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Comparison of Creep Behaviour in Alumina Based Ceramics Densified by SPS and HP

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Abstract

For more than a decade, the spark plasma sintering method (SPS) is an interesting alternative to classical densification processes for ceramic materials. Furthermore, SPS has recently been paid attention as an alternative method to obtain dense and fine-grained ceramics at low temperatures. SPS, also known as plasma activated sintering, is a method applicable for rapid sintering of metals and ceramics. Owing to the advantage of rapid heating, the alumina ceramics obtained by SPS have a grain size and density comparable to those of HPed ones. The increase of densification rate may be related to some difference in ion transport characteristics. In fact, if there is alteration in those transport characteristics, there may be some difference in all subsequent diffusion related to the processes such as grain growth, creep and high temperature deformation of SPS densified materials. This study describes creep behaviour and deformation mechanisms of alumina based materials densified by SPS, and compared with hot pressing (HP) to some extent. Pure alumina (SM8, Baikowski) was densified by SPS at 65 MPa (1200°C), and 45 MPa (1400°C) by hot pressing (HP).The grain size of the HP alumina was more twice bigger than the grain size of SPS sample (1000 nm versus 440 nm). The grain growth is more active during creep of SPS alumina (1300°C, σ = 30 MPa and final deformation 30 %) than during creep of HP alumina, about 70% versus 25%. Generally, the fineness of SPS materials microstructure shall speed up all processes related to diffusion.

Keywords: Creep, Alumina ceramics, Sintering, SPS, HP

PORÓWNANIE PEŁZANIA W CERAMICE KORUNDOWEJ ZAGĘSZCZANEJ METODAMI SPS I HP

Od ponad dekady metoda spiekania z plazmą iskrową (SPS) jest interesującą alternatywą dla procesów klasycznego zagęszczania materiałów ceramicznych. Dalej, na SPS zwrócono uwagę jako na alternatywną metodę otrzymywania w niskich temperaturach gęstej i drobnoziarnistej ceramiki. SPS, znana też jako spiekanie aktywowane plazmą, jest metodą mającą zastosowanie do szybkiego spiekania metali i ceramiki. Korzystając z szybkiego ogrzewania, ceramika korundowa otrzymywana za pomocą SPS charakteryzuje się rozmiarem ziarna i gęstością porównywalną z odpowiednikami prasowanymi na gorąco. Zwiększenie szybkości zagęszczania może być przypisane pewnej różnicy charakterystyk transportu jonowego. Faktycznie, jeśli istnieje zmiana w tych charakterystykach transportu pojawić sie może też różnica we wszystkich późniejszych cechach zależnych od dyfuzji takich jak: rozrost ziarna, pełzanie i deformacja wysokotemperaturowa materiałów zagęszczanych metodą SPS. Prezentowane badanie opisuje mechanizmy pełzania i deformacji materiałów korundowych zagęszczanych metodą SPS w porównaniu w pewnym zakresie do prasowanych na gorąco. Proszek korundu (SM8, Baikowski) zagęszczano metodą SPS przy 65 MPa (1200°C), i przy 45 MPa (1400°C) metodą prasowania na gorąco (HP). Rozmiar ziarna korundu HP był ponad dwa razy większy niż rozmiar ziarna próbek SPS (1000 nm przeciw 440 nm). Rozrost ziaren był aktywniejszy podczas pełzania korundu SPS (1300°C, σ = 30 MPa i deformacja końcowa 30 %) niż podczas pełzania korundu HP, około 70% przeciw 25%. Ogólnie, drobnoziarnistość mikrostruktury materiałów SPS będzie przyspieszała wszystkie procesy związane z dyfuzją.

