MICROSTRUCTURE OF COMPOSITES [CE-TZP] - [AL_2O_3] MODIFIED BY Yb^{+3} AND Ca^{+2}

[a]L.I.PODZOROVA, [a]A ,A. IL'ICHEVA, [a]N.A. ALAD'EV, [a]O.I. PEN'KOVA, [a]L. I. SHVORNEVA, [b]S.BEREZINA, [b]V.ŠKORIK,

[a]*A.A. Baikov Institute of Metallurgy and Material Science RAS, Moscow, Russia*

[b]*University of Žilina, Slovakia, E-mail: berezi@fyzika.uniza.sk*

Abstract

Scanning electron microscope and atomic force microscope were used to study the microstructure of the modified nanocomposites produced from Ceria-stabilized ZrO_2/Al_2O_3 ([Ce-TZP]-[Al_2O_3]) nano-powder blend with/without Ca^{+2}- and Yb^{+3}- modifiers. The presence of Me+2- and Me+3- ions determines the various processes of the phase formation of metastable tetragonal zirconia and thus affects the changes in the composition and size of the grains. The data on the qualitative phase composition, the crystallization degree of the powder and crystal lattice parameters of tetragonal ZrO_2 solid solutions were obtained. The microstructure of all composites designates two types of the grains: one corresponds to α-Al_2O_3- phase with habit close to hexagonal one and ZrO_2 grains with a soft smooth shape. It was found that the composite modified by Ca^{+2} contains also elongated prismatic grains. The composition analysis of these grains, given by energy dispersive spectrometry, detects the presence of elements Al, Ca and Ce in amounts close to the compound of $CaCeAl_3O_7$.

Key words: Nanocomposite, [Ce-TZP]-[Al_2O_3], modifier, AFM

INTRODUCTION

Ceramic composites on the base of ZrO_2 and Al_2O_3 are known materials for denture applications due to their high wear and heat resistance and excellent biocompatibility. In addition, the presence in phase composition of solid solution of tetragonal ZrO_2 (*t*- ZrO_2) allows obtaining materials with high performance strength and resistance to brittle fracture. However, the potential of improving them is not exhausted, and their approximation to natural tooth material in the first place is associated with the use of nano-sized powders and modifying compounds for ceramic synthesis. Modifying the composition of the original powder blend by metal ions is an important factor affecting phase transformation in nano-sized precursors, the sintering process, the formation of the dimensional characteristics and the composition peculiarities of the grains [1]. This work studies the effect of Ca^{+2} and Yb^{+3} modifiers on the processes of thermal phase formation, structuring of [Ce-TZP] – [Al_2O_3]-nano-particles and then on themicrostructure of the obtained nanocomposites.

SAMPLES

The original blend of powder precursors with composition of 65 mol.% ($88.ZrO_2$ - $12CeO_2$) -35 mol% Al_2O_3 and 1 mol % of modifier (CaO or Yb_2O_3) was used as a test one. The powder precursors were obtained by hydrosol version of the sol-gel process in the presence of polyvinyl alcohol and isobutanol as the complex surface-active substances [1], [3]. A simultaneous component precipitation process giving the best results in formation of *t*-ZrO_2 phase [2] was used. A concentrated solution of aqueous ammonia was taken as a precipitant. Gel-like precipitates were dried at 120°C, then obtained xerogel was heat treated at 950°C. The size of nano-particles of all precursors of the blend was about 20-30 nm. Composites sintered at a

temperature of 1650°C have density values higher than 99,0% of the theoretical one for the monolithic samples.

METHODS AND RESULTS

The thermogravimetric analysis showed that exoeffect correspondent to the process of crystal phase formation in three component (ZrO_2 – CeO_2 - Al_2O_3) system is shifted to the high-temperature range in comparison with two component ($88.ZrO_2$ – $12.CeO_2$) system. This can be related with effect of presence of the Al^{+3}-, Ca^{+2}- and Yb^{+3}-cations forming the *t* - ZrO_2 metastable solid solutions [4].

X-ray diffraction measurement by diffractometer DRON-3 was used for determining the crystal lattice parameters of *t* - ZrO_2 solid solutions (Table1). Changes in the crystal lattice at temperatures of 1100 and 1300°C are associated with the process of Al^{+3}- cations output from the structure and they are correlated with the bigger values of ionic radii of Me^{+2}- and Me^{+3}- input, respectively, R_{Al}^{+3} = 0.054 nm, R_{Ca}^{+2} = 0,100 nm and R_{Yb}^{+3} = 0.090 nm.

