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COMPOSITES THEORY AND PRACTICE

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MICROSTRUCTURE AND HARDNESS OF Al_2O_3-ZrO_2-Ti COMPOSITES

The aim of this work was to fabricate Al_2O_3-ZrO_2-Ti composites by slip casting and to analyse the influence of a pure titanium addition on the microstructure and density of the composites. For this purpose, two groups of samples were prepared by slip casting, with and without titanium. Experiments were performed using the samples: Al_2O_3 + 10 vol.% ZrO_2 and Al_2O_3 + 10 vol.% ZrO_2 + 10 vol.% Ti. The composites were characterized by XRD and SEM. Moreover, the density was measured using the Archimedes method. The hardness was measured as well. The obtained composites had a homogeneous microstructure and high relative density. It was found that a phase transformation in ZrO_2 occurred. The titanium content as a ductile phase can slightly reduce the Vickers hardness of the composites.

Keywords: ZTA composites, titanium, slip – casting method

MIKROSTRUKTURA I TWARDOŚĆ KOMPOZYTÓW Al_2O_3-ZrO_2-Ti

Celem pracy było wytworzenie kompozytów Al_2O_3-ZrO_2-Ti metodą odlewania z mas lejnych (slip-casting) oraz analiza wpływu dodatku czystego tytanu na mikrostrukturę i gęstość kompozytów. Przygotowano dwa zestawy próbek, różniących się brakiem lub obecnością dodatku tytanu: Al_2O_3 + 10% obj. ZrO_2 oraz Al_2O_3 + 10% obj. ZrO_2 + 10% obj. Ti. Wytworzone kompozyty charakteryzowano za pomocą dyfrakcji rentgenowskiej oraz skaningowej mikroskopii elektronowej. Zagęszczenie kompozytów wyznaczono metodą Archimedesa, natomiast twardość zmierzono metodą Vickersa. W badanych kompozytach otrzymano jednorodną mikrostrukturę oraz wysokie zagęszczenie. Zauważono również obecność przemiany fazowej zachodzącej w dwutlenku cyrkonu. Dodatek fazy plastycznej w postaci tytanu nieznacznie obniżył gęstość oraz twardość badanych kompozytów.

Słowa kluczowe: kompozyty ZTA, tytan, metoda slip-casting

INTRODUCTION

Zirconia toughened alumina (ZTA) was developed as an alternative to monolithic bioceramics in the early 1980s. These alumina matrix composites are reinforced with a secondary phase consisting of low yttria-doped zirconia up to 30 wt.%, as a toughening agent [1-3].

ZTA materials combine the outstanding properties of alumina, e.g. high hardness, wear resistance and biocompatibility, with the extraordinary fracture toughness of zirconia [4]. This combination allows one to obtain structurally toughened composites commonly used for orthopaedic and dental implants, due to the martensitic phase transformation between tetragonal zirconia (t-ZrO_2) metastable at ambient temperature to a thermodynamically stable monoclinic phase (m-ZrO_2) on cooling [5, 6]. To ensure the appropriate mechanical properties of Al_2O_3-ZrO_2 systems, high density of the matrix and the maximum amount of the metastable zirconia phase is necessary.

Research is now being conducted on Al_2O_3-ZrO_2 metal combinations, with toughening metal agents such as tantalum and niobium [7, 8]. There is little literature about the fabrication of ZTA systems with the most popular metallic biomaterial - titanium. Titanium belongs to lightweight metals because of its low density (4.5 g/cm^3) and is characterized by high mechanical strength with the highest Rm/ρ from metallic biomaterials [9]. In addition to its good mechanical properties, the reasons for using titanium as an additive to ZTA composites are its high melting point, biocompatibility and corrosion resistance [10, 11]. Because of these features, composites from the Al_2O_3-ZrO_2-Ti system can be used in medicine.

