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Anisotropic elastic moduli and internal friction of graphene nanoplatelets/silicon nitride composites

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ABSTRACT

Elasticity and internal friction of graphene nanoplatelets (3 wt.%)/Si_3N_4 composite is analyzed by ultrasonic methods. It is shown that the composite exhibits a degenerate (elliptic) form of transversal isotropy with the graphene nanoplatelets acting effectively as spheroidal voids and inducing significant softening in all directions. The shear internal friction is strongly anisotropic with the maximal value corresponding to the volume-preserving, 'breathing' vibrations of the nanoplatelets. Possible relations between the observed behaviors and the micromorphology of the composite are discussed.

1. Introduction

Graphene nanoplatelets (GNPs) were recently used as fillers for Si_3N_4 ceramic composites with the aim to obtain advanced materials with enhanced fracture toughness, or electric and thermal conductivity [1–5]. Due to the superior elastic properties of graphene (the in-plane Young's modulus equal to 1.1 TPa [10]), the presence of such particles in the ceramic matrix can be also expected to have some significant impact on the macroscopic elastic moduli of the composite, especially if they are arranged along some preferred directions and form, thus, a spatially anisotropic microstructure. In this paper, we study the case of silicon nitride ceramics with 3 wt.% of GNPs prepared by spark plasma sintering (SPS), where the preferred orientation of the platelets is induced by uniaxial stress applied during the sintering process [3–5]. The knowledge of elastic constants of such material is important not only with respect to its possible mechanical applications, but, as we show in this paper, enables also a deeper insight into micromechanics of the composite. In addition, the determination of elastic constants reported here is complemented by analysis of the anisotropic internal friction in the examined material, which is a parameter never discussed for graphene/ceramic composites so far. While the mechanical, micromechanical and vibrational properties of graphene/polymer nanocomposites have been studied numerous times and from numerous points of view (e.g. [6–8]), similar analysis for graphene/ceramic composites is still lacking; this paper aims to present one of the possible approaches how this gap can be filled.

2. Examined material

The examined composite was prepared by SPS (Dr. Sinter, SPS-510CE, Japan) from the mixture of α-Si_3N_4 powders (plus sintering additives: 2 wt.% Al_2O_3 and 5 wt.% Y_2O_3) and 3 wt.% of GNPs. The details on mixing, homogenization and SPS conditions were reported in [4]. The prepared specimen was cylindrical, with 20 mm in diameter and 2.7 mm in thickness. The density of this material was 3.18 g cm^{-3}, which equals to 99% of the theoretical one (calculated using values of 3.23 g cm^{-3} for Si_3N_4 and 2.2 g cm^{-3} for GNPs). The amount of β-Si_3N_4 phase in the composite estimated by X-ray methods was 50%. The GNPs in the composite showed average lateral size of 2 μm and variable thickness with maximum of 100 nm, and were regularly distributed, having one preferred orientation (perpendicularly to the pressing axis direction), as evidenced in Fig. 1. Such material can be expected to exhibit macroscopically the transversely isotropic (TI, e.g. [9]) elasticity, with all directions along the preferred orientation of the platelets being equivalent and forming the so-called *isotropic plane*, and with the *anisotropic axis* perpendicular to this plane.

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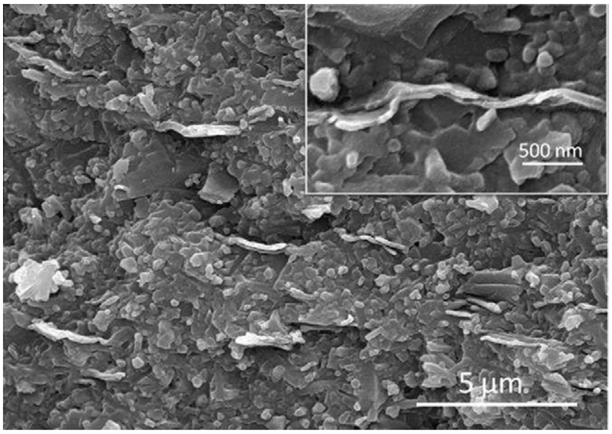

Fig. 1. Field emission scanning electron micrographs of the fracture surface of GNPs/Si_3N_4 composite showing the nanoplatelet orientation. The inset (zoomed area) evidences some waviness of the GNPs due to their tendency to follow the Si_3N_4 grain boundaries.

The elasticity of a TI material with the anisotropic axis denoted as x_3 is fully described by five independent elastic constants: $c_{11}, c_{12}, c_{13}, c_{33}$ and c_{44}. All other components of the Voigt's matrix c_{ij} are either zero, or can be calculated from the independent set as follows: $c_{22} = c_{11}, c_{23} = c_{13}, c_{55} = c_{44}$ and $c_{66} = (c_{11} - c_{12})/2$.

