and (d) : $\varepsilon = 0.20$.

B.2 Experimental method

Investigations on both TWIP steels and β -Ti alloys with grain sizes ranging over three decades have been performed.

The measurement of twinning characteristic lengths has been performed on SEM micrographs for all samples, except for the smaller grain size of the TWIP steel which has been observed in the TEM since the twins thickness was beyond the resolution limit of the SEM. The systematic

measurements have been performed by Perrine Tanguy for Ti-12Mo alloy and by Antoine Marsollier for Fe-Mn-C-V TWIP steel.

An example of the measurement of the grain size D , the twin thickness t and their inter-distance λ is shown in Figure B.2.

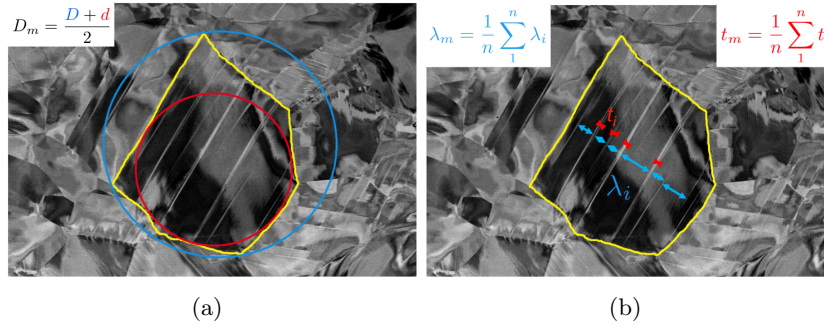


Figure B.2: *Illustration of the methodology used for (a) the grain size determination and (b) the twin thicknesses and inter-distances.*

Of course, a 2-dimensions measurement of plane-related defects like twins can be biased since an overestimation of the thickness will arise if the twin is not edge-on. A statistical evaluation of the accuracy of such measurements has been performed. Figure B.3 is a sketch of how this evaluation has been performed. A cube (Fig. B.3a) simulates a grain of size D , containing between two and ten twins spaced of λ_i , with $\lambda_i > t_i$. Also, each twin has its own thickness t_i , whose values are randomly taken in the interval $D/200 < t_i < D/50$.

Then, the cube is cut randomly (Fig. B.3b), and each values of λ and t are stored. Several thousand of cut plane orientations are simulated to reach a statistically meaningful result. The results of such analysis for a grain size D of $20\mu m$ are shown in the histograms of Figure B.4. It can be seen that for a high number of iterations, the mean measured values were about 25% higher for the thickness, but only of about 10% for the inter-distances.

The results presented in the following section are the mean values of the raw measurements, but it has little impact on the interpretation since they only vary from a multiplication factor compared to the real values.

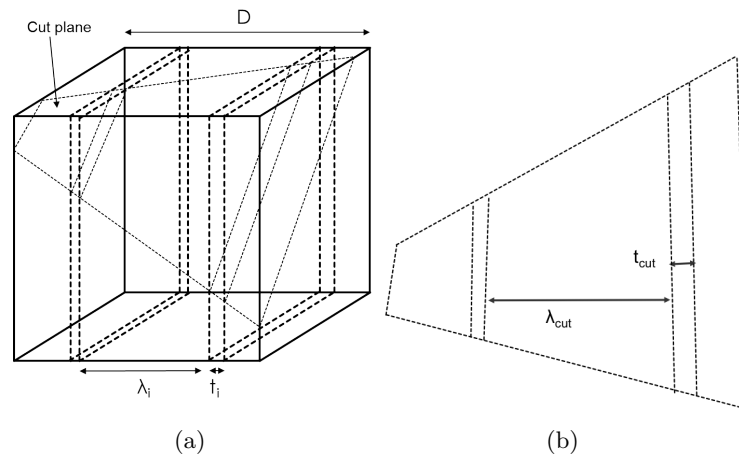
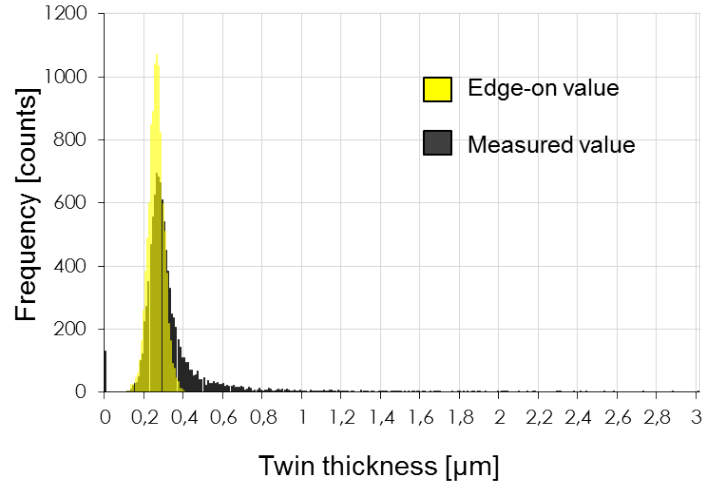
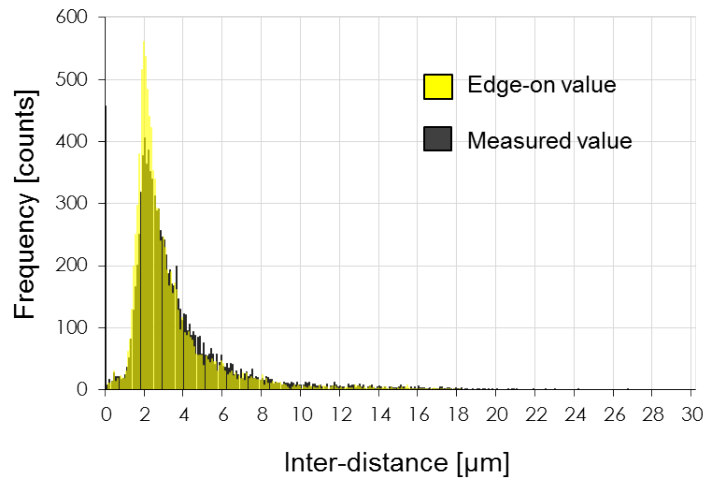


Figure B.3: (a) Cube simulating the samples observed in the SEM
 (b) 2D projection of the cut plane on which the real measurements are performed.



(a)



(b)

Figure B.4: Histograms highlighting the difference between the measured values and the real ones (edge-on) for (a) the twin thickness t and (b) their inter-distances. The grain size was set to $D = 20\mu\text{m}$.

B.3 Results

Measurements of λ and t for samples of Ti-12Mo strained up to 0.05 are gathered in Figure B.5. It can be seen that the data points in both cases are distributed around a straight line in a $\log - \log$ plot, meaning that a direct proportionality can be extracted. Interestingly, the data points coming from the literature for other Ti alloys exhibiting $\{332\}\langle 113 \rangle$ mechanical twinning also follow the same tendencies.

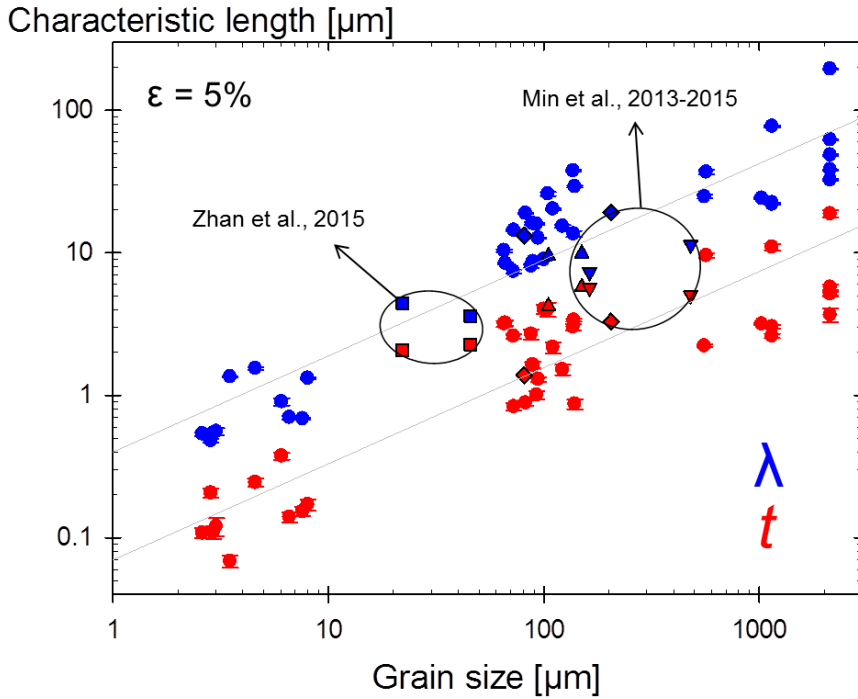


Figure B.5: Relationship between the grain size D , the twin thickness t and their inter-distance λ in a strained Ti-12Mo alloy ($\epsilon = 0.05$).

The same kind of graphs have been done for Fe-based TWIP alloys. Measurements for strain levels of 0.05 and 0.2 are plotted in Figures B.6 and B.7, respectively. It can be seen that the error bars are higher in the case of TWIP steels compared to β -Ti alloys, especially for the

$\varepsilon = 0.05$ datas. This difference comes mainly from the fact that the twin volume fraction is much smaller in the TWIP steel for the same amount of macroscopic plastic deformation [125]. Again, the data points from the literature fit well with the observed tendencies.

Characteristic length [μm]

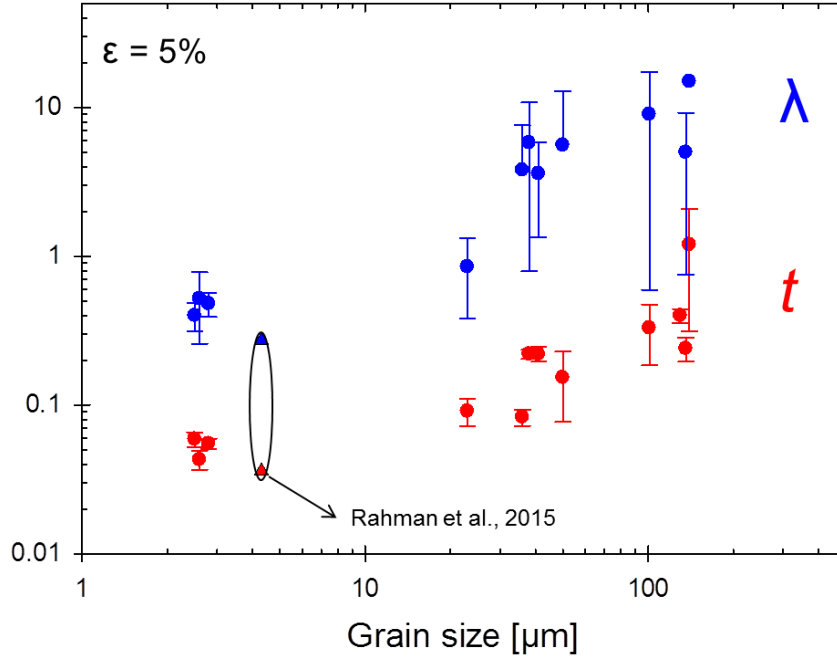


Figure B.6: Relationship between the grain size D , the twin thickness t and their inter-distance λ in a strained Fe-Mn-C TWIP steel ($\varepsilon = 0.05$).

