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Microstructural design for mechanical and electrical properties of spark plasma sintered Al_2O_3–SiC nanocomposites

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ABSTRACT

Al_2O_3–17 vol.% SiC nanocomposites were prepared by powder mixture of submicrosized α-Al_2O_3, nanosized γ-Al_2O_3 and different nanosized β-SiC. Materials were sintered by spark plasma sintering (SPS) technique at two temperatures (1400–1550 °C) and their electrical conductivity and mechanical properties were investigated. High-density composites have been achieved even at the lowest sintering temperatures and the microstructure characterization shows SiC particles located both within the Al_2O_3 matrix grains and/or at the Al_2O_3 grain boundaries.

It has been demonstrated that microstructure tailoring is possible by suitable selection of starting materials and fast sintering by SPS. Accurate design of nanocomposites microstructures allows obtaining moderately conductive (<100 Ω cm) or insulating (10^8 Ω cm) materials while the chemical composition is similar.

1. Introduction

Since the concept of structural ceramic nanocomposites had been proposed by Niihara in 1991 much attention has been focused on their processing routes and mechanical properties improvement [1]. Particularly, Al_2O_3–SiC nanocomposites in which submicrometre or nanometre alumina matrix is reinforced with silicon carbide nanoparticles have been widely studied. In the early 1990s different authors as Nakahira [2], Ohji [3] or Deng [4] revealed that the addition of low percentages of this material (5–17 vol.% of SiC particles) to an alumina matrix produced a large enhancement of the fracture strength and a markedly improved creep resistance on the final composite, compared to pure alumina.

In these materials, the most critical factors that appear to control the properties of use are: positioning of the second phase particles into the matrix (intragranular, intergranular or both), SiC and Al_2O_3 grain size (micrometric or nanometric) and the chemical composition (vol.% of SiC). Deng et al. showed the enhancement of the mechanical properties with a change in the mode of the alumina matrix fracture, from intergranular to transgranular, induced by the dispersion of SiC fine particles into the matrix. Besides the mechanical reinforcement, the electrical properties of composite materials can also be tailored. In particular, alumina based materials reinforced with conductive phases, or semiconductors such as silicon carbide, over the percolation threshold have received special attention. This is due to the advantages that can be offered by electro-conductive ceramics in wide variety fields of applications in industry. It is well known that mathematical calculations fixed a 17% relative volume of conductive phase as percolation threshold when the dispersed phase is formed by spherical particles [5,6].

Al_2O_3–SiC composites are usually sintered by hot pressing (HP) of powder mixtures [7,8]. Although the simultaneous heating and uniaxial pressure applied facilitates the densification of these composites, high temperatures up to 1800 °C are usually required. Due to the high sintering temperatures needed, alumina grain growth and the subsequent final microstructure control is limited. Recently, the spark plasma sintering (SPS) technique allows obtaining full dense materials in a very short time and lower temperatures than conventional sintering techniques [9]. The SPS, also known as field assisted sintering technique (FAST), is a sintering technique widely used in the processing of ceramic materials which can consolidate powder compacts applying an on–off DC electric pulse under uniaxial pressure [10]. This technique can work at heating rates of the order of hundreds degrees per minute combined with the external pressure assistance, reaching high temperatures in a very short time [11,12]. This sintering technique is being profusely applied in the preparation of a wide range of composites, but only three scientific publications can be found dealing with SPS sintered Al_2O_3–SiC materials [13–15]. All of them were focused on the SiC

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particles positioning in the final composite. Nevertheless, there is still no data about the influence that starting materials features and SPS parameters have on the design of these materials microstructure. In particular, raw materials features and processing and/or sintering conditions are especially relevant when the second phase content in the composite is close to the percolation threshold [16].

In the present work, the preparation of different inter/intragranular micro-nanocomposites of Al_2O_3–17 vol.% SiC by spark plasma sintering at relatively low temperatures is proposed. The resulting materials are evaluated in terms of microstructure, electrical conductivity and mechanical properties.

2. Experimental

2.1. Starting materials and mixed powders

The starting materials used in this study were three different commercial Al_2O_3 powders and two silicon carbide powders. Their characteristics have been provided by the suppliers and verified by DRX and TEM, these summarized in Table 1. The commercial alumina Taimei TM-DAR (T) is manufactured by Chemicals Co. Ltd, Japan, alumina Nanotek (N) by Nanophase Technologies Co., USA and alumina Sasol SPA 0.5 (S) by Ceralox Division, USA. These materials have a purity of 99.99%. As a second phase, β-SiC nano-sized powder (Hb) from Hubei Minmetals Corp., China with a purity >98% and β-SiC nano-sized powder (Tp) by Tespint S.A. Belgium with a purity >95% were used.