Temperature, °C	Modifier	a, Å	c, Å	V, Å^3
1100	0	5,131	5,225	137,5
	Ca	5,132	5,225	137,6
	Yb	5,135	5,228	137,8
1300	0	5,126	5,228	137,4
	Ca	5,140	5,236	138,4
	Yb	5,140	5,234	138,3
δ, Å		0,001	0,002	0,2

Tab. 1. Crystal lattice parameters of *t* - ZrO_2 solid solutions

Microscopic study of the composites microstructure with/without modifying was carried out by atomic force microscope ”NEXT” (NTMDT) and scanning electron microscope «LEO1420" (CARL ZEISS). The AFM-images of non-modified composite and one modified by Yb_2O_3 (Fig. 1) demonstrate that their morphology is quite similar: one can easily indentify 1-2 μm big grains of α - Al_2O_3 phase (corundum) with habit close to hexagonal drowned in solid solution of ZrO_2 with smooth surface.

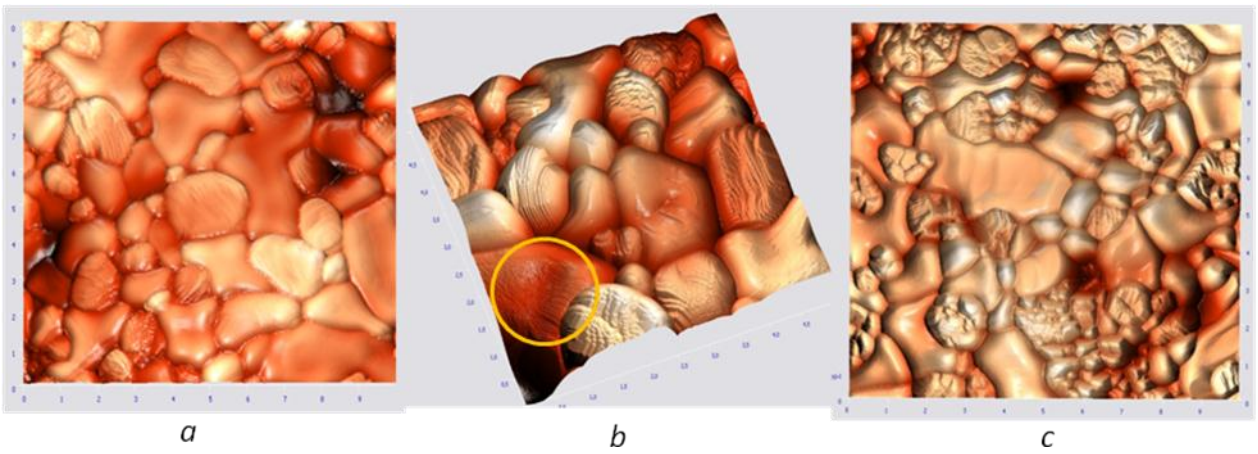

Fig.1. AFM images of the composites: non-modified (a,b) and modified by Yb_2O_3 (c).
Fields of view are 10 μm (a,c) and 5 μm (b)

The images do well show dislocation lines in Al_2O_3-grains, defining their mainly laminar substructure. The circle at the image of non-modified composite with 5 μm field of view (Fig. 1 *b*) illustrates the dislocation lines

in ZrO_2 solution. The distance between these lines is about 20-30 nm which is commeasurable with the size of nano-particles and corresponds to the high dislocation density (~10^{12} m^{-2}) of t-ZrO_2 solid solution.

The AFM images of the composite modified by CaO (Fig. 3 *a,b*) reveals besides the hexahedral Al_2O_3-grains a little amount of elongated prismatic grains. The *t* - ZrO_2 solid solution is visible here as shapeless grains with globular substructure. The elongated rod-shaped grains are well observed also at the SEM images (Fig. 3*c*).