The evolution of the normalised characteristic lengths (t/D and λ/D ratios) with applied strain is shown in Figure B.8 in the case of TWIP steel. The twin thickness is increasing with applied strain while their inter-distance is decreasing, meaning that both the number of twins is increasing as well as their mean thickness.

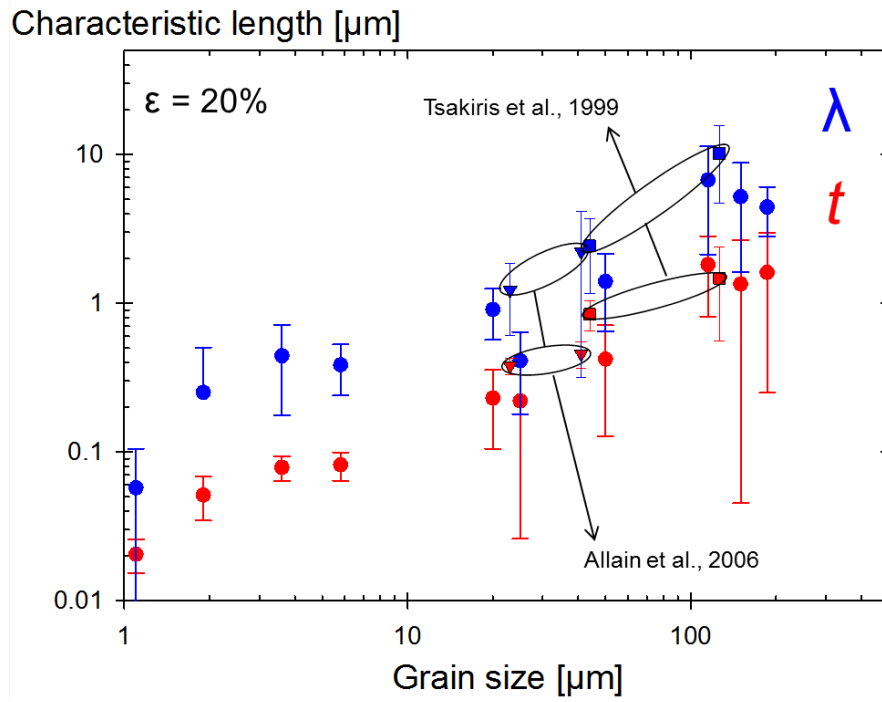


Figure B.7: Relationship between the grain size D , the twin thickness t and their inter-distance λ in a strained Fe-Mn-C TWIP steel ($\epsilon = 0.2$).

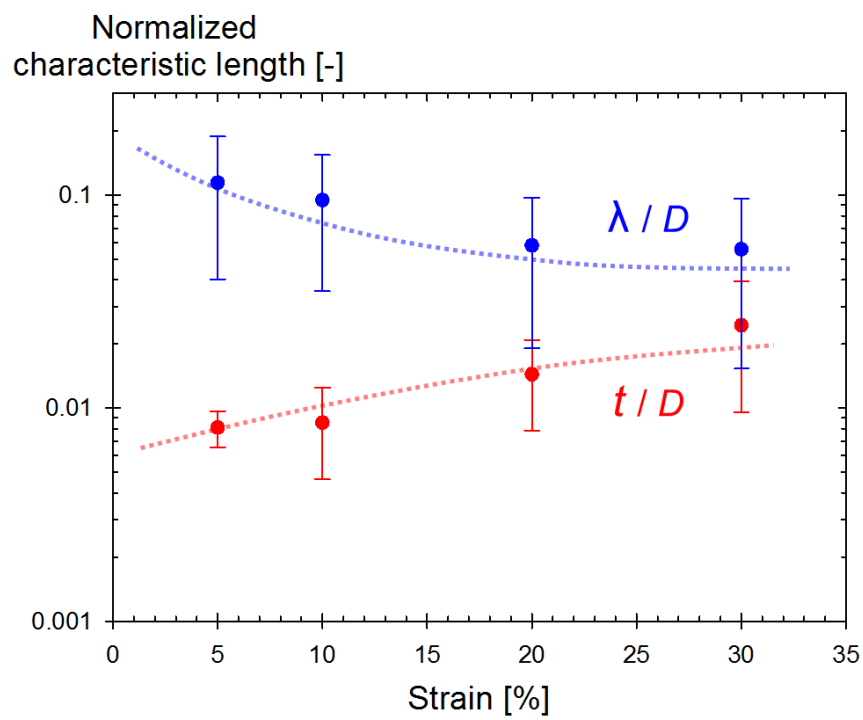


Figure B.8: Evolution of the ratios t/D and λ/D with plastic strain applied on the $Fe - Mn - C$ samples (the lines are guides for the eyes).

B.4 Discussion

It is obvious from the results of the systematic measurements of the three characteristic lengths in both TWIP steels and β -metastable Ti alloys that a proportionality relationship exists between the three parameters. Since this observation is not confined to one kind of material, it is proposed that this relationship comes from the mechanics of twinning.

To explain the observed grain-scaled dependence for twin thickness and inter-distance, a simple mechanistic approach is proposed. Let's consider that a given volume around the twins is forbidden due to the relaxation of elastic stresses. The formation of new twins in this volume will be much more energy consuming than in the rest of matrix since there exists a supplementary ΔG to overcome. At low strain levels (low twin volume fraction), the first twins will appear with a stochastic distribution that will depend on the initial dislocations distribution¹ (influence on the twinning initiation process). With the increase of the twins volume fraction, the formation of new twins will no longer be random, and the twins will form inside the existing twin arrangement. As new twins continue to appear within the grain, the inter-twin distance λ reaches its minimum due to elastic stress field heterogeneities at the grain scale. A schematic representation of the situation is sketched in Figure B.9. It should be noted that this scenario can explain the high variability of the λ parameter at low strain levels (see Fig. B.6 for example), and that its value seems to reach a minimum at high strain levels (see Fig. B.8).

The density of elastic energy that is relaxed in the matrix surrounding the twins is given by :

$$\Delta G_{elastic} \propto \mu \cdot \gamma^2 \cdot \frac{\lambda \cdot D^2}{D^3} = \mu \cdot \gamma^2 \cdot \frac{\lambda}{D} \quad [J/m^3] \quad (B.1)$$

where $\mu \cdot \gamma^2$ is the elastic energy of the twinning shear, $\lambda \cdot D^2$ is the excluded volume around the twin and D^3 is the grain volume.

If we consider that the trigger stress for dislocation motion is independent of D (asymptotic behavior of Hall-Petch law), then ΔG for the twin

¹This model implicitly implies that the twinning mechanism is dislocation-based.

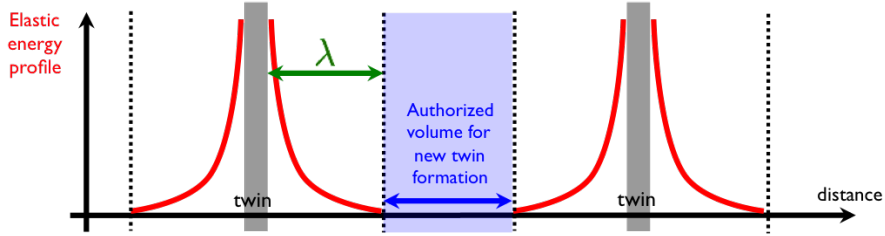


Figure B.9: Illustration of the elastic stress field around twins, and of the authorized volume for new twin formation.

creation will only depend on the twin thickness t since their length is $\approx D$. Thus, the ratio λ/D should be a constant.

The question at this point is then the following one : how does the grain “know” what should be the twin thickness ?

Let’s consider that t results from a compromise between the interfacial energy and the shear energy. The creation of new interfaces needs an extra amount of energy given by (for a iso-volume of twins situation) :

$$\Delta G^{M/T} \propto \sigma^{M/T} \cdot D^2 \cdot \frac{1}{t \cdot D^2} = \frac{\sigma^{M/T}}{t} \quad [J/m^3] \quad (B.2)$$

where $\sigma^{M/T} \cdot D^2$ accounts for the energy of the matrix-twin interface and $t \cdot D^2$ is the twin volume. On the other hand, the energy associated to the matrix $\rightarrow$ twin transformation can be expressed by :

$$\Delta G_{transf}^{M \rightarrow T} \propto \mu \cdot \gamma^2 \cdot \frac{t^2 \cdot D}{D^3} = \mu \cdot \gamma^2 \cdot \left(\frac{t}{D}\right)^2 \quad [J/m^3] \quad (B.3)$$

where $t^2 \cdot D$ is the free volume in the matrix influenced by the twin propagation front as illustrated in Figure B.10.

So, if the total amount of energy to provide is the sum of these two terms, we get :

$$\Delta G^{tot} = \Delta G_{transf} + \Delta G_{interface} = f(\gamma, \mu, \sigma^{M/T}, D) \quad (B.4)$$

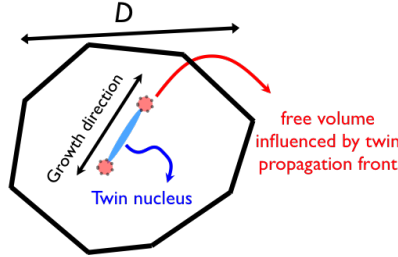


Figure B.10: Sketch of the most general growth situation of a mechanical twin in a grain, illustrating the free volumes involved in the expression of $\Delta G^{M \rightarrow T}$.

Among the parameters of the free Gibbs energy for twinning with this simple energetic approach, we see that ΔG is a function of the material parameters (μ and $\sigma^{M/T}$), the twinning mechanism (γ) and the micro-structure (D).

A qualitative plot of the ΔG^{tot} is shown in Figure B.11. One term varies with t^2 , while the second with $1/t$. An optimum value for t is thus theoretically possible to minimise the energy that has to be provided to the system. However, this approach does not take into account the increasing thickness of the twins, but it can reasonably argued that the initial thickness will be fixed by the grain size, and that their growth will be due to dislocation incorporation.

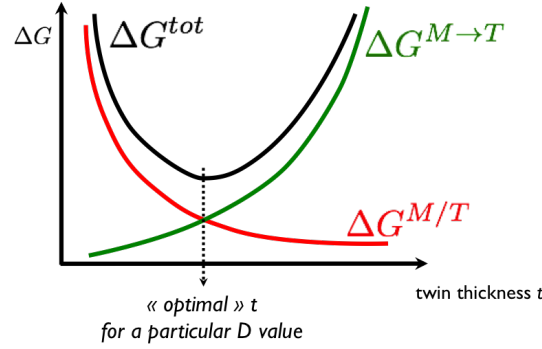


Figure B.11: Qualitative variation of the Gibbs free energies associated to twinning with the twins thickness t . $\Delta G^{M \rightarrow T}$ is associated to the lattice transformation, and $\Delta G^{M/T}$ to the creation of twin boundaries.

B.5 Conclusion and prospects

A relationship between the characteristic lengths of mechanical twinning has been observed in both TWIP steels and β -Ti alloys.