The mechanical properties of ZTA composites can be enhanced by incorporating titanium [12]. While zirconia increases the fracture toughness, it is still too low compared to metallic materials. Moreover, in ZrO_2 the phase transformation of t-ZrO_2 into m-ZrO_2 occurs. The two ways of enhancing fracture toughness: by phase transformation and ductile titanium particles, are synergistic [13]. Teng et al. conducted research

on ZrO_2-Ti composites. They reported a dependence between the titanium content and increasing volume fraction of m-ZrO_2 but on the other hand, the interfacial stresses arising from the plastic deformation of Ti and the thermal expansion mismatch of Ti and ZrO_2 were the driving forces for the phase transformation from t-ZrO_2 to m-ZrO_2 [12-14]. Furthermore, our works revealed the importance of adding titanium to ZrO_2 to improve the fracture toughness of ZrO_2-Ti composites [15].

In this paper, slip casting was chosen for sample preparation. This powder-based shaping method is based on the filtration process, in which usually water--based suspensions are poured into plaster moulds and consolidated under the influence of capillary forces. The advantages of slip casting are mainly good material homogeneity and simplicity. This method allows the use of powders with different particle sizes, which was important criterion during selection of the starting powders, from which titanium powder has a decidedly different particle size relative to Al_2O_3 and ZrO_2 powders [16, 17]. This work concerned fabrication by slip casting as well as characterization of the microstructure and hardness of the Al_2O_3-ZrO_2-Ti composite.

MATERIALS AND METHODS

The starting powder materials were: nano-sized alumina (Taimei Chemicals) and zirconia dioxide stabilized by 3mol% Y_2O_3 (TOSOH). For the Al_2O_3-ZrO_2-Ti composites micro-sized titanium powder (Alfa Aesar) was used. Figure 1 shows the morphology of the Al_2O_3, ZrO_2 and Ti powders obtained by scanning electron microscopy with the particle size distribution of each starting powder. Analysis of the histograms showed that the Al_2O_3 was characterized by particles with an average size of 0.114 ± 0.043 μm (Fig. 1a). It was found that the ZrO_2 was characterized by a particle size equal to 0.093 ± 0.065 μm (Fig. 1b). On the other hand, the histogram of the size distribution of the equivalent diameter of titanium shows that the powder is characterized by particles with a diameter of 9.58 ± 1.25 μm (Fig. 1c).

