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Structural and mechanical aspects of multilayer graphene addition in alumina matrix composites–validation of computer simulation model

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ABSTRACT

Since relationships between the structure and properties of ceramic-graphene composites are still not sufficiently defined, some numerical methods may facilitate the design of optimal material for new applications. In order to investigate such relationships, the methods for modelling the structure of composites with different sizes, shapes and spatial distributions of MLG (multilayer graphene) in the ceramic matrix have been developed. Using advanced methods of sintering SPS (Spark Plasma Sintering), two kinds of Al_2O_3 matrix composites were prepared with the participation of multilayer graphene flakes up to 2 wt.%. (3.56 vol.%). Studies of the microstructure and the basic mechanical properties suggesting a very strong impact of graphene flakes within a range of small volume additions. Thus there is a clear deterioration of the properties of composites with volume shares exceeding 1%, which may be due to changes of the graphene nanoplatelets and agglomerates shape.

1. Introduction

Graphene, a two-dimensional allotrope of carbon has unique electrical, thermal and mechanical properties: very high electron mobility, the thermal conductivity of more than 5000 W/mK and a Young's modulus of about 1 TPa, making graphene a promising material for applications in many branches of technology[1–3]. One such potential application of graphene may be the strengthening of ceramic materials, particularly by increasing their fracture toughness.

In the work of Porwal et al. [4] to strengthen oxide ceramics the graphene was prepared using liquid phase exfoliation and then applied. Al_2O_3—graphene composites with up to 5 vol.% content were densified (relative density $\boldsymbol{\rho} > 99\%$) using SPS. The fracture toughness of the material increased by 40% with the addition of only 0.8 vol.% graphene. Graphene changed the mechanism of crack propagation for the alumina matrix from inter-granular to trans-granular. Upon increasing the content of graphene in material, the effect of improving the fracture toughness decreased. The formation of an inter-connecting graphene network promoted easy fracture for concentration $\geq$2 vol.%. Another work of this author also shows the influence of the lateral size of flakes, obtained by of liquid exfoliation, on the mechanical properties of composites [5].

Similar results were achieved by Liu et al. [6] where the graphene content of 0.78 vol.% in the sintered alumina increased flexural strength and fracture toughness by 30% in comparison to the starting material. The authors explain the improved performance of material through mechanisms of crack deflection and crack bridging by the graphene platelets. The material with a higher content of graphene is characterized by increased porosity and platelets overlapping. The porosity acts as the areas initiating crack, thus resulting in the deterioration of the mechanical properties of the composite.

Slightly different results were achieved by Kim and colleagues [7]. Composites with volume fraction up to 1.5% of graphene were tested. The effect of increasing K_{Ic} was much stronger by up to 75% (from 3.1 to 5.6 MPa m$^{-1/2}$) but the volume fraction of chemically exfoliated (unoxidized) graphene was much smaller, between 0.25–0.5 vol.%. For these composites they found that flexural strength was also improved. As in previous work, further increasing the volume fraction of graphene caused a decrease in K_{Ic}. The observed strengthening was strongly dependent on the

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thickness of the flake in the microstructure. The most effective composites are found to contain agglomerate with the smallest thickness (2–5 nm). The thickness of the flake in the experiment was dependent on the centrifugation speed in the graphene preparation stage. Simultaneously with the reduction of the thickness, lateral dimension of the flakes decreased and the bridging mechanism in composites fracture were observed less frequently. The study also found decreasing of friction coefficient and remarkable improvements in the wear resistance for composites with 0.25–1 vol.% of graphene.

The presented research suggests a strong influence of an extremely small addition, less than 1% by volume, of MLG on the properties of the Al_2O_3 ceramic matrix composites. However none of these studies has given the answer for the fundamental question of what will happen in the microstructure of the composite with increasing volume fraction of the flakes and how these changes may affect the observed phenomena. An especially interesting question concerns the change of fracture toughness and phenomena responsible for those changes.

The authors undertook such an examination. The plan was to generate a three-dimensional model of the geometry of a polycrystalline composite matrix and then to perform analytical calculations based on data collected from the generated model. The generated models of given size distributions and particle shape allowed estimation of the surface of the grain boundaries in the structure and to carry out its visualization. In the context of analytical calculations we estimated the quantity of graphene that can be placed into the structure assuming graphene dispersion at the grain boundaries. The calculations took into account the possibility of agglomeration observed in real structures which manifests itself directly by increasing the thickness of the multilayered graphene flakes.

A dispersion in ceramic matrix composites is not a simple task. Homogenization processes involving graphene reinforcement are extremely difficult because of the need to provide even distribution and whilst avoiding the introduction of defects into graphene [8] in a single operation. Often you should consider using appropriate solvents to prevent agglomeration during colloid processing, such as: Isopropyl alcohol, NMP (*N*-methylpyrrolidone) or DMF (Dimetyloformamid). Another method used to obtain a good dispersion can be hetero coagulation [9].

