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Effect of homogenization treatment on the fracture behaviour of silicon nitride/graphene nanoplatelets composites

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Abstract

Si_3N_4 based composites with 7 wt.% of graphene nanoplatelets (GNPs) were prepared using different homogenization methods. Si_3N_4/GNPs powder mixtures were dispersed in isopropanol and homogenized by attritor milling, ball milling or planetary ball milling. The ball milling technique was also used for the homogenization of Si_3N_4/GNPs mixture in dry state. Fractography analysis was carried out in order to assess the individual homogenization treatment. Depending on the homogenization methods, the size of the processing flaws varied from 20 μm up to 400 μm. The agglomeration of the GNPs and the residual porosity were found as the most frequently observed types of the critical flaws. The planetary ball milling with previous ultrasonication of GNPs in isopropanol was found to be the most promising homogenization technique, resulting in the composites with the highest bending strength (average value is 740 MPa) and the lowest average size of the processing flaws (around 20 μm).

Keywords: Silicon nitride; Graphene nanoplatelets; Homogenization; Fractography; Bending strength

1. Introduction

Carbon is one of the most abundant elements on earth. The diversity in bonding makes carbon the most important element in a variety of disciplines. The ability to form large stable frameworks of interconnecting bonds with different hybridization allows carbon to form innumerable compounds with varying dimensionalities. A recent addition to this large family of carbon allotropes is graphene, a two-dimensional monolayer of sp2 carbon atoms arranged in a honeycomb lattice,[1] with exceptional charge transport, thermal, optical, and mechanical properties. Consequently, graphene in the form of graphene nanoplatelets (GNPs), graphene oxide (GO) or exfoliated graphene nanoplatelets (xGNPs) has become an ideal filler in fabrication of different polymer,[2] metal[3] or ceramic[4–8] composites. Ceramic composites with the addition of graphene nanoplatelets (stacks of graphene layers, with thickness in the range from few nanometer to tens of nanometers) has become an intense field of research due to the potential improvement of mechanical and functional properties, such as fracture toughness, bending strength, or tribological properties because of the lubricating nature of carbon.[9–12] One of the studied ceramic materials is silicon nitride, due to its excellent strength at room and elevated temperatures, good resistance to corrosive environments and excellent wear resistance.[13] When GNPs are introduced into the silicon nitride ceramic matrix several factors have a great impact on the final properties of the composite. First of all, it is the amount of GNPs added into the ceramic matrix. The addition of 1 wt.% multilayer graphene (MLG) increased the fracture toughness and Vickers hardness of hot isostatic pressed silicon nitride from 6.89 MPa $m^{1/2}$ to 9.92 MPa $m^{1/2}$, and from 15.38 to 16.38 GPa, respectively.[14] In the case of spark plasma sintered silicon nitride based ceramics, the addition of 1.5 vol.% of MLG resulted in the increase of the fracture toughness from 2.8 MPa $m^{1/2}$ to 6.6 MPa $m^{1/2}$.[15] However, the addition of a higher content of the graphene platelets deteriorated

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the mechanical properties; for example the four point bending strength of HIP-ed silicon nitride based ceramics with 3 wt.% of MLG[16] was reported to be 451 MPa, while the composite with 1 wt.% exhibited the bending strength of 642 MPa. Additionally, a type of graphene platelets can also modify the properties after sintering because of the different dispersion grade of the graphene platelets, which has a direct impact on the final density of the sintered materials.[10,16]

When considered silicon nitride based composites with several types of graphene platelets, the following sintering techniques have been used: hot isostatic pressing (HIP),[14] gas pressure sintering (GPS)[10] and spark plasma sintering (SPS).[15] However, to authors' best knowledge, the effect of the homogenization treatment of the graphene nanoplatelets on the final properties of the silicon nitride based composites has not been investigated yet. Moreover, fractography study on the silicon nitride based ceramics reinforced by GNPs has not yet been reported as well.

Therefore, the aim of the present contribution is to investigate the influence of various homogenization techniques of Si_3N_4/GNPs mixture on the fracture behaviour of the silicon nitride based composites prepared by hot press sintering. A relatively high amount of GNPs (7 wt.%) was used in order to assess critically the dispersion of GNPs, as it is well known that the dispersion of GNPs becomes difficult when the amount is increased. In order to disperse GNPs in the powder mixture of silicon nitride and sintering additives, five homogenization treatments were used. The isopropanol mixture of Si_3N_4/GNPs was planetary ball milled with or without using ultrasonication of GNPs prior to the addition of Si_3N_4 with the sintering additives into isopropanol; attritor milled with the ultrasonication of GNPs in isopropanol, ball milled with the ultrasonication of GNPs in isopropanol, and ball milled without using a liquid medium. Since the fractography analysis is a powerful tool for the evaluation of the processing routes and reveals the presence of the strength limiting flaws, a thorough fractography investigation is reported in the present work.

