

Submitted to *Journal of the European Ceramic Society*, November 2011.

Spark-plasma sintering of ZrB₂ ultra-high-temperature ceramics at lower temperature via nanoscale crystal refinement

V. Zamora^a, A.L. Ortiz^{a,*}, F. Guiberteau^a, M. Nygren^b

^a Departamento de Ingeniería Mecánica, Energética y de los Materiales,

Universidad de Extremadura, Badajoz, Spain

^b Department of Materials and Environmental Chemistry, University of Stockholm,

10691 Stockholm, Sweden

Abstract

~~We have explored~~ The feasibility of reducing the spark-plasma-sintering (SPS) temperature of additive-free zirconium diboride (ZrB₂) ultra-high-temperature ceramics via the crystal size refinement of the starting powder down to the nanoscale was tested. It is found that under the same SPS conditions nanoscale ZrB₂ can be densified at temperatures about 450 °C lower than the as-purchased, coarse ZrB₂, and at more than 250 °C below the typical submicrometre powders. It is also found that the elimination of the B₂O₃ impurities plays an important role in the complete densification. Finally, the unequalled sinterability of the nanoscale ZrB₂ powder highlights the need of using high-energy ball-milling for the comminution of the typical commercially-available ZrB₂ powders.

Keywords: ZrB₂; ultra-high-temperature ceramics; sintering; high-energy ball-milling.

* Corresponding author:

Angel L. Ortiz

Phone: +34 924289600 Ext: 86726

Fax: +34 924289601

E-mail: alortiz@materiales.unex.es

1. Introduction

Zirconium diboride (ZrB_2) is one of those few compounds that can be classed as ultra-high-temperature ceramic (UHTC) [1]. Its favourable set of properties (among others, melting point 3250 °C, hardness 23 GPa, elastic modulus >500 GPa, electrical resistivity $\sim 10^{-5} \Omega\cdot\text{cm}$, and thermal conductivity $>60 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) renders ZrB_2 a very attractive candidate material within the world of extreme environment engineering, for applications such as for example hypersonic flight, scramjet and rocket propulsion, atmospheric re-entry, refractory crucibles, plasma-arc electrodes, to cite some [2,3].

It is widely recognized by the ceramic community that one of the greatest obstacles that limits the successful development and implementation of the ZrB_2 UHTCs is its poor sinterability, to which contribute various intrinsic and extrinsic factors. On one hand there are the strong covalent bonding, the low self-diffusion coefficients, and the large particle sizes that together impose a very serious kinetic restrictions to the diffusion [2-5], and on the other hand there is the contamination by surface oxides that favours coarsening over densification [2,3,5]. The strategy typically adopted to tackle the problem of ZrB_2 unsinterability consists of introducing sintering additives (either liquid phase formers, or reactive agents), together with the refinement of the starting powders by ball milling (normally in the form of wet attrition mechanical) down to the submicrometre scale [2,3]. Regarding this latter point, in a recent study we investigated in details the spark-plasma sintering (SPS) kinetics of ZrB_2 without additives as a function of the crystal size from a couple of micrometres to a few nanometres (achieved by high-energy ball-milling), and concluded however that the breakthrough needed to obtain ZrB_2 powders with unmatched sintering behaviour requires going beyond the simple refinement to the submicrometre scale and that it is the nanoscale crystal refinement what indeed offers an unprecedented opportunity to significantly reduce the sintering temperature of ZrB_2 [6]. This latter expectation, which has not been confirmed experimentally thus far, arises from the observation that only the nanoscale crystal refinement promotes considerably greater grain-boundary diffusion at much lower temperatures in ZrB_2 [6], and this is the mass transport mechanism responsible for its densification. Elucidating this pending issue of the crystal refinement scale in the reduction of the sintering temperature of ZrB_2 is thus a fundamental question that requires a prompt experimental response not only because the lower-temperature sintering is doubtless one of the long-sought objectives in the field of UHTCs, but

also because, if confirmed, this might have important implications regarding the comminution practices utilized by the UHTC community.

With this in mind, the objective of present work is to extend the previous kinetics study providing the first extensive set of SPS experimental measurements carried out explicitly to explore by a detailed densification study the issue of the crystal refinement scale in the reduction of the sintering temperature of ZrB₂. For this proof-of-concept study, we have spark-plasma sintered without sintering additive six ZrB₂ powders with varied crystal sizes in the micrometer, submicrometre and nanometre scales, ~~so the crystal size effect can be investigated without any interference~~ (arriesgado, porque hay oxidos que se introducen en la molienda y por tanto no es exclusive del tamaño de cristales). The details of experiments and major findings are described below.

