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FABRICATION OF ZrO_2-Ti COMPOSITES BY SLIP CASTING METHOD

Slip casting is one of the most popular shaping method in ceramic technology which allows producing a large number of elements in small period of time. This shaping technique gives a possibility to fabricate ceramic or composite materials such as ZrO_2-Ti. Ti with its properties (low density, high melting point, high-temperature strength, good corrosion resistance and others) combine with ZrO_2 (high flexure strength, high compression resistance and very high K_{IC}) can be considered for different applications as constructional and functional materials. For the preparation of such composite nanometric zirconium oxide powder stabilized by 3 mol% Y_2O_3 and micrometric titanium powder were used. Water-based slurries with 35, 40, 45 and 50 vol.% solid phase content were prepared with 3, 10 and 15 vol.% addition of titanium powder. Zeta potential and pH of prepared slurries were considered. The pH changes were tested as a function of Ti content. The viscosity of the prepared slurries was measured. The sedimentation tests for selected slurries were performed. The casting rate for slurry of 35% solid phase with 10 vol.% Ti was examined. These measurements showed good stability of slurries. With the increasing of the solid phase concentration the density of the green bodies increased. However, the increase of the content of Ti powder reduced the density of green body samples. For selected samples the SEM observations was carried out. Composites produced by slip casting were characterized by a homogenous distribution of Ti particles in the ZrO_2 matrix.

Keywords: ceramic-metal composite, titanium, zirconium oxide, slip-casting

1. Introduction

Ceramic-metal composites with a ceramic matrix can be shaped for bulk materials by method such as die pressing [1] or methods based on colloidal processing such as slip casting [2-6]. Slip casting is one of the most common methods used in ceramic technology. Slip casting is a method in which aqueous suspension of ceramic particles is poured into a plaster mould. Samples are obtained by removing the liquid phase (solvent) through the pores of the form. The method enables the production, among others, ceramics or ceramics-metal composites with complex shapes [3-5].

The homogeneity of the slurry and the green density of casted samples affects the properties of the final material prepared by slip casting. Generally, the quality of the slurry must meet a number of requirements such as a highest possible solids content, high stability that prevent sedimentation, a low viscosity, good fluidity in order to evenly fill the form and to give the desired shape, exhibit the ability to flow even at very low amounts of addition of deflocculant and high casting rate [2-6].

Proper selection of the components of slips is highly dependent on powders used to create material. In order to produce ceramic-metal composite, preparation a mixture of ceramic powder and a suitable additive of metal powder. The slurry also consist, in addition to the powder, the solvent – usually water, deflocculant, binders, and surfactants. The preparation of the slurry for casting of ceramic metal composites focuses on preventing the sedimentation of heavy, usually micrometric metal particles. As a result, composites are produced with a homogenous distribution of metal particles in the volume of the ceramic matrix [2,5,7]. For the best properties ZrO_2 is additionally stabilized with a small content (3 mol%) yttrium oxide. This material has excellent resistance to thermal shock, corrosion resistance, high wear resistance, high strength and higher fracture toughness than many other ceramic materials [8-10]. Titanium is a metal characterized by a high strength relative to weight ratio, excellent corrosion resistance and biocompatibility. Titanium is used in many areas of advanced technology: aerospace, medicine and chemical industry. However, due to limitations resulting from low wear resistance titanium involves many complex processes [9-11]. The combination of both of these materials allows the formation of a composite with or improved properties and wide use even as thermal barriers. Despite to the used of couple ZrO_2-Ti will be limited to the properties temperature behavior of metal, the mechanical properties like fracture toughness of zirconia matrix with titanium particle may increase [8-10].

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The paper presents preliminary results of research on the production of composites from the ZrO_2-Ti system using slip casting method. There is no literature about the fabrication of ceramic metal composites from ZrO_2-Ti system by slip casting method.

2. Experimental details

For the preparation of slurries nano-sized powder of zirconium oxide ZrO_2 stabilized by 3 mol% Y_2O_3 (TOSOH) having a particle diameter below 100 nm (Fig. 1) and the micrometer titanium powder (MerckChemicals) with particle diameter d = 15,9 μm ±11,1 μm (Fig. 2) were used. The densities of the two powders were determined by a helium pycnometer AccuPyc 1340 II and were 5.88 g/cm^3 and 4.4 g/cm^3 for ZrO_2 and Ti respectively.

