

Liquid-phase assisted flash sintering of SiC from powder mixtures prepared by aqueous colloidal processing

Victor M. Candelario ^a, Rodrigo Moreno ^b, Richard I. Todd ^c, Angel L. Ortiz ^{a,*}

^a Departamento de Ingeniería Mecánica, Energética y de los Materiales,
Universidad de Extremadura, 06006 Badajoz, Spain.

^b Instituto de cerámica y Vidrio, Consejo Superior de Investigaciones Científicas,
28049 Madrid, Spain.

^c Department of Materials, University of Oxford, OX1 3PH, UK.

Abstract

The effects were investigated of the starting particle size (i.e., nanometer or submicrometer powders), content of $Y_3Al_5O_{12}$ additives (YAG; in the range 5–20 wt.%), and difference of size scales between the two particle types on the liquid-phase assisted flash sintering of SiC from powder mixtures prepared by aqueous colloidal processing. It was found that flash sintering benefits from the refinement of the particles size, the increase in additive content, and the smaller size scale of the particulate additive. It was also found that under the present flash sintering conditions (i.e., 900 °C furnace temperature, 13 A current, and 50 s in flash state) the resulting ceramics are, despite the formation of liquid phase, porous to a greater or lesser extent, and exhibit decreasing porosity gradients from their surface to the centre. These observations are rationalized to extract guidelines for powder batch design contributing to the pressureless ultrafast sintering of non-oxide advanced ceramics.

Keywords: SiC; Flash sintering; Liquid-phase assisted densification; Microstructure; Aqueous colloidal processing.

* Corresponding author:

Angel L. Ortiz

Phone: +34 924289600 Ext: 86726

Fax: +34 924289601

E-mail: **alortiz@unex.es**

1. Introduction

There is great interest within the ceramics community in the ultrafast sintering techniques, with the expectation of obtaining nanostructured ceramics beyond the possibilities of conventional sintering, of consolidating ceramic powders otherwise unsinterable, or simply of shortening markedly the normally long densification cycles at high temperatures of these materials (this latter leading to important savings in the production costs for the ceramics industry). Today, the best exponent of the ultrafast sintering techniques is doubtless spark-plasma sintering (SPS) [1,2], which is nonetheless an external pressure-assisted technique whose use is in general limited to the fabrication of geometrically simple pieces. There is no surprise in the current growing interest in pressureless ultrafast sintering techniques. Microwave sintering [3,4] and the recently established flash sintering technique [5] fall into this category. This latter essentially lies in applying a DC or AC electric field during the heat treatment in the furnace [6-14], to thus achieve the densification at lower temperatures in a matter of seconds. Flash sintering is certainly still in its infancy, but, if developed appropriately, could constitute a revolutionary breakthrough in the field of ceramics manufacture.

So far, flash sintering has successfully been used mainly on oxide ceramics, such as for example Y_2O_3 -stabilized ZrO_2 [15,16], MgO -doped Al_2O_3 [17], SrTiO_3 [18], Co_2MnO_4 [19], $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ [20], SnO_2 [21], TiO_2 [22], Y_2O_3 [23], $\text{Ce}_x\text{Gd}_{1-x}\text{O}_{1.9}$ [24], and ZnO [25], and to a lesser extent on non-oxide ceramics such as ZrB_2 [26,27], MoSi_2 [26], B_4C [28], and SiC [29-31]. This last which is an important advanced ceramic for both structural and functional applications, is hardly at all densifiable by solid-state flash sintering whether without additives or with Al-B-C additives [29]. It is however potentially densifiable by solid-state flash spark-plasma sintering [30,31] and also by liquid-phase assisted flash sintering with Y_2O_3 - Al_2O_3

additives [29], with each of them having their particular strengths and limitations. Concerning the latter, which is the one that could be used for the pressureless densification of SiC in typical industrial furnaces, there is a clear lack of systematic studies aimed specifically at elucidating powder preparation effects on the flash sinterability of SiC with $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ or other additives.

With these premises in mind, the present work was performed with the objective of investigating the effects of the particle size (i.e., nanometer or submicrometer) of the starting powders, of the relative content of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG; equivalent to the typical combination $3\text{Y}_2\text{O}_3\text{--}5\text{Al}_2\text{O}_3$) additives (i.e., 5, 10, or 20 vol.%), and of the difference of size scales between the SiC and YAG particles on the liquid-phase assisted flash sintering of compacts made from SiC–YAG powder mixtures prepared by aqueous colloidal processing. Aqueous colloidal processing was chosen because it is environmentally friendly, and in addition enables the green bodies used in flash sintering to be formed both directly by wet-shaping techniques (i.e., from the concentrated suspensions) and indirectly by dry-shaping techniques (i.e., from the powders obtained by spray-drying or freeze-drying the suspensions). Thus, the goal of the present study is only to extract guidelines for powder batch preparation, so that the optimization of the flash sintering is deferred for future work.

