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Pulsed electric current sintering and characterization of ultrafine Al_2O_3–WC composites

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ABSTRACT

Ultrafine Al_2O_3 powder mixtures with up to 80 vol% ultrafine WC were prepared and consolidated by pulsed electric current sintering (PECS) for 4 min at 1250–1750 °C under a mechanical pressure of 60 MPa. Fully dense composites with ≤40 vol% WC could be achieved when PECS at 1450 °C for 4 min, whereas 1650 °C was needed for the WC matrix composites. The microstructure, electrical conductivity and mechanical properties of the composites were assessed as a function of the WC content. Microstructural analysis showed that Al_2O_3 and WC grain growth was significantly suppressed due to secondary phase addition, resulting in ultrafine (<500 nm) microstructures. Excellent mechanical properties, combining a Vickers hardness of 25 GPa, fracture toughness of 4.8 MPa $m^{1/2}$ and flexural strength of 1000 MPa, as well as electrical conductivity of 1.09E+6 Ω^{-1} m^{-1} were obtained for the Al_2O_3–60 vol% WC composite.

1. Introduction

As one of the most commonly applied engineering ceramics, Al_2O_3 has great potential to be used in many applications where low density, high hardness, chemical inertness and good high-temperature properties are required [1,2]. The intrinsic low fracture toughness and modest flexural strength of bulk Al_2O_3 ceramics however limits the applicability of pure alumina under severe conditions such as for high-speed cutting tools. The incorporation of secondary phase particulates into a ceramic matrix on the other hand can largely improve the mechanical properties of ceramics. The flexural strength and fracture toughness of Al_2O_3 matrix ceramics can be enhanced by incorporating secondary phase particles such as WC [3–6], TiC [7–9], NbC [10] or TiB_2 [11–13]. Al_2O_3 reinforced with hard ceramic particles represents a new class of materials with improved mechanical properties, hardness and wear resistance when compared to monolithic alumina ceramics [3–13]. Al_2O_3 reinforced with WC has been investigated for metalworking applications, combining resistance to high service temperatures and improved toughness [3–6]. The presence of dispersed WC particles is reported to enhance the hardness and thermal shock resistance of Al_2O_3 ceramics [14]. Another advantage of Al_2O_3–WC composites is the thermo-mechanically compatibility of Al_2O_3 and WC due to their similar thermal expansion coefficients, i.e., 4–9 × 10^{-6}/°C for Al_2O_3 and 5–7 × 10^{-6}/°C for WC, limiting thermal residual stresses during thermal cycling.

One possible route for the production of nanometric WC dispersed Al_2O_3 composite is high-energy reactive milling of WO_3, Al and C powder mixtures and subsequent sintering at elevated temperature [15,16]. WC, W_2C and Al_2O_3 were concurrently formed during the reduction and carbonisation processes [15,16]. The sintered composite obtained from in situ synthesized mixtures however exhibits an uneven WC grain size distribution from 1 to 10 μm [15]. Another approach is to sinter Al_2O_3–WC particulate mixtures by means of pressureless sintering or hot pressing. Fully dense Al_2O_3-composites with up to 10 vol% WC were obtained by pressureless sintering with or without Y_2O_3 sintering additive [3–6]. When forming a percolating WC grain structure around 30 vol% WC, densification of Al_2O_3–WC composites was hard to achieve without applying external pressure, resulting in a modest hardness and flexural strength. Densification of such composites to closed porosity is only possible by pressure-assisted sintering or with the use of liquid phase forming sintering additives.

Despite numerous reports on the synthesis and characterization of Al_2O_3–WC composites, little information is available on fine grained composites with a substantial WC content. In the present study, Al_2O_3–WC composites with up to 80 vol% WC were densified by pulsed electric current sintering (PECS), also known as spark plasma sintering (SPS). This sintering method has the advantage of higher heating rates and shorter dwelling times in comparison with conventional sintering techniques like hot pressing, pressureless sintering and hot isostatic pressing [17,18]. Higher densities,

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refined microstructures, clean grain boundaries, surface impurity elimination as well as an overall improvement in materials performance have been reported for several PECS ceramic materials [18–20].

2. Experimental procedure

2.1. Materials preparation

Al_2O_3–WC composites were made from Al_2O_3 (TM-DAR, 0.2 μm, Taimei Chemicals Co. Ltd, Nagano, Japan) and WC (CRC-015, 0.5 μm, Wolfram Bergbau und Hütten GmbH, Austria) powders. Composite grades A20W, A40W, A60W and A80W, with 20, 40, 60 and 80 vol% WC, respectively were prepared by low energy multidirectional mixing (Turbula T2A, WAB, Switzerland) in ethanol for 24 h using Al_2O_3 milling balls (ϕ = 10 mm, grade AL9, Cerlim, France). After mixing, the suspension was dried in a rotating evaporator at 65 °C. PECS (Type HP D 25/1, FCT Systeme, Rauenstein, Germany) was performed in a vacuum of 4 Pa. A pulsed electric current was applied with a pulse duration of 10 ms and pause time of 5 ms throughout all the experiments. The powder mixture was poured into a cylindrical graphite die with an inner diameter of 30 mm and outer diameter of 56 mm and sintered for 4 min at 1250–1650 °C, under a maximum pressure of 60 MPa, with a heating and initial cooling rate of 200 °C/min. During PECS, the mechanical pressure was increased continuously from 7 to 30 MPa during heating from 450 to 1050 °C and from 30 to 60 MPa within 1 min at 1050 °C. The maximum pressure was retained until completion of a 4 min dwell section at the maximum temperature. Graphite paper was used to separate the graphite die/punch/powder set-up. A 10 mm thick porous carbon felt insulation was placed around the graphite die to obtain a homogeneous temperature distribution in the powder compact. The sintering temperature was measured by a two-colour pyrometer (400–2300 °C, Impac, Chesterfield, UK), focussed at the bottom of a central borehole in the upper punch, only 2 mm away from the top surface of the sample. The actual set-up and temperature monitoring procedure is described in detail elsewhere [21].