3. Experimental determination of elastic constants

From the SPS specimen, two rectangular parallelepipeds of dimensions approximately 4 × 3 × 2 mm^3 were prepared, oriented such that the shortest edge was always perpendicular to the preferred orientation of the platelets, i.e. that the largest face was always parallel to the expected isotropic plane. These two samples (denoted hereafter Sample 1 and Sample 2) were used for the determination of elastic coefficients by means of resonant ultrasound spectroscopy (RUS, [13,14]). In particular, the fully contact-less modification of RUS was employed, with the vibrations of the specimen both generated and detected by lasers, and with the modal shapes recorded by laser-Doppler interferometry (see [15,16] for instrumentation and further details). By this approach, 44 resonant modes for Sample 1 and 36 resonant modes for Sample 2 were identified in the frequency range 0.6–3 MHz and used for the determination of the elastic coefficients. The RUS measurements were complemented by pulse-echo measurements (30 MHz) of phase velocities of longitudinal waves in directions parallel and perpendicular to the preferred orientation of the GNPs. The results of the both ultrasonic methods were then simultaneously inverted, using the constrained inverse procedure described in [16], which resulted in the sets of elastic coefficients given in the upper part of Table 1. For these sets of elastic constants, the agreement between calculated and measured resonant frequencies for all detected modes was better than 1% (average error 0.17% for Sample 1% and 0.24% for Sample 2) and the values of longitudinal phase velocities were fitted with accuracy better than 0.5% as well. From Table 1, it is clearly seen that the results for both samples are in very good agreement, with slightly lower experimental uncertainty for Sample 1 (for which a higher number of modes was fitted with a lower misfit). Thus, for simplicity, we will restrict the further discussion to the results obtained for Sample 1 only, assuming that they represent well the behavior of the examined material.

Table 1
Resulting elastic constants of GNP/Si_3N_4 composite and pure Si_3N_4. For the composite, the independent constants $c_{11}, c_{12}, c_{13}, c_{33}$ and c_{44} are, for completeness, complemented by the constant c_{66} calculated as $(c_{11} - c_{12})/2$.

	Sample 1	Sample 2
GNP/silicon nitride composite		
c_{11} (GPa)	368.2 ± 0.8	369.5 ± 0.9
c_{12} (GPa)	120.0 ± 1.3	119.2 ± 1.8
c_{13} (GPa)	108.4 ± 0.8	104.5 ± 1.3
c_{33} (GPa)	288.8 ± 0.8	287.6 ± 1.0
c_{44} (GPa)	107.7 ± 0.2	108.5 ± 0.3
c_{66} (GPa)	124.1 ± 1.6	125.2 ± 2.0
Pure silicon nitride		
c_{11} (GPa)	396.2 ± 0.4	
c_{44} (GPa)	128.6 ± 0.4	

4. Discussion of elastic anisotropy

First of all, let us point out that the anisotropy induced by 3 wt.% of GNPs is surprisingly strong: the difference between the longitudinal moduli along the platelets (c_{11}) and perpendicular to them (c_{33}) is approximately 30% of c_{33}. The overall character of the anisotropy can be more easily seen from the directional dependence of the Young's modulus shown in Fig. 2. The Young's modulus in any given direction **n** can be calculated from the coefficients c_{ij} as

$$E = 1/s_{11}(\mathbf{n}), \quad (1)$$

where $s_{ij}(\mathbf{n})$ is a matrix inverse to the matrix c_{ij} rotated (*via* the rule for rotation of tensors) into a coordinate system with the x_1 axis aligned with the direction **n**. In Fig. 2, the results for the examined composite are compared with the isotropic Young's modulus of pure Si_3N_4. For the purpose of such comparison, a monolithic Si_3N_4 was prepared by SPS, having the same content of α- and β-phases as in the matrix of the composite. The elastic constants of this reference material were determined by conventional pulse-echo measurements with the results c_{11} = 396.2 GPa and c_{44} = 128.6 GPa, which gives the Young's modulus E = 324.0 GPa. It is clearly seen that the presence of GNPs leads to deterioration of elastic stiffness in all directions (E = 308. 3 GPa along the isotropic plane and E = 240.7 GPa along the anisotropic axis), including the

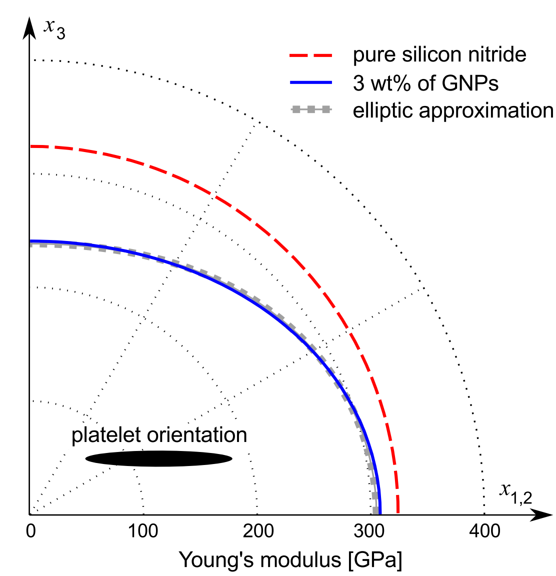

Fig. 2. Directional dependence of the Young's modulus of the examined material (thick solid line), compared with the isotropic Young's modulus of pure Si_3N_4 (dashed line) and with the elliptic approximation (3) (squares, see the text for more details).