2. Experimental procedure

The starting materials were commercially available powders of β -SiC and YAG with particle sizes in the nanometer or submicrometer ranges. More specifically, two β -SiC powders with average particle sizes of about 45–55 nm (SiC-n; Nanostructured and Amorphous Materials Inc., USA) and 0.7 μm (SiC- μ ; BF-12, H.C. Starck, Germany), respectively, were used; the corresponding values for the two YAG powders are ~40 nm (YAG-n; Nanostructured and

Amorphous Materials Inc., USA) and 0.3 μm (YAG- μ ; High Purity Chemical, Japan). Various powder batches were prepared from these four powders by aqueous colloidal processing. In particular, to investigate particle size effects on the flash sinterability both SiC-n+10wt.% YAG-n and SiC- μ +10wt.% YAG- μ powder batches were prepared. To study additive content effects, SiC-n+5wt.% YAG-n, SiC-n+10wt.% YAG-n, and SiC-n+20wt.% YAG-n powder batches were prepared. And lastly, to elucidate the influence of the difference of size scales between the SiC and YAG particles, SiC- μ +10wt.% YAG-n and SiC- μ +10wt.% YAG- μ powder batches were prepared. In all cases, the procedure of aqueous colloidal processing followed the standard protocol in which first the colloidal stability of the individual powders was studied in dilute suspensions (0.1 g/l) by zeta potential measurements (Zetasizer Nano-ZS, Malvern, UK) as a function of pH and deflocculant content, and next multi-component concentrated suspensions were formulated in accordance with the information extracted, and then deflocculated and characterized rheologically (MARS, Haake, Thermo, Germany) as a function of sonication time (UP400S, Hielscher Ultrasonics GmbH, Germany). Commercially available polyelectrolytes were used as deflocculants, in particular PKV (Produkt KV5088, Zschimmer-Schwarz, Germany) for SiC and PAA (DuramaxTM D-3005, Rohm & Haas, USA) for YAG [32-34].

Fresh optimized suspensions were placed in a rotary evaporator (RV10 basic, IKA, Germany) immersed in a liquid-N₂ bath, and once frozen were freeze-dried (Cryodos-50, Telstar, Spain) at -50 °C and 0.3 mPa for 24 h to thus obtain the powder mixtures. Green bodies (discs of ~5 mm height and diameter) were then prepared from these powder mixtures by cold pressing both uniaxially at 50 MPa and isostatically at 250 MPa. Those compacts were flash-sintered using the custom-made furnace and experimental setup described in detail elsewhere [29]. Briefly, this furnace consists of an induction-heated, cylindrical graphite susceptor to

provide pre-heating of the specimen. An electric field is applied to the specimen independently by sandwiching it between two graphite electrodes attached to a commercial DC power source (Elektro-Automatik, Viersen, Germany) by Mo wires. Electrical contact is maintained by the gravitational force on the upper electrode which exerts a small uniaxial compression of ~ 0.1 MPa on the specimen. In a typical test, the compacts were first heated at a rate of $15\text{ }^{\circ}\text{C}/\text{min}$ up to $600\text{ }^{\circ}\text{C}$ and then at $5\text{ }^{\circ}\text{C}/\text{min}$ up to the target temperature of $900\text{ }^{\circ}\text{C}$, in an Ar-gas atmosphere. At this temperature, the applied voltage was increased until the current began to increase significantly, leading to the “flash event”. The power supply was set to switch from voltage control to current control at a current of 13 A, giving a nominal current density of $\sim 0.66\text{ A}/\text{mm}^2$. This current was chosen as being close to the maximum limit of the power source. A dwell time of 50 s under constant current was applied before switching the current off. Other flash sintering conditions were tested too ($750\text{ }^{\circ}\text{C}$ with either 10 or 13 A current, and $900\text{ }^{\circ}\text{C}$ with 10 A current), but were found to be unsuitable and are not reported here. The voltage required to induce the flash event was registered directly (i.e., voltage was gradually increased in 5 V steps up to the occurrence of flash and the corresponding voltage was logged), while the power used to maintain the flash state was later calculated as the product of the steady state voltage and the current. Under current control, the specimen electrical resistance was computed as the ratio between the dissipated power and the square of the current [29], whereas the specimen temperature was estimated by equating the electrical power dissipation to the radiative heat loss (blackbody radiation mode) [9]. It should be noted that the temperatures calculated in this way are likely to be overestimates because they do not account for the additional heat loss to the graphite electrodes.

Finally, cross-sections were extracted from the central region of the flash-sintered specimens, and subsequently diamond polished to a 1- μm finish using routine ceramographic methods (but not etched) to examine the resulting microstructures by field-emission scanning electron microscopy (FE-SEM; Quanta 3D FEG, FEI, The Netherlands). The FE-SEM observations were taken with secondary and backscattered electrons, in locations at both the centre and the surface of these cross-sections.

3. Results and discussion

3.1. Effect of the particle size of the starting powders

As mentioned above, this effect was investigated using SiC-n+10wt.%YAG-n and SiC- μ +10wt.%YAG- μ compacts. The aqueous colloidal processing (colloidal stability and rheological properties) of the SiC-n+YAG-n mixture has been reported elsewhere [32], despite which it will be presented and discussed briefly here again as needed within the confines of the present work. The counterpart study on the SiC- μ +YAG- μ mixture however is original because the previous studies were performed on α -SiC [33,34], not β -SiC as in the present case. Fig. 1 shows the dependence of the zeta potential on pH for the individual dilute suspensions of the two types of SiC and YAG powders. Clearly, it can be seen that in the YAG case the isoelectric point is the same (i.e., pH \sim 8.8) regardless of the particle size, but not in the SiC case. This latter is indicative of differences in the surface chemical composition between the SiC-n and SiC- μ particles. In particular, the isoelectric point at pH \sim 3.6 indicates that the SiC- μ particles are completely passivated (i.e., surface SiO₂), while the higher isoelectric point at pH \sim 5.3 reflects that the SiC-n particles are only partially passivated due to the presence of surface hydrophobic amorphous carbon [32]. Fig. 2 shows the variation of the zeta potential on deflocculant content

