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Influence of conductive secondary phase on thermal gradients development during Spark Plasma Sintering (SPS) of ceramic composites

Maryse Demuynck [a,*], Jean-Pierre Erauw [a], Omer Van Der Biest [b], Francis Delannay [c], Francis Cambier [a]

[a] Belgian Ceramic Research Centre (Member of EMRA), Avenue Gouverneur Cornez 4, Mons, B-7000 Belgium
[b] MTM KULeuven, Kasteelpark Arenberg 44, Leuven, B-3001 Belgium
[c] EMPA UCLouvain, Place Sainte Barbe 2, Louvain-la-Neuve, B-1348 Belgium

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ABSTRACT

Spark Plasma Sintering (SPS) has attracted a lot of interest in recent years owing to its ability to enable the densification of a broad range of materials in a very short processing time. It is well documented in the literature that the very high heating rates that can be applied with this technology can lead to the apparition of large thermal gradients in the tool and thus affect the homogeneity of the compact.

In the present study, the influence of the compact thermal and electrical properties on the thermal gradients was studied. Al_2O_3, AlN and TiC powders were used to produce series of Al_2O_3-TiC and AlN-TiC composites (0, 25, 50, 75, 100 vol%TiC) showing different electrical and thermal conductivities. Two pyrometers were used in order to observe and measure the thermal gradients and the percolation of the current during sintering at a high heating rate and without insulation.

Electrical conductivity measurements were carried out on samples presenting different relative densities. This samples were obtained through interrupted sintering cycles at temperatures below and above the identified percolation threshold temperature.

It was shown that high thermal gradients can appear during SPS depending on the processing parameters (dimensions of the die and heating rate) but also on the composition of the compact (proportion of conductive phase) and on its density.

1. Introduction

SPS (Spark Plasma Sintering) is a rapid sintering technique that has attracted a lot of interest in recent years. It is a hot pressing technology that enables the densification of a broad range of materials in a very short processing time and at lower temperatures compared with more conventional sintering technologies. The sintering cycle is carried out in a chamber under vacuum or inert atmosphere. The tool (cylindrical die and punches) material is usually graphite. An electric current is directly applied to the punches and die system which heats by Joule effect (as well as the powder if it is electrically conductive) at very high heating rates (up to 200–1000 °C/min depending on the equipment used [1]). The low thermal inertia of the system and the absence of a massive insulation within the water cooled vessel, allow the shortening of the cooling step as well, thereby reducing significantly the overall thermal cycle.

Due to the very high heating rates, thermal gradients can appear in the SPS tool between its centre and the external part of the die [2] leading to a lack of homogeneity in the sample. Indeed, the temperature difference in the compact should ideally be close to zero in order to obtain a homogeneous sample.

Thermal gradients depend on several parameters like the conductivities of both the sample and the die, the sample dimensions, the current distribution during sintering, etc. SPS suppliers have already found solutions aiming to reduce these gradients, for example by using spacers between the powder and the punches (in order to influence the current distribution) or by using a thermal insulation around the die. They also have partially solve this problem for larger specimens (> 40 mm) through the use of hybrid systems aiming to reduce the radial thermal gradients by secondary resistive or inductive heating (this is of major interest for conductive materials).

However, it is sometimes necessary to add a correction to the measured temperature in order to be sure that the sample reach the desired temperature. This correction is dependent on the SPS

* Corresponding author.
E-mail address: m.demuynck@bcrc.be (M. Demuynck).

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equipment and on the way of controlling the temperature [3]. The electrical properties of the compact to be sintered has a great influence on the radial temperature gradient that can be observed in the system and in the sample. In the case of a high electrical conductor, the main part of the current flows through the sample while, on the contrary, the current is forced to flow through the die in the case of a strong electrical insulator [4–6]. The temperature control can thus be complicated when the sample goes from an insulating to a conductive behaviour during the densification process [7,8]. For example, a composite (powder or bulk) made of both an electrically conductive and an electrically insulating phases can be conductive or not. The electrical conductivity of the whole compact depends on the amount of conductive phase and on the number of contacts between conductive grains. This is known as "site-bond percolation" [9]. The electrical behaviour of the compact can also change over time, during the densification stage. Indeed, an insulating composite can become conductive if the amount of conductive phase is high enough and if the number on contacts between conductive grains increases during densification. It was also shown in the literature that the percolation threshold depends on the conductive phase (filler) grain size [10]. As a consequence, as the current applied in SPS contributes to the direct heating of the die/punches tool by Joule effect, it can also contribute directly to the heating of the compact in case of percolation.

The objective of this study was to highlight the creation of thermal gradients in the SPS tool during the sintering of ceramic composites and their influence on the temperature control during the densification process.