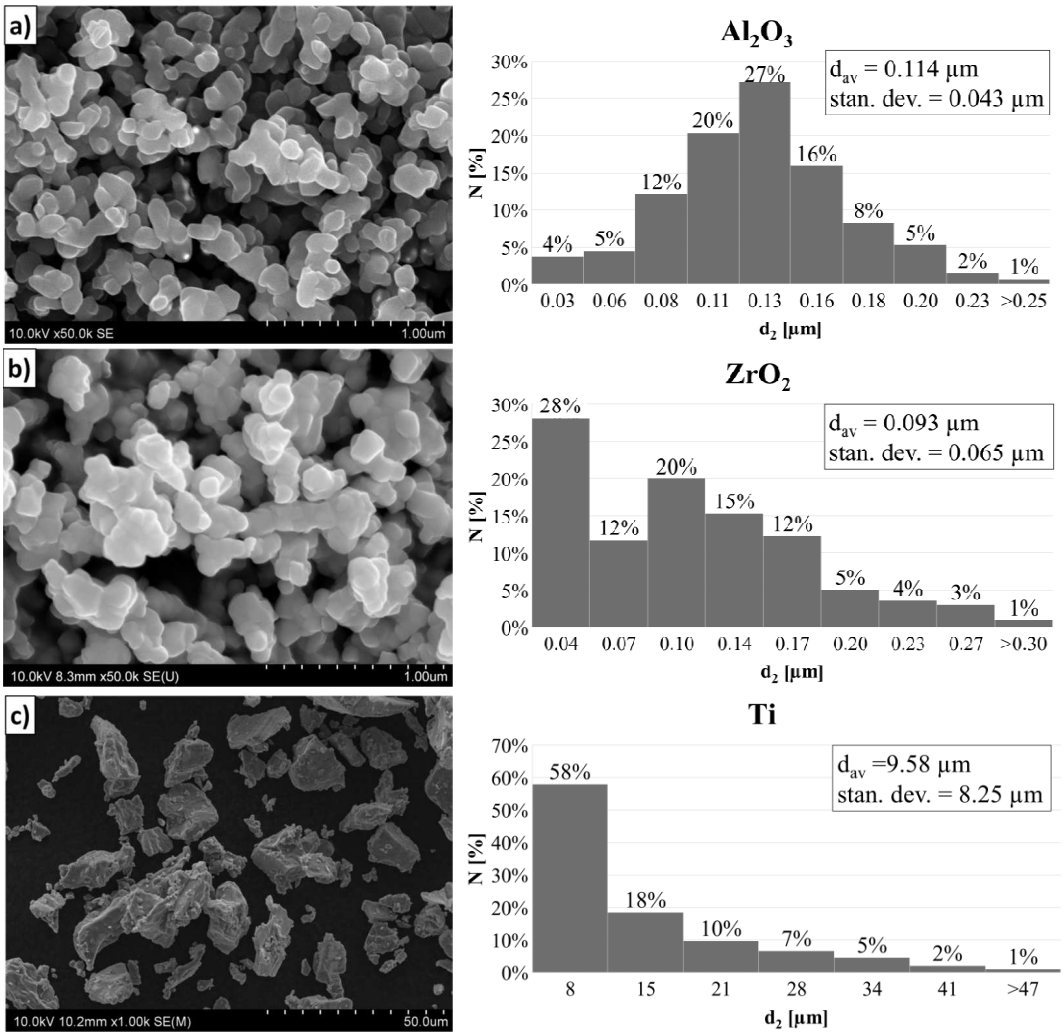

Fig. 1. Morphology of starting powders, scanning electron microscopy images and histograms of starting powders particle size distribution: a) Al_2O_3, b) ZrO_2 + 3 mol. % Y_2O_3, c) titanium

Rys. 1. Morfologia wyjściowych proszków, zdjęcia ze skaningowego mikroskopu elektronowego oraz histogramy rozkładu wielkości cząstek proszków wyjściowych: a) Al_2O_3, b) ZrO_2 + 3 mol. % Y_2O_3, c) tytan

The ceramic powders were selected in order to have particle sizes similar to each other. According to the literature data, as well as the authors' own work, the use of powders with a significant difference in particle size between the ceramic powders and metal powder may contribute to an increase in the density of composites. This is due to the fact that the small ceramic particles can be packed in open spaces between the large metal particles [18]. For both ceramic powders, a similar morphology and size were observed. The microscopic observations of the raw Al_2O_3 and ZrO_2 powders reveal that they were characterized by a spherical shape. It was found that both the ceramic powders were distinguished by a tendency to create agglomerates. Base on the SEM image of the metal powder it can be noticed that Ti powder has an irregular shape. The observations also revealed that the metal powder has numerous cavities. Differences in the morphology and size of the powders can significantly determine the density of composites and the deployment of metal particles in a ceramic matrix (Fig. 2).

Water-based slurries used for slip casting including the Al_2O_3, ZrO_2 and Ti powders as well as diammonium hydrocitrate (DAC) and citric acid (CA) as dispersants in the amounts of 0.3 wt.% and 0.1 wt.% respectively, were prepared. The following sample designations were introduced: Al_2O_3-ZrO_2 as A10Z3Y and Al_2O_3-ZrO_2-Ti as A10Z3Y + 10Ti. The slurry composition is shown in Table 1.

TABLE 1. **Participation of solid phase, alumina, zirconium and titanium powders in prepared slurries**
TABELA 1. **Udział fazy stałej, tlenku glinu, cyrkonu oraz tytanu w przygotowanych zawiesinach**

Sample	Content [vol.%]			
	Slurry solid phase	Solid phase composition		
		Al_2O_3	ZrO_2	Ti
A10Z3Y	45	90	10	-
A10Z3Y + Ti	45	80	10	10

The slurries were mixed in a PM10 Retsch planetary ball mill for an hour at the speed of 300 rpm. Then the aqueous slurry was poured into gypsum moulds. Afterwards, the samples were dried in a dryer at 25ºC for 48 hours. The dried samples were removed from the gypsum moulds and were sintered. The applied slip casting technique allowed cylindrical samples 4.5 mm in height and 17.6 mm in diameter to be created. The sintering process was conducted at 1450°C for 2 hours in argon atmosphere in a tubular furnace Carbolite RHF.

