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COMPOSITES THEORY AND PRACTICE

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THE PHASE STABILITY OF SINTERED COMPOSITES IN Al_2O_3-ZrO_2-$Y_3Al_5O_{12}$ SYSTEM

In recent years the technology of manufacturing dense composite sinters with submicrometric grains in the alumina/yttria-alumina garnet (Al_2O_3-$Y_3Al_5O_{12}$) system has developed. The garnet grains are very uniformly distributed in the alumina matrix due to applying special chemical methods. Such a material shows a higher hardness, comparable fracture toughness and almost a one order of magnitude lower wear susceptibility when compared to alumina sinters. The drawback of this material is its relatively low strength. This work presents the results of experiments on improving the mechanical properties of the Al_2O_3-$Y_3Al_5O_{12}$ (YAG)m composite by introducing grains of another phase (tetragonal zirconia) into the alumina matrix. The sintering of such a composition demanded temperature conditions which did not exclude the possibility of yttria atom diffusion between the garnet and zirconia grains. This phenomenon strongly influenced the phase composition of the final sinters. The paper discusses the microstructure of the sinters. The influence of the starting composition and sintering conditions on the final phase composition and selected mechanical properties of sinters were investigated.

Keywords: sintering, mechanical properties, Al_2O_3, YAG, ZrO_2

STABILNOŚĆ FAZOWA SPIEKANYCH KOMPOZYTÓW W UKŁADZIE Al_2O_3-ZrO_2-$Y_3Al_5O_{12}$

W ostatnich latach opracowano technologię uzyskiwania gęstych spieków kompozytowych o submikronowym rozmiarze ziaren w układzie korund/granat glinowo-itrowy (Al_2O_3-$Y_3Al_5O_{12}$), w którym ziarna granatu są niezwykle jednorodnie rozmieszczone dzięki zastosowaniu specjalnych metod chemicznych. Materiał ten cechuje się większą twardością, porównywalną odpornością na kruche pękanie oraz prawie dziesięciokrotnie mniejszym zużyciem ściernym w stosunku do spieków korundowych. Mankamentem tego tworzywa jest stosunkowo niska wytrzymałość na zginanie. Prezentowana praca przedstawia wyniki eksperymentalne prac nad poprawą właściwości mechanicznych kompozytu Al_2O_3-$Y_3Al_5O_{12}$ (YAG) poprzez wprowadzenie do niego trzeciej fazy - ziaren dwutlenku cyrkonu stabilizowanego itrem. Spiekanie takiego układu przebiega w warunkach, w których możliwa jest dyfuzja itru pomiędzy ziarnami granatu i dwutlenku cyrkonu. Powoduje to trudności z utrzymaniem założonego składu fazowego tworzywa. W pracy omówiono mikrostruktury spieków. Przedstawiono także zależności pomiędzy składem fazowym i wybranymi właściwościami mechanicznymi a warunkami spiekania i składem wyjściowym kompozytów w układzie Al_2O_3-ZrO_2-$Y_3Al_5O_{12}$.

Słowa kluczowe: spiekanie, właściwości mechaniczne, Al_2O_3, YAG, ZrO_2

INTRODUCTION

Composites in the Al_2O_3-Y_2O_3-ZrO_2 system could be promising materials in selected mechanical applications. Numerous works on the Al_2O_3-$Y_3Al_5O_{12}$ (Al_2O_3-YAG) system show that an addition of even 5 vol.% disspersed YAG significantly increased the Vickers hardness of pure α-Al_2O_3 material [1, 2], whereas, composites with an alumina matrix and disspersed zirconia grains showed very high bending strength and fracture toughness [3, 4]. There are many reports on the preparation of Al_2O_3-YAG-ZrO_2 (cubic) composites prepared by directional crystallization of the eutectic composition [5-11]. This method demands a very high processing temperature, which makes it very expensive. Additionally, the mentioned method excludes crystallization of the zirconia phase with tetragonal symmetry. Very few papers concerning sintered composites in the proposed Al_2O_3-Y_2O_3-ZrO_2 system report the utilization of YAG and cubic zirconia (5-33 vol.%) as dispersed phases [12]. In paper [13], the authors reported the possibility of pressureless sintering of three-phase materials composed of 45% Al_2O_3 - 38% YAG - 17% ZrO_2 and 43% Al_2O_3 - 39% YAG - 18% ZrO_2, respectively. The presented work shows the starting phase composition and sintering conditions on the final phase compositions of Al_2O_3-ZrO_2-$Y_3Al_5O_{12}$ sinters and their selected mechanical properties.