Al_2O_3-TiC or AlN-TiC composites should behave in a different manner regarding to direct heating of the samples and to the heat transfer to and/or from the die/punches tool. Indeed, Al_2O_3, AlN and TiC have opposite thermal and electrical properties (Table 1). Al_2O_3 is an electrically and thermally insulating material whereas AlN is thermally conductive and electrically insulating. TiC is both electrically and thermally conductive.

Unlike alumina [14], aluminium nitride is difficult to sinter without additives as reviewed elsewhere [15]. Indeed, AlN is a covalent compound with limited atomic mobility and it is thus difficult to fully sinter this material at low temperatures. Moreover, it is known that AlN decomposes at temperatures higher than 1600 °C [16]. That is why AlN is usually densified under high pressure with additives, the most used sintering aids being Y_2O_3, CaO or CaF_2 [17].

Due to its limited sinterability, TiC reduces strongly the sintering kinetics of alumina [18]. It forms an interconnected network that prevents to reach the maximum density. It is thus required to sinter at a higher temperature in order to increase the driving force for sintering, resulting however in matrix grain growth, or to heat at a lower temperature with the application of a uniaxial pressure and possibly adding sintering aids.

For Al_2O_3-TiC, the sintering aid is usually Y_2O_3 [19,20]. However, SPS could prevent the use of sintering additives but only limited information is available in the literature concerning the SPS densification of such composites [21–23]. They can be used, for example, for cutting and wear tools (with a TiC content of around 30 wt%) or as a substrate of magnetic heads due to their attractive mechanical properties (high temperature strength and thermal shock resistance) and good electrical conductivity [24].

AlN-based materials find application in refractories or in the electronic field due to their high thermal conductivity combined with their electrical insulating properties. The literature concerning AlN-TiC materials is poor as the main field of application of AlN substrate is in electronics where the electrical insulation is the major requirement. In this work, these composites have thus been chosen as a matter of comparison with Al_2O_3-TiC, to assess the influence of the thermal insulating behaviour or the heat transfer between the composite and the die.

2. Experimental

Commercial powders (Al_2O_3, AlN and TiC) were used as raw materials. Table 2 presents the grades that were chosen as well as their initial grain size (D50) and main impurities.

They were chosen for their different electrical and thermal properties. As said in the introduction, Al_2O_3 and AlN are electrically insulating powders ($\rho_{élec} > 10^{13}\ \Omega$ m) but they have different thermal conductivities: Al_2O_3 is thermally insulating ($\lambda \sim 30$–$40\ W\ m^{-1}\ K^{-1}$) while AlN presents good thermal properties ($\lambda \sim 200$–$300\ W\ m^{-1}\ K^{-1}$). TiC is a conductive material ($\rho_{élec} \sim 0.5 \times 10^{-6}\ \Omega$ m; $\lambda = 21\ W\ m^{-1}\ K^{-1}$) which was used as a second phase in Al_2O_3- and AlN-based composites in different proportions (25, 50 and 75 vol%) so that Al_2O_3-TiC and AlN-TiC composites with different electrical and thermal properties were produced.

Al_2O_3-TiC mixtures containing 25, 50 and 75 vol% of TiC were prepared by ball-milling during one night in isopropanol. Al_2O_3-TiC mixtures were dried in a rotational evaporator and sieved at 500 μm in order to break the larger agglomerates.

Due to the hygroscopic behaviour of AlN, AlN-TiC mixtures (25, 50 and 75 vol% of TiC) were mixed in dry conditions and sieved at 500 μm as well.

SPS experiments were conducted in an HPD25/1 equipment (FCT System, Germany) using a fixed pulse pattern of 10:5 ms on:off. The temperature was axially measured by an optical pyrometer focused on a point situated near the upper surface of the sample through a hole drilled in the upper punch (central pyrometer "CP").

Al_2O_3-TiC and AlN-TiC compacts were sintered at different temperatures in order to obtain samples with different densities (interrupted cycles). These sintering experiments were conducted in a die of 30 mm in diameter covered with a graphite felt insulation (in order to improve thermal insulation), with a heating rate of 200 °C/min and an applied load of 50 MPa. Table 3 summarizes the temperature and dwell time conditions of these tests. The density of each sample was measured using the Archimedes' immersion method (in water for Al_2O_3-TiC samples and in mercury for AlN-TiC samples).

The electrical conductivity of the composites was measured by the 4-points method (RZ-2001i, Osawa Science) between 25 and

Table 1
Electrical and thermal properties of Al_2O_3, AlN and TiC (from [11–13]).