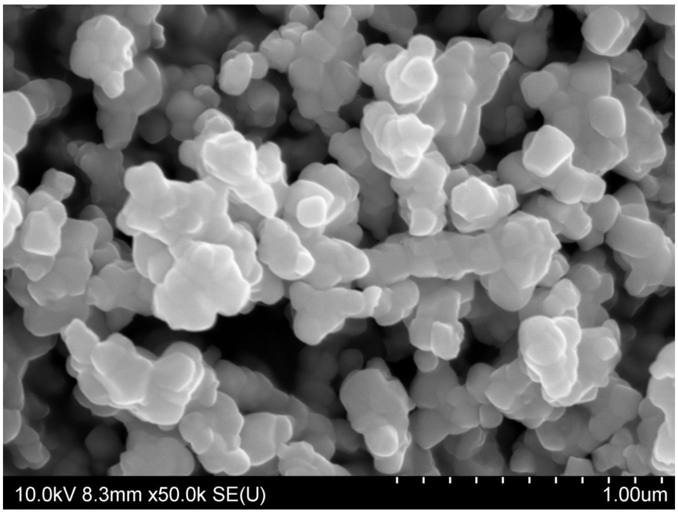

Fig. 1. SEM picture of agglomerated of zirconium oxide powder

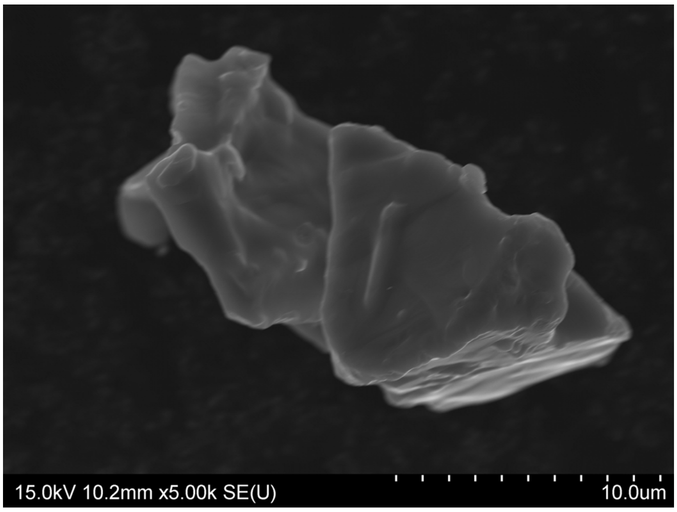

Fig. 2. SEM picture of microstructure of titanium powder

For the preparation of slurry as a solvent the distillate water was used. As deflocculant a diammonium citrate in an amount of 0.3 wt.% (in respect to the weight of solid phase) was used. The suspension was prepared by mixing for 1 h in a planetary ball mill Retsh PM 100. The prepared slurry was cast into plaster moulds. The volume fraction of powders was varied from 35 to 50 vol.% (Tab. 1). The concentration of Ti in the slurry was varied from 3 to 15 vol.% (Tab. 1).

TABLE 1

The participation of solid phase, titanium and zirconium powders in the prepared suspensions

	Solid phase content [vol.%]	**Ti content [vol.%]**	**ZrO_2 content [vol.%]**
I	35	10	90
II	40	10	90
IIIA	45	0	100
IIIB		3	97
IIIC		10	90
IIID		15	85
IV	50	10	90

The zeta potential of pure zirconia, titanium and the mixture of zirconia and titanium powders was measured using Zetasizer Nano ZS (Malvern Instruments). The concentration of powder in an electrolyte solution was about 100 ppm. The concentration of NaCl electrolyte was 10^{-3} M. Before the measurements every sample was sonicated for 5 min in ultrasonic bath EMMI 12HC (EMAG). The pH of the suspension was adjusted using 0.1 M HCl or NaOH solutions and varied from 3 to 11. The slurry should be characterized by a good stability in time, that uncontrolled agglomeration processes cannot take place. Instability of slurry would result in inhomogeneous density of green bodies after slip casting process, which would bring to the material stresses causing cracking of the material during sintering or significantly decrease the mechanical strength of the material. A key indicator of the stability of slurry is zeta potential which shows a degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion. It is assumed that the suspension is stable in a long period of time when the absolute value of the zeta potential is above 25-30 mV [12].

