Original Article

Fabricating eco-friendly nanocomposites of SiC with morphologically-different nano-carbonaceous phases

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ABSTRACT

A route based on aqueous colloidal processing followed by liquid-phase assisted spark-plasma-sintering (SPS) is described for fabricating eco-friendly nanocomposites of SiC with nano-carbonaceous phases (nanotubes, nanoplatelets, or nanoparticles). To this end, the conditions optimizing the aqueous colloidal co-dispersion of SiC nanoparticles, $Y_3Al_5O_{12}$ nanoparticles (acting as sintering additives), and carbon nanotubes (CNTs), graphene oxide (GO) nanoplatelets, or carbon black (CB) nanoparticles were first identified. Next, homogeneous powder mixtures were prepared by freeze-drying, and densified by liquid-phase assisted SPS, thus obtaining nanocomposites of SiC with CNTs, reduced GO (rGO) nanoplatelets, or pyrolized + graphitized CB (p + gCB) nanoparticles. It is also shown that these nanocomposites are dense and have a high hardness of ~20 GPa regardless of the nano-carbonaceous phase chosen, but are markedly tougher with CNTs and rGO (i.e., with high aspect ratio nano-carbonaceous phases). Finally, arguments are provided for the appropriate choice of nano-carbonaceous phases for engineering ceramic nanocomposites.

1. Introduction

There is great interest today in the fabrication of composites based on ceramic matrices with nano-carbonaceous second phases dispersed in the microstructure (i.e., carbon nanotubes (CNTs), nanoplatelets of graphene (GNPs), graphene oxide (GO) or reduced graphene oxide (rGO), graphite nanoparticles (NG), carbon black (CB), etc.) [1–5]. This is because these composites have enhanced mechanical and functional properties relative to conventional ceramics [4,5]. This approach is being applied successfully to liquid-phase-sintered (LPS) SiC, which is a prominent non-oxide engineering ceramic for structural applications at both room and high temperatures [6–20]. Certainly, with respect to mechanical properties, in LPS SiC enhancements have been observed in (i) toughness with NG [21], GNPs [22], rGO [22], and CNTs [23,24], (ii) strength, contact-damage tolerance, and machinability with GNPs [22,25,26] and rGO [22,25], and (iii) wear resistance with NG [21], GNPs [27], and CNTs [23]. Regarding functional properties, in LPS SiC with GNPs, high thermal and electrical anisotropies have been observed [28,29], as well as prominent local transport properties [30]. Electrically functional cellular porous structures of LPS SiC with GNPs have also been fabricated, using robocasting as shaping technique [31].

Cellular hybrid materials of LPS SiC with certain types of aligned CNTs have also been developed having superhydrophobic and superoleophilic properties [32]. Thus, these examples show that it is possible to "reinforce" and functionalize LPS SiC with nano-carbonaceous second phases.

There are two critical aspects making the fabrication of the composites of ceramics with nano-carbonaceous second phases very problematical. One is to correctly disperse the nano-carbonaceous phases in the ceramic matrix [5] without damaging them, and the other is to prevent their degradation during densification at high temperatures [5]. The problem is aggravated in the case of nanocomposites due to the additional difficulty of retaining nanograins during sintering, and becomes especially challenging if the condition of eco-friendly fabrication is imposed. This condition is met, for example, if the powder batches are first prepared by aqueous colloidal processing and next densified by spark-plasma sintering (SPS). The powder preparation stage is thus free from the safety and environmental concerns inherent in alcoholic slurries, and the densification stage is ultra-fast and energy efficient.

Accordingly, motivated by this challenge, we here explore the eco-friendly fabrication by aqueous colloidal processing plus liquid-phase assisted SPS of nanoceramics of SiC with varied-morphology nano-

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carbonaceous phases (i.e., nanotubes–CNTs, nanoplatelets–rGO, and nanoparticles–pyrolyzed + graphitized CB (p + gCB)), and compare their mechanical properties (hardness and toughness).