Powder	λ ($W\ m^{-1}\ K^{-1}$)	$\rho_{élec}$ (Ω m)
Al_2O_3	30–40	$> 10^{15}$
AlN	320 (Pure crystal) 180–220 (Sintered)	$> 10^{13}$
TiC	21	0.5×10^{-6}

Table 2
Raw materials.

Powder	Supplier	Grade	D50 (μm)	Impurities
Al_2O_3	Alcan	P172SB	0.4	600 ppm Na_2O, 900 ppm SiO_2, 600 ppm CaO, 120 ppm Fe_2O_3, 900 ppm MgO
AlN	H.C. Starck	Grade C	0.8–1.8	Fe < 50 ppm, O < 2%
TiC	H.C. Starck	HV120	1.0–1.5	free C, O max 1.3%

Table 3
Sintering conditions of Al_2O_3-TiC and AlN-TiC samples.

Mixture	TiC content (vol%)	Sintering T (°C)	Dwell time (min)
Al_2O_3-TiC	50	700–1500	0
	25–50–75	1500–1800	6
AlN-TiC	50	700–1600	0
	25–50–75	1600–1900	6

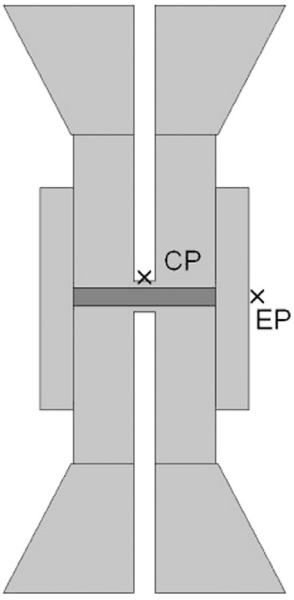

Fig. 1. Observation of the percolation phenomenon - Focus points of central (CP) and external (EP) pyrometers.

970 °C. These characterizations were realized under argon atmosphere, on small rectangular bars ($3 \times 3 \times 15$ mm) prepared by diamond saw cutting from the 30 mm cylinders.

Some sintering experiments were also carried out in a 40mm die on the raw materials (Al_2O_3, AlN and TiC) and on the composite mixtures at 1500°C with an applied load of 55MPa. These tests were conducted without insulation around the die and at a high heating rate (200°C/min) in order to induce the creation of thermal gradients in the system. The temperature was measured and controlled by the central pyrometer (CP). A second pyrometer focused on the outer surface of the die was also used to measure the temperature radially (external pyrometer "EP") (Fig. 1). These two ways of measuring the temperature in SPS were used simultaneously in order to assess the evolution of thermal gradients in the tool during the whole sintering step and to observe the percolation phenomenon.

3. Results

3.1. Thermal gradients and percolation threshold

In this section, the temperature difference between the centre and the external part of the die (T_{CP}-T_{EP}) is used to represent the thermal gradient appearing in the system. Figs. 2–4 present the evolution of this temperature difference as a function of the temperature in the centre of the system T_{CP} (which is the temperature used for the control of sintering). These figures concern the raw materials, Al_2O_3-TiC and AlN-TiC composites, respectively. The temperature difference observed during these experiments can be very high (up to 200 °C).

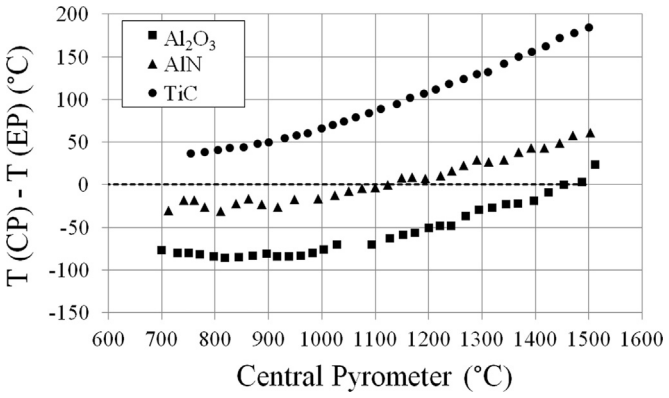

Fig. 2. Percolation phenomenon – Monolithic materials (Al_2O_3, AlN and TiC).

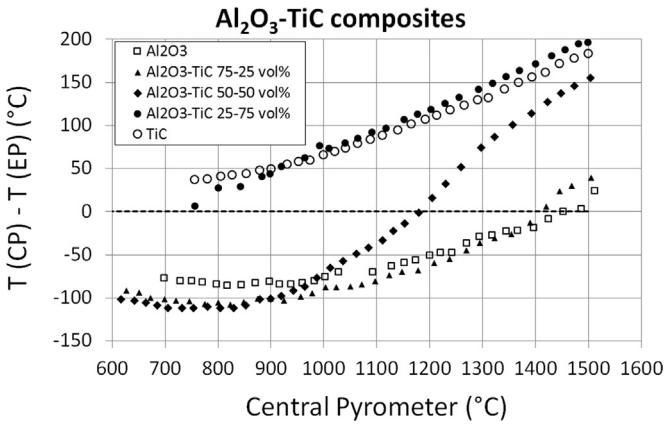

Fig. 3. Percolation phenomenon on Al_2O_3-TiC composites.

