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Alumina/zirconia composites toughened by the addition of graphene flakes

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ABSTRACT

The effect of added graphene flakes on the mechanical properties of a composite containing 20 wt% Al_2O_3 and 80 wt% ZrO_2 (stab. 3 mol% Y_2O_3) was studied. To obtain samples, a commercial ceramic powder produced by Tosoh (Japan), and graphene oxide (GO) made at the Institute of Electronic Materials Technology (Poland) were used. The obtained composites were based on aqueous mixtures of both components. After drying, they were sintered in an uniaxial pressure (HP) furnace. The composites contained from 0% to 3% of GO by weight. Results showed the influence of GO content i.e. fracture toughness has a maximum for 0.02% GO (increase by 42% in comparison to GO-free matrix) and afterwards decreased, strength decreased in the whole GO content range. Young's modulus and Vickers hardness remained constant up to 0.2% GO, and then decreased.

1. Introduction

ZrO_2 ceramics and its composites are, due to their corrosion resistance and mechanical properties, attractive structural material of great significance in technology. They are used as structural materials in the manufacture of refractory crucibles for melting pure metals, components of furnaces, engines, heat barriers, abrasion resistant components, blade cutting tools and wire mesh drawing machines, to name a few.

ZrO_2 exists in three polymorphic forms [1]. The stable polymorph at low temperatures (below 1273 K) has a monoclinic structure. In the intermediate temperature range (1273–1473 K), a tetragonal phase occurs. In the area of maximum temperatures (above 2643 K) to the melting temperature (2983 K), a stable phase of regular fluorite structure appears. During the cooling process, transition from the tetragonal to monoclinic phase occurs. This phenomenon leads to cracks due to the generation of a stress associated with volume expansion ranging from 3% to 5%. It was found that annealing at high temperatures (1273–1773 K) in the presence of some oxides stabilizes the tetragonal or regular ZrO_2. Commonly used stabilizing oxides are: CaO, MgO, CeO_2 or Y_2O_3 (the last is used most often). These oxides form a solid solution with ZrO_2, where in place of zirconium ions cations of oxide additive are embedded. The addition of these compounds to ZrO_2 lowers the temperature of polymorphic transformations, reduces the volume changes and blocks the transformation. As a result metastable phases of regular or tetragonal ZrO_2 are obtained at room temperature. The latter has outstanding mechanical properties i.e. high bending strength σ_c and fracture toughness K_{Ic} [2,3]. According to [2], for ZrO_2 stabilized with 3 mol% Y_2O_3 (approx. 100% of tetragonal phase), hereinafter referred to as 3Y-TZP, σ_c=1457 ± 134 MPa, and in turn for ZrO_2 stabilized with 12 mol% of CeO_2 [4] K_{Ic} is about 10 MPam$^{1/2}$. Even greater value (σ_c=1764 ± 204 MPa) was observed for Al_2O_3–ZrO_2 composite obtained in [5], by hot isostatic pressing (HIP). It contained 20 wt% Al_2O_3 and 80 wt% ZrO_2 stabilized with 2.4 mol% Y_2O_3. The main limitation of the wide use of ceramics as a structural material is its brittleness i.e. low fracture toughness in comparison with, for instance, a metal resistance to cracking. Increase of fracture toughness can be obtained by a variety of methods e.g. introducing a dopant material with a higher ductility than the primary phase, or blocking the development of catastrophic cracks which is combined with the increase of fracture energy. Examples of this introduction are metal particles such as Mo [6], SiC fibres [7] or carbon nanotubes [8]. In recent years graphene and graphene flakes have displayed unusual mechanical properties. Their addition to a ceramic matrix can also lead to improvement of mechanical properties. [9–17]. In Table 1, the literature data of ceramics strengthening by introducing graphene flakes were collected for various ceramics.

In [10,11,13–15,17], the samples were sintered in a vacuum by the SPS (Spark Plasma Sintering) technique. This method is characterized by very rapid heating (approx. 100 °C/min) and short holding time (approx. 5 min), accompanied by applied uniaxial pressure, and pulse current. The sintering process is much shorter than in other methods and results in the reduced likelihood of grain growth and damage of graphene flakes. In [9], the samples were sintered in a vacuum, in [12]

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Table 1
Improvement of fracture toughness ΔK_{Ic} and bending strength $\Delta\sigma_c$ for various ceramics as a result of graphene flake introduction into the matrix (based on literature).

Material	*Graphene content (%)*	*Grain size (μm)*	*Relative density (%)*	ΔK_{Ic} *(%)*	$\Delta\sigma_c$ *(%)*	*Literature*
Al_2O_3	0.02 vol.	5.8 ± 2.6	99.5	0	28	[9]
Al_2O_3	0.8 vol.	≈ 0.5	99.9	40	–	[10]
Al_2O_3	0.38 vol.	–	99.6	27.2	30.8	[11]
Al_2O_3	0.1 wt.	2.0 ± 0.3	99.2	37.0	30.0	[12]
Al_2O_3	0.2 wt.	1.9 ± 0.2	99.0	43.5	15	[12]
3Y-TZP	4.1 vol.	≈0.3	98.0	34	–	[13]
3Y-TZP	0.01 wt.	–	99.4	61	–	[14]
Al_2O_3–ZrO_2[a]	0.81 vol.	–	98.1	40	–	[15]
Si_3N_4	1.0 wt.	–	–	44	–	[16]
Y_2O_3	3.0 wt.	0.1 ± 0.03	97	80	28	[17]

- Lack of data.