for those suspensions at their natural pH (i.e., pH ~5.7, 6.2, 5.7, and 6 for SiC-n, YAG-n, SiC- μ , and YAG- μ , respectively). It can be seen that the deflocculant addition influences the colloidal stability in all four cases in the sense that the zeta potential increases in magnitude to a greater or lesser extent with increasing polyelectrolyte content, and also that the effect is more relevant for the two YAG powders in which cases not only is a change observed in the sign of surface charge from positive to negative but also the zeta potential variation is greater. Appropriate zeta potential values (i.e., about -40 mV) are reached with ~0.5 wt.% PKV, 0.25 wt.% PKV, 0.5 wt.% PAA, and 0.1 wt.% PAA for the dilute suspensions of SiC-n, SiC- μ , YAG-n, and YAG- μ , respectively. However, as justified elsewhere [32,33] (arguments also valid for the β -SiC powder), for the preparation of the multi-component concentrated suspensions it is highly recommendable to use a combination of greater deflocculant contents, and in particular 4 wt.% PKV plus 2 wt.% PAA for the SiC-n+YAG-n suspension [32] and 1.5 wt.% PKV plus 0.1 wt.% PAA for the SiC- μ +YAG- μ suspension [33].

Figs. 3A-B show selected flow curves for these concentrated suspensions of SiC-n+YAG-n and of SiC- μ +YAG- μ prepared at pH 10, respectively. The corresponding total solids loadings are 5 vol.% and 40 vol.%, respectively, chosen so as to ensure an appropriate suspension viscosity for the future shaping of green compacts by slip casting (not done in the present study). It can be seen that the SiC-n+YAG-n suspension exhibits, despite its low solid content, a shear-thickening behaviour attributable to coagulation [32], and that 6 min is its appropriate sonication condition. On the contrary, the SiC- μ +YAG- μ suspension exhibits the typical shear-thinning behaviour, with 2 min as most appropriate sonication condition. With this information, for the flash sintering studies, well-dispersed powder mixtures were obtained by freeze-drying the aforesaid fresh suspensions, thus circumventing the undesirable coagulation of

the SiC-n+YAG-n suspension (which is nonetheless something to bear in mind in the case of using wet-shaping techniques).

Figs. 4A-B show the curves of power dissipation as a function of time for the SiC-n+YAG-n and SiC- μ +YAG- μ compacts, respectively. Clearly, a “flash event” occurs in both compacts as inferred from the observation of the signature stage sequence, namely, first the pre-flash stage I (i.e., rising power dissipation under voltage control), then the transient stage II (i.e., power dissipation peak at switch of power supply to current control), and lastly the quasi-steady stage III (i.e., steady power dissipation under current control). However, it was found that flash sintering is influenced by the particle sizes in the powder mixture because the values of both the critical voltage associated with the onset of flash and the quasi-steady state power were lower for the SiC-n+YAG-n compact. Specifically, in the SiC-n+YAG-n case only 55 V were required to induce the flash event, while 75 V were needed in the SiC- μ +YAG- μ case. Also, as can be seen in Fig. 4, the quasi-steady state power is 0.64 W/mm³ for the former, but 0.87 W/mm³ for the latter. Therefore, it can be calculated that in the quasi-steady stage III SiC-n+YAG-n offered an electrical resistivity of $\sim 6.44 \cdot 10^{-3} \Omega \cdot m$ and reached a temperature of $\sim 1762^\circ C$, while the corresponding values for SiC- μ +YAG- μ are $\sim 9.31 \cdot 10^{-3} \Omega \cdot m$ and $\sim 1927^\circ C$.

Apart from the particle sizes, the other notable difference between the two cases lies in the surface chemical composition of the SiC particles. Thus, while SiC-n particles have some surface free carbon (i.e., incomplete passivation) [32], SiC- μ ones are passivated (i.e., surface SiO₂) [33]. It is then reasonable to think that this surface free carbon provides the SiC-n+YAG-n compact with higher electrical conductivity, in particular acting as internal electrodes in such a way that less voltage is required to induce the flash sintering relative to the SiC- μ +YAG- μ compact. Additionally, the smaller particle size favours a higher density of particle-particle

contacts in the SiC-n+YAG-n compact that also must be accompanied by a better electrical connectivity. It is worth mentioning that in the SiC-n+YAG-n case greater power fluctuations are observed during the stage III of flash sintering. Their origin is unclear at this moment, but since the results in Section 3.3 below rule out the possibility that they are caused by YAG-n it therefore has to be an effect attributable to SiC-n. Previous results in 3YSZ [13] suggest that the fluctuations may be connected with the details of the voltage-current-temperature response which can cause an apparent inversion of Ohm's law. The power supply struggles to cope with this and the spikes are a result. Their regular and uniform nature (as will become more evident in Section 3.2) would support this hypothesis.