2. Experimental Procedure

The six ZrB₂ powders used in the present study were taken from the ampler set of ZrB₂ powders already utilized in the previous SPS kinetics study [6], and thus here we will limit ourselves to summary their preparation protocol. Briefly, the coarse powder with an average crystal size of 2 μm was obtained from a commercial source (Grade B, H.C. Starck, Goslar, Germany). The powders with submicrometre and ultra-fine crystals (i.e., ~ 500 and 160 nm, respectively), and the three powders with nanometre crystals (i.e., ~ 70, 25, and 10 nm, respectively) were prepared by subjecting the commercial ZrB₂ powder to high-energy ball-milling in air in a shaker mill (Spex D8000, Spex CertiPrep, Metuchen, NJ, US) for different times as required to reach the desired average crystal size [6], using WC balls as milling media with a ball-to-powder weight ratio of 4. More details of the preparation and characteristics of these ZrB₂ powders can be found elsewhere [6-9].

The different ZrB₂ powders were individually loaded into 12-mm diameter graphite dies lined with graphite foil and surrounded by a ~~1 cm~~ 0.5 cm thick graphite blanket to minimize the heat loss, and were then spark-plasma sintered (Dr. Sinter SPS-2050, Sumitomo Coal Mining Co.) using 12ms on and 2ms off pulsed DC and under atmosphere of dynamic vacuum. Two types of SPS cycles were implemented: (1) heating at 100 °C·min⁻¹ up to target temperature under 75 MPa pressure, and soaking at these conditions of temperature and pressure for a certain time (hereafter abbreviated as simple SPS cycle), and (2) heating at 100 °C·min⁻¹ up to target temperature under

20 MPa pressure, followed by soaking at the target temperature under 75 MPa pressure for a certain time (hereafter abbreviated as complex SPS cycle). Details of another SPS cycle used only sporadically will be given along with results. For each powder the target temperature (measured by an optical pyrometer focused on the die) was a variable in this study, and was varied with the reference in mind of its transition temperature from surface diffusion to grain-boundary diffusion (T_{GBD}) determined in the previous kinetics study [6] (i.e., ~ 1550, 1650, 1740, 1765, 1785, and 1810 °C for the crystal sizes of 10, 25, 70, 160, 500, and 2000 nm, respectively). After the completion of the SPS cycle, the load was released and the electrical power was shut off to allow rapid cooling to room temperature (i.e., in 1-2 min). ~~The SPS furnace is equipped with a dilatometer of resolution better than 0.001 mm, connected to a computer to log the shrinkage curves.~~ The displacement resolution used to measure the shrinkage profile during densification is 1 μm . These curves were corrected for the expansion of the graphite parts (i.e., die, punches, and spacers) to give the real shrinkage curve of the powder itself, and converted to densification curves by considering the linear shrinkage and the bulk densities measured according to Archimedes's principle to get relative densities of the sintered samples. The sintered materials were observed by scanning electron microscopy (SEM; S-3600N, Hitachi) to validate the porosity data, and also to observe their microstructure. The SEM observations were done on fracture surfaces, at 5 kV without metal coating.

3. Results and Discussion

The data of T_{GBD} obtained in the previous SPS kinetics study [6] suggests that the ZrB_2 nano-powder with 10-nm crystals will exhibit the lowest sintering temperature of all powders investigated here, and for this reason the first set of SPS densification experiments will be focused on this powder. Figure 1 compares the densification curves as a function of time for this ZrB_2 nano-powder obtained with the simple SPS cycle after 15 min of soaking at 1450, 1500, 1550, 1600, and 1625 °C. It is very clear that the final degree of densification increases with increasing the target temperature, from ~91% at 1450 °C to ~98.5% at 1625 °C. This latter can be considered to be a dense UHTC. Since the densification curve at 1625 °C stabilized after 3.5 min of isothermal soaking, there is no reason to prolong further the sintering as this only will cause coarsening. It is noted that the target temperature of 1625 °C is pretty close to the corresponding value of T_{GBD} (i.e., ~ 1550 °C), with only ~ 75 °C difference. Hence, these results confirm the possibility of densifying

ZrB₂ UHTCs close to the temperature dictated by T_{GBD} under the appropriate isothermal soaking. This notion is further corroborated by the observation in Fig. 1 that the final degree of densification is relatively moderate and lower than 93% after 15 min of isothermal heating at 1450 and 1500 °C, which are temperatures both below the value of T_{GBD} , but increases notably above 96% when sintering for the same time at 1550 °C or at higher temperatures. This trend also became evident during the direct examination of the microstructures by SEM, as illustrated for example in the comparison of micrographs in Fig. 2 which shows incomplete densification at 1450 °C but pore absence at 1625 °C.

