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Silica-graphene nanoplatelets and silica-MWCNT composites: Microstructure and mechanical properties

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ABSTRACT

Silica-based composites were fabricated by powder metallurgy (PM) route using nanofillers like exfoliated graphite nanoplatelets (xGnPs) and multiwalled carbon nanotubes (MWCNTs) by both conventional sintering and spark plasma sintering (SPS) route. SiO_2-0.5, 3, 5 vol% xGnP and SiO_2-0.5, 3, 5 vol% MWCNT composites have been prepared and a comparative study of the effect of the addition of xGnP and MWCNT on the mechanical properties of the SiO_2-based composites has been done. The microstructural characterization of the various SiO_2-based composites was done by optical microscopy, SEM and HRTEM. In order to compare the effect of the addition of xGnP and MWCNT to SiO_2, various mechanical properties like hardness, fracture toughness and wear behaviour of the composites were determined. The results indicate that the SiO_2-xGnP composites possess better mechanical properties as compared to the SiO_2-MWCNT composites.

1. Introduction

Graphene is a monolayer of covalently bonded sp^2-hybridized carbon atoms having a combination of high specific surface area, high aspect ratio and outstanding electrical, mechanical and thermal properties. It has a density of ~2.26 g/cm^3, Young's modulus of ~1 TPa, intrinsic tensile strength of ~130.5 GPa and fracture strength of ~125 GPa. Its theoretical specific surface area is ~2630 m^2/g. The electrical resistivity of graphene is 10^{-6} Ω·cm and its in-plane thermal conductivity is among the highest of known materials and is ~5000 W/m·K [1, 2]. These properties make graphene an ideal reinforcement for composites. Graphene and its derivatives such as graphite nanoplatelets and graphite oxide have been explored as additives for the development of various new devices having superior properties. Bagheri et al. [3] reported an electrochemical sensor for the detection of melatonin and dopamine using graphene decorated with Fe_3O_4 magnetic nanoparticles on a carbon paste electrode. Carbon nanotubes (CNTs) on the other hand also have a unique structure and unrivaled properties. CNTs are very effective as reinforcement as they have a very high aspect ratio which is beneficial for effective load transfer in the matrix. Multiwalled carbon nanotubes (MWCNTs) have a density of ~2.6 g/cm^3, the aspect ratio in the range of 1000–10,000 and elastic modulus of > 1 TPa [4, 5]. Recently, Afkhami et al. [6] designed a potentiometric sensor for the rapid detection of nanolevel lead in hazardous wastes using a carbon paste electrode consisting of ionic-liquid/Schiff base/MWCNTs/nanosilica. Both 2D graphene and 1D CNTs are allotropes of carbon and are promising nanofillers for the development of composites. A novel sensor for sensitive determination of atropine in complex matrices, based on carbon paste electrode modified by Co_3O_4-reduced graphene oxide has been reported [7]. There is a rapid increase of interest in these nanomaterials for use as reinforcement in ceramic matrix composites (CMCs) as they can act as toughening elements to overcome the intrinsic brittleness and lack of mechanical reliability of monolithic ceramics which are otherwise attractive for their high stiffness and hardness as well as excellent functional properties. CMCs having a very low loading level of carbonaceous nanofillers like graphene and CNTs (< 5 vol%) are expected to have much higher toughness as compared to the monolithic ceramics. The synergetic effects of the nanofillers can enhance their mechanical properties to a significant extent [8, 9]. Among the various CMCs, silica-based composites have gained wide attention due to the excellent properties of silica. Silica (SiO_2) is chemically inert, has good abrasion resistance, high electrical insulation and better thermal stability because of which it is an ideal matrix for the development of composites. Silica is amorphous and porous. The density of amorphous silica is ~2.19 g/cm^3 and is lighter than both graphene (2.26 g/cm^3) and MWCNT (2.6 g/cm^3). Its melting point is 1713 °C and its tensile strength is ~110 MPa. Apart from high modulus (33.5–36.8 GPa), high hardness (4.5–9.5 GPa) and extreme temperature sustainability, silica is also water-soluble, nontoxic and biocompatible and is therefore ideal for biomedical applications [10]. Silica is used

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both as a precursor for the fabrication of other ceramic products as well as a material on its own. A sensor based on Fe_3O_4·SiO_2·TiO_2-MIP nanocomposite with a well-defined core-shell structure has been fabricated for the sensitive and selective determination of ephedrine in pharmaceutical dosage [11]. However, despite the numerous advantages and unique properties of silica, its low compressive strength, poor shock resistance, extremely high brittleness and very low dimensional tolerance during processing restricts its use in a wide range of applications. Several researchers have reported a significant improvement in the mechanical properties of the CMCs reinforced by graphene and CNTs at relatively low loading levels [12–14]. Therefore, the development of SiO_2 based composites by using these carbonaceous nanofillers can effectively enhance the physical and mechanical properties of monolithic SiO_2. The silica-based composites having low loading level of these carbonaceous nanofillers combine the advantages of both silica matrix and the excellent properties of the nano-reinforcement particles. However, one of the major challenges associated with the development of CMCs using nanofillers is their proper dispersion within the ceramic matrix which is essential to utilize their extraordinary properties. Nanofillers like the graphite nanoplatelets and the MWCNTs show a high tendency to agglomerate and the powder metallurgy (PM) technique is one of the most effective methods for dispersing them in the ceramic matrix. The other major challenge faced during the processing of bulk CMCs reinforced by nanofillers like graphite nanoplatelets and MWCNTs, is the poor thermal stability of these nanofillers at temperatures above ~600 °C, as ceramics start to densify and sinter at temperatures above 1000 °C [15–17].