Figs. 5 and 6 show representative sets of FE-SEM images taken at both the centre and the surface of the resulting SiC-n+YAG-n and SiC- μ +YAG- μ ceramics, respectively. Clearly, the ceramics are not fully dense, and have grain sizes of the same scale as the corresponding SiC starting powder. Also, it can be said despite the absence of quantitative density measurements that there is lower densification at the surfaces, indicating that these ceramics have increasing porosity gradients from their centre to their surface. Moreover, the SiC-n+YAG-n ceramic reached greater densification, and also developed a less pronounced porosity gradient. Another important difference is that the SiC-n+YAG-n ceramic exhibits isolated, closed porosity, while its SiC- μ +YAG- μ counterpart exhibits interconnected, open porosity. It then seems that the former reached at least the final sintering regime, whereas the latter did not surpass the intermediate sintering regime despite its temperature being $\sim 165^\circ\text{C}$ higher. This was perhaps somewhat to be expected because it is well-known that sintering kinetics benefits from the refinement of the starting powders and from the compaction of the green body. The lower density of the SiC- μ +YAG- μ specimen is also the explanation for the higher power dissipation

during the constant current stage III of the flash event as the higher porosity should increase the resistivity of the ceramic (as experimentally observed here).

The FE-SEM observations with backscattered electrons taken at the centres, such as those shown by way of example in Fig. 7A for the SiC- μ +YAG- μ ceramic (which is the most unfavourable case in terms of densification), indicate that the YAG particles melted, forming an intergranular secondary phase, whence it is inferred that the temperature reached in the central region of the compacts during the flash sintering is appropriate for the liquid-phase assisted densification despite the furnace temperature being set as low as only 900 °C. The melting point of YAG is ~1940 °C but this can be lowered substantially by the presence of SiO₂. Formation of liquid phase also appears to have occurred in the compacts' surface region because the FE-SEM observations rule out the existence of particulate YAG there too, as shown in Fig. 7B for the same specimen. It is then reasonable to think that the porosity gradients observed are due to the temperature reached during the flash sintering (definitely much higher than the furnace temperature) not being uniform across the compact's cross-section, but decreasing notably from its centre to its surface. Certainly, this conditions the densification through the liquid phase viscosity, which may be affected by the current [35] according to an earlier flash sintering study on Al₂O₃ with calcium-aluminium-silicate glass as sintering aid, and which is a very relevant factor in the initial sintering stage dominated by wetting, spreading, penetration, and rearrangement [36] as well as in the next sintering stage dominated by solution, diffusion, and reprecipitation [36]. As reported elsewhere [29], the temperature gradient arises from the rapid heat loss to the surrounding atmosphere and to the graphite conductors, whose temperature of 900 °C (i.e., the furnace temperature) could even become ~1000 °C lower than the temperature reached at the compact's centre. This heat loss phenomenon is reminiscent of what also occurs in

SPS, in which it is palliated by surrounding the die with a high-temperature blanket. Extending this approach to flash sintering, or developing other alternatives to mitigate the heat loss, is then an area for future work with a view to fabricating more homogeneous materials.

To summarise, the lesson to be learnt from this first study is that, as happens in conventional sintering (pressureless sintering and hot-pressing) and in non-conventional SPS, refinement of the starting powders facilitates the liquid-phase assisted flash sintering of SiC. Although the central objective of this study was only to elucidate this effect, it bears saying that to reach the complete densification not achieved here using a furnace temperature of 900 °C, current of 13 A, and in flash state dwell time of 50 s, it would be necessary to use a power source able to supply a greater current, as well as optimizing other flash sintering conditions (for example, furnace temperature and holding time under the flash state).

3.2. Effect of the proportion of liquid-phase forming sintering additive (YAG)

This effect was investigated using SiC-n+YAG-n compacts with different YAG proportions (i.e., 5, 10, or 20 wt.%). The choice of SiC-n+YAG-n was because it exhibits a greater flash sinterability than SiC- μ +YAG- μ . First, rheological aspects of the concentrated suspensions of SiC-n with 5 or 20 wt.% YAG-n will be discussed because the remaining aqueous colloidal processing results were presented above. Figs. 8A-B show selected flow curves of the concentrated suspensions (total solids loading of 5 vol.% and pH 10) of SiC-n+5wt.%YAG-n and SiC-n+20wt.%YAG-n. It can be seen in Fig. 8A that the former exhibits, for the sonication times used here, the same shear-thickening behaviour observed and discussed earlier for the SiC-n+10wt.%YAG-n suspension (Fig. 3A). A relevant quantitative difference is however that for the same sonication time the SiC-n+5wt.%YAG-n suspension displays a greater rheopexy and a

lower critical shear for coagulation than the SiC-n+10wt.%YAG-n suspension. These observations indicate that YAG-n helps to mitigate, and even to prevent, the SiC-n coagulation in water. This conclusion becomes much more evident in Fig. 8B for the SiC-n+20wt.%YAG-n suspension, which exhibits with increasing sonication time a change from shear-thickening behaviour to shear-thinning behaviour, in this latter case even with negligible thixotropy. This type of rheopectic–thixotropic change is not new and indeed has been observed for SiC-n when carbon nanotubes (CNTs) are added [32,37], in which case it was demonstrated that CNTs act as physical barriers against the SiC-n aggregation. Future studies (detailed rheological measurements together with extensive electron microscopy observations), which are beyond the scope of the present work, are needed to identify the underlying mechanism for the prevention of the coagulation in the present case with equiaxed YAG-n particles instead of with elongated CNTs. Finally, based on these rheological studies, the fresh SiC-n+5wt.%YAG-n and SiC-n+20wt.%YAG-n suspensions chosen for freeze-drying were those sonicated for 6 and 7 min, respectively.