A simple model based on energetic considerations provides first insights to explain the relationship between the grain size D , the twin thickness t and their inter-distances λ . It is proposed that the initial grain size D will fix an optimal twin thickness t , and that the elastic relaxation of the twin will be responsible for reaching a minimum value of the twin inter-distance λ as macroscopic strain level is increasing. The twin thickness increase is supposed to come from further dislocation incorporation.

The same kind of characterisation should be performed on other displacive transformations to gather more informations on this grain-scaled phenomenon in order to complete the modelling.

Appendix C

TTT diagram and investigations of some α/β Ti-12wt.%Mo alloys

C.1 Introduction

In materials subject to phase transformations during heat treatments, it is essential to be able to predict the phases that will be present in the sample for particular treatments conditions. A useful tool illustrating the transformation kinetics of a particular alloy is the Transformation-Time-Temperature (*TTT*) diagram. Basically, a *TTT* diagram shows the phases that will be present in that material after keeping the sample at a specific temperature during a certain time after cooling from the stable high temperature domain (the β domain in this case). The establishment of such a diagram is done by ageing samples under various conditions followed by systematic characterisation. Figure C.1 illustrates schematically the methodology.

The main purpose of this study is the selection of several $\alpha + \beta$ microstructure in order to study the effect of the introduction of α phase on the mechanical properties, which will induce a change of the chemical stability of the β matrix. An $\alpha + \beta$ microstructure exhibiting the deformation modes of the β phase studied in this work could result in a material with high work hardening coupled with an improvement of the

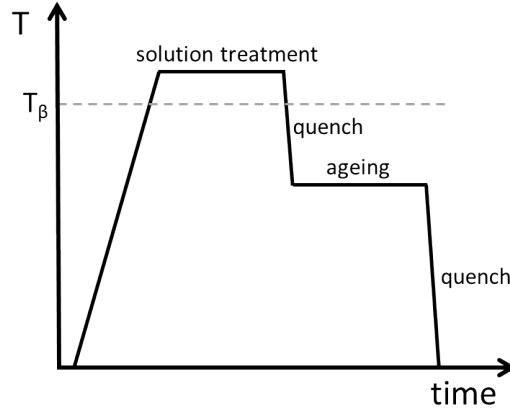


Figure C.1: *Qualitative diagram of the direct ageing process used in this work.*

yield stress due to second phase precipitation hardening.

C.2 Experimental procedure

The heat treatments have been carried out on the cold-rolled Ti-12wt.%Mo alloy in a tubular furnace for the solution treatment at 900°C and a fluidised bed furnace or a lead bath furnace for the ageing treatments at various temperatures. Table C.1 summarises the *time* – *T* couples performed in this work.

The samples have been polished and etched for proper SEM microscopy, and XRD has also been performed to identify the various phases present in the samples. Finally, hardness measurements as well as tensile tests on some chosen microstructure have been carried out.

Furnace	Temperature [$^{\circ}C$]	Time [min]
Lead bath	400	5, 15
	450	5, 15
	500	5, 15, 30, 60
Fluidised bed	600	5, 15, 30, 60
	650	5, 15, 30, 60
	720	5, 15, 30, 300
	750	5, 15, 30, 300
	780	5, 15, 30
	800	15, 60

Table C.1: Ageing treatments applied on *Ti – 12Mo*

C.3 Results

C.3.1 Ageing treatments

The microstructures obtained after all $T - time$ combinations of Table C.1 are displayed in Figures C.2 and C.3. It can be observed that some phase precipitation occurred in several samples. This phase has been identified as *HCP* α phase by XRD. The summary of the detected phases by XRD is shown in Table C.2. It has to be noted that no distinction is possible between ω_{ath} and ω_{iso} phases by XRD. Hardness measurements on aged samples have thus been performed to remove this uncertainty. The results of hardness tests are presented in Figure C.4.

At last, the α phase proportion has been measured for some samples by the grid method as explained in Chapter 4 for the measurement of twin volume fractions. The measured volume fraction are given in Table C.3.

C.3.2 Tensile tests

Tensile tests have been carried on several dual-phase alloys. The chosen ageing conditions are the listed in Table C.4 together with the resulting microstructure.

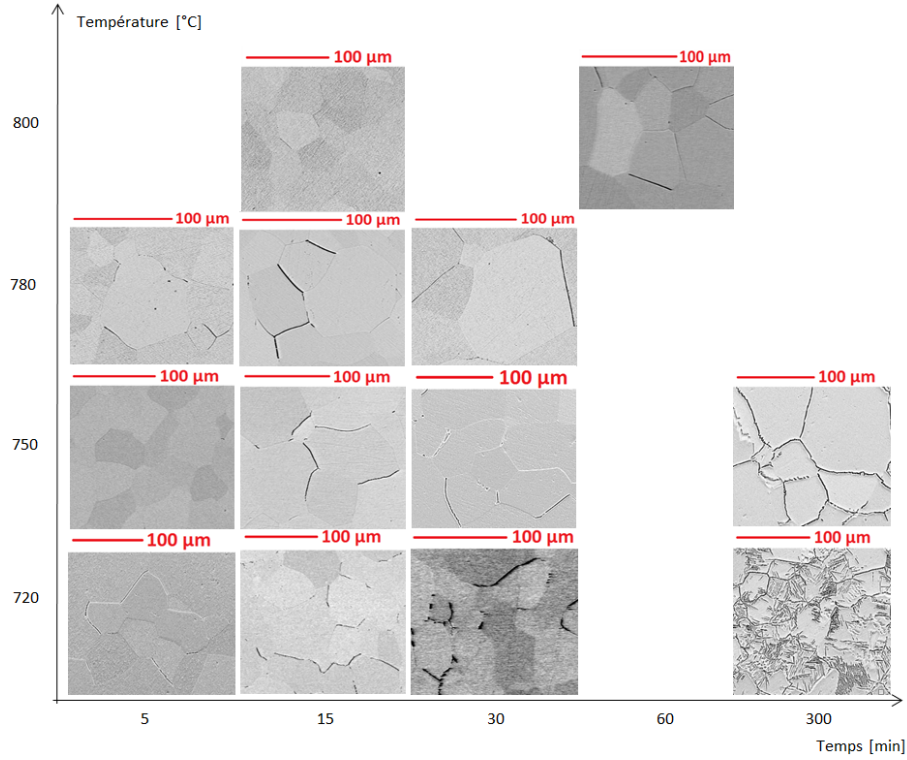


Figure C.2: Summary of the microstructures obtained after various direct ageing treatments between 720°C and 800°C.

The results of uniaxial tension are depicted in Figure C.5. The $\beta + \alpha_{GB}$ sample shows very similar tensile behaviour as compared to the as-quenched state ($\beta + \omega_{ath}$) in terms of yield stress and work-hardening behavior with a slightly reduced ductility. An increase of the amount of α phase induce an increase of the yield stress, together with a decrease of work-hardening capacity. Ultimately, the sample $\beta_{res} + \alpha_{disp}$ which contains its equilibrium amount of α phase ($\approx 94\%$) exhibits very high yield stress but nearly no work-hardening. The sample containing ω_{iso} phase shows a brittle behaviour.

The factured samples have been analysed by XRD and briefly observed in the SEM to check the potential activation of mechanical twinning or

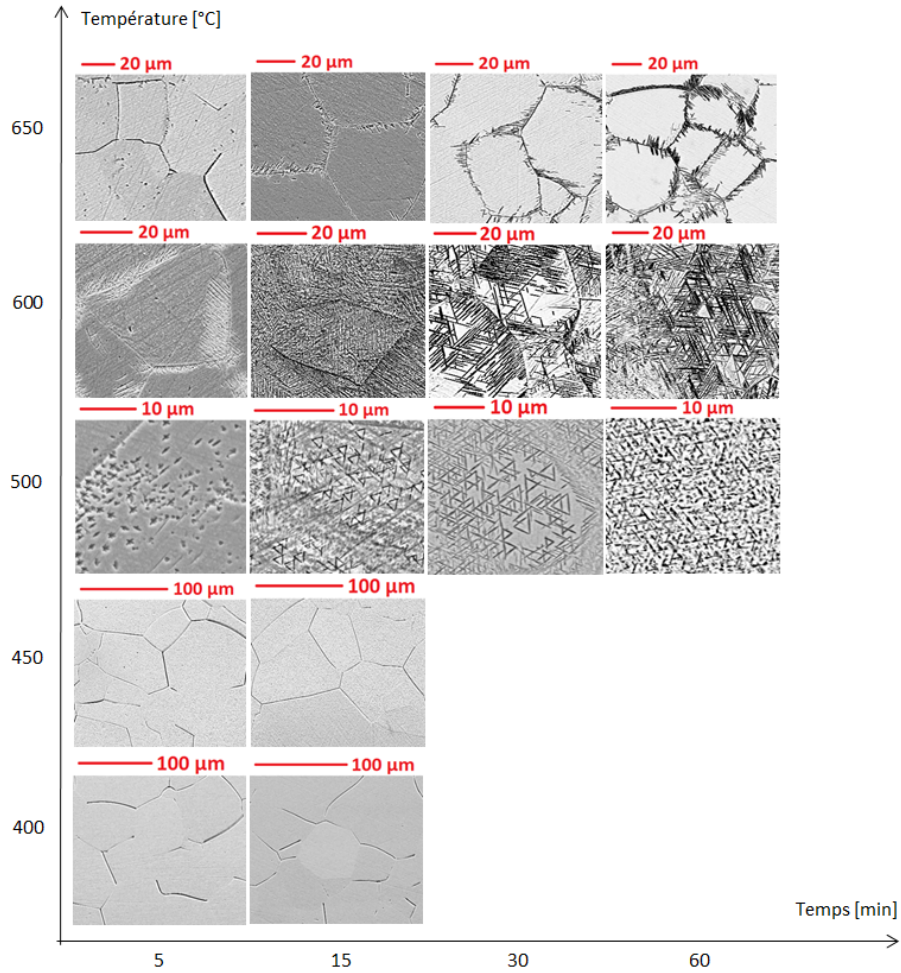


Figure C.3: Summary of the microstructures obtained after various direct ageing treatments between 650°C and 400°C.

martensitic transformation. The phases identified in each samples after fracture are gathered in Table C.5. No new phases were identified in the $\beta + \omega_{iso}$ and $\beta_{res} + \alpha_{disp}$ samples, but α'' diffraction peaks were observed in the two others, especially in the $\beta + \alpha_{GB}$ sample. The micrographs of the $\beta + \omega_{iso}$ and $\beta_{res} + \alpha_{disp}$ samples did not show any new interesting feature compared to the Figures C.2 and C.3. The

T [$^{\circ}\text{C}$]	Time [min]				
	5	15	30	60	300
800	-	β	-	β	-
780	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	-	-
750	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	-	$\beta + \omega + \alpha$
720	$\beta + \omega$	$\beta + \omega$	$\beta + \omega$	-	$\beta + \alpha + \omega$
650	$\beta + \omega$	$\beta + \omega + \alpha$	$\beta + \omega + \alpha$	$\beta + \alpha$	-
600	$\beta + \omega + \alpha$	$\beta + \omega + \alpha$	$\beta + \alpha$	$\beta + \alpha$	-
500	$\beta + \omega + \alpha$	$\beta + \omega + \alpha$	$\beta + \alpha$	$\beta + \alpha$	-
450	$\beta + \omega$	$\beta + \omega$	-	-	-
400	$\beta + \omega$	β	-	-	-

Table C.2: Results of XRD analysis of the samples subjected to ageing treatments.

microstructure of the two other samples are illustrated in Figure C.6. It can be seen that β grains are fulfilled with bands similarly to what is observed in as-quenched Ti-12Mo.