Another interesting observation in Fig. 1 is that all densification curves reached the plateau after various minutes of isothermal soaking, except the curve obtained at 1450 °C which has not flattened off after 15 min. It appears then that the ZrB₂ nano-powder would have densified further with a more prolonged soaking at 1450 °C. In consequence, we have measured the densification curve of the ZrB₂ nano-powder at 1450 °C until the stabilization of the graphite punches, which is shown in Fig. 3. The measurement indicates that ~ 98% relative density can be reached with the simple SPS cycle after 30 min at 1450 °C. Interestingly, this is almost the same final degree of densification reached at 1625 °C (~ 98.5%), and it is slightly higher than those reached at 1550 (~ 96%) and 1600 °C (~ 97%) and much higher than that at 1500 °C (~ 92%), in all cases after the corresponding curve stabilization. This is an expected finding because it is not what we would have predicted considering simply that the diffusion coefficients obey an Arrhenius-type law [10]. Therefore, to shed light on this issue we have examined by SEM the sample fabricated at 1450 °C. As can be observed in the micrograph of Fig. 4, the detailed SEM observations revealed that some grain faces exhibit what appears to have been a liquid phase. We believe that this liquid is boria, and that it is the responsible for the unexpected observation of the anomalously-high densification at 1450 °C because the presence of liquid boria not only facilitates the grain sliding but also the mass transport. This boria forms because the high-energy ball-milling was done in air and therefore ZrB₂ can oxidize superficially during the milling itself, and also because the resulting ZrB₂ nano-powder passivates spontaneously in contact with air [11]. The evolution of the vacuum level during the SPS test at 1450 °C supports the presence of liquid boria deduced from the SEM observations. Thus, the vacuum level did hardly change during the entire experiment (almost constant at ~ 3 Pa), indicating that no detectable boria gas emission occurred at 1450 °C and therefore that boria remained in liquid state. This scenario is however totally different from what occurred during the

SPS tests at higher temperatures for which gas release did was detected, with the vacuum level temporary dropping a couple of Pa or more and then recovering again its initial level. Armed with this information, it is reasonable to conclude that despite the SPS at 1450 °C eventually results in near-complete densification, this low-temperature densification is not useful because the residual boria will make the resulting ZrB₂ material to degrade in service when exposed to ultra-high-temperature applications. Thus, 1625 °C continues to be a more optimal SPS temperature.

Since the pursued objective is the lower-temperature SPS of boria-free ZrB₂ UHTCs, the next efforts will concentrate on the possible optimization of the SPS cycle between 1450 and 1625 °C. The SEM observations such as that shown in Fig. 5 for the UHTC processed at 1500 °C indicate that the residual pores in the UHTCs fabricated with the simple SPS cycle have a near-perfect spherical shape, thus suggesting that they originated due to the slow outward diffusion of the boria gas occluded when the pore distribution transformed very rapidly from open porosity to closed porosity in the presence of pressure^a. In consequence, one possible manner of facilitating the escape of the boria gas generated would be by applying a lower compaction pressure during the heating ramp, to delay the collapse of the open pore structure so the gasses can leave the sample more easily. To explore this possibility, we performed new experiments using the complex SPS cycle described in the experimental section. Figure 6 shows the resulting densification curves as a function of time for the ZrB₂ nano-powder obtained with the complex SPS cycle after 15 min of soaking at 1500, 1550, 1600, and 1625 °C. Recall that the temperature of 1450 °C has been excluded from further analysis due to the undesired presence of residual boria in the microstructure. As can be observed in Fig. 6, these curves exhibit the same trend as before in Fig. 1, with the final degree of densification increasing with increasing target temperature. The comparison between the densification curves obtained with the simple and complex SPS cycles is however very interesting. It can be inferred that in all cases the densification is better during the first moments (i.e., approximately the first 750 s) with the simple SPS cycle doubtless due to the greater compaction pressure (75 vs 20 MPa), but that the ultimate densification is essentially the same with both cycles (i.e., ~ 92.5% at 1500 °C, 96% at 1550 °C, 97% at 1600 °C, and 98% at