Figs. 9A-B show the curves of power dissipation as a function of time for the SiC-n+5wt.%YAG-n and SiC-n+20wt.%YAG-n compacts, respectively. The curve for the SiC-n+10wt.%YAG-n compact was shown in Fig. 4A, and therefore is not presented again. It can be seen in Figs. 9A, 9B, and 4A that it is possible to achieve flash sintering in the three cases, although under different experimental conditions depending on the YAG content. In particular, the voltages required to induce the flash event were 70, 55, and 55 V, and the quasi-steady state powers were 0.64, 0.64, and 0.62 W/mm³, for YAG contents of 5, 10, and 20 wt.%, respectively. Within the experimental errors and fluctuations, these quasi-steady state powers are to be considered as essentially the same. It can then be calculated that in the quasi-steady stage III

SiC-n+5wt.%YAG-n, SiC-n+10wt.%YAG-n, and SiC-n+20wt.%YAG-n essentially offered the same electrical resistivity of $\sim 6.20\text{--}6.44 \cdot 10^{-3} \Omega \cdot \text{m}$ and reached the same temperature of $\sim 1746\text{--}1762^\circ\text{C}$. Therefore, it can be inferred that apparently it is easier to induce the flash sintering as the YAG content increases above a certain threshold amount (i.e., $> 5 \text{ wt.}\%$), but also that, once reached, the YAG content no longer conditions the maintenance of the flash event. This effect seems in principle attributable to the YAG high-temperature conductivity because the fact that the powder mixtures were obtained from fresh suspensions (i.e., without shearing) and that the average particle size of the SiC-n and YAG-n are similar would rule out the influence of processing aspects. The influence of the YAG additions on the conditions required to initiate the flash event is also consistent with reference [29] in which the addition of Al_2O_3 and Y_2O_3 to “pure” SiC reduced the voltage required for a given furnace temperature substantially.

Figs. 10 and 11 show representative sets of FE-SEM images taken at both the centre and the surface of the resulting SiC-n+5wt.%YAG-n and SiC-n+20wt.%YAG-n ceramics, respectively, as those corresponding to the SiC-n+10wt.%YAG-n ceramic were presented in Fig. 5. It can be observed that the three ceramics are porous. Nonetheless, it is evident in qualitative terms that the degree of densification increases with increasing YAG proportion. In the three cases clear evidence of liquid-phase formation was observed, which is reasonable considering that the sintering additive is the same (i.e., YAG) and that the compacts reached the same temperature. Therefore, the FE-SEM observations are entirely consistent with what might be expected for very short-duration liquid-phase sintering, in which there is little densification by solution-reprecipitation. In this scenario, densification mostly occurs by liquid formation and particle rearrangement, both of which depend on the relative content of sintering additives and

then of liquid phase. Note that because the viscosity of the liquid phase is essentially the same, it does not play a relevant role. In particular, the case of low additive contents leads to the formation of what is known as "disconnected-liquid microstructure" in which the insufficient liquid formed becomes trapped at the interstices of the solid skeleton [36,38]. What occurs is that the little existing liquid is formed locally in the compact there where a YAG-n particle melts, and subsequently does not spread efficiently to fill other pores or to wet other neighbouring SiC-n particles with the result that compact densification is not favoured. In contrast, the case of high additive contents leads to the formation of a "connected-liquid microstructure", so that not only is there more liquid available to fill pores, with the attendant porosity reduction, but also the liquid can spread and wet particles more efficiently [36,38] in benefit of densification by rearrangement.

To summarize, the lesson to be learnt from this second study is that increasing the proportion of oxide sintering additives above a certain threshold also facilitates the liquid-phase assisted flash sintering of SiC, as is the case for conventional pressureless sintering [39,40]. Indeed, this processing guideline seems to be more general because it is also consistent with earlier observations on the liquid-phase assisted flash sinterability of Al_2O_3 with calcium-aluminium-silicate glass [35]. With this effect elucidated, it nevertheless bears saying that the YAG proportions used here (5–20 wt.%, equivalent to ~3.6–15 vol.%) are lower than that required (i.e., ~35 vol.%) to reach the complete densification exclusively by liquid formation and spreading [36,38], so that solution-precipitation events are necessary to eliminate the residual porosity. It is however anticipated that this stage of the densification by flash sintering is not expected to be affected by the sintering additive proportion because an earlier pressureless sintering study [41] has demonstrated that, under an Ar-gas sintering atmosphere, it is the solid-

liquid interface reaction, not the diffusion distance, which controls the kinetics of the Ostwald ripening process.

3.3. Effects of the particle size bimodality

Having demonstrated that the SiC- μ +YAG- μ compact has a poorer flash sinterability than its SiC-n+YAG-n counterpart and that the SiC-n+5wt.%YAG-n compact densifies insufficiently, it then seemed reasonable to investigate whether the flash sinterability of SiC- μ is enhanced when using 10 wt.% of YAG-n (instead of YAG- μ). First, rheological aspects of the concentrated suspension of SiC- μ +10wt.%YAG-n will be briefly discussed, which following the aqueous colloidal processing results presented above was prepared at pH 10 and deflocculated using 1.5 wt.% PKV for SiC- μ and 2 wt.% PAA for YAG-n. The entire preparation of the SiC- μ +10wt.%YAG- μ suspension has already been discussed in Section 3.1, and therefore is not presented again. Fig. 12 shows the flow curves of the concentrated suspension (total solids loading of 5 vol.%) of SiC- μ +10wt.%YAG-n as a function of sonication time. Clearly, it can be inferred that it exhibits an extremely low viscosity regardless of the sonication time, and that its thixotropy decreases gradually with the sonication even though this decrease is only slight because the thixotropy of the non-sonicated suspension is already very low. These low values of viscosity and thixotropy reflect that the SiC- μ and YAG-n particles are very homogeneously co-dispersed. Based on this rheological study, the fresh SiC- μ +10wt.%YAG-n suspension chosen for freeze-drying was that sonicated for 2 min.