For measurement of casting rate the slurry of 35% solid phase with 10 vol.% Ti was prepared. The suspension was cast into plaster mould in diameter of 30 mm and 30 mm deep. The slurry temperature before casting was 21°C. The forms were filled with slurry and after 5 min excess of suspension was decanted. This same procedure was repeated for 10, 15 and 20 minutes. Afterwards the green bodies were removed from the moulds and dried in 105°C. For all samples the thickness at the half high of walls (d) were measured. Subsequently, the casting rate (V) was calculated using the formula [13]:

$$V = \frac{d_2^2 - d_1^2}{t_2 - t_1} \cdot f \tag{1}$$

where: d_2 – wall thickness of cake after casting time t_2 [mm], d_1 – wall thickness of cake after casting time t_1 [mm], f – correction factor for the viscosity of the water depending on the temperature, (slurry temperature at 21°C).

The viscosity of slurries was measured by Kinexus Pro rheometer (Malvern Instruments) in a plate-plate geometry. The diameter of rotating geometry was 40 mm. The gap between plates was 0.5 mm. During the measurements, value of shear rate was increased from 0.1 to 500 s^{-1}. The measurements were done at 25°C.

For the prepared slurries pH was measured. The density of the green bodies after casting by geometrical method was measured, by height and width of samples. Then the basic mathematical dependence was used, and density of green bodies was calculated. The sedimentation test was conducted in a plastic tube up to 16 hours. Scanning electron microscopy picture (HITACHI SU-70) of microstructure of the fracture for selected samples were observed.

Distribution of Ti particles within ceramic matrix was characterized on sintered samples with the use of computer image analyzer. In order to determine the distribution of the metallic particles the Voronoi tessellation have been used [14].

3. Results and discussion

Selection of the appropriate slurry is crucial in the production of composite materials, because it can affect the density of the green bodies and consequently the density and quality of the final material.

Fig. 3 and Fig. 4 show the relationship between zeta potential as a function of pH of aqueous suspensions of ZrO_2, Ti and mixtures of both powders in a volume ratio of 90:10. For measurements of metal powders should be aware that their surface is easily oxidized. Therefore, in the case of Ti powder, we measure the zeta potential of oxidized Ti. In aqueous solution the Ti particles containing a surface layer of TiO_2 are generally covered by hydroxyl groups. Hence, the surface charge is a function of solution pH, which is affected by the reactions that occur on the surface. The measured zeta potential of oxidized Ti are comparable with literature data of TiO_2 zeta potential [15, 16].

As presented in Fig. 3, the zeta potential of Ti and ZrO_2 in all investigated range of the pH shows negative values. Theoretical stability of the slurry (zeta potential greater than 25 mV) is achieved above pH 5. However, from the practical point of view, the slurries are enough stable for slip casting above pH 6 and pH 7 for Ti and ZrO_2 respectively.

The dependence of zeta potential as a function of the pH of the aqueous slurry of ZrO_2 and Ti mixture in a volume ratio of 90:10 with the presence of 0.3 wt.% diammonium citrate is presented in Fig.4. One can see that the addition of a small amount of dispersant increases the absolute value of the zeta potential. It means that the addition of the diammonium citrate increases the stability of suspensions in comparison to the slurries without the addition of dispersant. The zeta potential at pH 8, which corresponds to the pH of the ceramic slurries used for slip casting (Fig. 5) is approximately 35 mV. This value ensures high stability during casting confirmed by sedimentation test shown in Fig. 6. This follows the fact that at a pH above the pKa (acid dissociation constant) of diammonium citrate (pKa = 3.13, 4.76, and 6.40), the dissociation of two ammonium groups and proton occurs. As a result of ionization, the carboxyl groups of adsorbed molecules got a negative charge ($-COO^-$) what increases the absolute value of the zeta potential.