Mechanical energy input during the process can lead to further delaminating of the multilayer flakes of graphene to obtain better dispersion [10]. However, regardless of the means, increasing the volume fraction of graphene in the actual structure leads to an overlapping of flakes, introduction of porosity [11] and consequently, when the volume fraction reaches approximately 3%, phase percolation appears [12].

Ensuring continuity of the conductive phase in the microstructure of the composite can improve the electrical conductivity and tribological properties but affects degradation of other mechanical properties and determine probable cracking mechanisms.

In order to verify this model we have designed and prepared composites with different volume fraction of MLG and examined their properties with particular attention to the fracture toughness. We also have described the changes of the morphology of produced flakes agglomerates and whole microstructural changes. Based on the presented literature and conducted calculations, we have included a small volume fraction of MLG from 0.36 to 3.58 vol.%.

2. Spatial distribution model

The starting point to generate a reference model of composites and estimate the amount of occupied grain boundaries was a microstructure of polycrystalline Al_2O_3 with 1.8 vol.% of MLG.

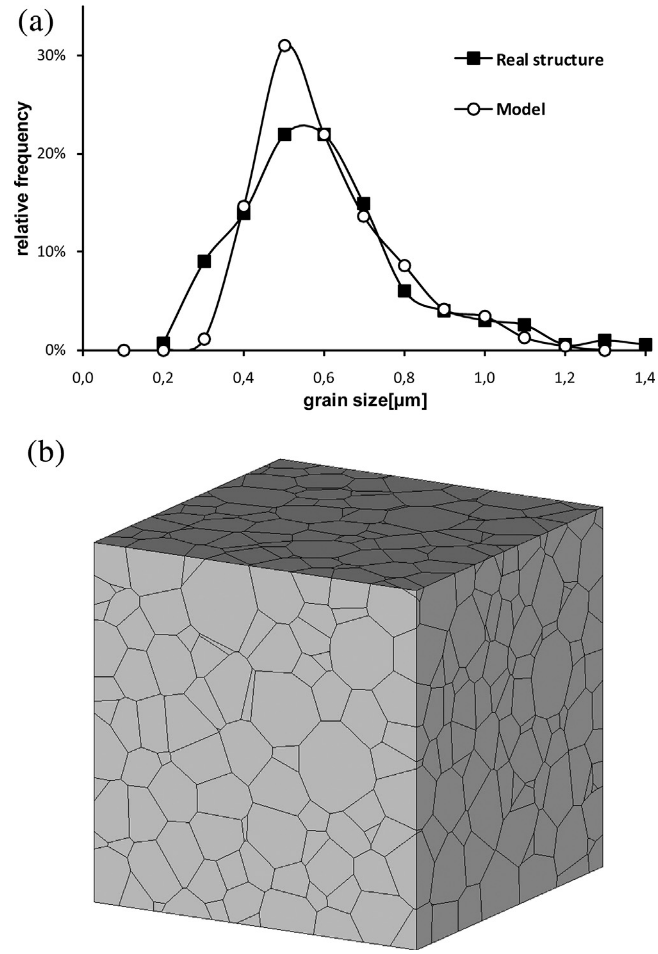

Fig. 1. Particle size distribution (a) and the 3D model (b) of a Al_2O_3 sinter grain structure.

The observed mean value of equiaxed grain size is 0.55 μm. Such a structure was observed in real composites (detailed later in this article) produced for testing mechanical properties. The figure below (Fig. 1) shows graphs of particle size distribution calculated based on the actual microstructure and matching obtained in the course of the numerical simulation. The following also shows a geometric model of the three-dimensional structures obtained.

In order to estimate capacity of Al_2O_3 polycrystalline structure to contain graphene a computer model of such structure was used. The model containing one thousand grains was generated using Laguerre–Voronoi tessellation (for details see [13,14]) on the basis of grain size distribution obtained from real Al_2O_3–graphene composite structure.

A generated model was used to calculate grain boundary area per unit volume $\mathbf{S}_v$ in the analyzed structure. The model assumed that graphene platelets reside at grain boundaries. This allowed to calculate the fraction of the surface of boundaries $\mathbf{A}_p$ covered by graphene platelets with defined thickness **t**

$$A_p = \frac{V_g}{t \cdot S_v} \tag{1}$$

where: $\mathbf{V}_g$ indicates volume fraction of graphene in the composite.

Under those assumptions maximum volumetric content of graphene in the structure (EC_{max}) can be estimated as:

$$EC_{max} = \frac{S_v \cdot t}{(1 + S_v \cdot t)} \tag{2}$$

where: **t** is graphene flakes thickness and $\mathbf{S}_v$ is grain boundary area per unit volume.