Fig. 13 shows the curve of power dissipation as a function of time for the SiC- μ +10wt.%YAG-n compact. The curve for the SiC- μ +10wt.%YAG- μ counterpart was shown in Fig. 4B, and therefore is not presented again. It can be seen in Fig. 13 that it is possible to

achieve flash sintering in this case too, and apparently a bit more easily than in the SiC- μ +10wt.%YAG- μ case because both the voltage required to induce the flash event and the steady-state power seem, if any, a little lower (70 V and 0.82 W/mm³ vs 75 V and 0.87 W/mm³). The same can be said for electrical resistivity (i.e., $8.87 \cdot 10^{-3}$ vs $9.31 \cdot 10^{-3}$ $\Omega \cdot m$) and temperature reached (i.e., 1903 vs 1927 °C) during the quasi-steady stage III. Note however that these small differences of only 5 V and 0.05 W/mm³ may lie within the experimental error and reproducibility of flash sintering, and therefore they have to be treated with caution. If really attributable to the specimens, then this slightly enhanced flash sinterability of SiC- μ when YAG-n is used instead of YAG- μ could be a consequence of the higher green-body density derived from a more efficient packing and to the more uniform distribution in the compact of a greater conduction surface, both being factors beneficial for the electrical circuit.

Fig. 14 shows representative sets of FE-SEM images taken at both the centre and the surface of the resulting SiC- μ +10wt.%YAG-n ceramic. The images for the SiC- μ +10wt.%YAG- μ counterpart were presented in Fig. 6. Although the porosity is evident, it is visually clear that the degree of densification increases appreciably when YAG-n instead of YAG- μ is used. These FE-SEM observations can also be explained by alluding to the favoured distribution and location in the compact of the YAG additives. In particular, as mentioned before, the expectation for a short-duration sintering as is the case of flash sintering is that the more uniform and homogeneous the distribution of liquid-phase forming particles, the greater the densification because this takes place predominantly by pore filling and particle rearrangement. This is certainly the trend observed when comparing the YAG-n and YAG- μ cases. This enhancement in sinterability has also been observed for conventional pressureless sintering when the additives, rather than particulate, are introduced as nano-films on the SiC particles [42].

To summarize, the lesson to be learnt from this third study is that, as occurs in the conventional pressureless sintering of a wide variety of materials [36,38], the use of particulate additives with a smaller size scale relative to the particle matrix also facilitates the liquid-phase assisted flash sintering of SiC. It therefore seems convenient to combine this guideline synergistically with that of larger proportions of oxide sintering additives, whose influence on densification appears to be greater due to the very short duration of flash sintering.

4. Conclusions

We have investigated separately the effects of the starting particle size, additive proportion, and difference of size scales between the two particle types on the liquid-phase assisted flash sintering of SiC with YAG additives, using to that end different powder mixtures all prepared by aqueous colloidal processing. Based on the results and analysis, the following conclusions can be drawn:

1. Despite the low furnace temperature (i.e., 900 °C), YAG additives melt during flash sintering thus promoting the liquid-phase assisted densification. Given the very short duration of flash sintering (i.e., 50 s), densification takes place essentially by pore filling and particle rearrangement, with a smaller contribution from solution-reprecipitation.
2. The smooth flash sintering conditions used (i.e., 900 °C furnace temperature, 13 A current, and 50 s dwell time in the flash state) result, to a greater or lesser extent, in porous SiC ceramics. These ceramics also exhibit inhomogeneous densification with gradients of increasing porosity from their centre to their surface, which is attributable to the thermal gradient induced by rapid heat losses to the surrounding.
3. The liquid-phase assisted flash sinterability of SiC with YAG additives benefits from the

refinement of the particle sizes, the increase in additive content above a certain threshold, and the smaller size scale of the particulate additive. Thus, the guidelines of powder batch design for flash sintering and conventional pressureless sintering of SiC are qualitatively the same, but should be used more judiciously in the former case given its short time scale.

Acknowledgements. This work was supported by the Ministerio de Economía y Competitividad (Government of Spain) and FEDER Funds under the Grants no. MAT2013-41012-P and MAT2015-67586-C3-2-R. Financial support from the Junta de Extremadura under the Grant n. GR15078, also co-financed with FEDER Funds, is gratefully acknowledged as well.