2. Experimental part

2.1. Powder characterization

The following starting materials were used for the preparation of Si_3N_4/GNPs ceramic composites: Si_3N_4 (grade SN-E10, UBE Industries, Japan), Yb_2O_3 (Pacific Industrial Development Corporation, purity 99.95%), α-Al_2O_3 (TAIMICRON TM-DAR, Taimei Chemicals Co., Ltd., Tokyo, α-Al_2O_3 99.99%, d_{50} = 150 nm, SSA 13.7 m^2/g) and Graphene Nanoplatelets – GNPs (Cheap Tubes Inc., USA, grade 4, purity 99%, SSA >700 m^2/g, highly crystalline), Fig. 1.

2.2. Preparation of Si_3N_4/GNPs mixtures – different homogenization techniques

Sintering of silicon nitride is usually performed by means of a liquid phase, which is provided by the addition of sintering additives, often oxides. In this work, alumina and ytterbium oxide were used as the sintering aids. The molar ratio of Si_3N_4:Al_2O_3:Yb_2O_3 was 93:5:2. The content of GNPs was 7 wt.% related to the mass of Si_3N_4/Al_2O_3/Yb_2O_3 mixture. Since it is well known that the dispersion of GNPs is complicated when their amount is high, 7 wt.% of GNPs was chosen as a relatively high content which can be used to assess critically the homogenization treatment. In order to find out the best homogenization technique for the preparation of Si_3N_4/GNPs composites the following procedures were used:

PBM – Si_3N_4 with the sintering additives was homogenized with 7 wt.% of GNPs in a planetary ball mill (RETSCH PM 100) in isopropanol at a speed of 250 rpm for 4 h. The grinding jar of a cylindrical shape (RETSCH) with an inner volume of 0.25 l, made of wear-resistant silicon nitride, and 30 g of grinding silicon nitride balls with a diameter of 5 mm were used for the homogenization. The slurry was dried in a rotary evaporator and the final powder was sieved through a 125 μm screen.

U-PBM – GNPs were dispersed in isopropanol by ultrasonication (Ultrasonificator SONOPLUS, UW 2200, BANDELIN electronic GmbH & Co. KG, 200 W input power, frequency 20 kHz, the amplitude 30%, 5 min). Later on, the silicon nitride with the sintering additives was inserted and the mixture was homogenized in a planetary ball mill at a speed of 250 rpm for 4 h. The slurry was dried in a rotary evaporator and the final powder was sieved through a 125 μm screen.

U-BM – GNPs were dispersed in isopropanol by ultrasonication, as in the case "U-PBM". Then, the silicon nitride with the sintering additives was inserted and the mixture was homogenized in a ball mill for 24 h. The laboratory ball mill consists of two rollers with a PE jar (0.25 l). The silicon nitride balls with a diameter of 5 mm were used as a stirring media (50 g). The slurry was dried in a rotary evaporator and the final powder was sieved through a 125 μm screen.

U-A – GNPs were dispersed in isopropanol by ultrasonication. Afterwards, the silicon nitride with the sintering additives was added into the solution and the mixture was homogenized in an attritor at a speed of 250 rpm for 4 h. The attritor mill (Reeves, Model X-V 25 HP 240 VAC 3 PHASE 01HD) with an agate jar (0.5 l), a silicon nitride stirrer rod and the silicon nitride balls with a diameter of 5 mm (approximately 250 ml), was used for the homogenization. The slurry was dried in a rotary evaporator and the final powder was sieved through a 125 μm screen.

D-BM – The silicon nitride with the sintering additives was homogenized in isopropanol using an attritor at a speed of 250 rpm for 4 h. The slurry was dried in a rotary evaporator and the powder was sieved through a 125 μm screen. GNPs were added into the dried and sieved mixture of the silicon nitride with the sintering aids and all together homogenized in a ball mill for 24 h without a subsequent sieving.

Ref. A – A reference mixture without GNPs; the silicon nitride with the sintering additives was homogenized in isopropanol using an attritor at a speed of 250 rpm for 4 h. The slurry was dried in a rotary evaporator and the powder was sieved through a 125 μm screen.