Słowa kluczowe: pełzanie, ceramika korundowa, spiekanie, SPS, HP

1. Introduction

A process of hot deformation of alumina base ceramic is limited by grain growth. Static and dynamic changes in grain size during deformation contribute to the overall growth which usually reduces continuously the super plastic capacity of the considered material. Different approaches have been experimented in order to control the grain growth during the deformation. The first approach, using some compounds (such as MgO and ZrO_2) in order to lower the grain boundary mobility and in impeding the grain growth of alumina. MgO has been added to alumina in order to lower the grain boundary mobility through solute drag and ZrO_2 particles have been particularly useful in impeding the grain growth of alumina by second phase pinning. However, the MgO effect is limited and one problem arises with the addition of ZrO_2 particles: their effectiveness is related to the homogeneity of their distribution which can evolve during the deformation of the material. Small carbon particles reduces greatly the grain growth during the sintering and during the compression

experiments. The super-plasticity of the carbon-containing alumina is greatly improved [1].

The second approach, using the new technique (such as SPS method) to obtain fine grained during sintering process of ceramic materials. Hot-pressing (HP) has been the widely used sintering technique for producing highly dense UHTCs (Ultra-high temperature ceramics) [2]. Spark plasma sintering (SPS) has recently been paid attention as an alternative method to obtain dense and fine-grained ceramics at low temperatures. During SPS of the alumina ceramics, the heating rate was very high (3150°C/min) and the holding time at sintering temperature was short (3–10 min). Owing to the advantage of rapid heating, the alumina ceramics obtained by SPS have a grain size and density comparable to those of HPed ones. For example, a fully dense (a relative density of ~100%) alumina with a grain size of 0.5 μm was obtained at 1200°C by SPS [3, 4]. Spark plasma sintering (SPS) has emerged as a nonconventional powder consolidation method in densifying a number of poorly sinterable ceramics in very short times [5]. In this technique, densification is stimulated by the application of a pulsed electric field, combined with resistance heating and pressure. Several experiments emphasized that high-rate and possibly low-temperature sintering are indeed characteristics of this technique [2].

High temperature shaping of ceramic materials has been investigated for a long time and studies are continuously reported by different authors. Studies of the hot forming of alumina or alumina-based ceramics are rare and investigations of the plastic deformation of these materials reveal the crucial importance of microstructural control during deformation. Indeed, for example, hot-forming of zirconia ceramics has been more extensively demonstrated due to lower microstructural evolution during deformation. However, alumina exhibits important dynamic grain growth, which is deleterious for further deformation capabilities. Super-plastic deformation of fine grained alumina as is a boundary diffusion process, involving mainly grain boundary sliding. Also, cavitations may become an important accompanying process for deformation when the mean grain size is over a few micrometers. From this basis, one of the necessary conditions for dense alumina to exhibit important deformation capabilities is to start with a submicrometre microstructure. The finer the initial microstructure, the better the plastic behaviour [6].

The aim of this paper is to assess the creep and deformation behaviour of alumina based ceramics densified by SPS and somehow compare it to the behaviour of HPed ones.

2. Experimental procedure

The starting material used in the study was an atomized commercial 500 ppm FeO-doped α-alumina powder (Baikowski, SM8) shown in Fig. 1. The nominal composition of the alumina powder is given in Table 1.

From this powder two types of dense alumina materials were produced. The first type was produced by HP method, whereas for the second type by SPS method. Discs were hot-pressed (45 MPa) during 30 min at T = 1450ºC in a graphite die, heating rate being 10ºC/min. SPS was performed under 45 MPa at 1200ºC. The obtained alumina discs had a diameter of 30 mm and a height of 10 mm.

Density of the resulting billets was determined by weighing in alcohol using the Archimedes' method. Final densities were reached greater than 99.4 % of theoretical for all billets, and 95.6 % of theoretical for samples FeO-doped. Samples for deformation experiments were cut from the pressed billets and the faces were made parallel. Typical sample sizes were a transverse square section of 3x3 mm^2 and a height of 7 mm.