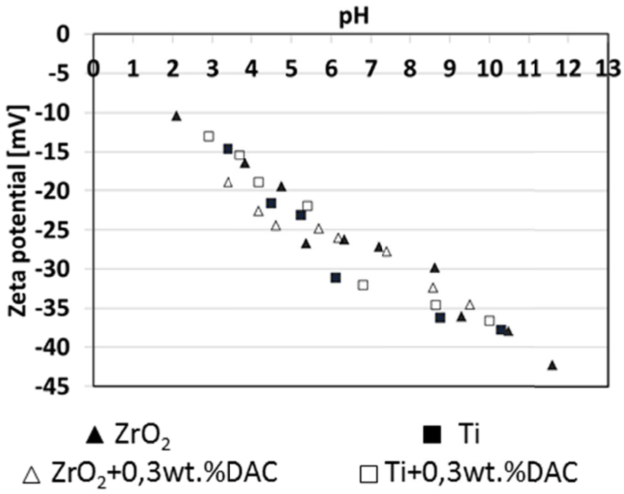

Fig. 3. Zeta potential as a function of pH of the aqueous suspensions of Ti and zirconia, with and without the presence of 0.3 wt.% diammonium citrate

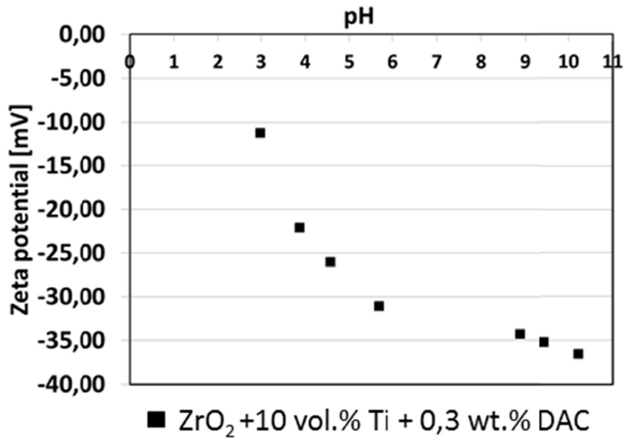

Fig. 4. Zeta potential as a function of the pH of the aqueous slurry mixtures of ZrO_2 and Ti powders in a volume ratio of 90:10 in the presence of 0.3 wt.% diammonium citrate

The conducted research have shown that the pH of the ceramic slurry depends on the amount of titanium in the suspension. The increase of titanium content decreases the pH of the slurry (Fig. 5). This may be due to attachment of water molecules to the Ti surface covered by layer of titanium oxide and the dissociation of hydrogen. As a result, the surface of titanium in an aqueous suspension can undergo hydroxylation releasing to solution H_3O^+ ions. Higher amount of titanium in slurry, the more hydrogen ions are released into solution decreasing the pH of suspension. This mechanism may be represented schematically as follows:

$$Ti + H_2O \rightarrow TiOH_2^+$$

$$TiOH_2^+ + H_2O \rightarrow TiOH + H_3O^+$$

However, it should be noted that the change in pH does not exceed 0.5 units, therefore, does not affect the overall stability of the composite slurry.

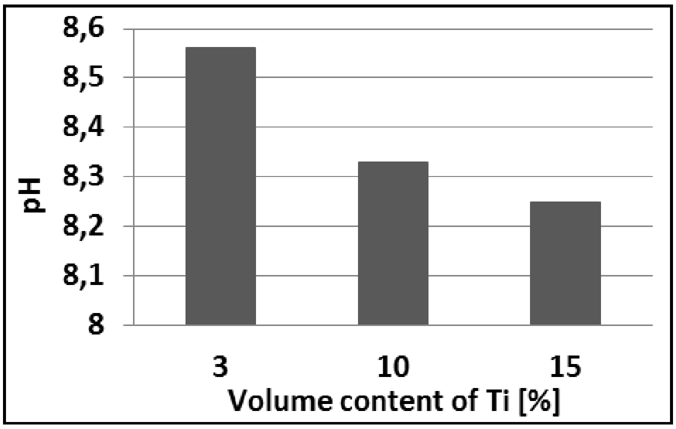

Fig. 5. The pH of suspension of different titanium content, for slurry with solid phase concentration of 45 vol.%

Fig. 6 shows the study of casting rate as a linear dependence of square of wall thickness of cake versus casting time. The used slurry was characterized by good castability, good fluidity and low sedimentation rate. The velocity of casting rate (*V*) is about 1,12 mm^2/min. It means that such slurry can be applied to obtain a ZrO_2-Ti composite with complex shapes with define wall thickness in quite short time.