2.2. Characterization

After PECS and sand blasting, the sintered discs had a thickness of 4 mm and diameter of 30 mm. The samples were subsequently cross-sectioned and polished to a 1 μm finish. The bulk density of the sintered composites was measured in ethanol. Phase identification was conducted by a θ–θ X-ray diffractometer (XRD, Seifert, Ahrensburg, Germany) using Cu Kα radiation (40 kV, 40 mA). The microstructure of the starting powders and sintered composites were examined by scanning electron microscopy (SEM, XL30-FEG, FEI, Eindhoven, The Netherlands). The Vickers hardness, HV_{10}, was measured (Model FV-700, Future-Tech Corp., Tokyo, Japan) with an indentation load of 98.1 N. The fracture toughness, K_{IC}, was calculated from the length of the radial cracks of the indentations according to the formula proposed by Anstis et al. [22]

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right), \quad (1)$$

where K_{IC} is the indentation toughness (MPa $m^{1/2}$), E the Young's modulus (GPa), H the Vickers hardness (GPa), P the indentation load (N) and c the half-length of the radial crack (m). The flexural strength at room temperature was measured in a three-point bending test (Series IX Automated Materials Testing System 1.29, Instron Corporation) with a span width of 20 mm and a crosshead displacement of 0.1 mm/min on rectangular (25 mm × 3 mm × 2 mm) bars, which were cut from the PECS discs by electrical discharge machining. All surfaces were ground (grinding wheel type D46SW-50-X2, Technodiamant, The Netherlands) on a Jung grinding machine (JF415DS, Göppingen, Germany). The edges of the rectangular bars were not chamfered. The elastic modulus, E, of the Al_2O_3–WC composites was measured on rectangular bars by the resonance frequency method [23]. The resonance frequency was measured by the impulse excitation technique (Grindo-Sonic, Lemmens N.V., Leuven, Belgium). The reported hardness, toughness and flexural strength values are the mean and standard deviation of five measurements. The electrical resistance of the samples was measured according to the 4-point contact method using a Resistomat (TYP 2302 Burster, Gernsbach, Germany).

3. Results and discussion

3.1. Densification behaviour

The densification during PECS, i.e. the shrinkage and shrinkage rate, of the Al_2O_3–WC composites was automatically recorded from the displacement of the upper piston of the equipment. Pure Al_2O_3 and WC powders were sintered as reference revealing that monolithic Al_2O_3 could be fully densified within 4 min at 1250 °C, whereas pure WC could only be densified at 1900 °C for 2–4 min at 60 MPa. The shrinkage behaviour of the A40W and A80W composite powders, PECS for 4 min at 1650 °C and 60 MPa, are compared in Fig. 1. Due to the high heating and cooling rate, the overall duration of the thermal cycle was less than 20 min. The onset of shrinkage at 1050 °C is due to the increased mechanical pressure from 30 to 60 MPa. For the Al_2O_3 matrix A40W composite (Fig. 1a), rapid densification was achieved during heating from 1150 to 1600 °C, with a maximum shrinkage rate at 1450 °C. Full density was reached after 1 min at 1650 °C under a pressure of 60 MPa. With increasing WC content, no apparent differences in the onset of densification and maximum shrinkage rate were detected in the WC matrix A80W composite. In contrast to the A40W ceramic, densification contin-

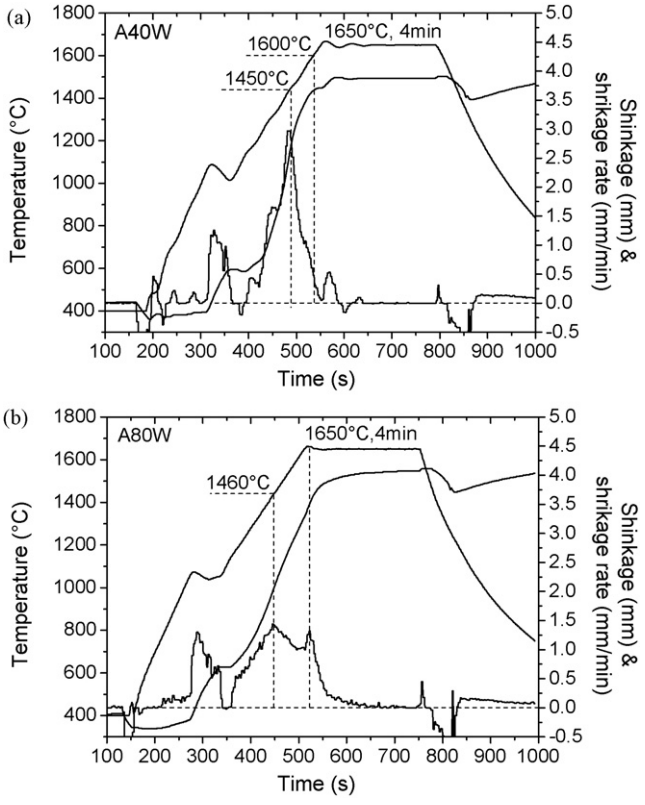

Fig. 1. Sintering behaviour of Al_2O_3 composites with 40 (a) and 80 (b) vol% WC during PECS for 4 min at 1650 °C and 60 MPa.