Table 1. Chemical and physical properties of α-alumina + 500 wt. (ppm) FeO before atomization

Element	Fe	Na	K	Si	Average particle size [nm]	Mean grain size [nm]	BET [m^2/g]
[ppm]	500	17	38	8	400	50	10

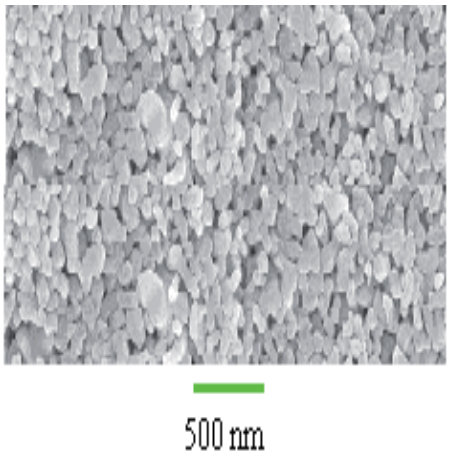


Fig. 1. Micrograph of pure α-alumina (Baikowski, SM8, mean average size 300 nm).

Compressive creep tests in air were carried out at different true stress up to 100 MPa and different temperatures (1200-1400ºC). From length change versus time curves, true strain rate versus true strain curves were obtained. The microstructures of as densified and of strained specimens were characterized by scanning electron microscopy (SEM) and by conventional transmission electron microscopy (TEM). For SEM investigations, diamond polished cross sections were thermally etched at T = 1270ºC for 30 min to reveal the microstructure (Fig. 2). The grain sizes were obtained by multiplying the square root of the average grain surface by 1.38 [7]. More than three hundred grains were numbered for each grain size calculation.

3. Results

3.1. Creep tests

Compression creep tests have been carried out in air at a temperature range (1200–1400ºC) and under true stresses up to 100 MPa, and then true strain rate ($\varepsilon^\circ = d\varepsilon/dt$) was plotted against true strain ($\varepsilon = \Delta l/l_o$).The graphs of true strain rate versus true strain (ε°-ε) at the temperatures of 1200ºC and 1300ºC under stress true 30 MPa for samples of alumina densified by SPS and at 1300ºC and 1400ºC

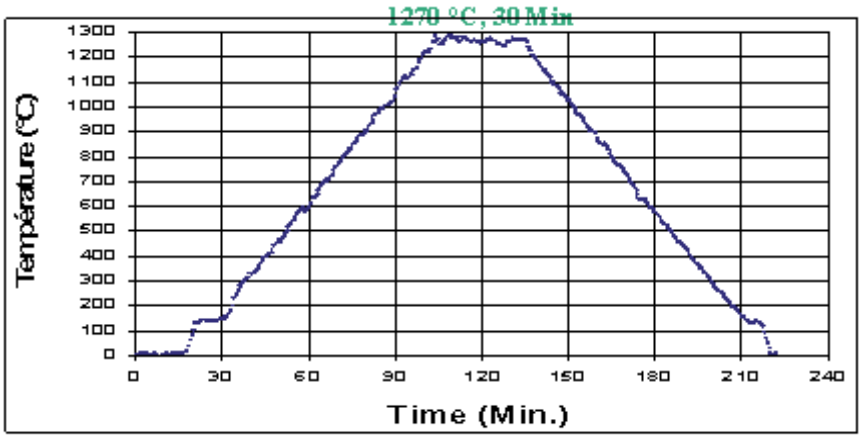


Fig. 2. Graph of thermal etching for SEM investigations.