[a] Al_2O_3–ZrO_2 composite in [15] was obtained by milling alumina powder in a planetary mill for 6 h where the container and balls were made of 3Y-TZP. Chemical composition (vol%) of the composite determined after grinding was: a) composite without graphene; 13.31% of ZrO_2, 0.79% of Y_2O_3 and 85.90% Al_2O_3, b) with graphene, respectively 12.87% of ZrO_2, 0.72% of Y_2O_3, 0.81% graphene and 85.60% Al_2O_3.

under uniaxial pressure (hot pressing - HP), and in [16] were hot isostatically pressed (HIP). As shown in Table 1, significant increase in strength and toughness was achieved in most cases with relatively small additions of graphene (less than 1% by volume or weight). The mechanisms of toughening were crack deflection, crack bridging and branching. The results achieved in several projects (presented in Table 1) encouraged the authors to undertake studies on the material with extremely high flexural strength (approx. 1.8 GPa) which is the composite of 20 wt% Al_2O_3 −80 wt% ZrO_2 [5]. Therefore, it was expected that reinforcing this composite by graphene flakes could lead to the production of a very strong material with high resistance to cracking.

2. Experimental procedure

The mixtures were prepared using Al_2O_3-ZrO_2 powder that consisted of 20 wt% Al_2O_3 and 80% ZrO_2 stabilized with 3 mol% Y_2O_3 (tetragonal phase) with a purity of 99.9%, crystallite size of 29 nm, and granule size of 60 μm supplied by Tosoh (Japan), and graphene oxide (GO) supplied by the Institute of Electronic Materials Technology (Poland). The GO was delivered in the form of an aqueous suspension with a concentration determined at 3.9 g/l. The GO suspension was sonicated and the SEM image of the GO flakes after the sonication is presented in Fig. 1.

The mixing was performed in a planetary Fritsch Pulverisette 6 mill for 15 min at a rotation speed of 250 rpm. The container and milling balls (5 mm diameter) were made of 3 mol% Y_2O_3 stabilized zirconia. The resulting mass was dried at 60 °C for 12 h. The mixtures with GO content of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 3 wt% were prepared and reference samples were made from pure Al_2O_3-ZrO_2 composite.

The batches were hot pressed under an uniaxial pressure of 30 MPa in an argon flow at 1400 °C for 1 h in the form of discs of approx. 33 mm diameter and approx. 4 mm thickness. The Archimedes method

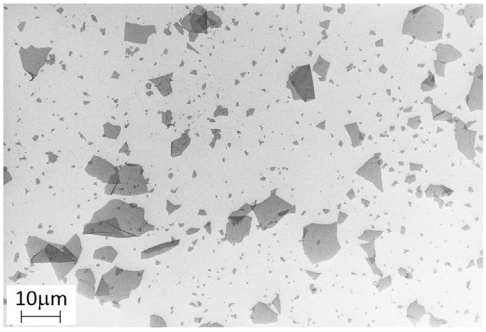

Fig. 1. GO flakes after sonication. Sonication resulted in formation of a larger fraction of the flakes of small size (approx. 1 μm).

was employed to measure the bulk density of the obtained discs in distilled water. The theoretical density was calculated by a rule of mixtures where densities of Al_2O_3–ZrO_2 and GO were 5.5 and 1.0 g/cm^3 (data from Tosoh and [13]) respectively.

Composite discs were cut into the beam size of approx. 0.95×1×12 mm for testing three-point bending strength σ_c, 0.95×2×12 mm for testing fracture toughness K_{Ic} and 0.95×2×23 mm for testing Young's modulus E, and Vickers hardness H. Samples for K_{Ic} tests (three-point bending method) was cut using a circular saw with a width of 0.2 mm to a depth of 0.8 mm and to a total depth of 1 mm with saw disc 0.025 mm width.

Strength tests were carried out using a three-point bending device with a span of L =8 mm with a crosshead displacement speed of 1 mm/min. Strength σ_c was calculated from Eq. (1):

$$\sigma_c = \frac{1.5P_cL}{bw^2} \tag{1}$$

where P_c is failure load, b is sample width (0.95 mm), w is sample thickness (1 mm), and the remaining symbols were defined previously.

The fracture toughness K_{Ic} was determined using the bending device described above. It was calculated from Eq. (2):

$$K_{Ic} = Y\frac{1.5P_cL}{bw^2}c_k^{0.5} \tag{2}$$

where Y is the geometrical factor for the notched beam calculated accordingly to [18], b=0.95, w=2 mm, c_k is the notch length (1 mm), and the remaining symbols were defined previously.

Young's modulus (E) was determined using a three-point device equipped with a deflection gauge. E was calculated from Eq. (3) [18]:

$$E = \frac{L^2}{bw^2C}\left[\frac{L}{4w} + \frac{(1+\nu)w}{2L}\right] \tag{3}$$

where L=20 mm, b=2 mm, w=0.95 mm, C=$\Delta y/\Delta P$ (Δy is the increase of deflection, ΔP is the increase of load), Poisson's ratio ν=0.3.

Hardness (H) was measured on polished surfaces of the samples using a hardness tester with a Vickers indenter under the indentation load P=98.1 N. H was calculated from Eq. (4):

$$H = 1.8544P/(2a)^2 \tag{4}$$

where a is half of an indent diagonal.

The mean and standard deviation of σ_c, K_{Ic}, E and H were calculated for 5 measurements. Tests of strength, fracture toughness, and Young's modulus were carried out at room temperature using a Zwick 1446 testing machine, and hardness testing using a Zwick 3202 hardness tester.

The microstructure of the samples were analysed on polished and etched surface of samples. The samples were thermally etched in a vacuum at 1250 °C for 30 min. Images of microstructures, fracture