2. Experimental procedure

The starting powders, obtained from commercial sources and used in their as-received condition, were: (i) β-SiC with a mean particle size of 45–55 nm, (ii) $Y_3Al_5O_{12}$ (YAG) with a mean particle size of ~40 nm, and (iii) multiwall CNTs with lengths of 0.5–2 μm, thicknesses of 10–20 nm and OH^- functionalization (the three from Nanostructured and Amorphous Materials Inc., USA), as well as (iv) GO with lengths of 1–4 nm and thicknesses of 0.7–1.2 nm (from Nanoinnova Technologies, Spain), and (v) CB with a mean particle size of ~32 nm (from Calblack N220, H.C. Starck, Germany). Nano-YAG was the sintering additive, and GO was chosen as starting material instead of rGO to facilitate the aqueous colloidal processing given that GO is then expected to transform into rGO during SPS. Three powder batches were prepared from these powders, as described next.

Firstly, dilute suspensions of nano-SiC, of nano-YAG, and of each of the nano-carbonaceous starting materials (i.e., CNTs, GO, or CB) were individually prepared to a solid content of 0.1 g/l in a solution of de-ionized water mixed with ethanol in a volume ratio of 9:1 together with KCl 10^{-2} M as inert electrolyte, and, once equilibrated, their colloidal stability was studied by zeta potential measurements (Zetasizer Nano-ZS, Malvern, UK) as a function of pH and deflocculant content (this latter done, as usual, at natural pH to allow free adsorption of the polyelectrolyte introduced to shift down the isoelectric point). The pH was adjusted in the acidic-basic range using 10^{-1} M HCl or KOH solutions, respectively. Commercially available polyelectrolytes were used as deflocculants, in particular, PKV (Produkt KV5088, Zschimmer-Schwarz, Germany) for nano-SiC and PAA (Duramax™ D-3005, Rohm & Haas, USA) for nano-YAG and CB. PKV is a synthetic anionic poly-electrolyte with unknown composition that has demonstrated its suit-ability for the dispersion of non-oxide ceramics (including carbides [24,33–38]), whereas PAA is an ammonium salt of polyacrylic acid that is known to be effective for oxide ceramics and metals [24,33–39]. Neither CNTs nor GO need deflocculants due to their surface functio-nalization. Secondly, multi-component suspensions with a total solids content of 5 vol.% were formulated with composition of 86.24 vol.% nano-SiC, 6.76 vol.% nano-YAG, and 7 vol.% nano-carbonaceous phase. The suspensions were prepared under continuous mechanical stirring with helices, using the following protocol of sequential addition. First, the pH of a mixture 9:1 by volume of de-ionized water and ethanol was adjusted to the desired value by dropwise addition of an aqueous so-lution of 25 wt.% tetramethylammonium hydroxide (TMAH, Aldrich-Chemie, Germany). Next, the desired amount of either CNTs, GO, or CB was added, followed by initial sonication, incorporation of the PAA content required for their appropriate dispersion, and stabilization for 5 min. Then, more PAA was added as needed to disperse the YAG na-noparticles, followed by addition of the nano-YAG powder and inter-mediate sonication for 1 min. Lastly, PKV was added as required to disperse the SiC nanoparticles, followed by addition of the nano-SiC powder and final sonication for different times to thus investigate its influence on the rheological behaviour of the suspension. The pH was maintained at the desired value throughout the entire process.

The rheological behaviour of the resulting suspensions was eval-uated using a rheometer (Mars, Haake, Thermo, Germany) operated in controlled shear rate mode. The measuring system consisted of a double-cone and plate, with cone angle of 2°, provided with a solvent trap to avoid evaporation. The measurement cycle of the flow curves involved a linear stretch of shear rate increase from 0 to 1000 s^{-1} in 300 s, then a plateau at 1000 s^{-1} for 60 s, and lastly a linear decrease to zero shear rate also in 300 s. The thixotropy/rheopexy was determined from the area of the flow curve's hysteresis loop, and the viscosity by direct reading at 1000 s^{-1} in the uploading stretch.