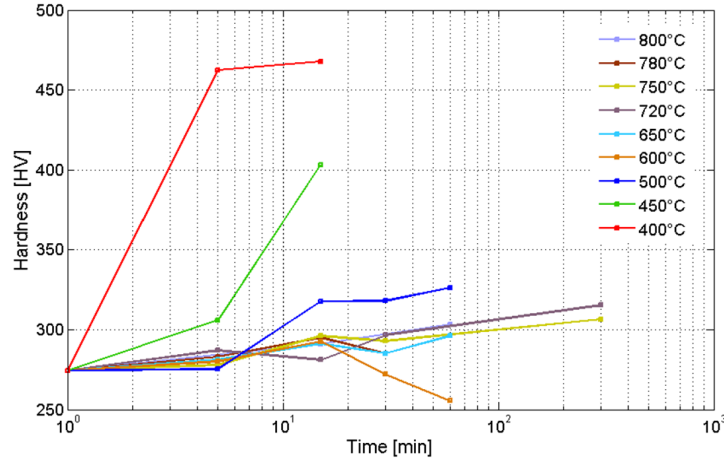


Figure C.4: Hardness evolution after ageing treatment and water quench.

T [$^{\circ}$ C]	Time [min]			
	5	15	30	60
650	≈ 0	2	10	26
600	13	88	95	<i>n.m.</i>
500	<i>n.m.</i>	76	93	<i>n.m.</i>

Table C.3: Calculated α phase proportion for some ageing treatments (*n.m.* is for “not measured”).

Ageing conditions	Microstructure
650°C for 30 min	$\beta + \alpha_{GB}$
500°C for 15 min	$\beta + \omega + \alpha_{disp}$
500°C for 60 min	$\beta_{res} + \alpha_{disp}$
450°C for 15 min	$\beta + \omega$

Table C.4: Dual-phase samples tested in uniaxial tension. α_{GB} means at grain boundaries, α_{disp} means homogeneously dispersed and β_{res} means residual.

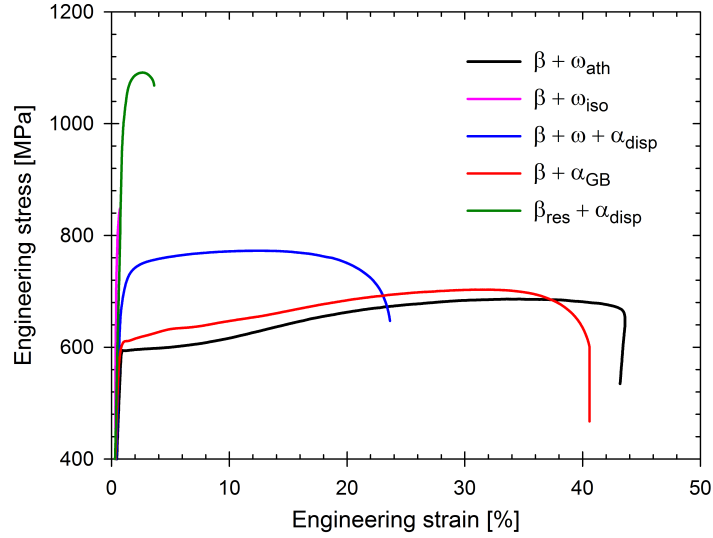
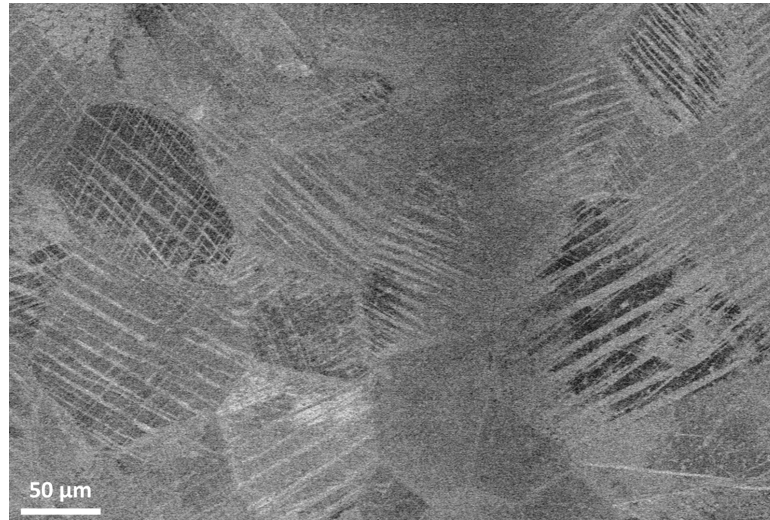


Figure C.5: Engineering stress-strain curves of the different dual-phase microstructures tested.

Ageing treatment	Before tensile test	After fracture
650°C for 30 min	$\beta + \alpha$	$\beta + \alpha + \alpha''$
500°C for 15 min	$\beta + \omega + \alpha$	$\beta + \alpha + \alpha''_{traces}$
500°C for 60 min	$\beta + \alpha$	$\beta + \alpha$
450°C for 15 min	$\beta + \omega$	$\beta + \omega$

Table C.5: Comparison of the phases detected by XRD before and after uniaxial tension for all tested samples.



(a)



(b)

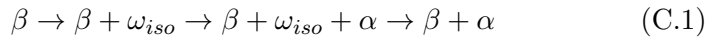
Figure C.6: SEM micrographs of fractured dual-phase Ti-12Mo alloy : (a) $\beta + \alpha_{disp}$ sample and (b) $\beta + \alpha_{GB}$ sample.

C.4 Discussion and prospects

C.4.1 Establishment of the TTT diagram

The gathering of the microscopy results, the hardness measurements and the XRD datas allow an accurate determination of the TTT diagram of Ti-12wt.%Mo. Indeed, the hardness evolution will give us clues about the nature of the ω phase present within the alloy. The intensities of XRD peaks is also a good criterion for such an analysis.

The two lower temperatures give the highest hardness evolution due to ω_{iso} precipitation. Indeed, the main effect of the presence of ω_{iso} is an increase of the hardness together with a drastic loss of ductility [16,93]. The increase in the 500°C treatment is attributed to the α phase precipitation, and the same trend should have been seen in the 600°C since the volume fraction of α phase is very similar for both cases (see Table C.3). In the second case, a softening is observed. The difference is supposed to come from a more homogeneous α precipitation for the 500°C samples. Indeed, in the 600°C samples, the precipitation appears preferentially on β grain boundaries and propagates in the grains. This difference comes from a different nucleation mechanism. Prima *et al.* proposed a model of α phase nucleation based on the presence of ω_{iso} [253]. It corresponds to the following scheme :



This sequence is believed to happen in the 500°C samples. On the other hand, the samples aged at higher temperature do not follow this sequence and undergo the classical $\beta \rightarrow \alpha$ allotropic transformation. Since grain boundaries are preferential sites for nucleation, the first α precipitates observed are mostly located there.

For the higher ageing temperature, the presence of a small amount of α phase induces a small precipitation hardening effect since the hardness is slightly higher than in the not aged sample. The ω phase detected by XRD is of athermal type and comes from quenching from the high temperature domain.

The correlation established between all these results allows the drawing of the TTT diagram of the Ti-12Mo alloy as shown in Figure C.7. It exhibits the typical *C* shape of a material presenting an allotropic transformation, and in this case two domains are present due to the different transformations occurring in metastable β -Ti alloys. Of course, the addition of other ageing conditions would increase the accuracy of the domains limits. Anyway, the major features of the materials behaviour under thermal treatments are presents.

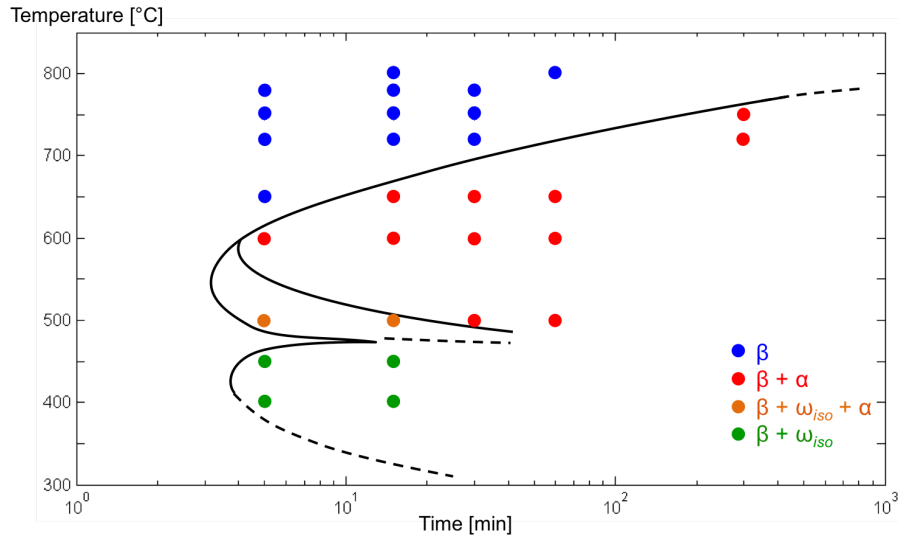


Figure C.7: *TTT diagram of Ti-12wt.%Mo. The dotted lines are assumptions of the domains limits.*

C.4.2 Conservation of deformation modes

The mechanical response of several dual-phase alloys has been tested under tensile loading. The results concerning the $\beta + \omega_{iso}$ sample are in agreement with literature, an hardening of the alloy and a drastic loss of ductile behaviour. The microstructure composed of mainly dispersed α phase with a small amount of residual β phase exhibits a very high yield stress. This is due to the fine grain size of the α needles (a few

micrometers in length) which are embedded in the residual β matrix. Dislocation transmission between the two phases is hindered by the differences of atomic packing, leading to an increase of the yield stress but to a low ductility as well.

Concerning the two last samples, XRD and SEM investigations highlighted very promising results. Indeed, α'' martensite has been detected in both samples after fracture, meaning that in these conditions, the β phase is still in a metastable state. Also, the dense pattern of deformation features resembles to the one of the as-quenched state. It is thus supposed that mechanical twinning was also activated. EBSD or TEM investigations should be performed on such samples to verify this hypothesis. The consequences on the mechanical properties are however not very convincing. The $\beta + \alpha_{GB}$ exhibits slightly higher yield stress and work-hardening rate at the beginning of plasticity while reaching earlier the necking point and the failure. The $\beta + \alpha_{disp}$ sample shows a consequent increase of yield stress together with more conventional work-hardening behavior (monotonic decrease) and a relatively low ductility regardless of the large amount of deformation features like illustrated in Fig. C.6(a).

