IOP Conf. Series: Materials Science and Engineering **140** (2016) 012009 doi:10.1088/1757-899X/140/1/012009

Composite materials based on high-modulus compounds for additive technology

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Abstract. The effect of adding nanocrystalline ZrO_2 and submicron TiC to ultrafine Al_2O_3 on mechanical properties and the microstructure of the composites developed by hot pressing was investigated. It was shown that by means of hot pressing in argon atmosphere at the sintering temperature of 1500 °C one can obtain the composites of Al_2O_3-ZrO_2-TiC with a fine structure and minimal porosity. It was shown that in the material a multi-scale hierarchical structure is formed, which possesses high physical and mechanical properties: the hardness and fracture toughness was 22 GPa and 5.2 MPa*$m^{1/2}$, respectively. It has been shown that mechanical properties of the composite are better than those of commercial composites based on aluminum oxide (Al_2O_3, ZTA, Al_2O_3-TiC) and are comparable to those of silicon nitride.

1. Introduction

Additive technologies are becoming more widely used for various applications. In particular, for example, layerwise printing methods in the aviation and aerospace industry enabled the creation of more complex parts, e.g. turbine blades, turbines etc.

There are various 3D printers that allow printing materials from plastic, metals, ceramic, which is important for the aerospace industry, especially for making very hard and heat resistant engine parts working at high temperatures [1, 2]. For such applications, there are composite materials based on high-modulus compounds like MeO-MeC, where MeO is matrix and MeC are strengthening particles, which increase the heat resistance of the material [3, 4].

Alumina-TiC composites are widely used in industry due to their machinability at higher speeds than cemented carbides and their superior hardness, toughness and strength as compared to alumina [5]. They are commonly known as *black ceramics*, consisting for 70% from alumina and for 30% of TiC, having high hardness of about 22 GPa, but insufficient toughness, not more than 4 MPa*$m^{1/2}$ [6]. Alumina-zirconia composites are also used in industry, where zirconia toughens the alumina matrix by stress induced by tetragonal to monoclinic martensitic phase transformation. The hardness and fracture toughness of Al_2O_3-ZrO_2 composites is only 18 GPa and 5 MPa*$m^{1/2}$, respectively [7]. It is well known that addition of either oxide or non-oxide additives improve mechanical properties of alumina. In this context, addition of both oxide and non-oxide additives may be an attractive option, as it may impart the beneficial effects of both additives to the resulting

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composites. It becomes even more attractive, if the oxides and non-oxides are nano sized as the majority of the nano particles may remain at grain boundaries and interact with cracks resulting in interesting features not observed in conventional composites.

Thus, the main goal of this paper is to study the structure and properties of ceramic composite materials based on alumina and additives therein of zirconia and titanium carbide in terms of the material applicable for additive technology.

2. Materials and experimental procedure

In these studies, we used commercial Al_2O_3 powders with average particle size of 4.7 μm and with purity of 99.0%, TiC powders with particle size of 5 μm and purity of 98.0% and ZrO_2 powders with nominal particle size of 30 nm and purity of 99.7%.

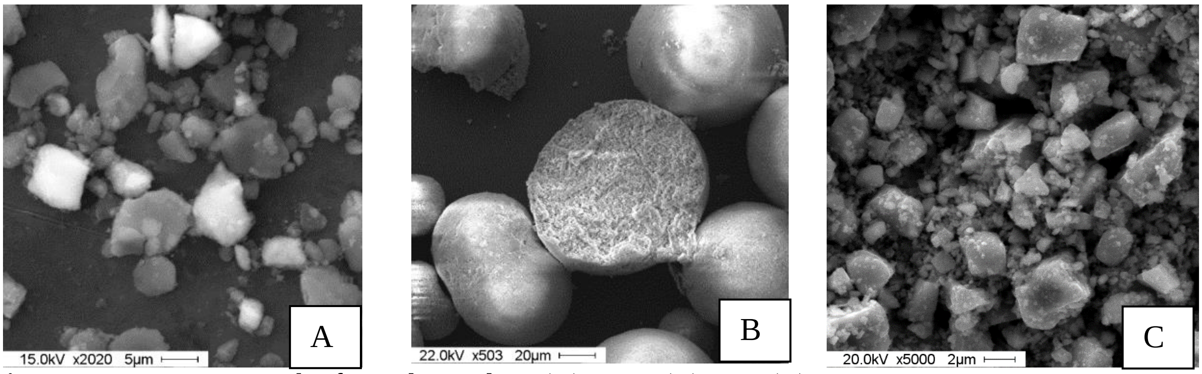

Figure 1. SEM micrograph of powders: Al_2O_3 (A), ZrO_2 (B), TiC (C)

The mixture of powders was prepared as follows: prepared individual water suspensions of components were mixed with each other with a magnetic stirrer, followed by suspension sonication. The resulting composition was deposited from the solution by flocculation of particles by raising the PH level followed by vacuum drying. The resulting composite mixture is shown in Table 1.

Table 1. The ratio of components in composites

Samples	Content		
	Al_2O_3 [%]	ZrO_2 [%]	TiC [%]
AZT-1	85	10	5
AZT-2	80	10	10
AZT-3	70	10	20
AZT-4	60	10	30

As it was shown earlier [8], the addition of zirconium dioxide of more than 10 wt% leads to reduced hardness of the composites; therefore, the zirconia content was 10 wt%. Ceramic composites were obtained by hot pressing in argon atmosphere at the sintering temperature of 1500 °C, with a pressing under 50 MPa. The holding time was 10 minutes. The heating rate up to hot pressing was 50, 150 and 300 °C/min.