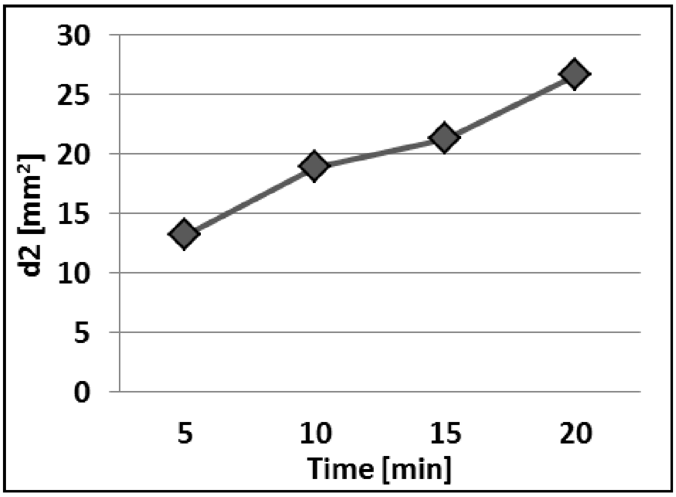

Fig. 6. Square of wall thickness of cake (d^2) versus casting time (slurry of 35% solid phase with content 10 vol.% Ti)

The effect of solids content on viscosity as a function of shear rate is showed in the Fig. 7. For slurry with 35 vol.% of solid phase the viscosity had the lowest value. Between suspension of 40 and 45 vol.% of solid phase different in viscosity was slight. For the slurry with 50 vol.% of solid phase the viscosity was much higher. However, the viscosity of all slurries was low enough to pour them into the mould and it filled the mould properly.

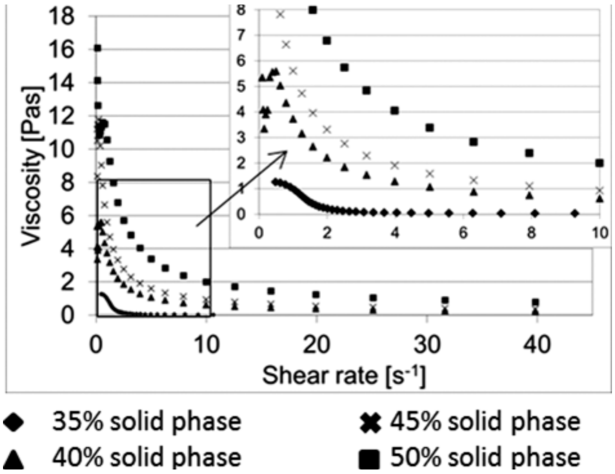

Fig. 7. Viscosity of the prepared slurries with different concentration of solid phase and 10 vol.% Ti content as a function of shear rate

The viscosity of slurries with different volume content of Ti is showed in the Fig. 8. The highest viscosity was observed for slurry without titanium particles. The slurry with 10 and 15 vol.% of titanium characterized by similar depending on viscosity and shear rate. With the increase of titanium volume content, the viscosity of slurries decreased.

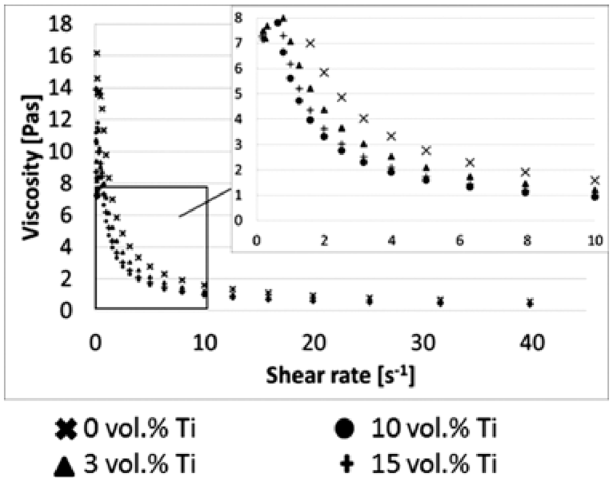

Fig. 8. Viscosity of the prepared slurries of 45% solid phase with various volume content of Ti as a function of shear rate