The density of the composites was calculated using the Archimedes method according to the PN-76/6-06307 standard. The samples were polished with abrasive paper, using 100, 400 and 800 gradations. Phase identification of the composites was carried out using a Rigaku MiniFlex II Desktop X - ray Diffractometer for $2\theta = 0.05^o$ values ranging from 20^o to 100^o with CuKα radiation and $\lambda = 1.54178$ Å. The analyses were performed on cross-sections of the samples.

The microstructure of a fracture of the composites was characterized by scanning electron microscopy, using a Hitachi SU-70. Before the investigation the samples were covered with a thin layer of copper. Furthermore, EDS analysis was carried out.

The hardness was estimated by means of a Vickers hardness tester (HVS - 30T, Huatec Group Corporation), with a 10 kG (98 N) load and a 10-second holding time. For each sample, at least 10 measurements were made.

RESULTS AND DISCUSSION

The green bodies were compacted without cracks or pores. Table 2 shows the density of the green and sintered bodies and the relative density of the prepared materials measured by the Archimedes method. It was noticed that the sintered A10Z3Y had a high relative density of about 95% of the theoretical density. Elezz et al. conducted research on ZTA sintered at 1450ºC and obtained samples with a density equal to 92% [19]. However, this value is not high enough. It is possible to receive fully dense ZTA composites at higher sintering temperatures. Exare et al. reported that the optimum sintering temperature regarding the density and limitation of grain growth stands around 1500ºC [20].

Densification of the A10Z3Y + 10Ti composites was lower than the A10Z3Y sample and equal to 90%. It might be a consequence of the difference in particle size between the ceramic powders: Al_2O_3, ZrO_2 ~ 100 nm and Ti powder ~ 10 μm. Despite the possibility that the smaller ceramic particles can be located in the spaces between the titanium particles, the large titanium particles could make densification difficult.

TABLE 2. **Densification of green and sintered bodies of ZTA and ZTA-Ti composites**
TABELA 2. **Zagęszczanie surowych i spiekanych kompozytów ZTA i ZTA-Ti**

Relative density [%]	A10Z3Y	A10Z3Y + Ti
Green body state	57%	61%
Sintered state	95%	90%

Because of the differences in powder density: ZrO_2 equal to 6.00 g/cm^3 and Al_2O_3 (3.97 g/cm^3) [21, 22], ZrO_2 can sediment faster. The use of titanium powder with a micrometric particle size may, on the one hand, impede densification due to its size and the formation of micro- and nano-pores. On the other hand, nanometric ceramic particles can overlap the titanium particles and block them in the composite structure (Fig. 2), according to a literature report [15, 18].

Furthermore, sintering can lead to thermal strains anisotropy because of the difference between the thermal expansions each of powder. The average thermal

expansion coefficient of alumina is $8.2 \cdot 10^{-6o}C^{-1}$, of zirconia is $9.6 \cdot 10^{-6o}C^{-1}$ and of titanium is $8.2 \cdot 10^{-6o}C^{-1}$ at room temperature to 100ºC, which can also influence the density of the sinters [14].

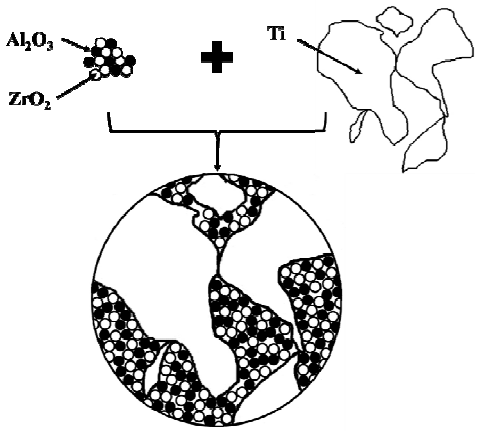

Fig. 2. Diagram of particle arrangement in sintered state with different sizes of ceramic and metal particles

Rys. 2. Schemat rozmieszczenia cząstek w spieku o różnej wielkości cząstek ceramicznych i metalu

The X-ray diffraction patterns of A10Z3Y and A10Z3Y + Ti sample cross-sections after sintering are shown in Figure 3. The XRD analysis indicated that Al_2O_3 and t-ZrO_2 are the only crystalline phases present in the A10Z3Y sample, whereas in the A10Z3Y + Ti sample, a single peak from the m-ZrO_2 phase was also observed. Two phases of titanium were revealed - pure titanium and titanium oxides.