Well-dispersed suspensions of nano-SiC + nano-YAG + CNTs/GO/ CB were then frozen within a rotatory evaporator (RV10 basic, IKA, Germany) immersed in a liquid–N_2 bath and subsequently freeze-dried (Cryodos-50, Telstar, Spain) at −50 °C and 0.3 mPa, after which the resulting powder mixtures were examined by scanning electron mi-croscopy (SEM; Quanta 3D FEG, FEI, The Netherlands). Next, each of the three powder mixtures was densified by SPS (Dr. Sinter SPS-2050, Sumitomo Coal Mining Co., Japan), under the following conditions: atmosphere of dynamic vacuum (which is indeed slightly reducing), peak temperature of 1700 °C, heating ramp of 100 °C min^{-1}, soaking time of 5 min, and uniaxial pressure of 75 MPa. The resulting nano-composites were characterized using SEM and Raman spectroscopy (Nicolet Almega XR, Thermo Scientific, UK). The Raman spectra of the as-received CNT, GO, and CB powders were also acquired, and com-pared with those of the corresponding nanocomposites to elucidate possible changes during SPS. The relative density of the nanocompo-sites was measured using the Archimedes method.

Lastly, the nanocomposites were characterized mechanically by Vickers indentation tests (MV-1, Matsuzawa, Japan) at 98 N load (ten separate indentations on each material) to thus determine their hard-ness and fracture toughness by standard procedures and formulae [40].

3. Results and discussion

The first step of the routine for the eco-friendly fabrication of these appealing ceramic nanocomposites is to optimize the aqueous colloidal co-dispersion of nano-SiC, nano-YAG, and either CNTs, GO, or CB, in the desired proportions. Fig. 1 shows the evolution of the zeta potential as a function of pH for the individual dilute suspensions of nano-SiC [33–35], nano-YAG [33–35], CNTs [33,34], GO, and CB. It can be seen that nano-SiC and nano-YAG have their isoelectric points at pH ~5.3 and 8.8, respectively. It can also be seen that CNTs and GO have their surface negatively charged in the whole range of pHs investigated, and that their isoelectric point will occur at pH < 2. This is because CNTs are intentionally functionalized with hydroxyl surface groups, whereas GO has carboxylic acid, hydroxyl, epoxy, and carbonyl surface groups [41]. Thus, unlike rGO, GO is hydrophilic and therefore preferable as starting material when preparing suspensions, inks, and pastes in aqu-eous media. Finally, it can also be seen that CB behaves as nano-SiC does because the nano-SiC surface is enriched with some amorphous carbon [33]. By imposing the co-dispersion condition (i.e., the same sign of surface charge for the three compounds being mixed with zeta potential of the order of ~ ± 20 mV) it is inferred that the nano-SiC + nano-YAG + CNTs/GO/CB suspensions have to be prepared at pH~12. To avoid these extreme conditions, anionic polyelectrolytes
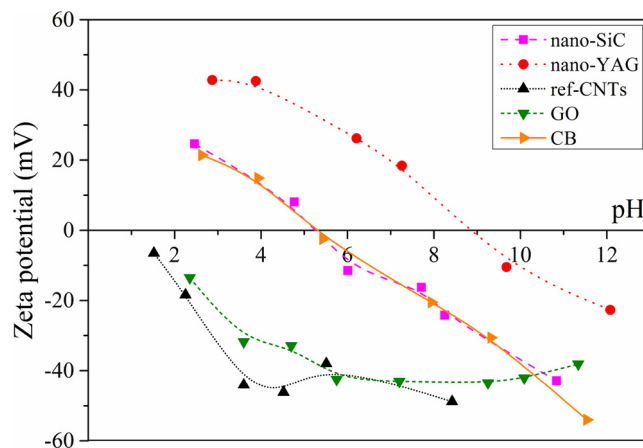

Fig. 1. Dependence on pH of the zeta potential for the individual dilute sus-pensions of nano-SiC [33–35], nano-YAG [33–35], CNTs [33,34], GO, and CB. Lines are to guide the eye.