The decrease of viscosity could be connected with particle sizes of powders. Generally for the same volume fraction of powder the suspensions with smaller particles shows higher viscosity than the suspension with bigger particles. This effect is related with amounts of particles and distance between them which is greater in suspensions containing bigger particles. Therefore, the particles do not collide so often so the friction between particles is smaller and hence viscosity is reduced. In this research some volume of small zirconium particles is replaced by the same volume of bigger particles of Ti. It is mean that the average distance between particles increases while the number of particles in slurry decreases. As a result the viscosity decreases with increasing content of Ti.

As it was mentioned, one of the important features of the suspension for slip casting is preventing sedimentation. Although the stability of slurry can be predicted by zeta potential measurements, the sedimentation of "real" ceramic suspension can occurs. Usually this is due to low volume fraction of powder, low viscosity and especially high density of powders. That is why the sedimentation test gives an important information about behaviour of slurry during casting. In the study, the sedimentation test was carried out for two slurries with 10 vol.% of Ti and solid concentration of 40 and 50 vol.%. This test showed that in both cases after 1 hour, 8 h and 16 h no phase separation were observed. In Fig. 9 the results of sedimentation test after 16 h are presented.

The high concentration of solid phase makes the distance between the particles of powder quite small what allows them to stabilize together by mutual repulsion on the principle of electrostatic interactions. If the concentration of solid phase was not so high that despite the high value of zeta potential large particles of titanium with a relatively high density sediment in the gravitational field of the earth.

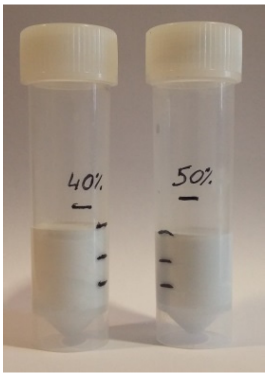

Fig. 9. Sedimentation test for selected slurries, picture after 16 h

Research has shown that with increasing concentration of solid phase for the fixed concentration of Ti, the density of green bodies formed by slip casting increases (Fig. 10). A higher solid content promotes more particle- particle interaction, hence decreases the space between particles occupied by water and consequently increasing the relative density [17]. However for increasing Ti concentration in slurries with defined solids content the relative density of green samples decreases. (Fig. 11). This may be related to the wide diversity of powder size. Micrometric sized titanium particles probably block rearrangement of particles during settling and decreasing the particles packing.

The selected slurry with the solid phase concentration of 45 vol.% and the titanium content of 10 vol.% was used to prepare samples for SEM observations of fracture of green body and sintered sample.

The observations of green body fracture showed homogenous distribution of titanium particles in ZrO_2 matrix. Single metal particles were closely surrounded by nano-size powder particles of ZrO_2 (Fig. 12). The microstructure of composite also includes pores resulting from the fact that the sample has approx. 51% of relative density. Such good homogeneity of samples was obtained due to the sufficiently high zeta potential and a high volume fraction of powders.

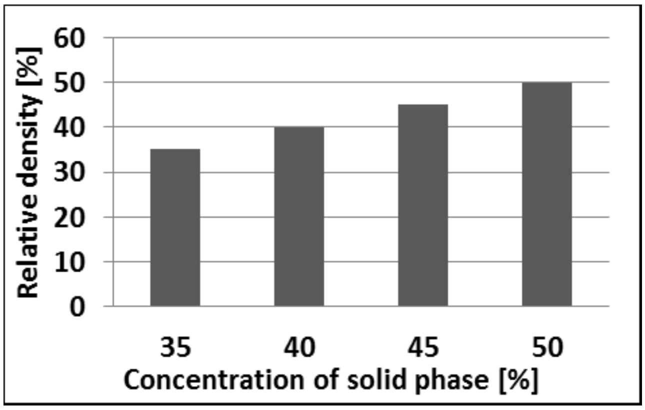

Fig. 10. Dependence of the concentration of solid phase in slurry (10 vol.% Ti) on green density