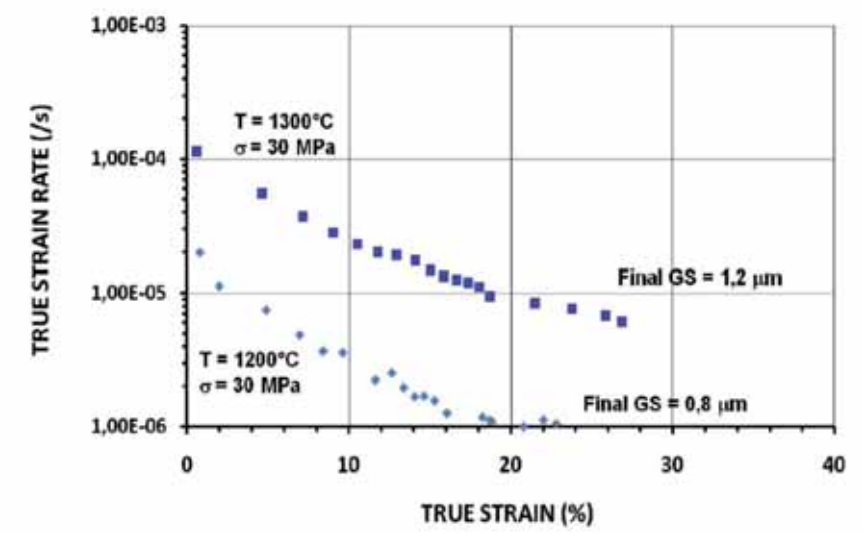


Fig. 3. True strain rate versus true strain curves (ε°-ε) at the temperatures of 1200ºC and 1300ºC, σ = 30 MPa for the SPS alumina.

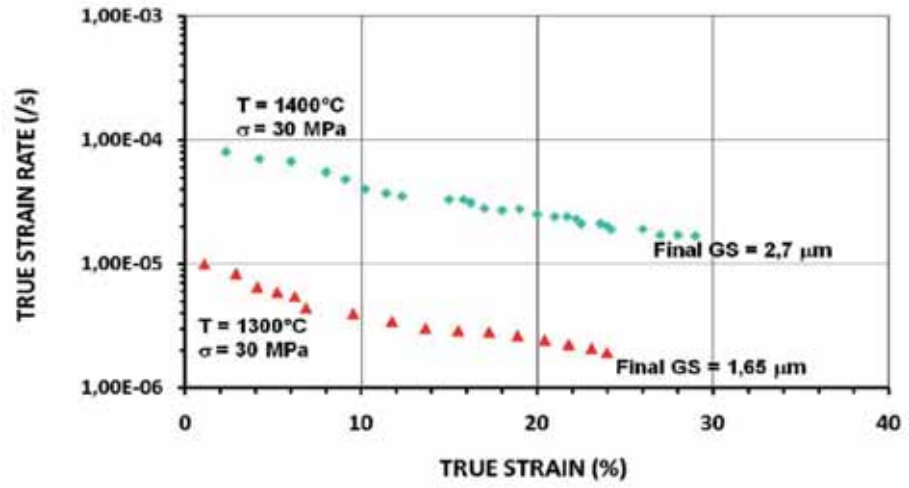


Fig. 4. True strain rate versus true strain curves (ε°-ε) at the temperatures of 1300ºC and 1400ºC, σ = 30 MPa for the HP alumina.

under the same true stress for samples densified by HP are presented in Figs. 3 and 4.

As a matter of fact, the graph corresponding to the creep SPS alumina at 1300ºC and 30 MPa is very comparable to the graph of creep HP alumina at 1400ºC and the same stress level.

Concerning the calculation grain size of deformed samples observed by SEM at different temperatures, σ = 30 MPa and final deformation ~25%, the graph of grain growth was obtained in both types of samples (Fig. 5). The grain growth is more active during creep of SPS alumina than during creep HP alumina.

3.2. SEM studies

Figs. 6 and 7 show SEM micrographs of both SPS and HP alumina as densified and deformed at T = 1300ºC, σ = 30 MPa and final deformation 30%.

