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ALUMINA MATRIX CERAMIC-NICKEL COMPOSITES WET PROCESSING

The main advantage of ceramic-metal composites is the increase of fracture toughness of the brittle ceramic matrix. The slip casting moulding method is widely used in the ceramic industry, which gives the possibility to obtain products of complicated shapes without green machining. Good quality and homogeneity of powder consolidation is crucial in the ceramic and ceramic matrix composite fabrication process as it influences the properties of the material.

In the case of such complex systems as powder mixture dispersions in a liquid medium (slurry), it is indispensable to investigate the phenomena taking place at the solid-liquid interface which determines dispersion stability and governs the interaction characteristics between the particles of different types (ceramic and metallic).

In the paper, the results concerning ceramic matrix ceramic-metal composite fabrication via the slip casting method are presented. The following materials were used: alumina powder (TM-DAR, Tamei Japan) of average particle size D_{50} = = 0.21 µm, specific surface area of S_{BET} = 14.5 m^2/g and density of d = 3.8 g/cm^3, and nickel powder (Sigma-Aldrich) of average particle size D_{50} = 2.17 µm, specific surface area of S_{BET} = 2.1 m^2/g and density d = 8.9 g/cm^3. Ceramic and metallic powders show great differences in electrokinetic behavior, which can cause the heteroflocculation effect to take place in the suspension. In order to investigate the particles interaction character, the zeta potential of each powder and its mixture was measured. The zeta potential measurements were performed on diluted suspensions that contained deflocculants, as a function of pH. Additionally, the particle size distribution of the diluted slurries was conducted in order to investigate the agglomeration characteristics. Rheological measurements of the slurries were performed. Furthermore, the chosen physical and mechanical properties of sintered bodies were examined (i.e.: bending strength, hardness and fracture toughness)

Keywords: ceramic-metal composite, alumina, nickel, zeta potential, slip casting

KOMPOZYTY TLENEK GLINU-NIKIEL O OSNOWIE CERAMICZNEJ FORMOWANE METODAMI OPARTYMI NA ODLEWANIU Z GĘSTWY

Zapotrzebowanie na tworzywa ceramiczne znacznie wzrosło w ciągu ostatnich lat ze względu na niepowtarzalne właściwości ceramiki, niemożliwe do osiągnięcia przy zastosowaniu innych materiałów. Do korzystnych cech ceramiki można zaliczyć dużą twardość, sztywność, odporność na ścieranie oraz niską gęstość. Jednak kruchość tych materiałów ogranicza obszar ich zastosowania. Jedną z metod zwiększenia odporności na kruche pękanie jest realizowane poprzez wprowadzenie plastycznych cząstek metalu do osnowy ceramicznej, na których energia rozprzestrzeniającego się pęknięcia ulega rozproszeniu.

Do tej pory do formowania kompozytów ceramika-metal o osnowie ceramicznej wykorzystywano głównie metody oparte na formowaniu z mas sypkich, spośród których można wyróżnić: prasowanie, prasowanie na gorąco, prasowanie izostatyczne czy metodę wtrysku. Jednak wszystkie te metody mają pewne ograniczenia. Głównym ograniczeniem wymienionych wyżej metod formowania kompozytów są olbrzymie trudności z formowaniem wyrobów o skomplikowanym kształcie i o znacznych wymiarach.

W artykule przedstawiono wyniki badań nad otrzymywaniem kompozytów o osnowie z tlenku glinu z rozproszonymi cząstkami niklu metodą bezciśnieniowego odlewania z mas lejnych w porowatych formach gipsowych na bazie proszków metalicznego i ceramicznego. Zastosowano tlenek glinu (proszek α-Al_2O_3, TM-DAR, Tamei, Japan) o średniej wielkości ziarna 0,2 µm i gęstości 3,8 g/cm^3 oraz niklu (Aldrich) o średniej wielkości ziarna 2,13 µm i gęstości 8,9 g/cm^3.