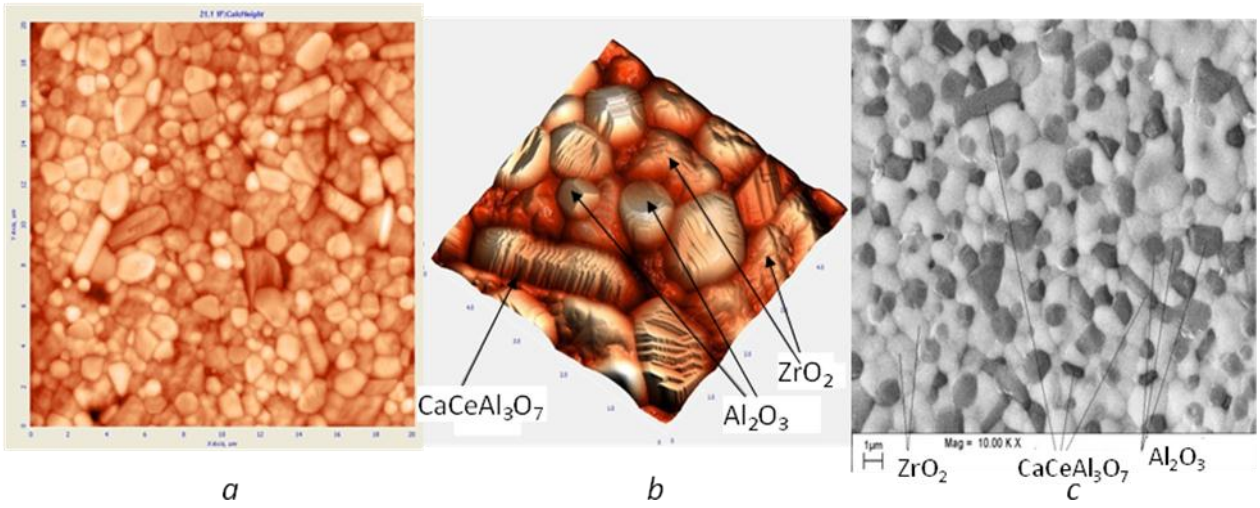

Fig. 3. The images of composite surface with Ca^{+2} modifier obtained by AFM (*a,b*) and SEM (*c*)

Composition analysis of modified composites was carried out by energy dispersive X-ray spectrometer "INCA Energy 300" (OXFORD INSTRUMENTS) coupled with SEM «LEO1420". Table 2 presents the content of main elements in different grains in the samples noted as 2 and 3 modified by CaO and Yb_2O_3, respectively. The measurement error depends on the accuracy of superposition of measured area (~1 μm) with specific chosen grain (i.e. there is a possibility of entering into a zone of grains of another species). As can be seen from Table 2, the phase containing aluminum is found primarily in dark or black grains, while the white grains correspond to phase containing zirconium.

Element	Element composition, at.%				
	Black elongated grains	Black hexahedral grains		White grains	
	Sample 2	Sample 2	Sample 3	Sample 2	Sample 3
O	71,5	70,6	67,5	63,7	68,1
Zr	3,6	4,2	3,1	30,6	22,9
Al	18,3	24,3	28,8	0,0	3,0
Ce	2,9	0,8	0,4	5,3	3,9
Hf*	0,0	0,0	0,0	0,3	0,4
Ca	1,0	0,0	0,0	0,1	0,0
Yb	0,0	0,0	0,1	0,0	0,6

Tab. 2. Content of the main elements in the grains in the ceramics modified by CaO (sample 2) and by Yb_2O_3 (sample 2). (* Hf is included in the basic elements because it is non detachable impurity of Zr).

So, one can identify the white grains with ZrO_2 and black hexahedral grains with corundum. Black elongated grains shows the presence of elements Al, Ca and Ce in amounts close to the compound of $CaCeAl_3O_7$.

CONCLUSION

It was shown that microstructure of the composite modified by Yb_2O_3 is not substantially different from the microstructure of non-modified composite: both of them have grains of corundum drown in ZrO_2 solid solution. Adding CaO to the blend of precursors leads to the sintering three-phase composite with hexahedral grains of corundum, shapeless ZrO_2-grains with globule substructure and prismatic elongated grains which are likely related to the $CaCeAl_3O_7$. AFM images reveal also the process of various dislocation growing for the grains of different habit.

ACKNOWLEDGEMENT

The work was done with the financial support of the VEGA project 1/0564/10 of MŠ SR and SRDA project LPP-0242-09.

LITERATURA

[1] SHEVCHENKO V.Ya., GLUSHKOVA V.B., et al. Obtaining the ultrafine powders of tetragonal solid solution in the system ZrO_2-CeO_2. Neorg. Materials, 2001, vol. 37, N7,pp. 821-827

[2] PODZOROVA L.I, ILJICHEVA A.A., MICHAJLINA N.A. et al., Phase formation in system ZrO_2-Al_2O_3-Ce_2O_3 . Neorg. Materials. 2002, vol. 38, N12, pp. 1455-1461

[3] PODZOROVA L. I., IL'ICHEVA A. A., SHVORNEVA L. I. et al., Phase formation of nanosize precursors *t-ZrO_2* - Al_2O_3 and formation of the microstructure of ceramics based on them. *Fiz. Khim. Stekla,* 2007, vol. 33 **(**5**),** pp. 703 - 709

[4] YASHIMA M., TAKASHINA H. et al. Low-tempeature phase equilibria by the flux method and the metastable-stable phase diagram in the ZrO_2 – CeO_2 system. J. Amer. Ceram.Soc. 1994, vol. 77, N 7. pp.1869 – 1874