EXPERIMENTAL PROCEDURE

The preparation method of Al_2O_3-YAG-ZrO_2 composite powders consisted in the precipitation of a yttrium oxide precursor in a water suspension of α-Al_2O_3 (TM-DAR Taimicron) and ZrO_2 (TZ-3Y Tosoch) powders. The preparation procedure was as follows: yttria powder (purity 99.9%) was dissolved in nitric acid. The alumina and zirconia powders were mixed with water. The prepared suspension has a solid content of 50 vol.%. The pH of the suspension was stabilized at the level of 8.5 by the addition of a water solution of $(NH)_4CO_3$. It allowed the yttrium oxide precursor to precipitate quantitatively. Consequently, the yttrium nitrite solution was instilled into the suspension at the speed of a few drops per minute. The whole volume of the suspension was intensively mixed. During the precipitation process and after it the pH was 8.5. The ready mixtures were dried at 105°C for 24 hours. After that, the mixtures were heat treated at 600°C for 1 hour. It was enough to crystallize the nanometric yttrium oxide [2]. The mentioned thermal treatment of the suspension gave a uniform mixture of submicrometric alumina, nanometric zirconia and nanometric yttrium oxide grains. Additionally, this α-Al_2O_3, ZrO_2 (3Y-TZP) and Y_2O_3 mixture was homogenized in an attritor mill for 30 minutes in an isopropanol environment. The milling media was 2 mm zirconia balls (made by Tosoh). The balls/powder ratio was 20:1. After homogenization, the suspension was rapidly dried at 120°C.

Cylindrical samples of 20 mm in diameter and 1.6 - 1.7 high were uni-axially pressed under 50 MPa and consequently re-pressed isostatically under 300 MPa. The samples were pressureless sintered at 1450°C in an electrical furnace equipped with Superkanthal heating elements in air atmosphere. The temperature was increased 25°C/min. The soaking time was 120 minutes.

Alumina-yttria garnet synthesis occurred during the sintering of the composite powders as a result of chemical reaction between α-Al_2O_3 and Y_2O_3. The composition of the starting powders was calculated for 5, 7.5 or 10 vol.% content YAG and zirconia phases in the composites. The apparent densities (d_{app}) of the sinters were determined according to the Archimedes method. The phase compositions were determined by means of the XRD method utilizing an Empyrean (PANalytical) apparatus. Measurements were performed for the monochromatic CuK_α line in the 2θ angle range changing from 10 to 90°. The phase content was calculated by means of Ritveld procedures.

Vickers hardness (*HV*) tests were performed utilizing an FV-700 apparatus (Futur-Tech). Polished surfaces were loaded with 9.81 N for 10 s. The applied load was selected to prevent cracking in indentation corners. The bending strength (σ) measurements were performed by the bi-axial bending method [14] using a Zwick/Roell Z150 testing machine.

The critical stress intensity factors (K_{Ic}) were determined by the standard method [14] of three point bending tests of the samples with a notch. The microstructures were examined utilizing SEM equipment Nova-Nano SEM200 (FEI).

RESULTS AND DISCUSSION

Figure 1 illustrates the XRD diffractograms of the composites sintered at 1450°C. It proves that the only phases present in the materials are alumina, yttrium-aluminium garnet and a zirconia-yttria solid solution. The results of the quantitative phase analysis are presented in Table 1.