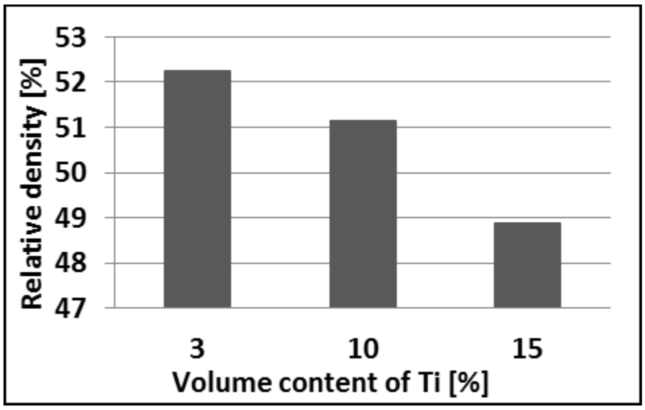

Fig. 11. The effect of Ti concentration on green density of slurry with 45 vol.% solid phase

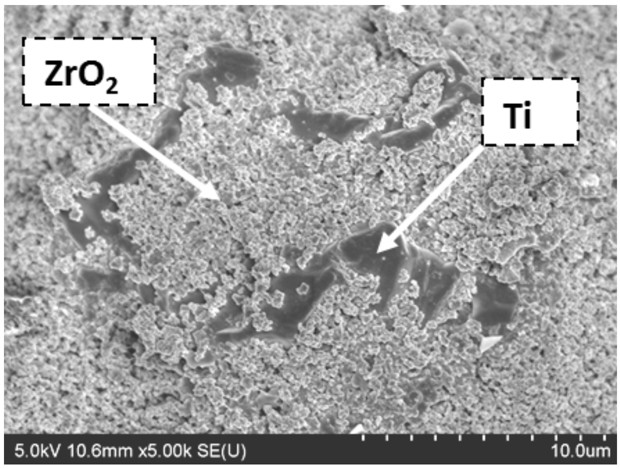

Fig. 12. The fracture of the green body, ZrO_2 – 10 vol.% Ti composite from slurry with 45 vol.% of the solid phase

Preliminary observations of fracture of the sintered at 1450°C for 2 h in Ar atmosphere samples also showed a homogenous distribution of titanium particles in a ceramic matrix

(Fig. 13). The observed particle size of the titanium powder in composite corresponds to size of starting metal particles. There was no delaminations and cracks on the border between the Ti particles and the ceramic matrix. The microstructure of the composite showed the presence of pores with varying size.

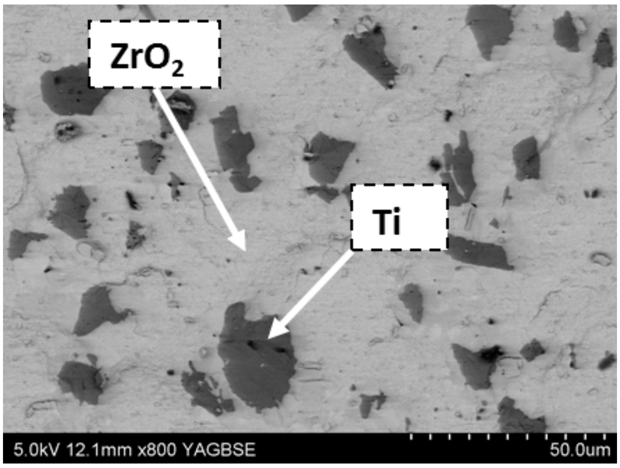

Fig. 13. The fracture of the sample after sintering, ZrO_2 – 10 vol.% Ti composite from slurry with 45 vol.% of the solid phase

4. Conclusion

Composite from ZrO_2-Ti system with different ratio of powders can be formed by slip casting method. The addition of 0.3 wt.% of diammonium citrate allows achieving high enough stability of slurry in pH above 7 to obtain homogenous samples with good dispersion of Ti particles in ceramic matrix in green state and after sintering.