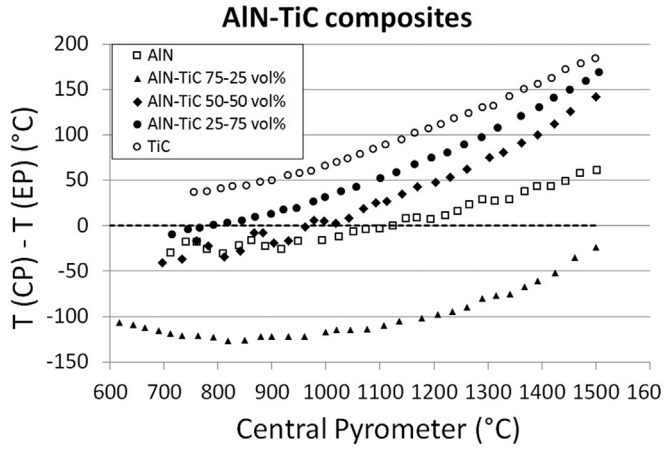

Fig. 4. Percolation phenomenon on AlN-TiC composites.

Fig. 2 shows that the thermal difference is negative for electrically insulating powders like alumina ($T_{EP} > T_{CP}$) and positive for electro-conductive powders like TiC ($T_{EP} < T_{CP}$). For AlN, while being a thermal conductor and an electrical insulator, this difference is lower and closer to zero.

Fig. 3 (Al_2O_3-TiC composites) shows that, with an increasing amount of TiC, Al_2O_3-TiC composites move from an insulating behaviour like alumina (0 vol% and 25 vol% TiC) to a conductive behaviour like TiC (75 vol% and 100 vol%TiC). For the intermediate composition (50 vol% TiC), the percolation phenomenon occurs during the sintering step at around 1200 °C.

For the AlN-TiC composites (Fig. 4), the percolation phenomenon can also be observed for the compositions containing 50 and

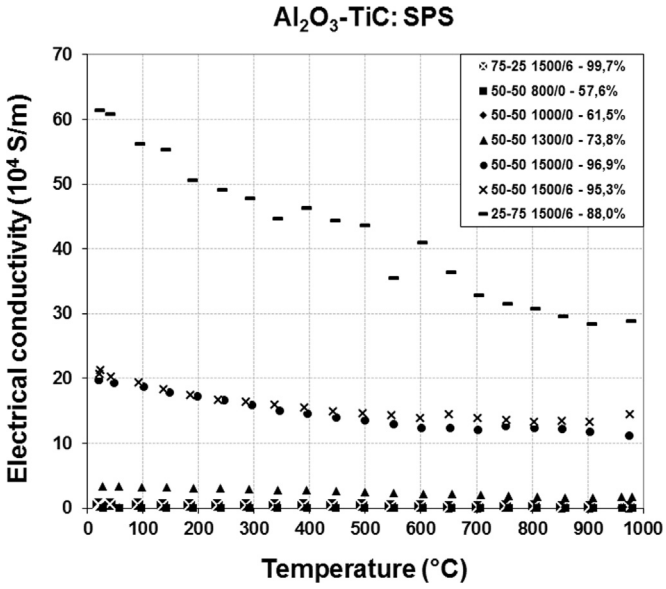

Fig. 5. Electrical conductivity of SPS-sintered Al_2O_3-TiC samples.

75 vol% of TiC but at a lower temperature (around 1000 °C and 800 °C, respectively). The results obtained for AlN-25vol%TiC are similar to those of pure alumina (Fig. 2). Indeed, for this composition, the thermal difference is negative ($T_{EP} > T_{CP}$) and tends to decrease during sintering. The AlN-25vol%TiC compact behaves as an electrical insulator and the thermal gradients are higher than for a monolithic AlN compact.

3.2. Electrical conductivity measurements

Samples for electrical conductivity measurements (rectangular bars) were prepared from SPS compacts sintered at different temperatures in order to study the influence of both the composition and the density on the electrical conductivity.

Figs. 5 and 6 show the variation of the electrical conductivity between room temperature and 980 °C for Al_2O_3-TiC and AlN-TiC composites, respectively. Values indicated in the legends represent the composition (for example, "75–25" means 75 vol%Al_2O_3 or AlN and 25 vol%TiC), the sintering conditions (1500/6 for 1500 °C and 6 min dwell) and the relative density of the sample.