X-ray diffraction data were obtained using an X-ray diffractometer with CuK source; grain-size and elemental analyses of the composites were carried out using LEO EVO 50 (Zeiss, Germany) scanning microscope.

The densities of sintered samples were determined by Archimedes' method with distilled water. For hardness measurements, the sintered samples were polished by diamond paste up to 1 μm grains. Vickers hardness was determined using a 5 kg load with ten indentations for each sample as:

$$Hv = 1.854 \cdot P/d^2 , \qquad (1)$$

where P is load [N]; d is the diagonal of indentation [μm].

Fracture toughness was determined as follows:

$$K_{1c} = 0.035 \cdot \left(H \cdot a^{1/2}\right) \cdot \left(E\varphi / H\right)^{0.4} \cdot \left(l / a\right)^{-0.5}, \qquad (2)$$

where H is hardness [GPa]; E is Young's modulus [MPa]; a is half-diagonal indentation [μm]; l is the crack length from the corner indentation [μm]; φ is a constant.

3. Results and discussion

Elemental analysis of the fractured surface of Al_2O_3–$10ZrO_2$–20TiC composite has shown that all phases are distributed randomly, but titanium carbide has a higher grain size. Measuring of the average grain size of the individual components has shown that that for alumina is 1.5 microns; for zirconia, 0.8 microns; for titanium carbide, 2.5 microns; thus, the average grain size of individual components in the structure of the composites is not significantly higher than the average particle size of the initial powders.

XRD analysis showed that alumina in composites is in α-modification (corundum), zirconia is cubic and tetragonal modifications of titanium carbide has NaCl-cubic lattice.

Density of the samples was close to the theoretical one, and they had less than one-percent porosity. Evidently, Figure 2 shows that the hardness and fracture toughness of the composites linearly increases with TiC content and is not affected by the heating rate during sintering process.

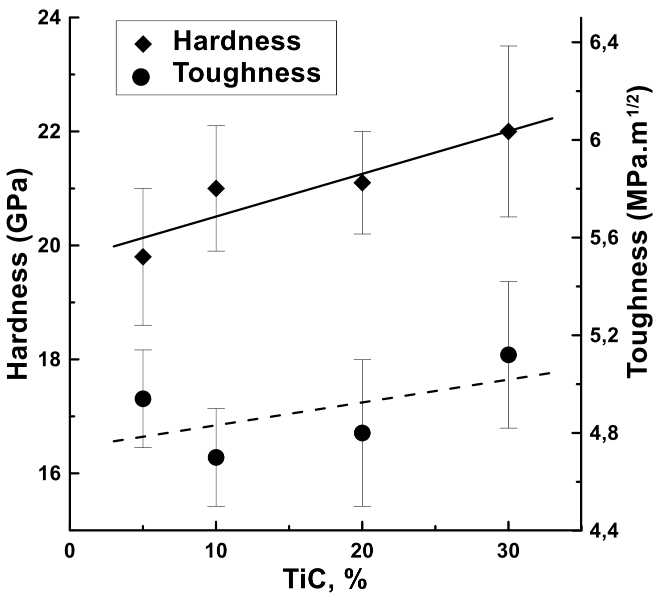

Figure 2. Variation of hardness and fracture toughness vs. titanium carbide content

Such behavior is not in line with data [9, 10], where TiCN and ZrB2 (ZrO2) was added to alumina matrix and had maximum hardness and toughness for TiCN content of 20wt%, and we may expect that the addition of titanium carbide of more than 30% will yield improved hardness and toughness.

The comparison of the strength and toughness of commercially available ceramic composites are shown in Figure 3. Obviously, the mechanical properties of the composite are better than those of commercial composites based on aluminum oxide (Al_2O_3, ZTA, Al_2O_3-TiC) and are comparable to silicon nitride.

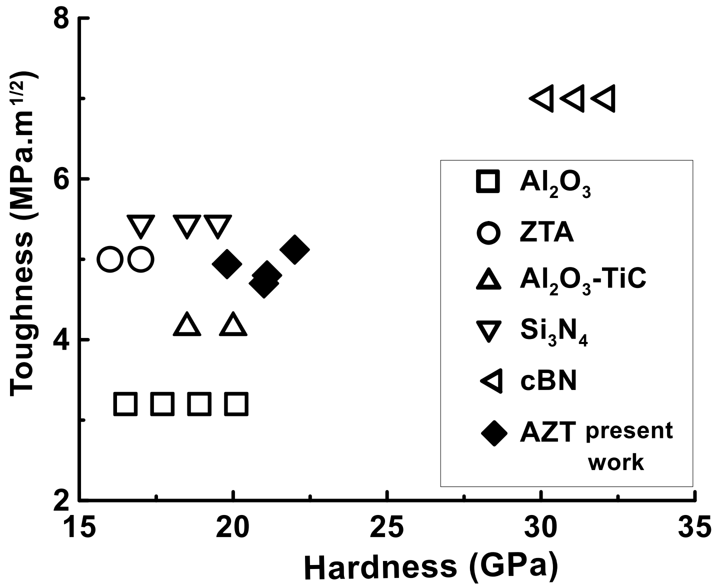

Figure 3. Hardness and toughness of composites compared with different commercial ceramic analogues [11]

4. Conclusions

1. It was shown that hot pressing of Al_2O_3-ZrO_2-TiC composites in argon atmosphere and sintering temperature of 1500 °C yielded very low-porosity and fine structure with uniform distribution of ZrO_2 and TiC phases in alumina matrix without phase changes as compared to initial mixtures.

2. It was demonstrated that hardness and fracture toughness increase linearly with the increase of titanium carbide content in composites, and these mechanical characteristics are very similar to the best values obtained elsewhere.

Acknowledgement
This research was partially supported by RFBR; contract No. 26 16-33-00889\16.

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