The presence of deformation bands similar to the one observed in the as-quenched samples is a very promising results, since it seems possible to form $\alpha + \beta$ Ti alloys where the β phase is in a sufficiently metastable state to exhibit mechanical twinning and α'' SIM transformation. A fine tuning of the alloy composition, together with appropriate thermo-mechanical processing could lead to even better combination of strength (brought by dual-phase aspect) and work-hardening capacity (brought by β metastability).

Appendix **D**

Elastic distortion gradients maps & densities of GND

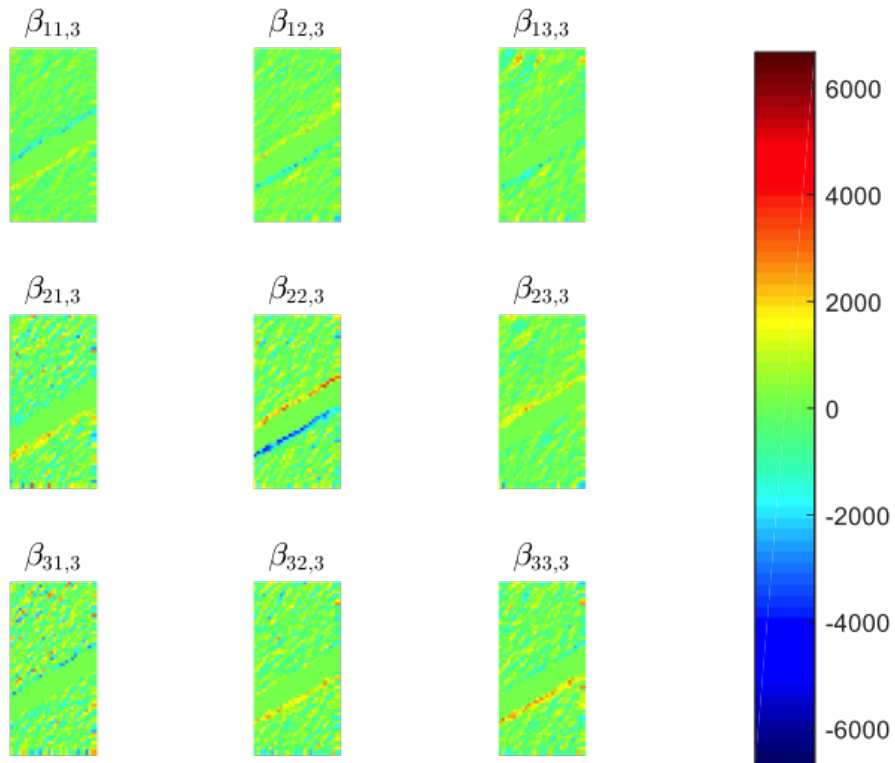


Figure D.1: Mapping of the non-zero components of the elastic distortion gradient tensor ($\beta_{ij,3}$) of the matrix around an α'' plate.

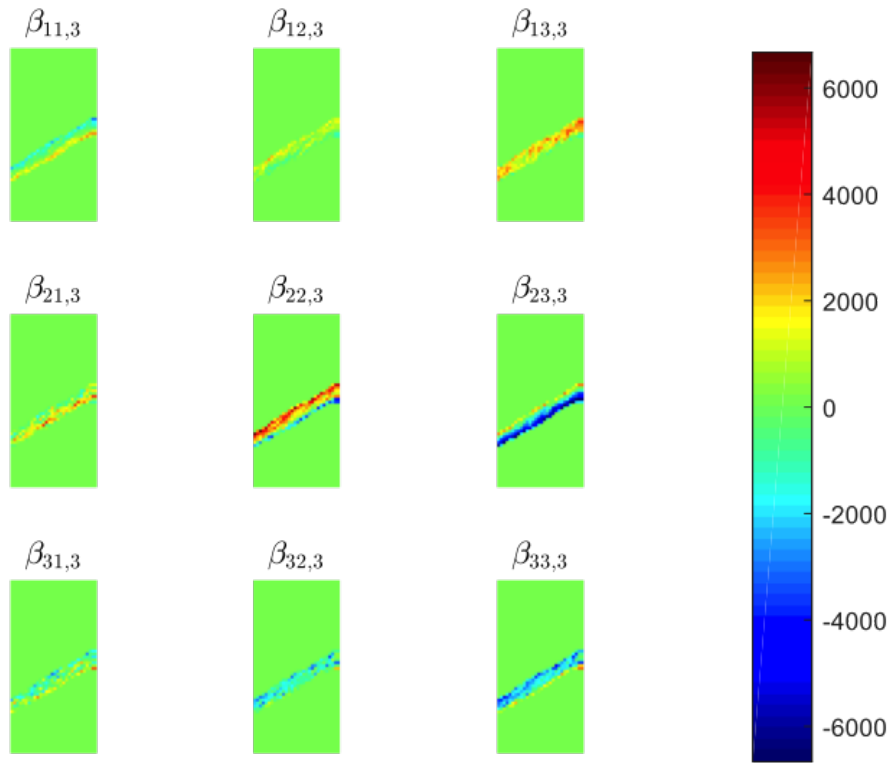


Figure D.2: Mapping of the non-zero components of the elastic distortion gradient tensor ($\beta_{ij,3}$) of the α'' plate.

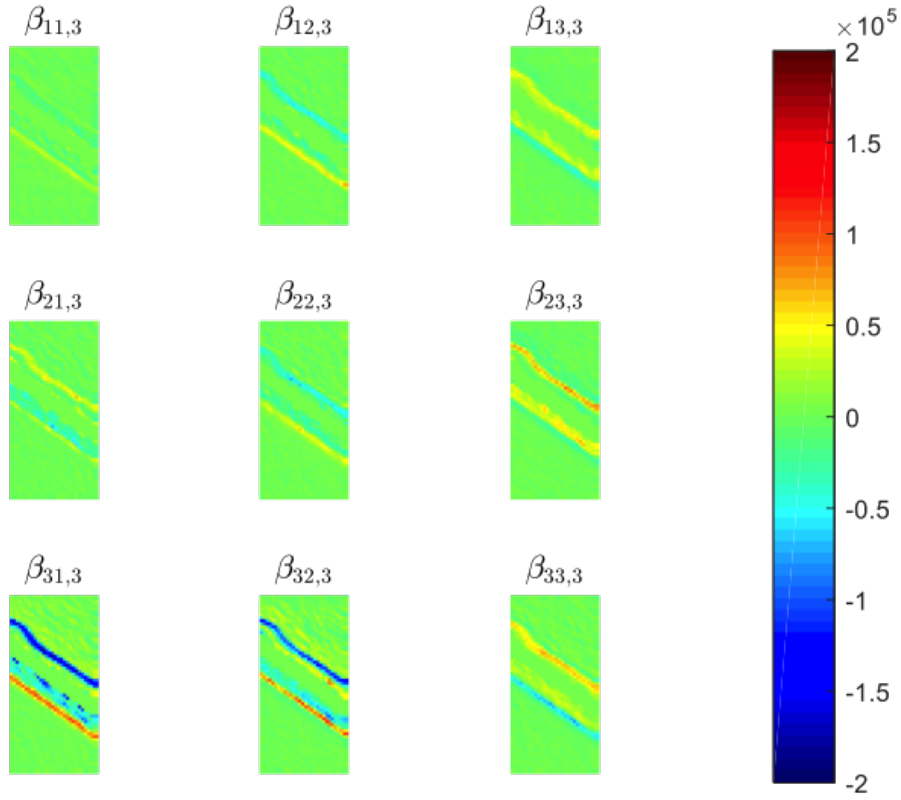


Figure D.3: Mapping of the non-zero components of the elastic distortion gradient tensor ($\beta_{ij,3}$) of the matrix around a $\{332\}\langle 113 \rangle$ mechanical twin.

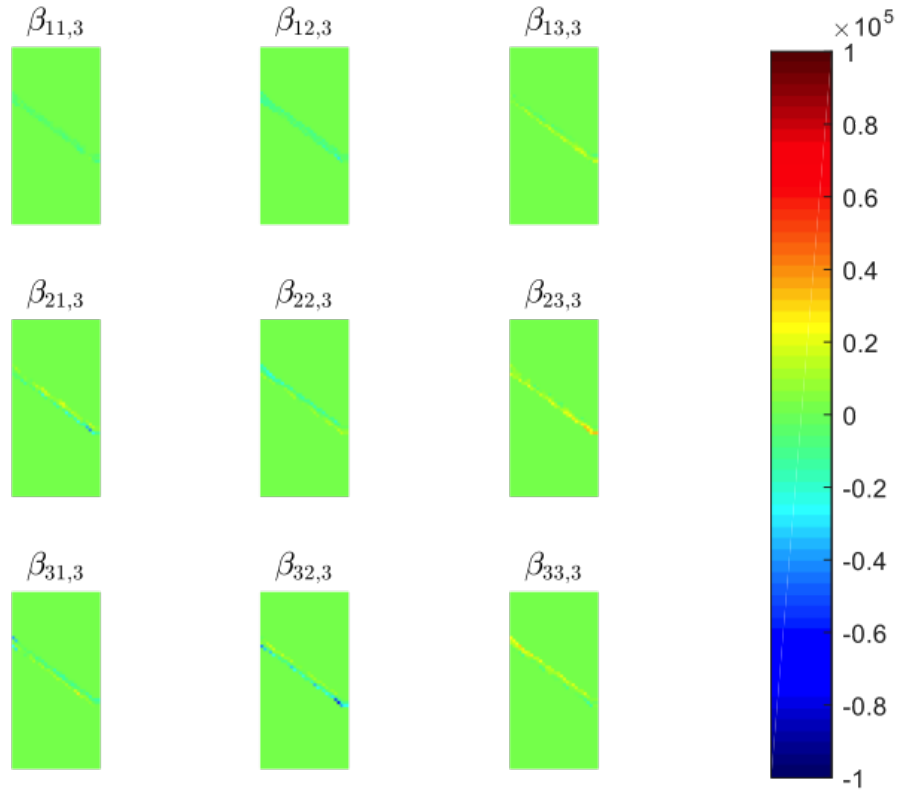


Figure D.4: Mapping of the non-zero components of the elastic distortion gradient tensor ($\beta_{ij,3}$) of the $\{332\}\langle 113\rangle$ mechanical twin.