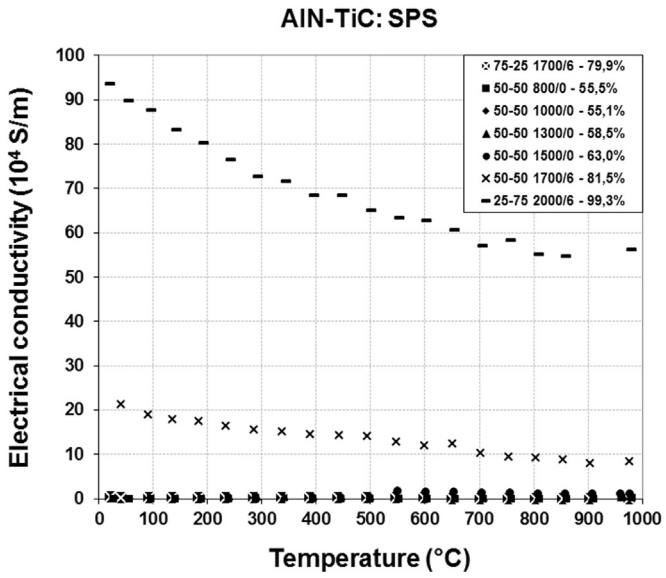

Fig. 6. Electrical conductivity of SPS-sintered AlN-TiC samples.

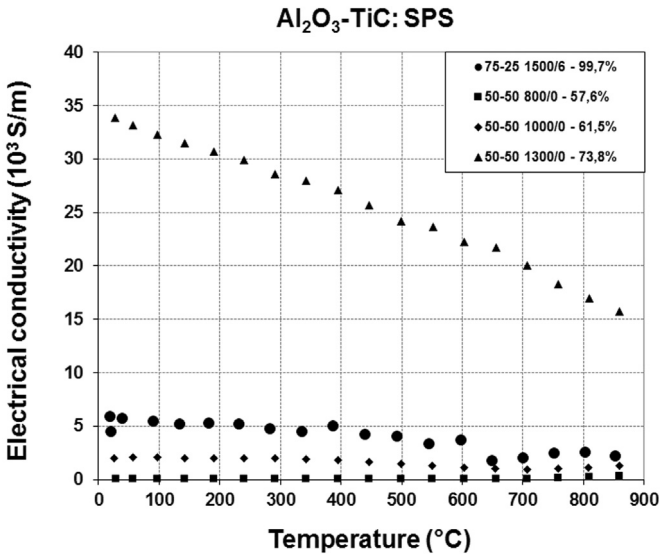

Fig. 7. Electrical conductivity of SPS-sintered Al_2O_3-TiC samples (low densities).

These results confirm that the samples containing 25 vol% TiC are electrically insulating even if their relative density is high (99.7% for Al_2O_3-TiC and 79.9% for AlN-TiC).

Composites containing 50 vol%TiC with the lower relative density (~60%) are electrically insulating. Their conductivity increases with increased density.

For Al_2O_3-50vol%TiC and AlN-50vol%TiC presenting a relative density of 95–96% and 81.5% respectively, the electrical conductivity evolves from 2.10^5 down to 10^5 S/m between the room temperature and 980 °C.

The conductivity of compacts containing 75 vol%TiC is very high and can reach 9.10^5S/m in the case of AlN-75vol%TiC with a density higher than 99%.

In can be noticed that, when Al_2O_3-TiC and AlN-TiC are electrically conductive, the conductivity decreases when the temperature increases. This has to be related to the metallic behaviour of TiC [25,26].

Results presented on Figs. 7 and 8 concern the samples with

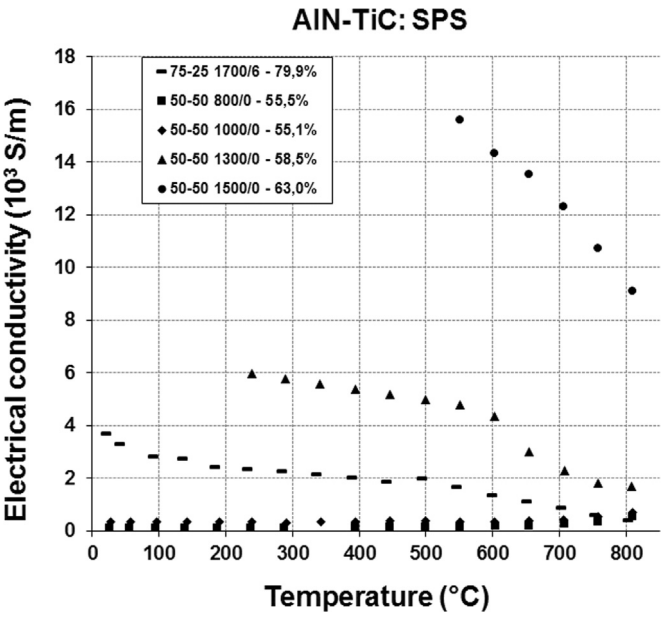

Fig. 8. Electrical conductivity of SPS-sintered AlN-TiC samples (low densities).