^a The solid-state sintering theory has established that the transformation from open porosity to closed porosity occurs during the intermediate stage of sintering, which covers normally the interval of relative densities between 70 and 90% [12]. Thus, 90% densification represents typically the onset of the final stage of sintering, that is the sintering regime where the closed porosity is eliminated [12]. In consequence, within the confines of the present study in what follows 90% relative density will be taken as the moment of the collapse of the open pore structure.

1625 °C). One can thus conclude that the complex SPS cycle is not effective by itself in improving the final degree of densification. Neither seems the complex SPS cycle to affect appreciably the grain size, as deduced by comparing for example the SEM micrograph in Fig. 7 for the sample fabricated with the complex cycle at 1625 °C with the corresponding one in Fig. 2B for the simple SPS cycle. These observations indicate that the microstructure (i.e., porosity and grain size) is dictated essentially by the high-pressure/high-temperature stretch. Nevertheless, the comparison between the curves in Figs. 1 and 6 still deserves more attention. Clearly, it can be observed that the shape of the densification curves at 1550, 1600 and 1625 °C is very similar for the two SPS cycles, and that at these temperatures the use of the complex SPS cycle delays little the end of the collapse of open pore structure (i.e., ~ 90, 30 and 20 s, respectively). Consistently with this scenario, we measured at 1550, 1600 and 1625 °C only a marginal difference between the evolution of the vacuum levels during the simple and complex SPS cycles. The densification curves obtained at 1500 °C exhibit however a relevant variation in shape, as with the complex SPS cycle the approximation towards the limiting value of ~ 92.5% is much more gradual. Indeed, the open pore structure collapses much later, that is, ~ 500 s later. Interestingly, we did not note at 1500 °C a relevant difference in the boron emission; in particular, with the complex SPS cycle not only the gas emission peak was 2 Pa more intense and lasted for more time than with the simple SPS cycle, but also reached at 1500 °C the same level than at 1625 °C with the simple SPS cycle despite the temperature being 125 °C lower. Unfortunately, despite the better elimination of boron gas at 1500 °C with the complex SPS cycle, the final degree of densification reached is however still moderate due to the insufficient diffusion at that temperature.

Taking all these analyses together into consideration, it seems very reasonable to implement a two-step SPS cycle with a first step at 1500 °C for ~10 min under a moderate pressure of 20 MPa to eliminate the boron impurities while densifying the compact up to ~ 90% relative density with little coarsening, followed by a shorter second step at 1600 °C under higher pressure of 75 MPa to promote the complete pore elimination. This expectation has indeed been confirmed experimentally because, as shown in the densification curve of Fig. 8 and in the SEM micrograph of Fig. 9, a fully dense ZrB₂ compact can be obtained with this two-step SPS cycle. Note that although the here-proposed two-step cycle and the one used typically to process nano-ceramics pursue the same objective of densification with little grain boundary migration, they are reversed with respect to each other [13] because in the latter the powder is first heated at the high

temperature for a short period and then is rapidly cooled down to a lower temperature and maintained there for a long period. This difference is because in the present case the major concern is the elimination of the boron impurities, which requires of a “smooth” intermediate stage of sintering, while in the case of the nano-ceramics the major concern is the inhibition of the grain growth, which requires of a “smooth” final stage of sintering.

