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Improving the sliding wear resistance of SiC nanoceramics fabricated by spark plasma sintering via gentle post-sintering annealing

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Experimental evidence is presented for the improvement of the sliding wear resistance of an SiC nanoceramic processed by spark plasma sintering (SPS) with post-sintering annealing. It is inferred that gentle annealing without nanograin growth strengthens the grain boundaries induced by the ultrarapid nature of SPS, and the consequent improvement in grain cohesion delays the onset of the severe-wear regime without affecting the rates of mild and severe wear. Implications for the fabrication of highly wear-resistant nanoceramics are discussed.

Keywords: Sliding wear; Nanoceramics; Spark plasma sintering; Tribological properties

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Grain refinement down to the nanoscale increases hardness and reduces the size of incipient grain boundary flaws, factors which are very important for improving the wear resistance of polycrystalline ceramics [1–3]. Nanostructuring has therefore emerged as a prime strategy for the processing of advanced, highly wear resistant triboceramics [1], with the consequent growing interest in the fabrication of nanoceramics by ultrarapid sintering techniques. Recent observations made of the abrasive wear of an Al_2O_3 nanoceramic (150 nm grain size) fabricated by the technique of self-propagating high-temperature synthesis plus quick pressing point to the possibility of achieving further improvements in wear resistance via post-sintering annealing (PSA) aimed at relaxing the non-equilibrium grain boundaries (GBs) induced by ultrarapid densification [4]. A different study of the mechanical properties, but not the wear, of a fine-grained Al_2O_3 (0.5–2 μm grain size) prepared by spark plasma sintering (SPS) has also shown the existence of strained GBs and their relaxation with PSA [5]. The non-conventional nature of the GBs in these advanced nanostructured ceramics seems reasonable because the ultrarapid sintering techniques used in their processing have in common the use of ultrarapid heating and cooling ramps, together with very short soaking times [6–8].

Today, SPS is by far the most popular of the ultrarapid sintering techniques, and is being used to process a multitude of nanoceramics and ultrafine-grained ceramics, including triboceramics (SiC, Si_3N_4, Al_2O_3, B_4C, etc.) [1,4,9–15]. Thus, in view of the previous grinding and polishing wear studies in Al_2O_3 [4], investigation of the possible effects of PSA on the wear resistance of spark plasma sintered nanoceramics under sliding contact is fundamental for its technological consequences. This was the central objective of the present study, in which the sliding wear resistance of the same SiC nanoceramic fabricated by SPS using liquid-phase-forming additives (i.e. $Y_3Al_5O_{12}$ or YAG) is compared before and after gentle PSA. A liquid-phase-sintered (LPS) SiC was chosen so as to provide the study with greater generality, and to extend it to two-phase ceramics since the two previous studies [4,5] were conducted with single-phase Al_2O_3.

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Commercial nanocrystalline powders (Nanostructured and Amorphous Materials Inc., USA) of SiC (~45–55 nm average particle size) and YAG (~40 nm average particle size) were mixed in appropriate amounts to produce an LPS SiC ceramic with 10 vol.% YAG as a secondary phase. The homogenized powder mixture was loaded into a graphite die (12-mm diameter) lined with graphite foil and surrounded by a 1 cm thick graphite blanket to minimize heat loss, then spark plasma sintered (Dr. Sinter SPS-2050, Sumitomo Coal Mining Co.) in dynamic vacuum (i.e. ~6 Pa) at 1800 °C under 75 MPa pressure using a heating ramp of 100 °C min^{-1} up to 1750 °C and 50 °C min^{-1} there onwards to avoid overshooting. Once 1800 °C was reached, the electrical power was shut off to allow rapid cooling to room temperature (i.e. in 1–2 min). Figure 1A is a representative scanning electron microscopy (SEM; Quanta 3D FEG, FEI, Eindhoven, The Netherlands) micrograph of the fracture surface of the resulting ceramic showing its complete densification (confirmed by the Archimedes method) and the nanoscale size (i.e. ~83 ± 2 nm) of its SiC grains. This demonstrates the feasibility of obtaining nanostructured SiC ceramics by liquid-phase-assisted SPS, the conditions of which have to be optimized to reach full densification with minimal grain growth, depending on the features of the SiC nanopowder and the amount and type of sintering aid. For the comparative sliding wear study, the as-processed nanoceramic was annealed at 1200 °C (heating and cooling ramps of 10 and 20 °C min^{-1}, respectively) for 12 h in vacuum. The choice of this particular PSA was based on preliminary tests aimed at identifying a high-temperature heat treatment sufficiently gentle to retain the original size of the SiC nanograins (i.e. ~84 ± 3 nm), as confirmed in the SEM micrograph of Figure 1B. Nevertheless, the grain structure seems to be somewhat more faceted after PSA and the fracture surface exhibits less grain pull-out, which suggests improved grain cohesion due to strengthened GBs. According to the two XRD patterns shown in Figure 2, the PSA did not affect the phase composition, which in both cases consists of β-SiC nanograins and YAG secondary phase. This is important as it rules out any phase-composition effect in this comparative study of wear resistance.