Powders mixtures containing 17 vol.% of nano-SiC component were prepared by roll milling using ethanol (Panreac Quimica) as solvent in a PET container. High purity (99.5%) alpha alumina balls media of 2 mm diameter were added in a relation to media/powders 4/1. Rotating speed was fixed at 100 r.p.m. and rolling times of 48 h were used to achieve a good dispersion between both phases. After roll milling, the resultant slurry was dried at 60 °C and the dried powder was sieved under 60 μm. The samples were labelled with the capital letters in brackets from each material.

2.2. SPS processing and characterization of sintered bodies

The composite powders mixtures were placed into a graphite die with an inner diameter of 20 mm and cold uniaxially pressed at 30 MPa. Then, they were introduced in a spark plasma sintering apparatus HP D 25/1 (FCT Systeme GmbH, Rauenstein, Germany) under low vacuum (10^{-1} mbar) and sintered at 1400 °C and 1550 °C for 1 min of dwell time and heating rate of 100 °C min^{-1}. Samples were initially pressed at 16 MPa and this load was kept from room temperature up to 600 °C. Then, pressure was increased while heating, reaching 80 MPa within the next 100 °C and being maintained up to the maximum temperature and during dwell time. Real density of the starting powders has been measured by helium picnometry. The obtained values were 3.90 ± 0.2 g cm^{-3} and 3.55 ± 0.2 g cm^{-3} for alpha and gamma alumina powders, respectively, and 3.11 ± 0.1 g cm^{-3} in the case of silicon carbide. The apparent densities of the sintered composites were measured by the Archimedes method using water as medium (ISO-3369) and the real density by He pycnometry. The relative density was calculated as the apparent/real densities ratio.

The samples for hardness and fracture toughness analysis were previously polished (Struers, model RotoPol-31) with diamond to 1 μm roughness. The hardness of the materials was determined using the indentation technique (Buehler, model Micromet 5103) with a conventional diamond pyramid indenter. The diagonals of each indentation were measured using an optical microscope. Thirty diagonals were tested for each composition. Measuring conditions for the Vickers hardness, H_v, were an applying load of 2 N for 10 s and the standard specification ASTM E92-72. To estimate the indentation fracture toughness (K_{IC}), 98 N Vickers indentations were performed on the surface of the samples, inducing Palmqvist cracks, from which the indentation fracture toughness was obtained by method of Niihara [17]. After polishing and thermally etching in vacuum, sintered samples were characterized by field emission scanning electron microscopy (FE-SEM, Zeiss Ultraplus). The electrical resistivity of composite materials was determined according to ASTM C611. The specimens were placed between two sheets of copper connected to a power supply, which allowed working at different current intensities. The measurements were carried out by fixing the intensity of the current at 0.5 A using a multimeter of fixed contacts (9.55 mm separation), determining the voltage drop.

The alumina average grain size of the sintered composites was calculated from the FE-SEM micrographs of the polished and thermally etched surface. For this purpose, the lineal intercept technique for measuring grain size in composites, developed by Wurst and Nelson [18] was used. More than 100 grains were taken into account by this method.

Table 1
Particle size and crystal structure of the powders.

Raw materials	Crystal structure	Mean particle size, d_{50} (nm)
Al_2O_3 (Nanotek)	70(gamma):30(delta)	45
Al_2O_3 (Taimei)	Alpha	150
Al_2O_3 (Sasol)	Alpha	350
SiC (Hubei)	Beta	50
SiC (Tespint)	Beta	80

3. Results and discussion

3.1. Sintering behaviour and mechanical properties

Two temperatures were used for spark plasma sintering tests (1400 °C and 1550 °C). In both cases, nearly fully dense samples (>99.0% relative density) were obtained for all Al_2O_3–17 vol.% SiC composites prepared through the different raw materials combinations tested. In Figs. 1, the microstructures of nanocomposites obtained at 1400 °C and 1550 °C can be observed, where alumina (grey) and silicon carbide (black) can be distinguished and no porosity is observed. When similar composite powder (Al_2O_3–SiC) is sintered by hot-press, it is needed at least 1650 °C and 1 h soaking time [19–21] for total densification, even if the total SiC content is lower (5 vol.%). Then, SPS sintering technique allows attaining total densification of this type of composites in very short processing times and at relatively low temperatures. The strong reduction in processing times is critical if a control of alumina grain growth is desired.

Moreover, the residual porosity was always <0.5% except for NTp at 1400 °C sample that has 0.9% porosity. In this case, the phase transformation of the alumina Nanotek from gamma/delta to alpha during the sintering cycle delays the densification process. If the sintering temperature is increased (1550 °C) the residual porosity is completely removed.

The effect of pressure on sintering has been widely discussed in the literature. The pressure has a mechanical role (higher packing density of particles, rearrangement, breakdown of agglomerates, etc.) as well as an intrinsic role (by increasing the driving force of sintering). Jaafar et al. have reported that the densification of alumina–SiC material by SPS was drastically reduced from 99% to 85% by half reducing the applied pressure from 80 to 40 MPa and maintaining the sintering temperature [13]. Then, the full densification of samples achieved in this work, for both sintering temperatures (1400 °C and 1550 °C) can be favoured by the high