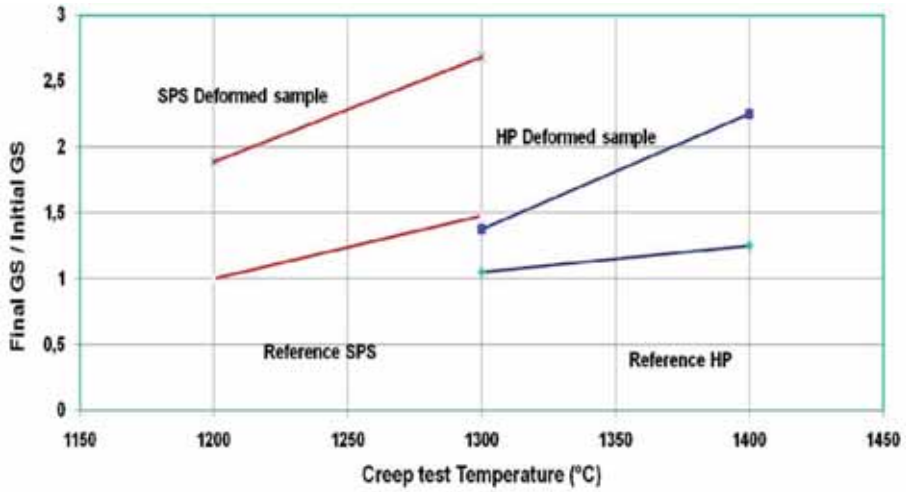
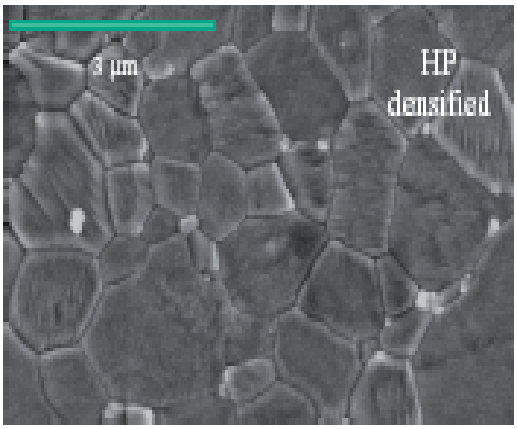
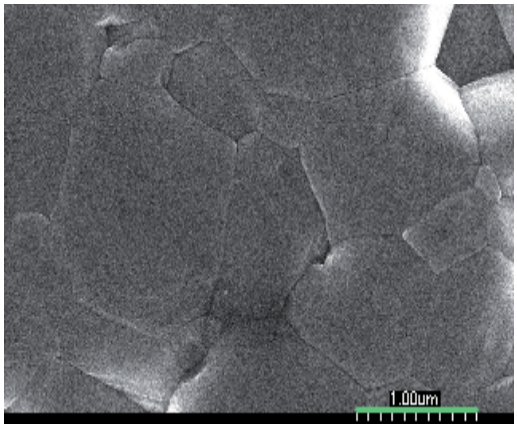


Fig. 5. The static and dynamic grain growth, reference and deformed samples respectively, at different creep temperatures, σ = 30 MPa and final deformation ~25 % for both SPS alumina and HP alumina.

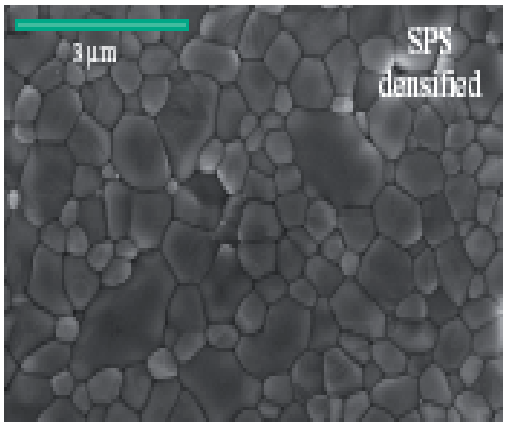


a)

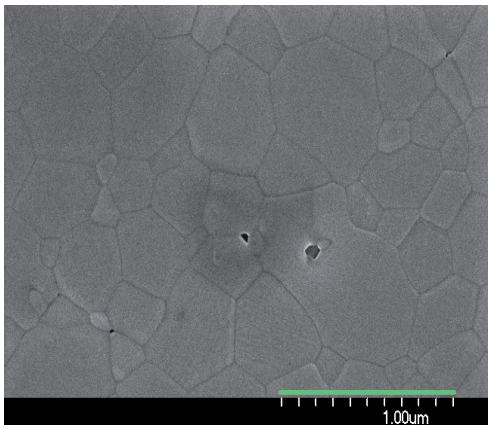


b)

Fig. 6. SEM micrographs of HP alumina samples: a) as-densified and b) deformed at T = 1300ºC, σ = 30 MPa and final deformation 30 %. Grain size was increased from 1000 nm to 1220 nm for the sample deformed at these conditions.



a)



b)

Fig. 7. SEM micrographs of SPS alumina samples: a) as-densified and b) deformed at T = 1300ºC, σ = 30 MPa and final deformation 30 %. Grain size was increased from 440 nm to 50 nm for the sample deformed at these conditions.