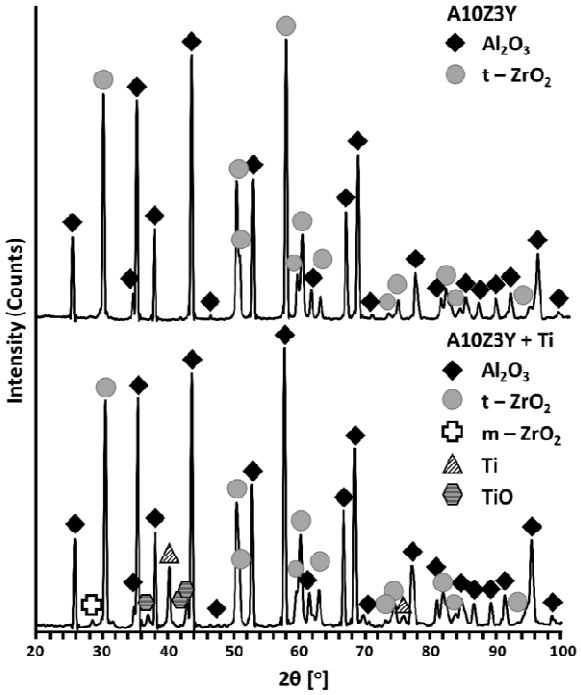

Fig. 3. Diffractograms of: a) ZTA and b) ZTA - Ti composites

Rys. 3. Dyfraktogramy wytworzonych kompozytów: a) ZTA i b) ZTA - Ti

Figure 4 shows the microstructure of the A10Z3Y and A10Z3Y + 10Ti composites sintered at 1450ºC. The images show highly homogeneous microstructures with some agglomerates and without visible pores. EDS analysis indicates the Al_2O_3 and ZrO_2 grains as dark and bright respectively and the presence of Al_2O_3-ZrO_2 as the matrix. In the A10Z3Y + 10Ti microstructure, titanium appears as grey areas with a low contrast.

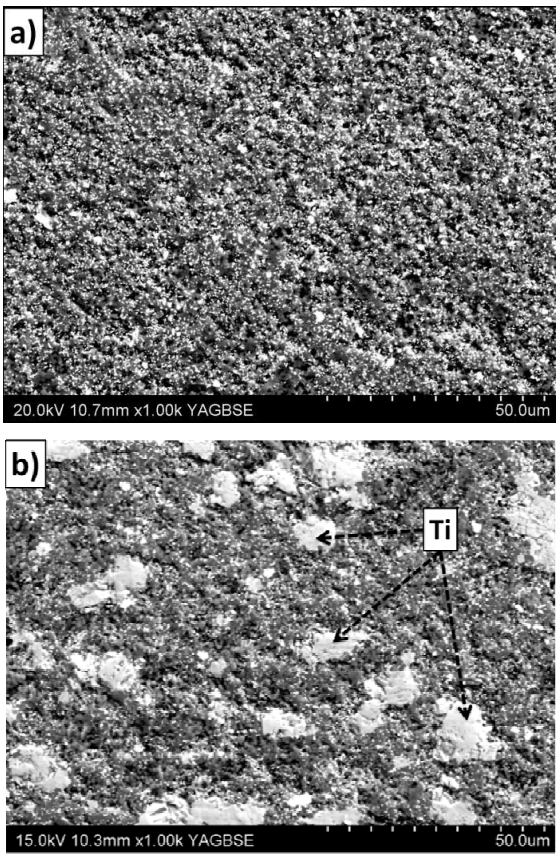

Fig. 4. SEM photograph of: a) A10Z3Y, b) A10Z3Y + 10Ti composite (Ti - light contrast)

Rys. 4. Zdjęcia SEM: a) A10Z3Y, b) A10Z3Y + 10Ti kompozytu (Ti - jasny kontrast)

The EDS analysis (Fig. 5) revealed the elements of the matrix (Al, Zr, O) in the area of the Ti particles which can be a result of the diffusion and formation of a Ti rich phase with the presence of a solid solution of these elements. On the other hand, EDS signals from Al, Zr in the Ti areas can come from a deeper part of the material or from the surrounding area. The EDS analysis also confirmed the presence of nitrogen in the samples. As can be observed, the titanium grains are uniformly dispersed in the Al_2O_3-ZrO_2 matrix. It was found that the Vickers hardness of A10Z3Y after sintering at 1450ºC was close to 17 GPa. This result is satisfying compared to literature data. In accordance with the research presented in the study by Moazzan Hossen et al., the ZTA composites were characterized by a 14 GPa hardness obtained by uniaxial pressing at 60 MPa and sintering at 1450°C [23].