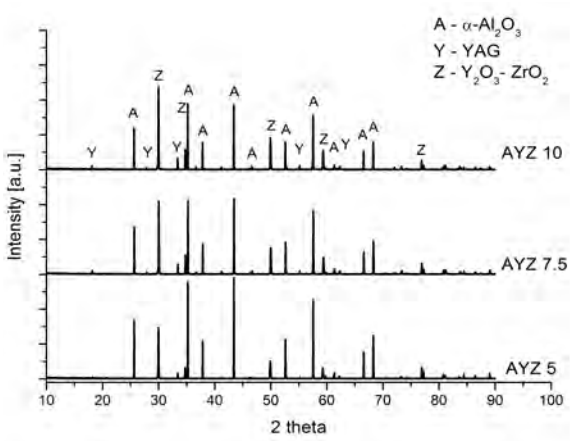

Fig. 1. XRD diffractograms of obtained composite sinters

Rys. 1. Dyfraktogramy XRD otrzymanych spieków kompozytowych

TABLE 1. **Quantitative phase composition of obtained composite sinters**

TABELA 1. **Ilościowy skład fazowy uzyskanych spieków kompozytowych**

Material	α-Al_2O_3		Y_2O_3·ZrO_2 solid solution		YAG	
	Measured [vol.%]	Theoretical [vol.%]	Measured [vol.%]	Theoretical [vol.%]	Measured [vol.%]	Theoretical [vol.%]
AYZ 5	92.3	90	6.8	5	0.9	5
AYZ 7.5	87.4	85	9.8	7.5	2.8	7.5
AYZ 10	83.8	80	12.7	10	3.5	10

Ritveld analysis of the XRD data confirmed that during sintering, a chemical reaction between alumina and yttria took place and as a result, the YAG phase was created. The amount of YAG phase was smaller than intended in all the prepared composites (Table 1). It suggests that the composition of the zirconia-yttria solid solution changed significantly during the sintering process. Detailed analyses of the chemical compositions gave the real content of yttria in the zirconia-yttria solid solution. This content changed from 13 to 16.7 mole % Y_2O_3. The results are presented in Table 2. Such results unambiguously indicate that during sintering, the yttrium atoms diffused into the zirconia, which caused chemical stabilization of the cubic zirconia phase. This phenomenon is not profitable because the starting

tetragonal zirconia phase has better mechanical properties that the cubic one.

TABLE 2. **Mean mole content of Y_2O_3 in ZrO_2 grains**
TABELA 2. **Średni udział molowy Y_2O_3 w ziarnach ZrO_2**

Material	mol.% Y_2O_3 in ZrO_2	zirconia phase symmetry
AYZ 5	16.7	cubic
AYZ 7.5	13.0	cubic
AYZ 10	13.1	cubic

TABLE 3. **Densification and mechanical properties of investigated materials**
TABELA 3. **Zagęszczenie oraz właściwości mechaniczne badanych materiałów**

Material	d_{app} [g/cm^3]	$d_{rel.}$ [%]	HV [GPa]	K_{Ic} [MPa·m$^{1/2}$]	σ [MPa]
Al_2O_3	3.96 ±0.002	99.3 ±0.7	16.7 ±0.6	4.0 ±0.2	632 ±107
AYZ5	4.02 ±0.002	98.1 ±1.2	14.3 ±1.3	2.9 ±0.6	598 ±105
AYZ7.5	4.02 ±0.001	96.7 ±1.0	16.8 ±1.4	3.0 ±0.7	544 ±133
AYZ10	4.10 ±0.003	96.8 ±0.3	16.2 ±1.0	2.6 ±0.3	551 ±72

Table 3 compares the densification level of the manufactured materials. As the reference sample, a polycrystalline α-Al_2O_3 sinter prepared at 1400°C was used. The relative densities (d_{rel}) of the composites were calculated using the real phase composition of the materials and real densities of the constituent phases (α-Al_2O_3, YAG and Y_2O_3·ZrO_2 solid solution). The densification level of the composites was distinctly lower than that measured for pure alumina. Such a phenomenon is well known and observed in many multiphase sintered systems [15]. The presence of rigid inclusions of second and optionally third, phases weakened the sintering driving forces in the matrix. It is worth noticing that there was a distinct difference between the densification level of composite AYZ5 and the others (AYZ7.5 and AYZ10). It was probably due to the different phase arrangement (Figs. 2-5). The BSED mode applied for SEM observations linked to the EDS analysis results allowed us to identify the phase composition of individual grains (Fig. 2). Of course EDS gave information about the chemical composition of the surrounding area about 1 micrometer in diameter only, but comparison of these results with the phase contrast presented in the BSED images with distinctly visible grain boundaries strongly suggested the phase composition of the individual grain. The lightest grains were supposed to be composed of a zirconia-yttria solid solution; the darkest ones were supposed to be alumina grains. Grains of a medium grey colour were most probably YAG inclusions.