4. Discussion

Creep tests have been carried out mainly at σ = 30 MPa, and σ = 75 MPa. The presented graphs correspond to the creep tests at σ = 30 MPa and different temperatures. The creep behaviour of SPS densified alumina under these conditions can be compared to the one of hot-pressed alumina. The similarity of creep behaviour is perceptible. As a matter of fact, the curve corresponding to the creep of SPS alumina at σ = 30 MPa and T = 1300°C is very comparable to the one of HP alumina at σ = 30 MPa and T = 1400°C.

Considering the expression of the constitutive equation of superplastic deformation, mean values of stress exponent, strain size dependant factor and activation have been obtained for the SPS alumina and those are comparable to

the ones for HP alumina [1 and present work], as follows calculated values are close for both materials.

$$\dot{\varepsilon}_{(SPS)} = C_1 \cdot \sigma^{2.2} \exp\left(-\frac{490\,kJ}{RT}\right) \quad (1)$$

$$\dot{\varepsilon}_{(HP)} = C_2 \cdot \sigma^{1.92} \exp\left(-\frac{510\,kJ}{RT}\right) \quad (2)$$

Interestingly, when considering the second equation, a decrease of temperature of 100°C (from 1400°C down to 1300°C) is compensated by the difference of grain size observed between SPS alumina and HP alumina. This would explain the presented similarity of creep curve. This shall mean that the creep mechanisms which are active in creep of HP alumina are those active in creep of SPS alumina.

From the analysis of grain growth at σ = 30 MPa and at different temperatures, the grain growth is more active during creep of SPS alumina than during creep of HP alumina. This may be the counterpart of the high densification rate obtained at lower temperatures in the SPS process. The high rate shall limit the reaching of equilibrium in the microstructure during SPS densification. Hence the microstructure of SPS material shall be less stable. Also, there are several cavitations in triple grain boundary; it results in decreasing of mobility of grain boundary or grain growing. So, the grain size of HPed samples are more stable during creep test than SPSed samples.

5. Conclusions

The grain growth is more active during sintering of SPS alumina than during sintering of HP alumina.

Considering the analysis of grain growth at σ = 30 MPa and at different temperatures, the grain growth is more active during creep of SPS alumina than during creep of HP alumina.

The high rate shall limit reaching the equilibrium in the microstructure during SPS densification. Hence the microstructure of SPS material shall be less stable.

The grain size of the HP alumina was more twice bigger than the grain size of SPS sample (1000 nm versus 440 nm). Generally, the fineness of SPS materials microstructure shall speed up all processes related to diffusion.

Considering the investigation of microstructure of HPed samples, there are several cavitations in triple grain boundary; it results in decreasing of mobility of grain boundary or grain growing. So, the grain size of HPed samples are more stable during creep test than SPSed samples.

The ratio dynamic to static grain growth in SPSed samples is more than twice HPed samples during creep test.

References

[1] Bataille A., Crampon J., Duclos R.: „Upgrading super plastic deformation performance of fine-grained alumina by graphite particles", Ceramics Int., 25, (1999), 215-222.
[2] Monteverde F.: „Ultra-high temperature HfB_2–SiC ceramics consolidated by hot-pressing and spark plasma sintering", J. Alloys Compd, 428, (2007), 197–205.
[3] Shen, Z., Johnsson, M., Zhao, Z., Nygen, M.: „Spark plasma sintering of Alumina". J. Am. Ceram. Soc., 85, (2002),1921–1927.
[4] Dobedoe, R.S., West, G.D., Lewis, M.H.: „Spark plasma sintering of ceramics", Bull. ECerS, 1 ,(2003), 19–24.
[5] Nygren M., Shen Z.: „On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering", Solid State Sci., 5, (2003), 125–131.
[6] Bataille A., Crampon J.: „Investigation and simulation of hot forming of alumina based materials", J. Mater. Sci., 38, (2003), 3245–3248.
[7] Carry C., Mocellin A.: „Structural superplasticity in single phase crystalline ceramics", Ceram. Int. 13, (1987), 89.

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