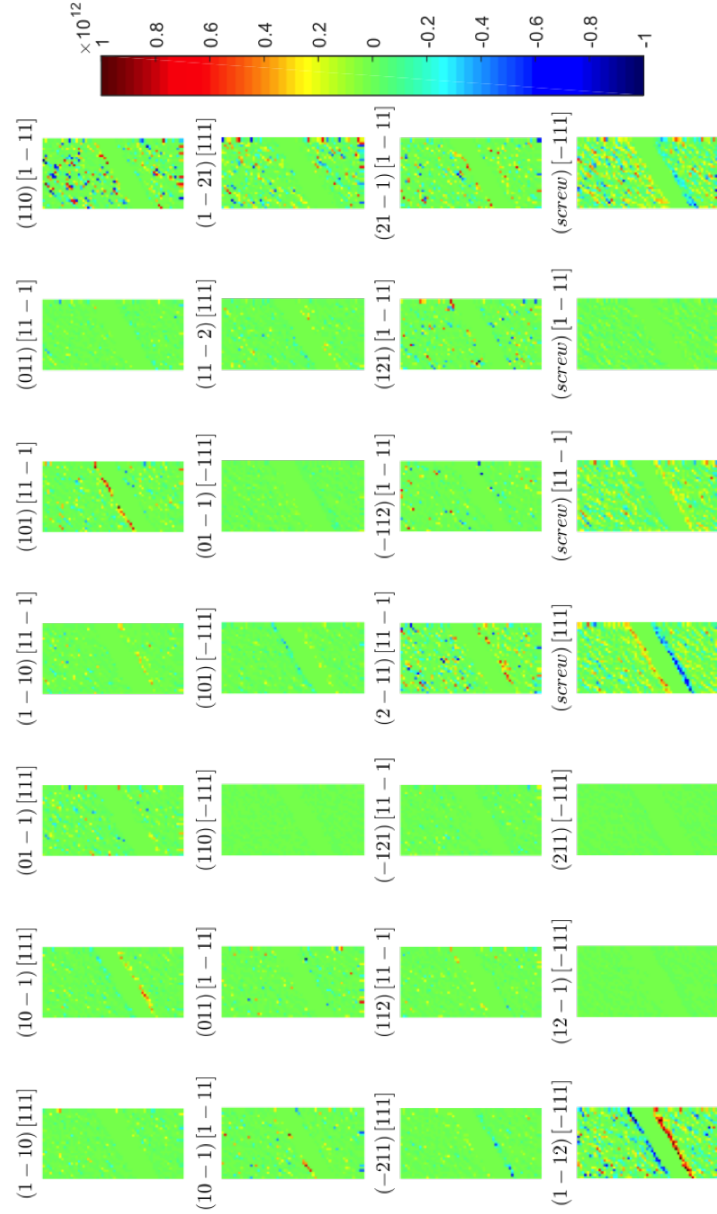


Figure D.5: Estimated GND density (in m^{-2} - meters of dislocation line per cubic meter of material) from Nye tensor for β matrix around an α'' plate.

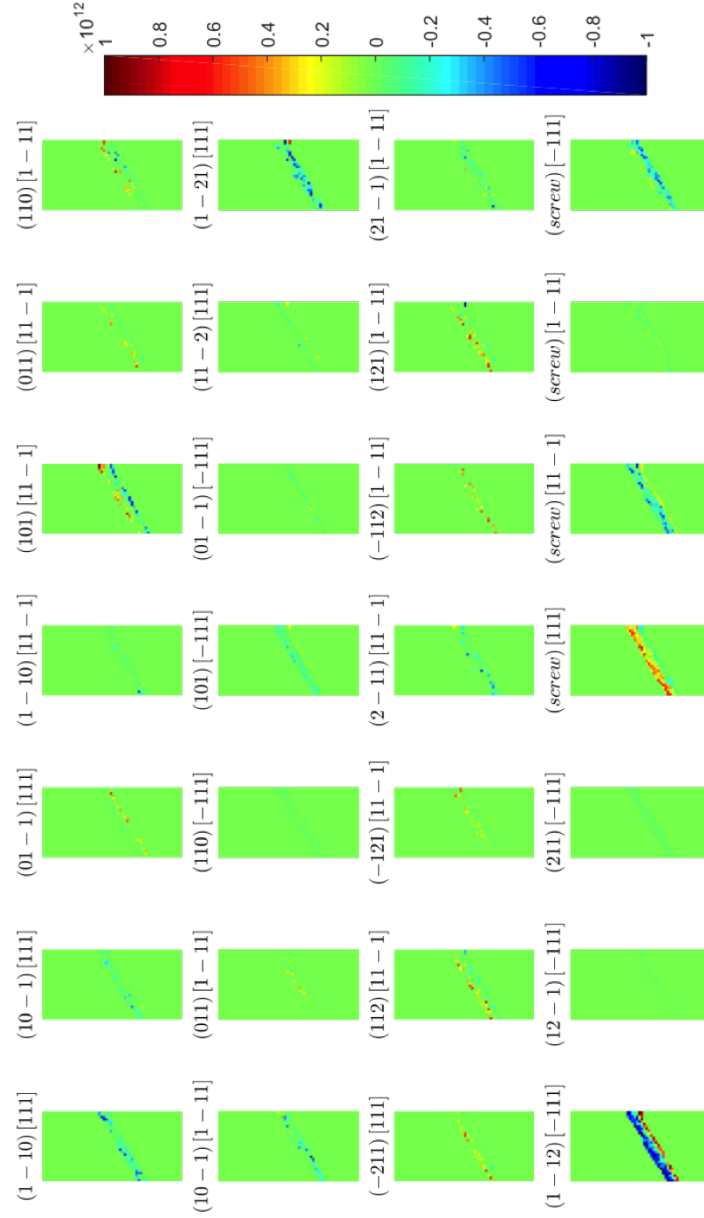


Figure D.6: Estimated GND density (in m^{-2}) from Nye tensor for the α'' plate (in terms of BCC slip systems).

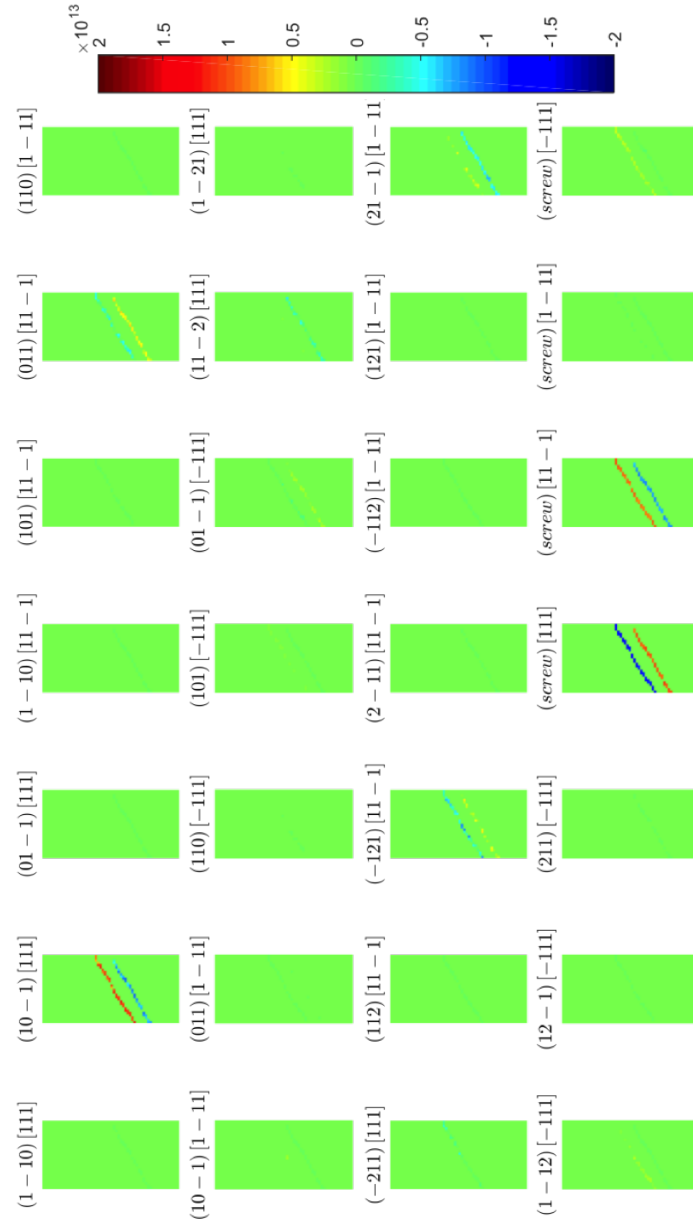


Figure D.7: Estimated GND density (in m^{-2}) from Nye tensor for the β/α'' interface.

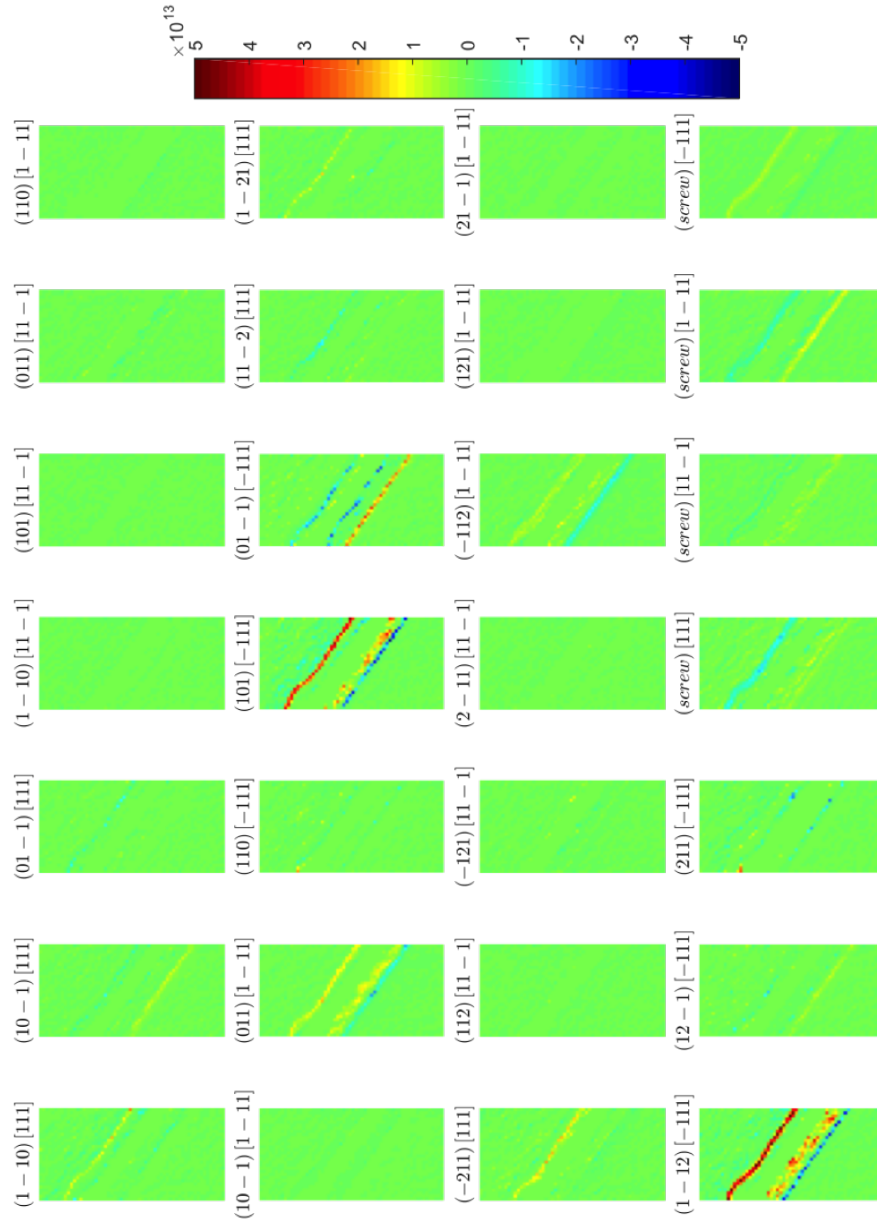


Figure D.8: Estimated GND density (in m^{-2}) from Nye tensor for β matrix around a mechanical twin.