To put the results of the ZrB₂ nano-powder with 10-nm crystals results in perspective, the above SPS data will be compared with those of the ZrB₂ powders with larger crystal sizes of ~ 25, 70, 160, 500, and 2000 nm. Given that the experimental observations indicate that the simple and complex SPS cycles yield eventually the same degree of densification and similar microstructure, the SPS experiments in the rest of ZrB₂ powders with larger crystal size will be carried out using only the simple SPS cycle. Clearly, this is enough within the confines of the present comparative study. Figure 10 compares the lowest-temperature densification curves for all these ZrB₂ powders, when the condition of reaching at least 95% densification is imposed. Note that the elucidation of these curves has required to conducting many SPS experiments at different temperatures for each of these ZrB₂ powders as we did previously for the nano-powder with 10-nm crystals, although these densification curves will not be presented for the sake of brevity. As can be observed, the curves in Fig. 10 demonstrate clearly that the crystal size refinement progressively reduces the SPS temperature of ZrB₂, and also show that the reduction is only moderate with the refinement to the ultra-fine range and however very marked with the refinement to the very nanoscale. Indeed, since according to Fig. 1 the ZrB₂ nano-powder with 10 nm crystals reached 96% densification at 1550 °C, which is the densification reached by the as received powder at 2000°C (fig 10), it can thus be concluded that the nanoscale crystal refinement reduced the SPS temperature by no less than 450 °C. This is very relevant because this reduction is similar or even higher than those previously achieved with the help of liquid-phase former sintering additives (for example with MoSi₂ or with TaSi₂) [2,3]. In addition, the oxygen contamination (which is known to promote coarsening [2,3,14-16]) was not prevented here by any use of an inert atmosphere during the milling, suggesting that there could be still room for further reductions in the sintering temperature, but at the expense of making the comminution routine more tedious and costly.

Finally, the present study has interesting implications concerning the comminution practice in the UHTC community. In particular, it emerges that the preparation of ZrB₂ powders with unequalled sintering behaviour requires necessarily the use of high-energy ball-milling because

the typical wet attrition milling, which has been so far the gold-standard comminution treatment, is a form of conventional milling that does not generate the high compressive stresses in the ball-to-ball collisions needed for the refinement of the crystal sizes down to nanoscale. This, however, does not rule out the use of attritors because it can also function as a high-energy ball-mill if operated in dry under a high ball-to-powder ratio ($> 40:1$) and with a high peripheral speed of the agitator (> 3 m/s). This would be another way of achieving the nanoscale crystal refinement needed to make the lower-temperature sintering of ZrB_2 possible

4. Concluding remarks

Acknowledgements This work was supported by the Ministerio de Ciencia y Tecnología (Government of Spain) under Grant N° MAT 2007-61609.

References

- 1) Wuchina E, Opila E, Opeka M, Fahrenholtz W, Talmy I. UHTCs: Ultra-High Temperature Ceramic Materials for Extreme Environment Applications. *Interface* 2007;**16**(4) 30–36.
- 2) Fahrenholtz WG, Hilmas GE, Talmy IG, Zaykoski JA. Refractory Diborides of Zirconium and Hafnium. *J Am Ceram Soc* 2007; **90**(5):1347–64.
- 3) Guo S-Q. Densification of ZrB₂-Based Composites and their Mechanical and Physical Properties: A Review. *J Eur Ceram Soc.* 2009;**29**(6):995–1011.
- 4) Telle R, Sigl LS, Takagi K. Boride-Based Hard Materials; pp. 802–945 in *Handbook of Ceramic Hard Materials*, Vol. 2, Edited by R. Riedel. Wiley-VCH, Weinheim, 2000.
- 5) Thompson M, Fahrenholtz WG, Hilmas G. Effect of Starting Particle Size and Oxygen Content on Densification of ZrB₂. *J Am Ceram Soc.* 2011;**94**(2):429–35.
- 6) Zamora V, Ortiz AL, Guiberteau F, Nygren M. Crystal-Size Dependence of the Spark-Plasma-Sintering Kinetics of ZrB₂ Ultra-High-Temperature Ceramics. *J Eur Ceram Soc*, in press.
- 7) Galán CA, Ortiz AL, Guiberteau F, Shaw LL. Crystallite Size Refinement of ZrB₂ by High-Energy Ball Milling. *J Am Ceram Soc.* 2009;**92**(12):3114–7.
- 8) Galán CA, Ortiz AL, Guiberteau F, Shaw LL. High-Energy Ball Milling of ZrB₂ in the Presence of Graphite. *J Am Ceram Soc.* 2010;**93**(10):3072–5.
- 9) Zamora V, Ortiz AL, Guiberteau F, Shaw LL, Nygren M. On the Crystallite Size Refinement of ZrB₂ by High-Energy Ball-Milling in the Presence of SiC. *J Eur Ceram Soc.* 2011;**31**(13):2407–14.
- 10) Mehrer H. *Diffusion in solid metals and alloys.* Springer-Verlag; 1990.
- 11) Ortiz AL, Zamora V, Rodríguez-Rojas F. On the Oxidation of ZrB₂ Powders during High-Energy Ball-Milling in Air. *Ceram Int.*, submitted 2011.
- 12) German RM. *Sintering Theory and Practice.* Wiley, New York; 1996.
- 13) Chen I-W, Wang X-H. Sintering Dense Nano-Crystalline Ceramics without Final Stage Grain Growth. *Nature* 2000;**404**(6774):168–71.
- 14) Chamberlain AL, Fahrenholtz WG, Hilmas GE. Pressureless Sintering of Zirconium Diboride. *J Am Ceram Soc.* 2006;**89**(2):450–6.
- 15) Zhang SC, Hilmas GE, Fahrenholtz WG. Pressureless Densification of Zirconium Diboride