Wyznaczono krzywe zależności potencjału zeta i rozkładu wielkości cząstek od pH zawiesiny dla poszczególnych proszków i ich mieszanin w wodzie oraz w wodzie z dodatkiem substancji upłynniających w masie lejnej. Proszki wykorzystane w badaniach charakteryzują się dużą różnicą ich właściwości elektrokinetycznych, przez co w ich mieszaninie może dochodzić do efektu heteroflokulacji (przyciągania się elektrostatycznego cząstek różnego rodzaju i o różnym ładunku). Prowadzić to powinno do równomiernego rozmieszczenia cząstek metalicznych w kompozycie ceramika-metal. W wyniku powstawania przeciwnych ładunków podwójnej warstwy elektrycznej poszczególnych proszków dochodzi do elektrostatycznego przyciągania cząstek ceramicznych i metalu (tzw. efekt heteroflokulacji). Dzięki temu zjawisku kompozyt charakteryzuje się równomierną dystrybucją cząstek metalu w osnowie ceramicznej.

W niniejszej pracy przedstawiono opis zjawisk elektrokinetycznych występujących w układzie tlenek glinu i nikiel na podstawie pomiarów potencjału zeta sprzężonych z pomiarem rozkładu wielkości cząstek dla czystych proszków oraz ich mieszanin zarówno w wodzie, jak i w roztworze upłynniaczy stosowanych w masie lejnej. Ponadto przeprowadzono badania lepkości dynamicznej i naprężeń ścinających przy zmiennej szybkości ścinania mas lejnych o różnych zawartościach proszku niklu. Przedstawiono także wybrane właściwości fizyczne i mechaniczne spieczonych kompozytów.

Słowa kluczowe: kompozyt ceramika-metal, tlenek glinu, nikiel, potencjał zeta, masa lejna

INTRODUCTION

Ceramic-matrix composites due to their unique properties find applications in diverse fields. The presence of a ductile metal phase hinders the propagation of cracks in a ceramic matrix originating from a strain exhibited in the material. This results in, among others, an increase in fracture toughness and thermal shock resistance in comparison to ceramic material.

So far, most investigations concerning ceramic matrix ceramic-metal composite fabrication focused on methods based on powder processing (pressing, hot pressing etc. [1, 2]). These moulding methods lead to high densification and the process can be easily automated, however, they have some limitations. Namely, pressing methods can be applied only to the fabrication of small elements of simple shapes. Isostatic, hot isostatic pressing and injection moulding offer many more possibilities as far as the shape of the produced element is concerned, however, such methods require sophisticated apparatus that can withstand high pressure, which increases production costs. This is the reason why in recent years the wet processing of ceramic matrix ceramic-metal composites gained importance [3-7]. Slip casting, listed among wet processing methods, is a method where slurry poured into a porous mould is filtrated so that the solidified material settles on the mould surface replicating its shape.

The slip casting method gives the possibility of product shape control without green machining. It also guarantees good quality and homogeneity of powder consolidation which is crucial in ceramic and ceramic matrix composite fabrication as it influences the properties of the material.

However, powder suspension is a very complex system, in which case it is indispensable to investigate the phenomena taking place at the solid-liquid interface that determines slurry quality. In the case of a ceramic matrix composite, where the ceramic phase dominates, care must be taken so that the surface charge of ceramic particles is high enough and that the particles do not agglomerate in the suspension. Metallic particles are much more difficult to stabilize in water, as the high polarizability of metal causes the van der Waals attraction to govern their interaction characteristics, thus metallic particles are prone to agglomerate.

Furthermore, the suspension of mixed powders which show a certain degree of incompatibility in surface charge may interact with each other - heteroflocculation takes place [8, 9]. The particles of different kinds in a mixture tend to agglomerate. This phenomenon has both positive and negative results. High agglomeration caused by the heteroflocculation effect in the slurry may lead to the deformation and fluctuation of density in the green body [8]. Nonetheless, heteroflocculation may be desirable in the case of slurries containing a mixture of powders of different density [7]. The interaction between particles prevents the segregation of heavier material.