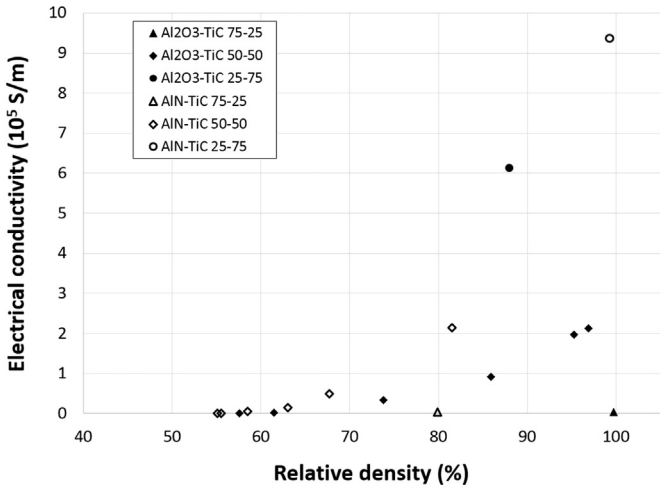

Fig. 9. Electrical conductivity at room temperature as a function of the relative density.

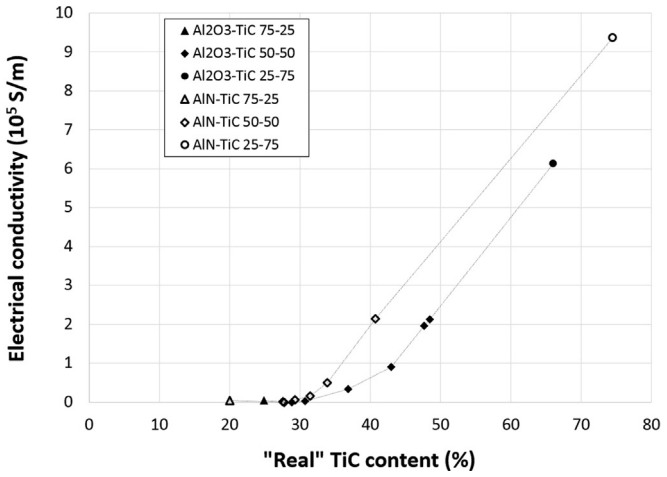

Fig. 10. Electrical conductivity at room temperature as a function of the amount of conductive phase.

the lower densities (25 and 50 vol%TiC) in order to appreciate the moment when the conductivity starts to increase. It is to be noted that the small increase observed on the curves above 800 °C is not significant (artefact of measuring).

Al_2O_3- and AlN-based samples containing 25 vol%TiC present a very low electrical conductivity ($\sim 5.10^3$ S/m), even when their relative densities reach 100% and 80% respectively.

For 50 vol%TiC-containing compositions, the conductivity starts to increase when the relative density reaches ~60% for Al_2O_3-TiC (see Fig. 7) and ~55% for AlN-TiC (see Fig. 8). These results indicate that the conductivity depends on the composition but also on the density of the compact.

Fig. 9 represents the evolution of the electrical conductivity at room temperature as a function of the relative density for the Al_2O_3-TiC and AlN-TiC composites. This figure shows that, except for composites containing 25 vol%TiC which remain insulating during the whole densification process (Figs. 3 and 4), the conductivity starts to increase from a relative density of around 60% for Al_2O_3-TiC and AlN-TiC composites.

If we consider that there is no reaction between the insulating phase (Al_2O_3 or AlN) and TiC, there is no change in the mass m ($m_{Al2O3/AlN}+m_{TiC}$) of the sample nor in the respective volume of each phase (V_{TiC} and $V_{Al2O3/AlN}$). The only thing that changes is the volume of the sample:

$$\text{for a porous sample: } V_{TOT\ sample} = V_{TiC} + V_{Al2O3/AlN} + V_{poro} \quad (1)$$

$$\text{for a dense sample: } V_{TOT\ theo} = V_{TiC} + V_{Al2O3/AlN} \quad (2)$$

The relative density can be expressed as:

$$\rho_{rel} = \rho_{sample}/\rho_{theo=}\left(m/V_{TOT\ sample}\right)/\left(m/V_{TOT\ theo}\right) = V_{TOT\ theo}/V_{TOT\ sample} \quad (3)$$