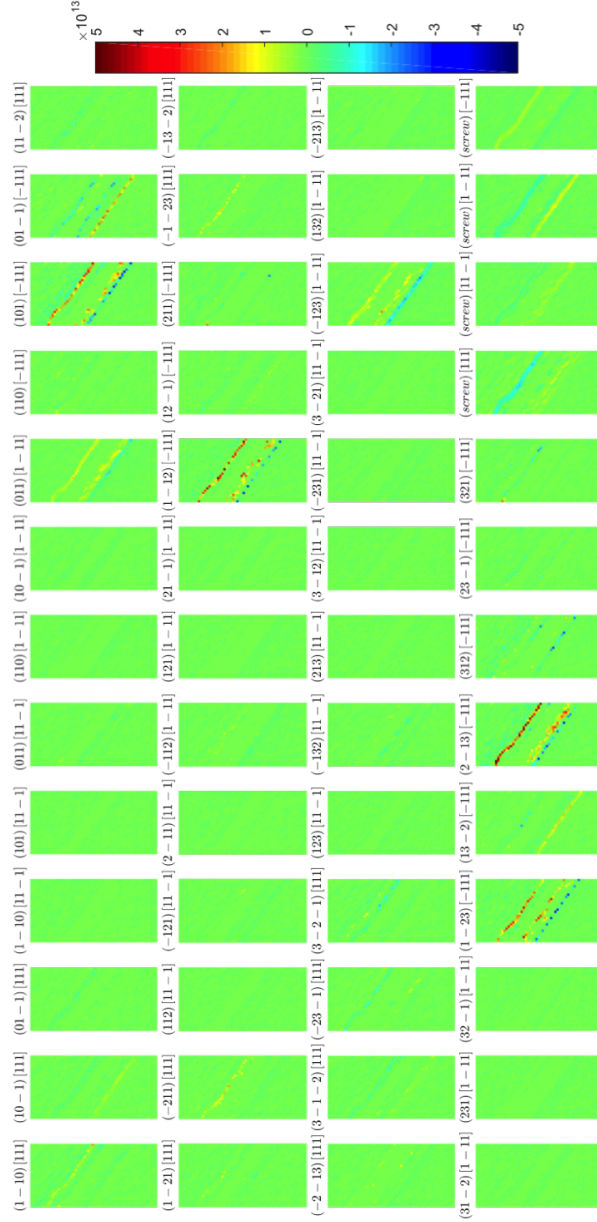


Figure D.9: Estimated GND density (in m^{-2}) from Nye tensor for β matrix around a mechanical twin with additional 24 equivalent $\{321\}\langle 111 \rangle$ slip systems.

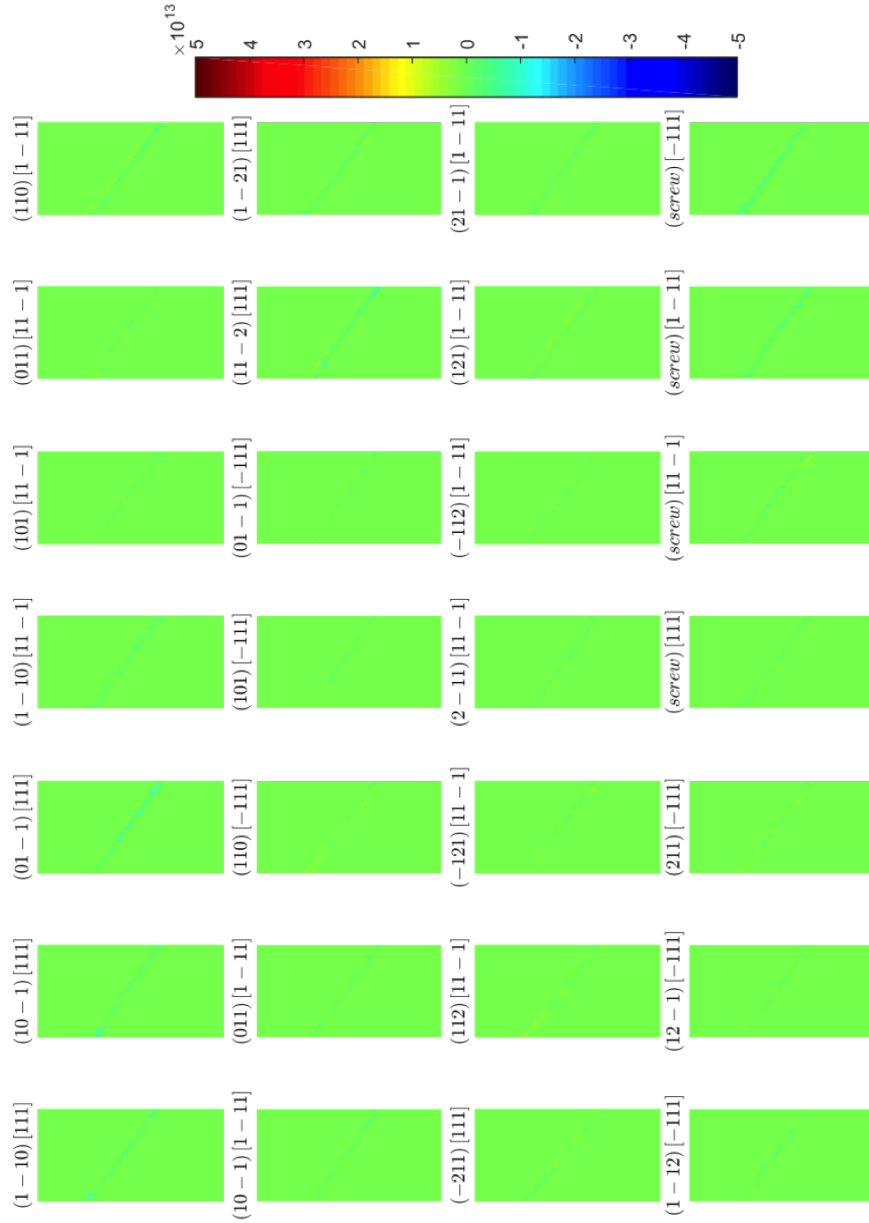


Figure D.10: Estimated GND density (in m^{-2}) from Nye tensor inside the β twin.

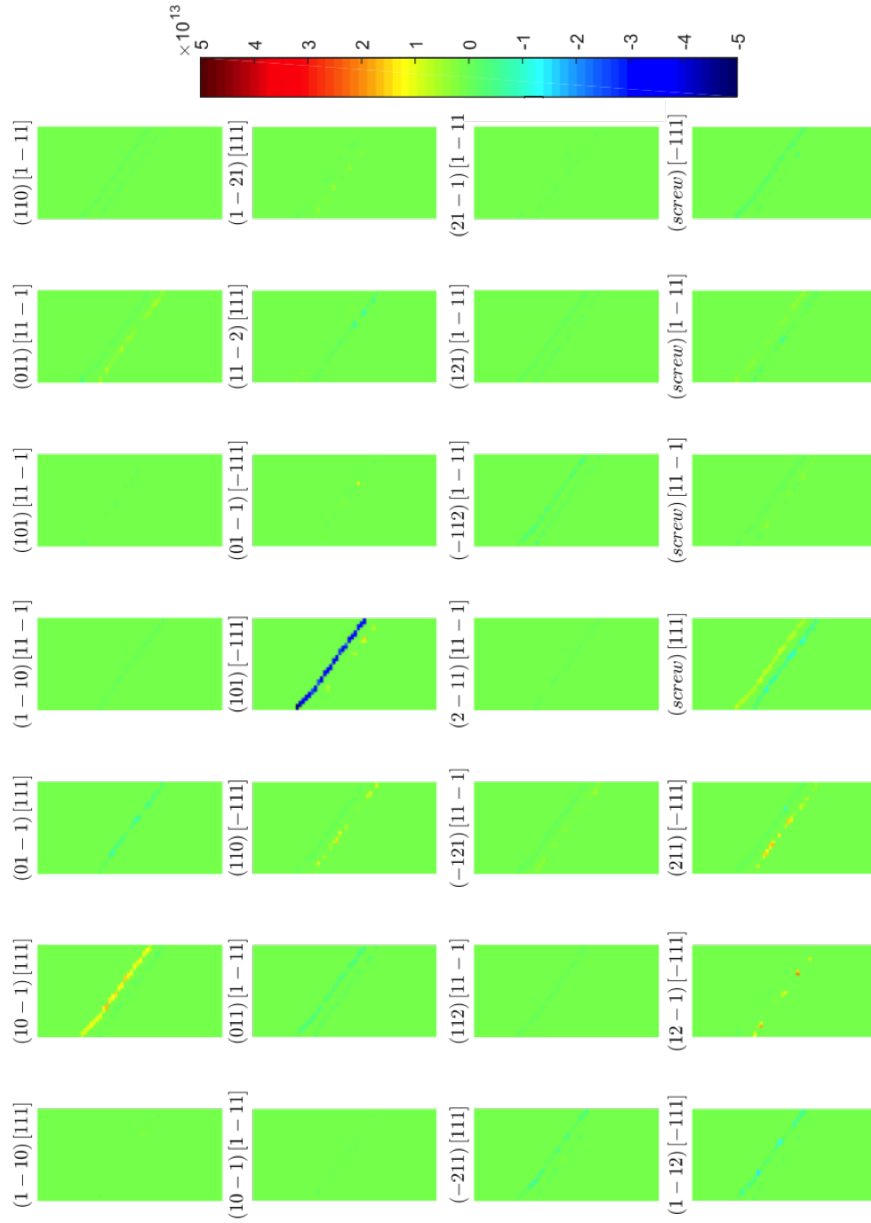


Figure D.11: *Estimated GND density (in m^{-2}) from Nye tensor at the twin boundaries.*

Appendix E

Strain tracking procedure during *in situ* tensile test in the TEM

The calculation of the strain during the *in situ* tensile test in the TEM has been performed using a tracking method with the help of Ir. Florent Hannard. Indeed, the dynamical contrast due to the electron beam is problematic in order to apply a conventional DIC method since there is no conservation of the gray level. Each frame of the video is sampled in a grid of an arbitrary shape, depending on the objects that have been chosen for the tracking (in this case : microstructural defects like grain boundary or FIB defects). The main difficulty was to find such kind of objects to track in both grains since a lot of care had been taken to avoid the introduction of defects during FIB-milling.

A first guess done by eye-tracking of some features in both grains has been performed to ensure that the computer-automated tracking was correctly performed. The results of this guess are given in Figure E.1. The error bars correspond to an error of one pixel for the centre position of the tracked features.

