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Spark plasma sintering of fine-grained alumina ceramics reinforced with alumina whiskers

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ABSTRACT

Densification of alumina whisker-reinforced alumina ceramics by spark plasma sintering (SPS) has been investigated with the aim of obtaining a fine-grained microstructure and also studying the effect of whisker addition on the room-temperature mechanical properties. It was found that whisker addition retards slightly the sinterability of alumina by whisker hindering of particle rearrangement. Besides, the internal stress on the alumina matrix particles reduced due to the presence of a whisker network structure of strong rigid boundaries. Nevertheless near fully-dense and fine-grained alumina ceramics with alumina whisker content between 3 wt% and 10 wt% could be obtained under appropriate SPS conditions. The hardness of alumina ceramics with 3 wt% was comparable to that of pure alumina ceramics (~26 GPa) whereas its fracture toughness (5.6 MPa $m^{1/2}$) was higher (4.2 MPa $m^{1/2}$). Crack bridging by well-dispersed whiskers and whiskers pull-out were identified as the main toughening mechanisms.

1. Introduction

Alumina ceramics have attracted the highest investment as structural ceramics due to its excellent chemical stability, good mechanical properties and oxidation resistance together with a low production cost. However, its intrinsic low fracture toughness is a limiting factor for a broader application range [1–3]. It is well known that the microstructural refinement by advanced sintering techniques like spark plasma sintering (SPS) can improve their strength, hardness and to some extent fracture toughness [4–8]. Another efficient approach to this goal is the microstructural reinforcement by addition of secondary phases [9–24]. Accordingly, several secondary phases, either particles or whiskers/fibers, such as SiC particles – Al_2O_3 [9–11], SiC whiskers – Al_2O_3 [12], TaC whiskers – Al_2O_3 [13], carbon nano tubes (CNT) – Al_2O_3 [14–21], BN – Al_2O_3 [22,23], metal – Al_2O_3 [24] have been used to fabricate alumina-based composites. It is reported that the addition of SiC particles or SiC whiskers to Al_2O_3 matrix enhances hardness and fracture toughness by changing the fracture mode from intergranular in pure alumina polycrystals to mixed intergranular-transgranular mode in alumina-based composites [10–12]. Moreover, the recent studies have shown that the carbon nanotubes are also efficient additives to the aim of improving fracture toughness and flexure strength of Al_2O_3 ceramics whereas the hardness is generally reduced [17–21].

In many high-temperature structural applications, alumina-based composites with high oxidation resistance are required. This is the main drawback of the non-oxide secondary phases (SiC, CNT, or metals): their mechanical properties degradation at elevated temperatures under air [3,23]. Furthermore, the bonding character between alumina grains and second phases in alumina-based composites like CNT/Al_2O_3 ceramics [17] is not still clear and depends strongly on the processing procedure. Indeed, the bonding character can affect mechanical properties relevantly [17]. The improved fracture toughness of SiC whiskers-reinforced Al_2O_3 ceramics [10–12] or CNT-reinforced ones [17–21] confirm that whiskers are promising candidates for Al_2O_3 ceramics reinforcement. In order to overcome the drawback of non-oxide additives, an appropriate alternative is the use of Al_2O_3 whiskers/fibers, that obviously cannot oxidize and do not have bonding incompatibility with the matrix. Surprisingly, the reinforcement of Al_2O_3 ceramics with Al_2O_3 whiskers has not been studied previously. Fortunately, Al_2O_3 whiskers produced by vapor-liquid-solid deposition (VLS) techniques [25,26], are available at industry level at competitive cost. In addition to this, Al_2O_3 has previously been compacted successfully by spark plasma sintering (SPS) and the systematic study of SPS sintering conditions with limited grain growth and higher hardness values has been reported before [4–8]. Therefore it seems

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quite reasonable to get advantage of the SPS technique to prepare whiskers-reinforced alumina ceramics with enhanced mechanical properties. This is the objective of this study, which is aimed at investigating the effect of the additions of Al_2O_3 whiskers on the sinterability and room-temperature mechanical properties of SPSed alumina composites.

2. Experimental procedure

Al_2O_3 powders (Sumitomo Chemical Co., Ltd, Tokyo, Japan) of > 99.99% purity, with particle size 0.3 – 0.5 μm and BET surface area 5 – 10 m^2/g and Al_2O_3 whisker (Neoker, S. L., Milladoiro, Spain) of > 5 μm in length and with aspect ratio 3:1 were used as raw materials. Three powder batches were prepared with different compositions, one of which contains only Al_2O_3 powders, while other ones are Al_2O_3 powders with 3 wt% and 10 wt%Al_2O_3 whiskers, respectively. Hereafter, the pure Al_2O_3 sample is labelled as AW00, the composite with 3 wt% whiskers as AW03, and consequently the 10 wt%-whiskers composite as AW10. The powder mixtures were subjected to ball-milling with Si_3N_4 balls for 24 h in ethanol. Later on, the resulting slurry was dried on a hot plate in air.