By replacing (1) and (2) in (3):

$$\rho_{rel} = \left(V_{TiC} + V_{Al2O3/AlN}\right)/\left(V_{TiC} + V_{Al2O3/AlN} + V_{poro}\right) \quad (4)$$

The "real" volume percentage of TiC (*real %vol TiC*) in the sample takes into account the amount of porosity in the sample and can be expressed by:

$$real\ \%vol\ TiC = V_{TiC}/V_{TOT\ sample} \quad (5)$$

So, from (1), (4) and (5):

$$real\ \%vol\ TiC = \left[V_{TiC}/\left(V_{TiC} + V_{Al2O3/ALN}\right)\right].\ \rho_{rel} \quad (6)$$

$$real\ \%vol\ TiC = theo\ \%vol\ TiC.\ \rho_{rel} \quad (7)$$

So the results presented in Fig. 9 can also be represented as a function of the "real" volume percentage of TiC by multiplying the theoretical TiC content (vol%) by the relative density of the sample (Fig. 10). In other words, we consider here the porosity as a third phase with an insulating behaviour. This graph shows that the electrical conductivity of the Al_2O_3-TiC and AlN-TiC composites increases from TiC contents above 30 vol% which is the percolation threshold for the materials used in this study.

It seems that, for similar density and (real) TiC content, the AlN-TiC composites are more electro-conductive than the Al_2O_3-TiC compacts. This is probably due to the difference in grain size distribution of the raw materials. Indeed, the alumina grains (d50=0.4 μm) are smaller than the TiC grains (d50=1–1.5 μm) while AlN (d50=0.8–1.8 μm) and TiC have nearly the same grain size. As a consequence, the alumina grains tend to form an insulating layer around the TiC particles thus reducing the amount of contacts between electroconductive grains.

4. Discussion

Experiments conducted with the two pyrometers (central and external) showed differences in the thermal gradients appearing in the SPS tool and their evolution during sintering and densification. When an electrically insulating material is tested, the current flows through the die and the punches and not through the powder, resulting in a higher Joule effect in the graphite SPS tool. As a consequence, the temperature at the external surface of the die is much higher than in the centre of the system (negative value for T_{CP}-T_{EP}).

Alumina is an electrically and thermally insulating material. For instance, with the sintering parameters applied here, the thermal gradient at the beginning of the densification is around 75 °C. During sintering, the thermal gradient tends to decrease following the homogenization of the temperature.

The thermal gradients are much lower in the case of AlN which is also an electrically insulating material. However, the very high thermal conductivity of this material results in a fast homogenization of the temperature in the assembly.

An opposite effect (positive value of T_{CP}-T_{EP}) is found for a conductive material. In that case the current can pass directly through the powder and the Joule effect could be higher in the centre of the system. Indeed, due to the cooling of the sintering chamber, the temperature gradient tends to increase and can

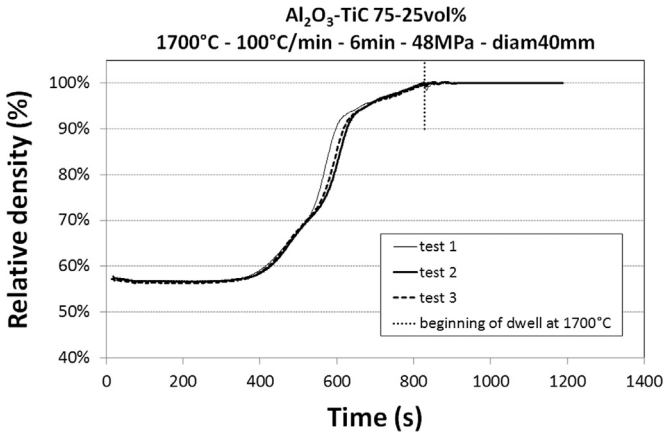

Fig. 11. Evolution of the relative density of Al_2O_3-TiC composites (25 vol% TiC) during a SPS cycle.

reach several tens of degrees (up to 200 °C with TiC for example).

For both the Al_2O_3-TiC and AlN-TiC composites, the TiC content has to be higher than 25 vol% in order to observe the percolation phenomenon.