- with Boron Carbide Additions. *J Am Ceram Soc.* 2006;**89**(5):1544–50.
- 16) Thompson M, Fahrenholtz WG, Hilmas G. Effect of Starting Particle Size and Oxygen Content on Densification of ZrB_2 . *J Am Ceram Soc* 2011;**94**(2):429–35.
- 17) ----
- 18) ----
- 19) ----
- 20)
- 1) ---
- 2)
- 3) W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium, *J. Am. Ceram. Soc.* 90 (5) (2007) 1347–1364.
- 4) -----A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, Pressureless sintering of zirconium diboride, *J. Am. Ceram. Soc.* 89 (2) (2006) 450–456.
- 5) S.C. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Pressureless densification of zirconium diboride with boron carbide additions, *J. Am. Ceram. Soc.* 89 (5) (2006) 1544–1550.
- 6) .
- 7) S.-Q. Guo, Densification of ZrB_2 -based composites and their mechanical and physical properties: a review, *J. Eur. Ceram. Soc.* 29 (6) (2009) 995–1011.
- 8) S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, S. Zhang, Pressureless sintering of zirconium diboride using boron carbide and carbon additions, *J. Am. Ceram. Soc.* 90 (11) (2007) 3660–3663.
- 9) W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, S. Zhu, Pressureless sintering of zirconium diboride: particle size and additive effects, *J. Am. Ceram. Soc.* 91 (5) (2008) 1398–1404.
- 10) C. Herring, Effect of change of scale on sintering phenomena, *J. Appl. Phys.* 21 (4) (1950) 301–303.
- 11) R. Telle, L.S. Sigl, K. Takagi, Boride-Based Hard Materials; pp. 802–945 in *Handbook of Ceramic Hard Materials*, Vol. 2, Edited by R. Riedel. Wiley-VCH, Weinheim, 2000.
- 12) S.L. Dole, S. Prochazka, R.H. Doremus, Microstructural coarsening during sintering of boron carbide, *J. Am. Ceram. Soc.* 72 (6) (1989) 958–966.
- 13) S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, Pressureless sintering of carbon-coated zirconium diboride powders, *Mat. Sci. Eng. A* 459 (1-2) (2007) 167–171.
- 14) H. Zhang, Y. Yan, Z. Huang, X. Liu, D. Jiang, Pressureless sintering of ZrB_2 -SiC ceramics:

- the effect of B₄C content, *Scripta Mater.* 60 (7) (2009) 559–562.
- 15) S.C. Zhang, G.E. Hilmas, W.G. Fahrenholtz, Mechanical properties of sintered ZrB₂-SiC ceramics, *J. Eur. Ceram. Soc.* 31 (5) (2011) 893–901.
 - 16) X.-G. Wang, W.-M. Guo, G.-J. Zhang, Pressureless sintering mechanism and microstructure of ZrB₂-SiC ceramics doped with boron, *Scripta Mater.* 61 (2) (2009) 177–180.
 - 17) C.A. Galán, A.L. Ortiz, F. Guiberteau, L.L. Shaw, Crystallite size refinement of ZrB₂ by high-energy ball milling, *J. Am. Ceram. Soc.* 92 (12) (2009) 3114–3117.
 - 18) C.A. Galán, A.L. Ortiz, F. Guiberteau, L.L. Shaw, High-energy ball milling of ZrB₂ in the presence of graphite, *J. Am. Ceram. Soc.* 93 (10) (2010) 3072–3075.
 - 19) V. Zamora, A.L. Ortiz, F. Guiberteau, M. Nygren, L.L. Shaw, On the crystallite size refinement of ZrB₂ by high-energy ball-milling in the presence of SiC, *J. Eur. Ceram. Soc.* (2011), in press.
 - 20) B.R. Lawn, *Fracture of brittle solids*. Cambridge University Press. Cambridge, UK; 1993.
 - 21) C. Suryanarayana, Mechanical alloying and milling, *Prog. Mater. Sci.* 46 (1-2) (2001) 1–184.
 - 22) P.R. Soni, *Mechanical alloying. Fundamental and applications*. Cambridge International Science Publishing. Cambridge, UK; 2001.
 - 23) V. Zamora, A.L. Ortiz, F. Guiberteau, M. Nygren, Crystal-size dependence of the spark-plasma-sintering kinetics of ZrB₂ ultra-high-temperature ceramics, *J. Eur. Ceram. Soc.* (2011), submitted.
 - 24) J. Watts, G. Hilmas, W.G. Fahrenholtz, D. Brown, B. Clausen, Measurement of thermal residual stresses in ZrB₂-SiC composites, *J. Eur. Ceram. Soc.* 31 (9) (2011) 1811–1820.
 - 25) L. Huerta, A. Durán, R. Falconi, M. Flores, R. Escamilla, Comparative study of the core level photoemission of the ZrB₂ and ZrB₁₂, *Physica C* 470 (9-10) (2010) 456–460.
 - 26) D. Alfano, L. Scatteia, F. Monteverde, E. Bêche, M. Balat-Pichelin, Microstructural characterization of ZrB₂-SiC based UHTC tested in the MESOX plasma facility, *J. Eur. Ceram. Soc.* 30 (11) (2010) 2345–2355.

Figure Captions

Figure 1. Densification curves as a function of time for the ZrB_2 nano-powder with 10-nm crystals, obtained with the simple SPS cycle for target temperatures of 1450, 1500, 1550, 1600, and 1625 °C. The closed points are data measured during the heating ramp up to the target temperature, while the open points are data measured during the soaking.

Figure 2. SEM micrographs of the UHTCs fabricated from the ZrB_2 nano-powder with 10-nm crystals using the simple SPS simple for 15 min at (A) 1450 °C and (B) 1625 °C.

Figure 3. Densification curve as a function of time for the ZrB_2 nano-powder with 10-nm crystals, obtained with the simple SPS cycle for a target temperature of 1450 °C. The closed points are data measured during the heating ramp up to 1450 °C, while the open points are data measured during the soaking at 1450 °C.

Figure 4. High-magnification SEM micrograph of the UHTC fabricated from the ZrB_2 nano-powder with 10-nm crystals using the simple SPS cycle at 1450 °C for 30 min.

Figure 5. Low-magnification SEM micrograph of the UHTC fabricated from the ZrB_2 nano-powder with 10-nm crystals using the simple SPS cycle at 1500 °C for 15 min.

Figure 6. Densification curves as a function of time for the ZrB_2 nano-powder with 10-nm crystals, obtained with the complex SPS cycle for target temperatures of 1500, 1550, 1600, and 1625 °C. The closed points are data measured during the heating ramp up to the target temperature, while the open points are data measured during the soaking.

Figure 7. SEM micrographs of the UHTCs fabricated from the ZrB_2 nano-powder with 10-nm crystals with the complex SPS cycle at 1625 °C for 15 min.

Figure 8. Densification curves as a function of time for the ZrB_2 nano-powder with 10-nm crystals, obtained with the two-step SPS cycle composed of a first complex SPS cycle with a target temperature of 1500 °C, followed by a second simple SPS cycle with a target temperature of 1600

°C. The closed points are data measured during the heating ramp up to the target temperatures, while the open points are data measured during the corresponding soakings.

Figure 9. SEM micrographs of the UHTCs fabricated from the ZrB₂ nano-powder with 10-nm crystals with the two-step SPS cycle at 1600 °C for 15 min.

Figure 10. Densification curves as a function of time for the ZrB₂ coarse, submicrometre, ultra-fine, and nanometre powders, obtained with the simple SPS cycle at the lowest target temperatures that resulted in final densification degrees greater than 95%. The closed points are data measured during the heating ramp up to the corresponding target temperature, while the open points are data measured during the soaking. The fact that the degree of densification at the onset of the SPS cycle first increases and then decreases is simply because the powder's mechanical-packing density scales inversely with the particle sizes, not with the crystal sizes, and the nano-crystals achieved with the long-time high-energy ball-milling are actually agglomerated [6,8,9].



