In the present study, SiO_2-0.5, 3, 5 vol% xGnP and SiO_2-0.5, 3, 5 vol % MWCNT composites have been fabricated by PM route. Powder mixtures of SiO_2-xGnP and SiO_2-MWCNT prepared by blending in a ball mill were compacted and later sintered. The various composites were prepared by both conventional sintering and spark plasma sintering (SPS). Conventional sintering was carried out at 1350 °C for a period of 4 h in inert atmosphere whereas SPS was carried out at 1350 °C under 40 MPa pressure for a period of 10 min. In order to find out the effect of the addition of xGnP and MWCNT on the various properties of silica, pure silica samples were also prepared by both conventional sintering and SPS.

2. Experimental

2.1. Synthesis of nanofillers

Powder metallurgy (PM) route was adopted to develop the SiO_2-xGnP/MWCNT composites in order to achieve uniform dispersion of the nanofillers in the SiO_2 matrix. For the development of the composites, silica powder having a size in the range of 100–200 mesh was procured from Thermo Fischer Scientific Pvt. Limited, India. However, both the nanofillers have been synthesized individually and processed carefully before their introduction into the SiO_2 matrix. The xGnP has been synthesized by thermal exfoliation of the graphite intercalation compound (GIC) (Fig. 1) [18, 19].

MWCNTs were synthesized by the low-pressure chemical vapor deposition (LPCVD) technique. Due to their high aspect ratio and tendency to agglomerate, de-agglomeration of the MWCNTs is a major challenge. The MWCNTs were acid functionalized for their homogeneous dispersion in the SiO_2 matrix [20, 21]. Schematic diagram showing the route opted for the synthesis of MWCNTs and their acid functionalization process have been shown in Fig. 2.

2.2. Fabrication of SiO_2-xGnP and SiO_2-MWCNT composites

Powder processing route was opted for the fabrication of SiO_2-xGnP/MWCNT composites in order to achieve uniform dispersion of the nanofillers in the SiO_2 matrix. The detailed procedure for the fabrication of SiO_2-xGnP and SiO_2-MWCNT composites from the milled powder mixtures has been described in the schematic diagram in Fig. 3.

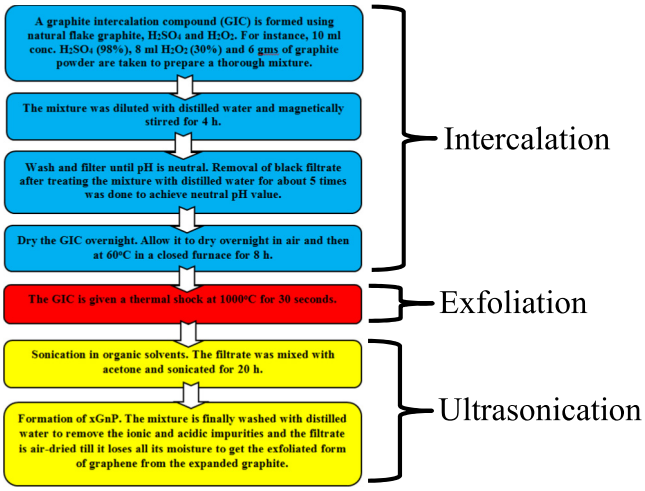

Fig. 1. Synthesis of xGnP.

Pure SiO_2 and SiO_2-0.5, 3 and 5 vol% xGnP and SiO_2-0.5, 3 and 5 vol % MWCNT composites were fabricated by both conventional sintering and SPS.

2.3. Sintering

For the consolidation of the SiO_2 based composites, both pressureless and pressure-assisted sintering routes were opted. In the case of conventional sintering, green compacts are prepared in a uniaxial cold compaction machine under a load of 310 MPa, which were later sintered at 1350 °C for 4 h in inert Ar atmosphere. For the pressure-assisted sintering, SPS was carried out at 1350 °C for 10 min using Dr. Sinter 515S apparatus (SPS Syntex Inc., Kanagawa, Japan) with a pulse on-off ratio of 12:2. A heating rate of 100 °C/min and pressure of 40 MPa was applied. The powder mixture, loaded in a graphite die of diameter 15 mm was placed inside the SPS chamber between two graphite electrodes under a vacuum of 6 Pa and high purity Ar was then purged at a flow rate of 2 L/min in the chamber to ensure minimal oxidation of the powders. During SPS a constant voltage of 20 V was maintained and the current flow was around 1200 A. The pressure was removed at the end of the sintering and the samples were cooled naturally. The SPS profile used for the development of the composites is shown in Fig. 4 [22].

2.4. Characterization

The morphology of the sintered composites was analyzed using Zeiss Axio Scope.A1 optical microscope, a JEOL-JSM-6480LV scanning electron microscope (SEM) and a Nova NanoSEM 450/FEI field emission scanning electron microscope (FESEM) both enabled with energy-dispersive x-ray (EDX) analysis system. The morphology of the ball milled blended powders was also analyzed using a JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) at an acceleration voltage of 200 keV. The structural evolution and the formation of any new phase on sintering were analyzed using x-ray diffraction (XRD). The blended powders and the sintered composites were characterized by a Rigaku Ultima-IV diffractometer using Cu Kα (λ = 1.5409 Å) radiation.

2.5. Mechanical testing

The various mechanical properties like hardness, wear behaviour and fracture toughness of the sintered composites were determined. For pure SiO_2 and various SiO_2 based composites, the hardness values were