The AYZ5 microstructure consists of isolated YAG and zirconia-yttria solid solution grains dispersed in the alumina matrix (Figs. 2, 3). Such a phase arrangement was relatively the best from the sintering point of view. Isolated grains in small amounts slightly hindered matrix densification. The additives in the composites marked as AYZ7.5 and AYZ10 created continuous chains of grains which hindered the matrix densification process.

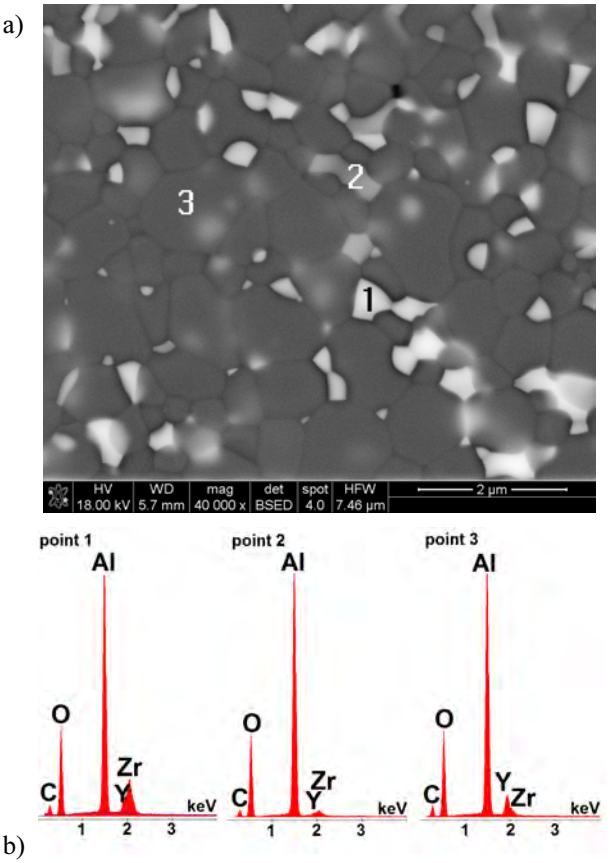

Fig. 2. Typical SEM image of AYZ5 composite (a); EDS spectra indicates chemical composition qualitatively in marked places (b)

Rys. 2. Typowy obraz SEM kompozytu AYZ5 (a); widma EDS wskazują jakościowo skład chemiczny w zaznaczonych miejscach (b)

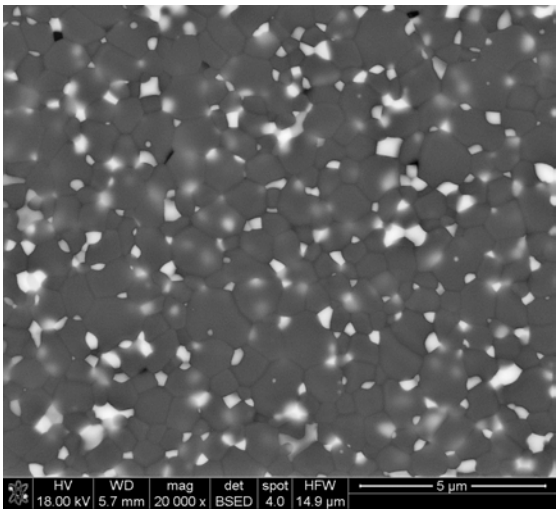

Fig. 3. Typical SEM image of AYZ5 composite

Rys. 3. Typowy obraz SEM kompozytu AYZ5

The densification level influenced the mechanical properties of the materials. The Vickers hardness (HV) of the AYZ5 composite was lower than that measured

for α-Al_2O_3. This was caused by lower densification and a smaller than assumed YAG content (0.9 instead of 5.0). The hardness increase reported in literature [1, 2] was detected in the Al_2O_3-YAG materials with at least 5 vol.% YAG phase.