The research shows that green density is dependent on volume fraction of powders and increases with increasing solid content. However, the increase of Ti concentration in slurry has negative effect on green density although, in the same time, the viscosity decreases with increasing Ti content what theoretically should improve the packing of particles during slip casting.

Due to good castability and low viscosity in quite wide range of solid content, the ZrO_2-Ti slurry could be adjust to slip casting of complex-shape element with define wall thickness in reasonable short time.

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REFERENCES

[1] K.L. Lin, C.C. Lin, Reaction between titanium and zirconia powders during sintering at 1500°C, J. Am. Ceram. Soc. **90**, 2220-2225 (2007).

[2] A. Tsetsekou, C. Agrafiotis, A. Milias, Optimization of the rheological properties of alumina slurries for ceramic processing applications, Part I: Slip-casting, J. Eu. Ceram. Soc. **21**, 363-373 (2001).

[3] H. Hassanin, K. Jiang, Fabrication and characterization of stabilised zirconia micro parts via slip casting and soft moulding, Scripta Mater. **69**, 433-436 (2013).

[4] M. Gizowska, M. Szafran, Moulding ceramic materials with slip casting, Ceram. Mater. **61**, 3, 173-178 (2009).

[5] K. Konopka, M. Szafran, E. Bobryk, Fabrication of Al_2O_3-Fe gradient composites by slip casting method, Composites **6**, 57-61 (2006).

[6] Y. Li, J. Lin, J. Gao, G. Qiao, H. Wang, Fabrication of reaction--bonded SiC ceramics by slip casting of SiC/C suspension, Mater. Sci. Eng. **A483-484**, 676-678 (2008).

[7] D. Huo, Y. Zheng, X. Sun, X. Li, S. Liu, Preparation of transparent Y_2O_3 ceramic by slip casting and vacuum sintering, J. Rare Earths **30**, 1, 57-62 (2012).

[8] W. Acchar, Y.B.F. Silva, C.A. Cairo, Mechanical properties of hot-pressed ZrO_2 reinforced with (W,Ti)C and Al_2O_3 additions, Mater. Sci. Eng. **A527**, 480-484 (2010).

[9] L.D. Teng, F.M. Wang, W.C. Li, Termodynamics and microstructure of Ti-ZrO_2 metal-ceramic functionally graded materials, Mater. Sci. Eng. **A293**, 130-136 (2000).

[10] K. Yousefipour, A. Akbari, M.R. Bayati, The effect of EEMAO processing on Surface mechanical properties of the TiO_2-ZrO_2 nanostructured composite coatings, Ceram. Int. **39**, 7809-7815 (2013).

[11] J. Zhu, A. Kamiya, T. Yamada, W. Shi, K. Naganuma, K. Mukai, Surface tension, wettability and reactivity of molten titanium in Ti/yttria-stabilized zirconia system, Mater. Sci. Eng. **A327**, 117-127 (2002).

[12] L. Kucharska, Reologia i fizykochemiczne podstawy procesów ceramicznych, Wydawnictwo Politechniki Wrocławskiej, Wrocław (1976).

[13] Norma branżowa, Ceramika, Metody badań, Oznaczanie szybkości nabierania czerepu, BN-86 7011-36.

[14] S. Ghosh, Z. Nowak, K. Lee, Quantitative characterization and modeling of composite microstructures by Voronoi cells, Acta Mater. **45**(6), 2215-2234 (1997).

[15] M.I. Nieto, C. Baudı´n, I. Santacruz, Reaction sintering of colloidal processed mixtures of sub-micrometric, alumina and nano-titania, Ceramics International **37**, 1085-1092 (2011).

[16] K. Suttiponparnit, J. Jiang, M. Sahu, S. Suvachittanont, T. Charinpanitkul, P. Biswas, Role of Surface Area, Primary Particle Size, and Crystal Phase on Titanium Dioxide Nanoparticle Dispersion Properties, Nanoscale Res. Lett. 6-27 (2011).

[17] J.A. Lewis, Colloidal processing of ceramics, J. Am. Ceram. Soc. **83**(10), 2341-59 (2000).