Subsequently, the as-received Al_2O_3 powders and the ball-milled powder mixtures of with 3 wt% and 10 wt%Al_2O_3 whiskers were densified by SPS (Dr. Sinter SPS-515S, Fuji Electronic Industrial Co., Ltd., Kanagawa, Japan), using a graphite mold with inner diameter of 15 mm. The amount of powders was set to obtain a 3 mm thick of fully dense sintered body. A thermal insulating carbon foil was placed surrounding the graphite mold to limit the heat loss. Temperature of the graphite mold surface was monitored by an optical pyrometer and the SPS pulse sequence was set to 12:2. SPS was carried out in dynamic vacuum (i.e.,~6 Pa) and the following parameters were studied: (i) sintering temperature, in the range 1150–1400 °C and (ii) sintering dwell time, in the range 1–10 min. In all cases, the SPS was performed under uniaxial mechanical pressure of 75 MPa (applied during the whole sintering process, including heating and cooling ramps) with heating rate set at 200 °C/min and cooling rate of 100 °C/min.

The relative density of the samples was measured by the Archimedes method in distilled water as the immersion media. The microstructural characterization was carried out by scanning electron microscopy (FE-SEM; HITACHI S5200, Hitachi High-Technologies, Tokyo, Japan). SEM observations were done on fracture surfaces and on polished-gold-coated surfaces polished to a 1 μm-finish using conventional ceramographic methods. The polished surfaces were thermally etched at 1150 °C for one minute dwell time with a heating rate of 20 °C/min and cooling rate of 10 °C/min. The equivalent planar diameter d was measured from SEM photographs, counting more than 380 grains.

In order to study the compaction behavior during SPS, the following experiment was performed: one SPS test at 1300 °C in the same graphite mold used previously with constant pressure of 27 MPa applied during heating (minimum contact pressure for safety reasons) up to 1300 °C. Then, the temperature was held for one minute to ensure thermal stability. Later on, while keeping this temperature, pressure was increased up to 100 MPa and then it was relieved. Temperature, pressure and powder shrinkage were monitored. The length from the top to the bottom of punches was measured after the die cooled down to room temperature and the sample thickness was calculated considering the length of the two punches used. Additionally, a blank test was also carried out by setting die, punches and graphite sheet without sample powder following the same procedure mentioned above. By means of this blank test, the effect of thermal expansion and elastic deformation of the graphite elements can be calibrated.

The hardness (H_v) and fracture toughness (K_{IC}) of the selected specimens were measured by Vickers indentation tests on polished samples using a Vickers indentation tester (Struers A/S, DK-2750 Bullerup, Denmark) equipped with a diamond Vickers indenter, under a load of 9.8 N and dwell time of 10 s. At least 10 measurements per specimen were recorded to average the hardness and the fracture toughness. The hardness and toughness were determined using the standard expressions $H_v=2P/a^2$ and $K_{IC}=0.016(E/Hv)^{0.5}Pc^{-1.5}$ [27,28] where a and c are the length of the diagonal of the residual impression and the semi-length of the surface trace of the radial cracks measured by optical microscopy, respectively, and E, P the Young modulus and indentation load, respectively.

Table 1
Processing conditions and microstructural features of the AW00, AW03 and AW10 alumina-based ceramics by SPS.

Composition	Sintering temperature (°C)	Dwell time (min)	Relative density (%)	Grain size d (μm)	Standard deviation (μm)
AW00	1150	10	95.4	0.226	0.096
(Alumina	1200	3	97.9	0.351	0.163
powder	1300	1	99.8	0.510	0.248
100%)		3	99.9	0.581	0.357
		5	100.0	0.708	0.297
		10	100.0	1.010	0.527
	1400	3	100.0	2.169	1.144
AW03	1200	3	90.4	0.282	0.118
(Whisker 3	1300	1	97.2	0.441	0.222
mass%)		3	99.0	0.446	0.244
		5	99.9	0.739	0.494
	1400	3	99.5	0.772	0.281
AW10	1200	3	90.2	0.216	0.169
(Whisker 10	1300	1	93.8	0.307	0.158
mass%)		3	95.5	0.306	0.159
		5	95.9	0.304	0.185
		10	95.8	0.325	0.186
	1400	3	96.9	0.440	0.252

3. Results

3.1. Sintering behavior

Results of relative density, mean grain size, and grain size distribution of sintered bodies obtained at different SPS conditions are summarized in Table 1. Both the relative density and grain size evolution as a function of sintering dwell time are plotted in Fig. 1(a) and (b), respectively for the test at 1300 °C. Additionally, the evolution of the relative density and grain size with SPS temperature for 3 min of SPS dwell time is shown in Fig. 1(c) and (d), respectively. A heating rate of 200 °C/min, cooling rate of 100 °C/min and pressure of 75 MPa were applied for these SPS experiments. As it is shown in Fig. 1(a) and (c), near fully-dense AW00 specimens (relative density higher than 98%) was obtained at SPS temperatures higher than 1200 °C for any dwell time, while grain size increases with dwell time and remarkably with sintering temperature. It can be concluded that the optimal SPS conditions for the pure alumina powders are 1300 °C for 1–3 min with near fully-dense specimen and limited grain size of 0.5–0.6 μm. When whiskers are added, it is clear from Fig. 1(a) and (c), that 3 wt% whiskers addition retards densification slightly compared to pure alumina at the same SPS conditions while it limits grain growth strongly. In the case of higher whisker addition (10 wt%), the densification inhibition (Fig. 1(a) and (c)) is more relevant and grain growth is hindered effectively and decreases to much lower values than those of as-received and 3 wt% whiskers-added under identical SPS conditions (Fig. 1(b) and (d)). It is especially remarkable the grain size evolution of AW10 at 1300 °C, which remains constant (0.3 μm) whatever the sintering dwell time value. Moreover, grain growth was hardly observed at 1400 °C in AW10. Therefore, it seems that Al_2O_3 whiskers addition promotes microstructure refinement and stability.