References

1. Munir ZA, Anselmi-Tamburini U, Ohyanagi M. The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method. *J Mat Sci* 2006;**41**(3):763–77.
2. Munir ZA, Quach DV. Electric current activation of sintering: a review of the pulsed electric current sintering process. *J Am Ceram Soc* 2011;**94**(1):1–19.
3. Sutton WH. Microwave processing of ceramics — an overview. *Mater Res Soc Symp Proc* 1992;**269**:3–20.
4. Rybakov KI, Olevsky EA, Krikun EV. Microwave sintering: fundamentals and modeling. *J Am Ceram Soc* 2013;**96**(4):1003–20.
5. Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in <5 s at 850 °C. *J Am Ceram Soc* 2010;**93**(11):3556–9.
6. Ghosh S, Chokshi AH, Lee P, Raj R. A huge effect of weak dc electrical fields on grain growth in zirconia. *J Am Ceram Soc* 2009;**92**(8):1856–9.
7. Yang D, Raj R, Conrad H. Enhanced sintering rate of zirconia (3Y-TZP) through the effect of a weak dc electric field on grain growth. *J Am Ceram Soc* 2010;**93**(10):2935–7.
8. Yang D, Conrad H. Enhanced sintering rate of zirconia (3Y-TZP) by application of a small ac electric field. *Scr Mater* 2010;**63**(3):328–31.
9. Raj R. Joule heating during flash-sintering. *J Eur Ceram Soc* 2012;**32**(10):2293–2301.
10. Francis JSC, Raj R. Influence of the field and the current limit on flash sintering at isothermal furnace temperatures. *J Am Ceram Soc* 2013;**96**(9):2754–8.
11. Narayan J. A new mechanism for field-assisted processing and flash sintering of materials. *Scr Mater* 2013;**69**(2):107–11.

12. Naik KS, Sglavo VM, Raj R. Flash sintering as a nucleation phenomenon and a model thereof. *J Eur Ceram Soc* 2014;**34**(15):4063–7.
13. Todd RI, Zapata-Solvas E, Bonilla RS, Sneddon T, Wilshaw PR. Electrical characteristics of flash sintering: thermal runaway of Joule heating. *J Eur Ceram Soc* 2015;**35**(6):1865–77.
14. Hewitt IJ, Lacey AA, Todd RI. A mathematical model for flash sintering. *Math Model Nat Phenom* 2015;**10**(6):77–89.
15. Downs JA, Sglavo VM. Electric field assisted sintering of cubic zirconia at 390°C. *J Am Ceram Soc* 2013;**96**(5):1342–4.
16. Muccillo R, Muccillo ENS. An experimental setup for shrinkage evaluation during electric field-assisted flash sintering: application to yttria-stabilized zirconia. *J Eur Ceram Soc* 2013;**33**(3):515–20.
17. Cologna M, Francis SCJ, Raj R. Field assisted and flash sintering of alumina and its relationship to conductivity and MgO-doping. *J Eur Ceram Soc* 2011;**31**(15):2827–37.
18. Karakuscu A, Cologna M, Yarotski D, Won J, Raj R, Uberuaga BP. Defect structure of flash sintered strontium titanate. *J Am Ceram Soc* 2012;**95**(8):2531–6.
19. Prette ALG, Cologna M, Sglavo V, Raj R. Flash-sintering of Co_2MnO_4 spinel for solid oxide fuel cell applications. *J Power Sources* 2011;**196**(4):2061–5.
20. Muccillo R, Muccillo ENS, Kleitz M. Densification and enhancement of the grain boundary conductivity of gadolinium-doped barium cerate by ultra fast flash grain welding. *J Eur Ceram Soc* 2012;**32**(10):2311–6.
21. Muccillo R, Muccillo ENS. Electric field-assisted flash sintering of tin dioxide. *J Eur Ceram Soc* 2014;**34**(4):915–23.

22. Jha SK, Raj R. The effect of electric field on sintering and electrical conductivity of titania. *J Am Ceram Soc* 2014;**97**(2):527–34.
23. Yoshida H, Sakka Y, Yamamoto T, Lebrun JM, Raj R. Densification behaviour and microstructural development in undoped yttria prepared by flash-sintering. *J Eur Ceram Soc* 2014;**34**(4):991–1000.
24. Jiang T, Wang Z, Zhang J, Hao X, Rooney D, Liu Y, Sun W, Qiao J, Sun K. Understanding the flash sintering of rare-earth-doped ceria for solid oxide fuel cell. *J Am Ceram Soc* 2015;**98**(6):1717–23.
25. Schmerbauch C, Gonzalez-Julian J, Röder R, Ronning C, Guillon O. Flash sintering of nanocrystalline zinc oxide and its influence on microstructure and defect formation. *J Am Ceram Soc* 2014;**97**(6):1728–35.
26. Zapata-Solvas E, Gómez-García D, Domínguez-Rodríguez A, Todd RI. Ultra-fast and energy-efficient sintering of ceramics by electric current concentration. *Sci Rep* 2015;**5**:8513.
27. Grasso S, Saunders T, Porwal H, Cedillos-Barraza O, Jayaseelan DD, Lee WE, Reece MJ. Flash spark plasma sintering (FSPS) of pure ZrB_2 . *J Am Ceram Soc* 2014;**97**(8):2405–8.
28. Niu B, Zhang F, Zhang J, Ji W, Wang W, Fu Z. Ultra-fast densification of boron carbide by flash spark plasma sintering. *Scr Mater* 2016;**116**:127–30.
29. Zapata-Solvas E, Bonilla S, Wilshaw PR, Todd RI. Preliminary investigation of flash sintering of SiC. *J Eur Ceram Soc* 2013;**33**(13-14):2811–6.
30. Grasso S, Saunders T, Porwal H, Milsom B, Tudball A, Reece M. Flash spark plasma sintering (FSPS) of α and β SiC. *J Am Ceram Soc* 2016; in press.