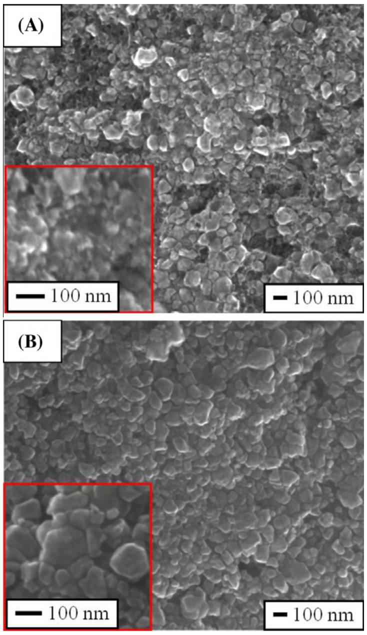

Fig. 1. SEM micrographs of fracture surfaces of the broken SiC nanoceramic (A) in its as-processed condition and (B) after PSA at 1200 °C for 12 h in vacuum. The inset in (A) is a magnified region with tiny nanocrystals (~10 nm size). The inset in (B) is also a magnified region.

Figure 3A and B shows bright-field transmission electron microscopy (TEM; Titan 80-300 TEM/STEM, FEI, USA) micrographs of the SiC nanoceramic before and after PSA, respectively, taken at 300 kV. In the as-processed condition, the microstructure consists of β-SiC nanograins and YAG nanoparticles (as confirmed by transmission electron diffraction and fast Fourier transform patterns from high-resolution TEM (HRTEM) images – not shown), as well as pockets filled with tiny SiC nanocrystals (as confirmed by energy-dispersive X-ray spectrometry – not shown) ~10 nm in size (as also seen by SEM in the inset of Fig. 1A) and amorphous phase (see the inset of Fig. 3A). The β-SiC nanograins have mostly a relatively rounded morphology, with sizes in the range of 50–300 nm. After PSA, the microstructure had changed little, except that the GBs seemed somewhat flatter than before and the grains more faceted, as one also infers from the high-angle annular dark-field (HAADF) STEM, bright-field TEM and HRTEM images (see the three insets in Fig. 3B). The effects of PSA, which are more pronounced with increasing PSA temperature, have been observed before, in nanocrystalline Al_2O_3 [4,5], and attributed to the GBs reaching a more equilibrium state (in turn resulting in better grain cohesion and strengthened GBs). To confirm the increasing flatness of the GBs and grain faceting, the as-processed SiC nanoceramic was also annealed at 1400 °C for 6 h in vacuum, and its microstructure was again examined by TEM. As can be seen in the bright-field TEM and HAADF STEM (as inset) micrographs in Figure 3C, the grains become more faceted and the GBs flatter. This was further corroborated by the SEM observation of the corresponding fracture

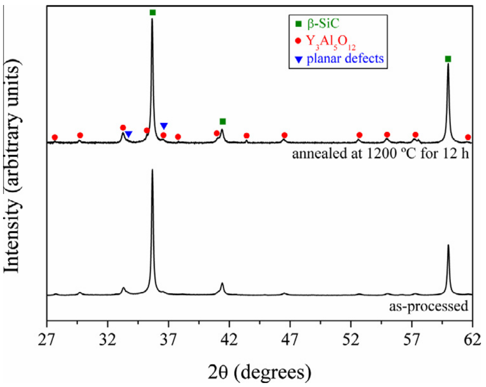

Fig. 2. XRD patterns of the SiC nanoceramic before and after PSA at 1200 °C for 12 h in a vacuum. The phase identification, performed with the aid of the PDF2 database, is indicated.