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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3359–3364
www.elsevier.com/locate/jeurceramsoc

Hardness degradation in liquid-phase-sintered SiC with prolonged sintering

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Available online 1 May 2007

Abstract

The effect of the sintering time on the Vickers hardness of liquid-phase-sintered SiC with 10 wt% YAG additives was studied for materials fabricated in Ar and N_2 atmospheres. The hardness of the Ar-sintered materials was found to decrease markedly with increasing sintering time, whereas, in contrast, the decrease was only marginal for the N_2-sintered materials. Berkovich nanoindentation tests showed that the softening could not be attributed in either case to degradation of the SiC grains, thereby pointing to the intergranular YAG phase as the responsible. That the cause was degradation of the YAG phase was confirmed by X-ray energy-dispersive spectrometry and Hertzian indentation tests. The far more pronounced softening observed for the Ar-sintered materials reflects the more severe degradation that the YAG phase undergoes during sintering in this atmosphere.

Keywords: Liquid-phase sintering; SiC; Hardness; Mechanical properties

1. Introduction

Liquid-phase sintering is the most effective way of densifying silicon carbide (SiC) at a moderate processing temperature without the simultaneous application of external pressure,[1–8] and therefore at low cost. In this context, the most widely studied additive system for SiC is Y_2O_3–Al_2O_3, especially when these components are chosen in the form $Y_3Al_5O_{12}$. Typically, prolonged sintering in an Ar atmosphere is used to process such a liquid-phase-sintered (LPS) SiC to improve its long-crack toughness,[8–13] since the sintering duration promotes grain coarsening, and the crack-bridging toughening mechanism in LPS SiC is more efficient with increasing grain size.[14] However, it has been shown that LPS SiC resulting from prolonged sintering, the so-called "in situ toughened SiC", are much softer than those sintered for shorter times.[8,10,13,15] Whereas reduced hardness facilitates machining of LPS SiC parts, it can limit their utility in various structural applications. Although hardness degradation with prolonged sintering is a well-documented effect, to the best of the authors' knowledge no studies have explored the underlying causes of the phenomenon.

Thus, the present study was designed with two objectives in mind. The first was to evaluate the influence of the sintering atmosphere (Ar or N_2-gas) on the hardness degradation in LPS SiC with prolonged sintering. For this propose, we used exclusively Vickers indentation tests. Our results showed that the Vickers hardness is much more stable when the sintering is performed in an N_2 atmosphere. The second objective was to investigate the origin of the softening in the two atmospheres. To this end, we combined mechanical tests of Berkovich nanoindentation, which allows the evolution of the SiC grain hardness to be followed, and Hertzian indentation, which allows the progression of the interface weakness to be monitored through the yield stress values. The results point to intergranular phase degradation as being the key to the softening in both cases, as was also confirmed by direct X-ray energy-dispersive spectrometry.

2. Experimental procedure

2.1. Processing

α-SiC powder (UF-15, H.C. Starck, Goslar, Germany) with 4.29 wt% Al_2O_3 (AKP-30, Sumitomo Chemical Company, New York, NY, USA) and 5.71 wt% Y_2O_3 (Fine Grade, H.C. Starck, Goslar, Germany) as additives was ball-milled for 24 h in ethanol

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0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.189

using ZrO_2 balls. This batch composition yields LPS SiC ceramics with 7.3 vol.% YAG after sintering. The slurry was dried, and the resulting powder deagglomerated and sieved. Compacts were made by uniaxial pressing (C, Carver Inc., Wabash, IN, USA) at 50 MPa, followed by isostatic pressing (CP360, AIP, Columbus, OH, USA) at 350 MPa. Sintering was performed (1000-3560-FP20, Thermal Technology Inc., Santa Rosa, CA, USA) at 1950 °C for 1–7 h in a flowing Ar- or N_2-gas atmosphere. Additional details of the processing procedure have been given elsewhere.[5,8,16] Surfaces for microstructural and mechanical characterizations were diamond-polished to 1 μm finish.

2.2. Microstructural characterization

Densities of the sintered ceramics were measured using the Archimedes method, with distilled water as the immersion medium. Cross-sections of all materials were plasma-etched (PT 1750, Fissions Instruments, East Sussex, UK), and were then observed under the SEM (S-3600N, Hitachi, Japan). Grain morphology analysis was performed from the SEM micrographs by image analysis on no less than 300 grains/ceramic. The nitrogen content in the N_2-sintered samples was measured using the inert gas (helium) fusion method (TNT-414, Leco Corporation, St. Joseph, MI, USA). Analysis of the chemical composition in selected samples was performed using the X-ray energy-dispersive spectrometer (XFLASH Detector 3001, Röntec GmbH, Germany) attached to the SEM.