The behaviour of alumina, Al_2O_3-TiC and AlN-TiC composites containing 25 vol% of electroconductive phase (TiC) are very similar. In the case of the alumina-based composites, the mean grain sizes of the raw materials are very different ($d50_{Al2O3}$=0.4 μm; $d50_{TiC}$=1–1.5 μm) inducing a good dispersion of the alumina grains around the TiC particles and thus reducing the possibility for the current to flow through the sample. However, as AlN and TiC have a similar grain size distribution ($d50_{AlN}$=0.8–1.8 μm; $d50_{TiC}$=1–1.5 μm) and also because the mixing was carried out dry, the compaction of these particles is not optimized resulting in a lot of voids (pores) in the compact. Indeed, this difference in compaction can also be observed on Fig. 11 and Fig. 12 where it is evident that the green density of Al_2O_3-TiC samples is higher than the green density of AlN-TiC samples. Fig. 9 also shows that the density of Al_2O_3-TiC sample has to be higher than for AlN-TiC compacts in order to reach the same electrical conductivity level.

This means that these porosities can be assimilated to a third electrically insulating phase. Moreover, TiC has a low thermal conductivity, comparing to AlN, which explains why the AlN-25vol%TiC behaviour is similar to the one of alumina.

For any TiC content higher than 25 vol%, a percolation phenomenon occurs and the compacts become progressively more and more conductive. This transition is related to the amount of

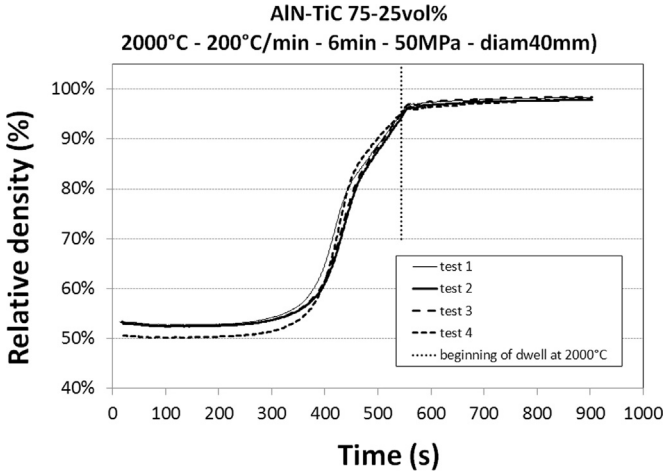

Fig. 12. Evolution of the relative density of AlN-TiC composites (25 vol% TiC) during a SPS cycle.

conductive grains and to the densification (increasing the number of "links" between particles according to percolation models [2]). That means that, in order to be conductive, a composite material must contain enough conductive grains, but of course these grains have to be in contact (site-bond percolation).

The electrical conductivity measurements show that the composites containing 25 vol%TiC are mostly insulating: a very low conductivity (~50 S/cm) is measured even if the sintered sample presents a high density (relative density of 100% for Al_2O_3-25vol% TiC and more than 80% pour AlN-25vol%TiC).

The percolation phenomenon can occur in samples prepared from mixtures containing between 25 and 50 vol% of TiC. When the percolation threshold is reached, the higher is the TiC content, the higher is the conductivity at a specific density. The electrical conductivity starts to increase from a density of 60% and 55% for Al_2O_3-50vol%TiC and AlN-50vol%TiC, respectively. At the same relative density and the same TiC content, an AlN-TiC sample is more conductive than an Al_2O_3-TiC compact. As explained before, this is attributed to the arrangement of the grains in the compact. An Al_2O_3-50vol%TiC sample with a relative density of 95% has the same conductivity as an AlN-50vol%TiC sample with a density of 81.5%.

The tests carried out in this study showed that the electrical conductivity of the composites depends not only on the amount of conductive phase but also on its relative density and on the number of contacts between conductive grains. For Al_2O_3-TiC and AlN-TiC compositions, it was shown that the electrical conductivity starts to increase from 30 vol% of TiC taking into account the volume of porosity in the compact.

5. Conclusion

Sintering experiments with two pyrometers (one focused on the external part of the die and the other one focused in the centre of the system) and electrical conductivity measurements on samples with different densities allowed to observe the current percolation phenomenon in composites containing a mixture of electrically insulating and electrically conductive phases.

Thermal gradients were observed during the sintering of Al_2O_3-TiC and AlN-TiC composites (from 0 to 100 vol% TiC) between the centre of the SPS tool and the outer surface of the die. Depending on the tool dimensions and on the sintering parameters, this temperature difference can be very high (up to 200 °C). These gradients can also reverse during the densification step following the increase of the number of contacts between conductive grains. This is called percolation. This work thus put forward the importance of a good optimization of the sintering conditions (mainly heating rate and temperature control) and of the tool design, in order to minimize the thermal gradients and to obtain a homogenous sample. It was also defined that, for the materials used in this study, the percolation is reached when the conductive phase (TiC) represent about 30% of the sample volume (taking the porosity into account). This result depends on the grain size and morphology of the raw materials but it will probably be in the same range for other conductive materials. The composition of the material and its density are thus of major influence.

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