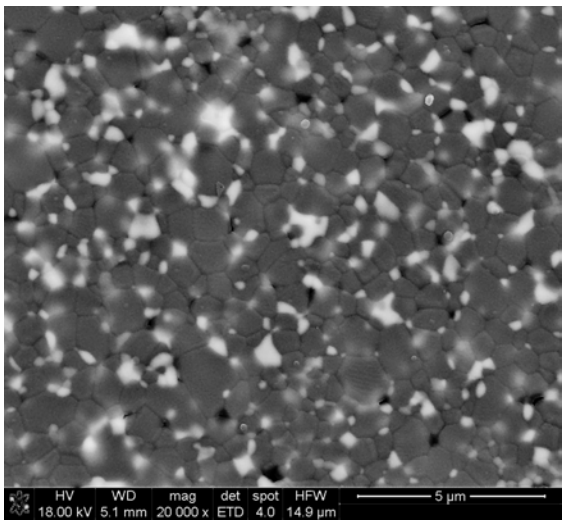

Fig. 4. Typical SEM image of AYZ7.5 composite
Rys. 4. Typowy obraz SEM kompozytu AYZ7.5

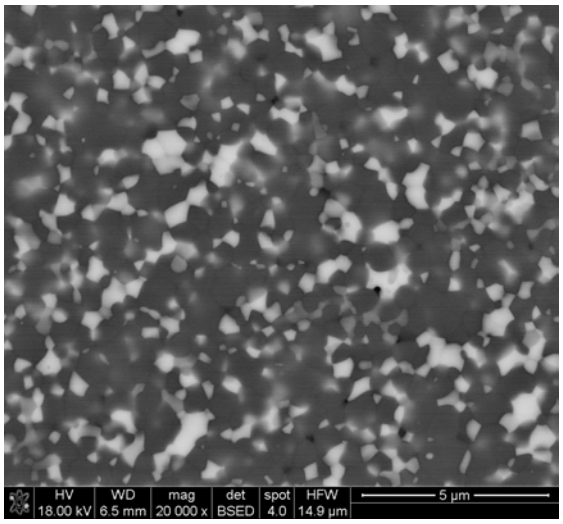

Fig. 5. Typical SEM image of AYZ10 composite
Rys. 5. Typowy obraz SEM kompozytu AYZ10

The Vickers hardness of the AYZ7.5 and AYZ10 composites was on the level of the alumina matrix hardness despite the relatively low density and lower YAG phase content. The bending strength (σ) and fracture toughness (K_{Ic}) of the composites were lower than those demonstrated by the alumina matrix material (Table 3). Such an effect probably appeared due to stabilization of the cubic zirconia phase instead of the tetragonal one. This fact eliminated the important toughening mechanism connected with the tetragonal to monoclinic phase transformation which was reported as the main factor influencing the very good mechanical properties of materials containing zirconia [16].

CONCLUSIONS

The concept of introducing tetragonal zirconia into the α-Al_2O_3-YAG composite as the third additional phase, assumed synergic action of both additives. Consequently it should improve the mechanical properties of the material.

The intensive diffusion of yttrium atoms durin composite sintering prevented proper phase composition of the final materials. The mentioned diffusion caused stabilization of the cubic zirconia phase, which is unprofitable for mechanical properties. It turned out that this diffusion was so intensive that it was impossible to preserve any traces of tetragonal zirconia in the manufactured composites. Additionally, the diffusion of the yttrium atoms significantly decomposed the YAG phase. It is worth mentioning that this decomposition was full, that means no other phases from the Al-Y-O system (YAP, YAM) were detected. The YAG decomposition resulted in alumina formation and the yttrium atoms went to zirconia-yttria solid solution grains. The described phenomena did not improve the mechanical properties of the manufactured composite sinters. The performed tests of pressureless sintering of triple phase composites manufactured from very fine, uniformly homogenized particles proved that in such sintering conditions it was not possible to limit yttrium atom diffusion enough to protect the material from significant YAG decomposition and cubic zirconia formation. Further works should focus on using faster and more effective sintering methods in order to limit unfavourable phenomena occurring during sintering.

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