The final properties of composite elements are also sensitive to the last step of a ceramic matrix composite, which is sintering. Metallic particles may act as an inclusion that inhibit mass transport - hindering densification. Thus pressure is often applied during the sintering process of such materials. The second solution, leading to good densification, is the application of ceramic powders that are more sintering active.

The presented work gives an overview of each step of alumina-nickel composite fabrication with an insight to colloid chemistry. The used materials are characterized by their electrokinetic properties and basing on the results of the research the characteristics of particle interaction are given. Furthermore, the influence of metallic particles on slurry properties is described. Last but not least, the chosen mechanical properties of the sintered bodies are presented.

EXPERIMENTAL PROCEDURE

For the experiments the following materials were used: alumina powder (TM-DAR, Tamei Japan) of average particle size D_{50} = 0.21 μm, specific surface area of S_{BET} = 14.5 m^2/g and density of d = 3.8 g/cm^3, and nickel powder (Sigma-Aldrich) of average particle size D_{50} = 2.17 μm, specific surface area of S_{BET} = = 2.1 m^2/g and density d = 8.9 g/cm^3.

Ceramic water-based slurries with 50 vol% solid content were prepared with 0 and 3 vol% of nickel powder with respect to total solid volume. A composition of deflocculants i.e. citric acid (p.a., POCH Gliwice) and diammonium citrate (p.a., Aldrich), as well as a surface active agent - defoamer (octanol, Reachim) were added. The slurry also contained a binder (Duramax™ B-1000, Rohm and Haas) to increase strength. The ingredients were homogenized in a planetary mill with a rotating speed of 250 r.p.m. for 80 min. Afterwards, the air absorbed on the particle surface was removed by submitting the slurries to low pressure (10 hPa) for 15 min.

Zeta potential and particle size distribution measurements were conducted by means of a zeta potential analyzer (Zetasizer Nano ZS, Malvern Instruments) for diluted suspensions, which in the case of measuring powders without additives, underwent ultrasonication (BioLogics Inc., Ultrasonic 3000) for 10 min prior to measurement. The ionic strength was fixed with 10^{-3} M NaCl. The zeta potential as a function of pH was investigated. The pH value was set by the addition of HCl and NaOH. Rheological measurements were performed by means of a Brookfield DV II pro rheometer. The tests were carried out by an increasing and decreasing shear rate.

The samples were sintered in an argon flow at a temperature of 1300°C for 5 h. The physical parameters (porosity, apparent and relative density) of the sintered samples were estimated by means of the hydrostatic method. The theoretical density used to determine relative density was calculated from the rule of mixtures equation. Shrinkage was calculated from a change in sample dimensions.

The bending strength was estimated by the ball-on-ring test. The values were computed using Kirstein and Wooley's equation (1) [10, 11]:

$$\sigma_{max} = \frac{3P(1-\nu)}{4\pi t^2} \cdot \left[1 + 2ln\frac{a}{b} + \frac{(1-\nu)}{(1+\nu)}\left\{1 - \frac{b^2}{2a^2}\right\}\frac{a^2}{R^2}\right] \quad (1)$$

where *P* is the load, *t* - disk thickness, *a* - radius of the circle of the support points, *b* - radius of the region of uniform loading at the center, *R* - radius of the disk and *ν* - Poisson's ratio.

In order to estimate the fracture toughness value, a method based on the length measurement of cracks on the sample surface, originating from a Vickers diamond indentation, was used. The indentations were made under a load of 10, 20 and 30 kg. However, the hardness and fracture toughness only for indentations obtained under a load of 20 kg are given. Only central cracks were taken into account and the K_{IC} value was computed using the equation (2) [12]:

$$K_{IC} = 0{,}067 \cdot \left(\frac{E}{H_V}\right)^{0,4} \cdot \left(\frac{c}{a}\right)^{-1,5} \cdot H_V \cdot \sqrt{a} \quad (2)$$

where *a* is the half of the indent diagonal ($a = 0.5d$), H_V - Vickers hardness ($H_V = 1.8544F/d$), *E* - Young modulus, *c* - crack length.