2.3. Mechanical characterization

Vickers indentations were made (MV-1, Matsuzawa, Tokyo, Japan) at a load P of 98 N to measure the hardness of composites, determined[14] as $H_V = P/2d^2$, where d is the impression half-diagonal measured by optical microscopy. Ten separate indentations were performed on each material, and the mean of the measured values is reported here.

Nanoindentations were made (Micromaterials, Wrexham, UK) on selected composites using a Berkovich indenter (tip radius <100 nm) to measure the hardness of the constituents in these two-phase materials. Tests were conducted at variable load, such that the penetration depth was always 50 nm. Depth-sensing indentation hardness was evaluated from the indentation load–displacement curves, using the Oliver and Pharr method.[17,18] The hardness values reported here are the means of 100 indentations/sample.

Hertzian indentations were made (5535, Instron, Canton, MA, USA) using a tungsten carbide sphere of radius $r = 1.58$–7.94 mm, at peak loads in the interval $P = 15$–4000 N. Measurements of the contact radius a (made visible by first coating the specimen surfaces with a gold field) at each given load P and sphere radius r enabled indentation stresses, $p_0 = P/\pi a^2$, and indentation strains, a/r, to be calculated for the construction of the indentation stress–strain curves.[19–21] Indentation yield pressures p_Y were evaluated from the threshold indentation stresses at which the indentation data first deviated from linearity, and they were then used to calculate the yield stressses Y through the expression $Y = p_Y/1.1$ (see Fig. 1).

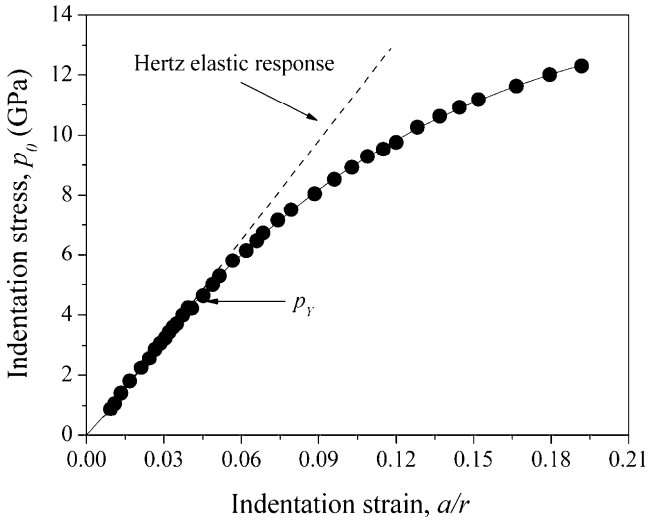

Fig. 1. Typical indentation pressure-strain curve at room-temperature for single-cycle Hertzian contacts in LPS SiC. The points are the experimental data for the material sintered for 1 h in the Ar atmosphere. The solid line through the data is a guide for the eye. The dashed line represents Hertzian-elastic response. The error bars for experimental data are lower than the point size.

3. Results and discussion

Fig. 2A–D shows SEM micrographs of the microstructures obtained for the extreme sintering times (1 and 7 h), in the two atmospheres. One observes that, consistent with the densities measured by the Archimedes method that indicated complete densification, the materials are pore free. With respect to the microstructure of the Ar-sintered materials, as shown in Fig. 3, up to 5-h sintering the grains have almost equiaxed form and sizes that increase with increasing sintering time. On the contrary, the 7-h sintered material contains both elongated and equiaxed grains, whose sizes are even larger than before (see Fig. 3). A detailed explanation of the microstructural evolution in LPS SiC fabricated in Ar atmosphere is given elsewhere.[16,22,23]

The grains in all the materials sintered in N_2 atmosphere have a nearly equiaxed form (aspect ratio 1.4), as shown in Fig. 3. With respect to the grain size, no appreciable change was observed with increasing sintering time, the value remaining within the ultrafine scale (see Fig. 3). The high viscosity of the liquid phase during sintering due to the incorporation of nitrogen from the atmosphere is the cause of the inhibition of grain growth mechanisms.[24] Indeed, we measured nitrogen contents of 0.3133 wt% and 0.6477 wt% after 1 h- and 7 h-sintering in the N_2 atmosphere. A detailed description of the microstructural evolution in LPS SiC fabricated in a N_2 atmosphere is given elsewhere.[24]

The hardness values obtained by Vickers indentation are shown in Fig. 4. One observes that the Ar- and N_2-sintered materials had similar hardnesses at 1 h-sintering, but the N_2-sintered materials were increasingly harder than their Ar-sintered counterparts with increasing sintering time. Furthermore, the hardness of the Ar-sintered materials decreased continuously by 5 GPa with increasing sintering time from 1 to 7 h, whereas the N_2-sintered materials decreased only marginally (by 1 GPa).