31. Grasso S, Kim E-Y, Saunders T, Yu M, Choi S-H, Tudball A, Reece M. Ultra-rapid crystal growth of textured SiC using flash spark plasma sintering (FSPS) route. *Cryst Growth Des* 2016; in press.
32. Candelario VM, Moreno R, Ortiz AL. Carbon nanotubes prevent the coagulation at high shears of aqueous suspensions of equiaxed nanoparticles. *J Eur Ceram Soc* 2014;**34**(3):555–63.
33. Candelario VM, Nieto MI, Guiberteau F, Moreno R, Ortiz AL. Aqueous colloidal processing of SiC with $Y_3Al_5O_{12}$ liquid-phase sintering additives. *J Eur Ceram Soc* 2013;**33**(10):1685–94.
34. Candelario VM, Guiberteau F, Moreno R, Ortiz AL. Aqueous colloidal processing of submicrometric SiC plus $Y_3Al_5O_{12}$ with diamond nanoparticles. *J Eur Ceram Soc* 2013;**33**(13–14):2473–82.
35. Gonzalez-Julian J, Guillon O. Effect of electrical field/current on liquid phase sintering. *J Am Ceram Soc* 2015;**98**(7):2018–27.
36. German RM. Liquid phase sintering. New York, US: Plenum Press; 1985.
37. Candelario VM, Moreno R, Shen Z, Ortiz AL. Aqueous colloidal processing of nano-SiC and its nano- $Y_3Al_5O_{12}$ liquid-phase sintering additives with carbon nanotubes. *J Eur Ceram Soc* 2015;**35**(13):3363–8.
38. German RM. Sintering theory and practice. New York, US: John Willey and Sons; 1996.
39. Mulla MA, Krstic VD. Low-temperature pressureless sintering of β -silicon carbide with aluminum oxide and yttrium oxide additions. *Am Ceram Soc Bull* 1991;**70**(3):439–43.

40. Lee JK, Kang HH, Shim DJ, Lee EG, Kim H. Effects of YAG-phase amount on the microstructure and phase transformation during the liquid-phase sintering of β -SiC. *Key Eng Mat* 1999;**161-163**:263–6.
41. Ye H, Pujar VV, Padture NP. Coarsening in liquid-phase-sintered α -SiC. *Acta Mater* 1999;**47**(2):481–7.
42. Ortiz AL, Borrero-Lopez O, Quadir MZ, Guiberteau F. A route for the pressureless liquid-phase sintering of SiC with low additive content for improved sliding-wear resistance. *J Eur Ceram Soc* 2012;**32**(4):965–73.

Figure Captions

Figure 1. Dependence on pH of the zeta potential for the individual dilute suspensions of SiC-n [32], YAG-n [32], SiC- μ , and YAG- μ [33]. Lines are to guide the eye.

Figure 2. Dependence on deflocculant content (PKV for SiC and PAA for YAG) of the zeta potential for the individual dilute suspensions of SiC-n [32], YAG-n [32], SiC- μ , and YAG- μ [33], at natural pH. Lines are to guide the eye.

Figure 3. Selected flow curves of the concentrated suspensions of (A) SiC-n+10wt.% YAG-n [32] and (B) SiC- μ +10wt.% YAG- μ subjected to different sonication times (sonication times below 4 min were unsuitable for the former). The arrows indicate the uploading and downloading stretches of the flow curves.

Figure 4. Power per unit volume as a function of time for a limiting current of 13 A at furnace temperature of 900 °C for the (A) SiC-n+10wt.% YAG-n and (B) SiC- μ +10wt.% YAG- μ compacts. Time 0 has been defined as the moment of maximum power dissipation. In (A), the three stages of flash sintering are indicated.

Figure 5. Representative secondary-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC-n+10wt.% YAG-n ceramic.

Figure 6. Representative secondary-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC- μ +10wt.% YAG- μ ceramic.

Figure 7. Representative backscattered-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC- μ +10wt.% YAG- μ ceramic. The inset in (A) is a micrograph at higher magnification to show details.

Figure 8. Selected flow curves of the concentrated suspensions of (A) SiC-n+5wt.% YAG-n and (B) SiC-n+20wt.% YAG-n subjected to different sonication times (sonication times below 4 min were unsuitable for their dispersion). The arrows indicate the uploading and downloading stretches of the flow curves.

Figure 9. Power per unit volume as a function of time for a limiting current of 13 A at furnace temperature of 900 °C for the (A) SiC-n+5wt.% YAG-n and (B) SiC-n+20wt.% YAG-n compacts. Time 0 has been defined as the moment of maximum power dissipation.

Figure 10. Representative secondary-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC-n+5wt.% YAG-n ceramic.

Figure 11. Representative secondary-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC-n+20wt.% YAG-n ceramic.

Figure 12. Selected flow curves of the concentrated suspensions of SiC- μ +10wt.%YAG-n subjected to different sonication times. The arrows indicate the uploading and downloading stretches of the flow curves.

Figure 13. Power per unit volume as a function of time for a limiting current of 13 A at furnace temperature of 900 °C for the SiC- μ +10wt.%YAG-n compact. Time 0 has been defined as the moment of maximum power dissipation.

Figure 14. Representative secondary-electron FE-SEM micrographs at the (A) centre and (B) edge of the central cross-section of the flash-sintered SiC- μ +10wt.%YAG-n ceramic. The inset in (A) is a micrograph at higher magnifications to show details.