Scan imagining was performed by means of a LEO 1530 scanning microscope. For better contrast of the composite components, the back scattered electrons detection technique was used.

RESULTS AND DISCUSSION

Alumina and nickel powder show great difference in their electrokinetic behavior. Pure alumina powder in water (10^{-3} M NaCl electrolyte) shows a point of zero charge at a pH of 9.3 (Fig. 1) and nickel - 4.6. Such colloidal incompatibility drives particles to interact, which can affect the slurry quality as the particles form large clusters. However, the zeta potential characteristic of alumina can be changed with the addition of deflocculants that have carboxylate groups in their molecule structure. One of such deflocculants is citric acid and its derivatives. Citric acid molecules adsorb at the alumina particle surface (via carboxylate groups). Not all carboxylate groups present in the citric molecule take part in adsorption. Thanks to those groups that are not coordinated to the surface, a negative charge on the alumina particles is created [13].

Depending on the amount of this additive, the point of zero charge (i.e. pH by which the zeta potential for alumina equals zero; pH_{pzc}), can be significantly decreased [13]. In this case, the pH_{pzc} of alumina with deflocculants in the amount that was used in the slurries, dropped to 5.75 (Fig. 1). Deflocculants do not change the zeta potential curve vs. the pH of the nickel powder significantly and the pH_{pzc} = 4.2. Alumina-nickel composite slurries showed a pH of about 7÷7.5. However, the characteristics of the zeta potential curve of the alumina-nickel mixture in the presence of deflocculants is very similar to the one obtained for alumina (in the presence of deflocculants), which can indicate that heteroflocculation takes place (Fig. 1).

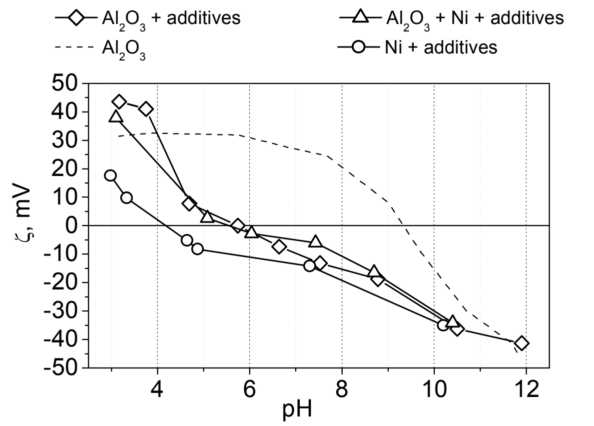

Fig. 1. Zeta potential as a function of pH of Al_2O_3, Ni powders and their mixture

Rys. 1. Potencjał zeta w funkcji pH proszku Al_2O_3, Ni i ich mieszaniny

Figure 2 represents the curves of the measured particle size distribution of the alumina slurry, nickel and alumina-nickel slurry. In the latter, there are no peaks corresponding to either the alumina or nickel peaks visible in the particle size distribution curves. The maximum of the curve of composite suspension is shifted to higher diameters, which indicates that some agglomeration takes place. This suggests that despite the fact that in the slurry, the pH of both nickel and stabilized alumina have a negatively charged surface, the particles agglomerate.