For the grain *G1*, the dark features in the upper right corner of the image were good candidates, together with the grain boundary. Moreover, since no additional features appeared within the grain (except for the slight changes in the bend contours) during the tensile test, the tracking

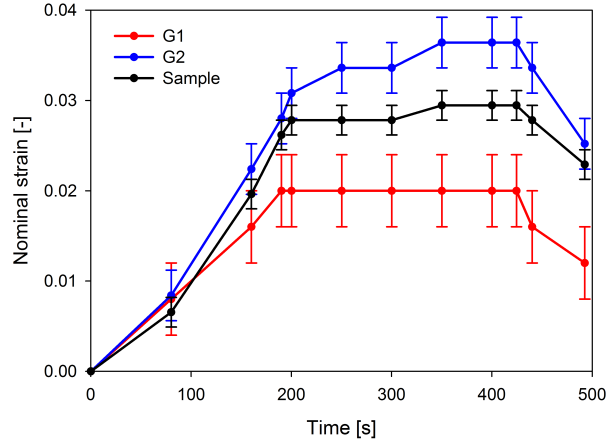


Figure E.1: Strain-time curves for both grains and the entire sample obtained by the eye-tracking method.

was easily performed and the noise with quite low. Figure E.2 shows two tracking steps used for $G1$ strain determination. The strain for each points of the final curve is a mean of all relative displacement measurements.

By contrast, the entire strain determination of $G2$ was much more trickier for two main reasons : (i) the dynamical contrast shows much stronger variations and (ii) a large amount of defects arises within a few successive frames.

To overcome these difficulties, the tracking has been segmented in two parts : the elastic loading and the plateau. Indeed, the stiffer contrast variations are due to the appearance of the twin embryos. Since the strain level is low, the different parts can be added without introducing a large error on the strain level (certainly lower than the error associated to the tracking method in such low contrast conditions). Example of the tracking is shown in Figure E.3. It can be seen that the tracking does not seem much reliable before the appearance of the defects, as illustrated by the tensile curve in Figure E.3(b).

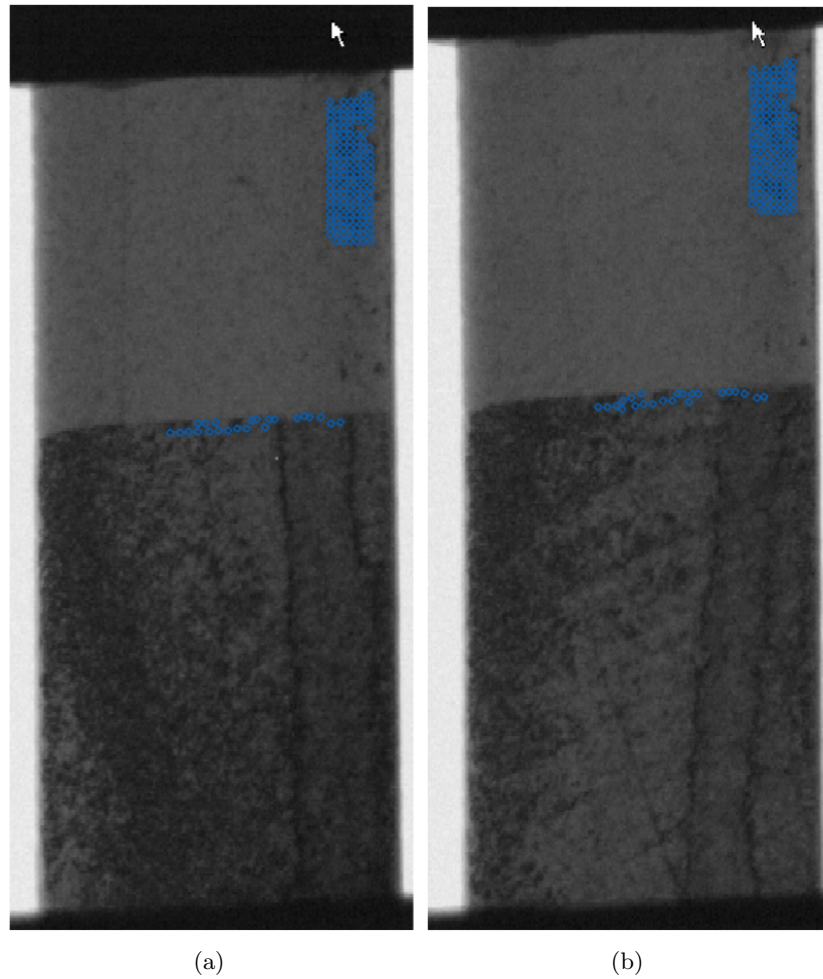


Figure E.2: Example of object tracking in G1. (a) Time = 0s and (b) Time = 220s.

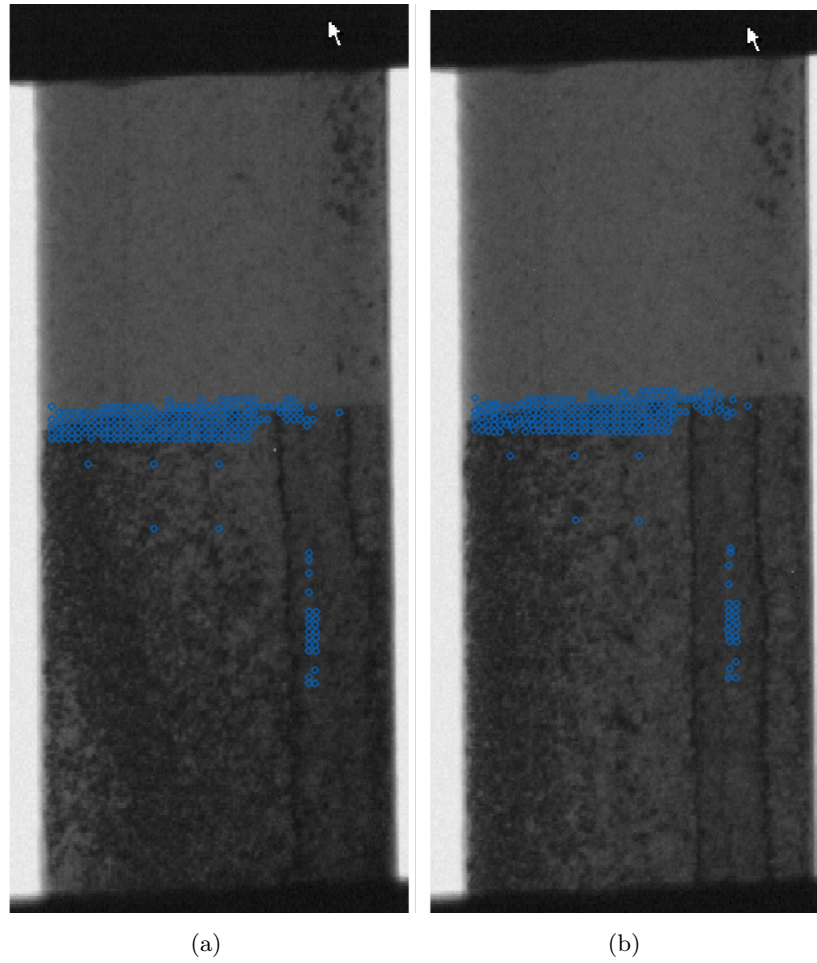


Figure E.3: *Example of object tracking in G2. (a) Time = 0s and (b) Time= 95s.*

List of symbols and abbreviations

α_{ij}	ij^{th} term of the Nye's tensor
β_{ij}	ij^{th} term of the elastic distortion gradient tensor
$\dot{\epsilon}$	Strain rate [s^{-1}]
γ	Shear strain [-]
$\hat{H}$	Hamiltonian
$\hbar$	Reduced Planck constant [m^2kg/s]
λ	Wavelength [nm]
$\langle uvw \rangle$	Crystalline direction of uvw indices
∇^2	Laplace operator
ν	Poisson ratio [-]
Φ	Approximated wave function
Ψ	Wave function
ρ	Density [g/cm^3]
ρ^i	Density of dislocation of type i [m/m^3]
σ	Stress [MPa]
τ	Shear stress [MPa]

Θ	Work-hardening rate [MPa]
θ	Diffracting angle [$^{\circ}$]
ε	Strain [-]
ε_0	Vacuum permittivity [F/m]
$\vec{b}$	Burgers vector
$\vec{g}$	Reciprocal lattice vector
$\vec{l}$	Dislocation line
$\{hkl\}$	Crystalline plane of hkl indices
$\{hkl\}\langle uvw \rangle$	Slip or twinning system
a, b, c	Lattice parameters [$\text{\AA}$]
A_f	Austenitic finish temperature [$^{\circ}C$]
A_s	Austenitic start temperature [$^{\circ}C$]
Bo	Bond order
C_{ij}	ij^{th} term of the elastic constant tensor [GPa]
D	Grain size [μm]
d_{hkl}	Interplanar distance of the hkl planes [nm]
E	Energy [J]
e	Electron charge [J]
e/a	Number of valence electrons per atom
eV	Electron-volt [J]
f	Volume fraction
F_{hkl}	Structure factor

hkl	Miller indices
I_{hkl}	Diffacted intensity
M	Atomic mass [g/mol]
m	Mass [kg]
m_e	Electron mass [kg]
M_f	Martensitic finish temperature [$^{\circ}C$]
M_s	Martensitic start temperature [$^{\circ}C$]
Md	d orbital energy level
s	Magnitude of shear
T	Temperature [$^{\circ}C$]
T_{β}	Temperature of the β transus [$^{\circ}C$]
w^p	Aspect ratio of particles
Z	Atomic number
E	Young's modulus [GPa]
G or μ	Shear modulus [GPa]
AsB	Back-scattered electron detector
BCC	Body-centered cubic
BF	Bright field
BSE	Backscattered electron
CBED	Convergent beam electron diffraction
CCD	Charge coupled device
CRSS	Critical resolved shear stress

CSL	Coherent site lattice
DF	Dark field
DFT	Density functional theory
DIC	Digital image correlation
DV	Discrete variational
EBSD	Electron back-scattered diffraction
EBSP	Electron back-scattered pattern
ECCI	Electron channeling contrast imaging
EDM	Electrical discharge machining
FCC	Face-centered cubic
FEG	Field emission gun
FFT	Fast Fourier transform
FIB	Focused ion beam
FWHM	Full width at half-maximum
GB	Grain boundary
GND	Geometrically necessary dislocation
GPFE	Generalised plane fault energy
GSFE	Generalised stacking fault energy
HCP	Hexagonal close-packed
HR	High resolution
ICP	Inductively coupled plasma
IFFT	Inverse fast Fourier transform

IPF	Inverse pole figure
KPQ	Kikuchi pattern quality
LCAO	Linear combination of atomic orbitals
LVDT	Linear variable differential transformer
MAD	Mean absolute deviation
MEMS	Micro electro-mechanical system
NBD	Nano beam diffraction
PC	Pattern center
PF	Pole figure
PTMC	Phenomenological theory of martensite crystallography
PTP	Push-to-pull device
ROI	Region of interest
SAD	Selected area diffraction
SE2	Secondary electron detector
SEM	Scanning electron microscopy
SF	Stacking fault
SFE	Stacking fault energy
SIM	Stress-induced martensite
SSD	Statistically stored dislocation
SXRD	Synchrotron X-ray diffraction
TB	Twin boundary
TEM	Transmission electron microscopy

TM	Topological model
TMP	Thermomechanical processing
TRIP	Transformation induced plasticity
TTT	Transformation-time-temperature
TWIP	Twinning induced plasticity
UTS	Ultimate tensile strength
XRD	X-ray diffraction

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