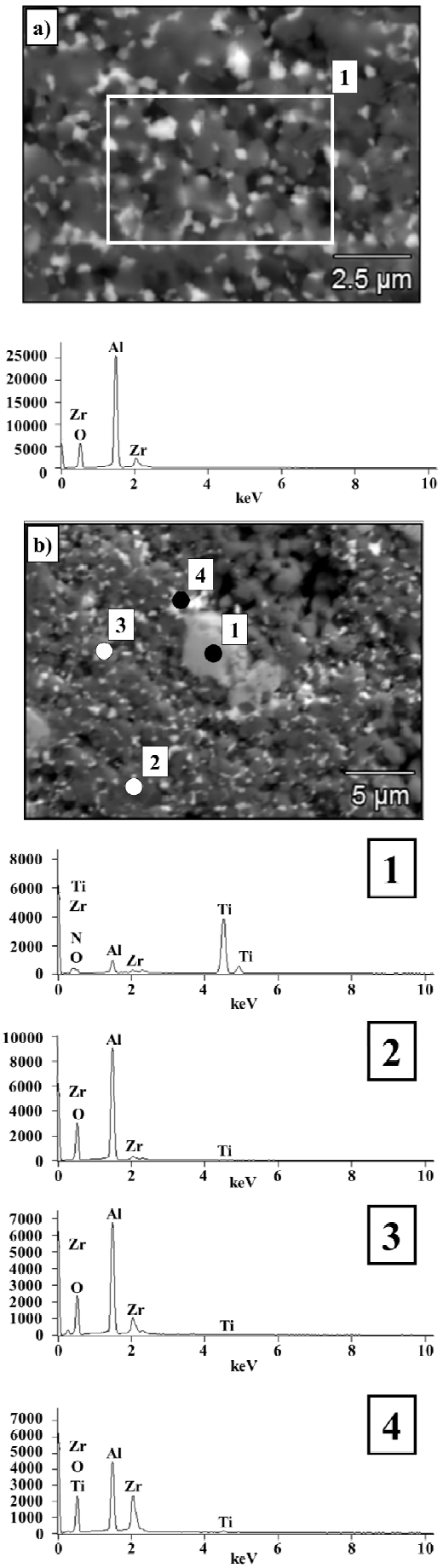

Fig. 5. EDS analysis of samples: a) A10Z3Y and b) A10Z3Y + 10Ti

Rys. 5. Analiza EDS próbek: a) A10Z3Y i b) A10Z3Y + 10Ti

Based on the hardness measurements, it can be concluded that composites with the titanium addition were characterized by a lower Vickers hardness in relation to the reference A10Z3Y composite and it was equal to 10 GPa. The lowering of the hardness is undoubtedly influenced by the clearly lower densification of these composites, which is consistent with the literature reports on the ZrO_2-Ti system [24]. The reduction in hardness is also associated with the presence of plastic titanium particles [11].

SUMMARY AND CONCLUSIONS

The result of the presented work showed that slip casting can be successfully used to fabricate dense composites of the Al_2O_3-ZrO_2 and Al_2O_3-ZrO_2-Ti systems. The density of the A10Z3Y + 10Ti composite was lower than the A10Z3Y, which probably can be the effect of Ti, as well as the difference between the size of the Ti particles and ceramic powder particles. The microstructure of the composites with Ti are highly homogeneous, however, titanium phase agglomerates are present. The lower density of the Al_2O_3-ZrO_2-Ti than the Al_2O_3-ZrO_2 is responsible for the decrease in the hardness. Investigations of the fracture toughness of the composites are in progress.

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