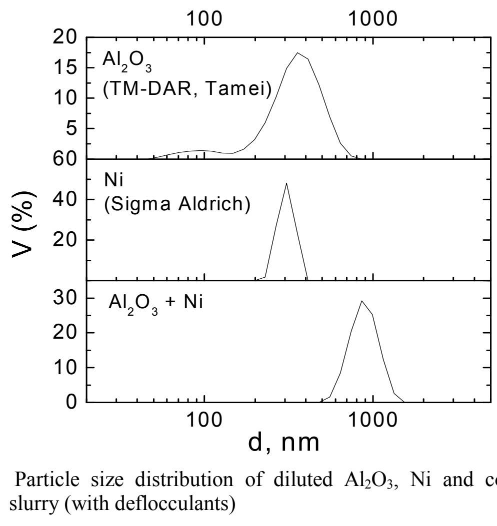

Fig. 2. Particle size distribution of diluted Al_2O_3, Ni and composite slurry (with deflocculants)

Rys. 2. Rozkład wielkości cząstek w masie lejnej proszku Al_2O_3, Ni i ich mieszaniny z zawartością upłynniaczy i innych dodatków

In this case, the interaction of nickel particles with alumina may compete with the phenomena of the adsorption of citric acid at alumina particles surface.

The rheological measurement (Fig. 3) showed that the presence of nickel particles in the slurry cause a significant increase in viscosity, however, the viscosity is low enough so that it is possible to pour it into the mould and it fills the mould properly. Furthermore, no sedimentation of nickel particles was observed.

The increase in viscosity may be a result of the alumina-nickel cluster presence that forms as a result of a difference in surface charge. When applying shear stress, greater shear friction occurs between such agglomerates. The slurry containing nickel particles exhibits shear thinning properties, however, the loop in the flow curve (Fig. 3) indicates time dependency.

Both alumina and coma) site green bodies are comparably well-densified and their measured relative density is respectively: 61 and 59%. In Table 1, the properties of the obtained sintered bodies are listed.

a)

b)

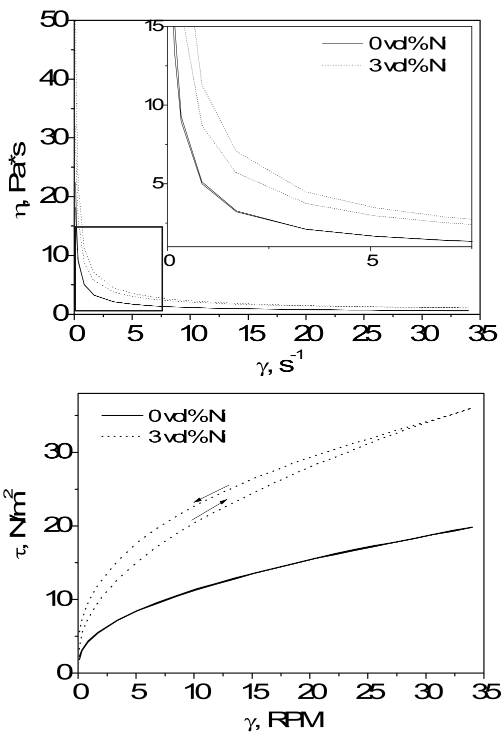

Fig. 3. Shear stress (a) and viscosity (b) as a function increasing (→) and decreasing (←) shear rate of Al_2O_3 and Al_2O_3-3 vol.%Ni slurries

Rys. 3. Zależność naprężenia ścinającego (a) i lepkości (b) od szybkości ścinania przy wzrastającej szybkości obrotów (→) oraz przy malejącej szybkości obrotów (←) masy lejnej z tlenku glinu oraz masy lejnej tlenek glinu-3%obj. niklu

The sintering conditions were selected as optimal for the alumina matrix. Alumina used in experiments is sintering active as it densifies already at 1300°C, a temperature at which nickel is in a solid state. In this situation, it is granted that the nickel particles will not melt and coalescent. However, the high surface area and higher reactivity of alumina powder results in higher reactivity with other species. Although the sintering process was carried out in an inert atmosphere, one can not avoid the remains of air or water adsorbed on the particles in green bodies. Hence a high system reactivity spinel phase forms at the sample surface. However, no spinel phase was observed at the alumina-nickel interphase.

TABLE 1. **Physical and mechanical properties of sintered Al_2O_3 and Al_2O_3-3 vol.% Ni composite samples**

TABELA 1. **Podstawowe właściwości fizyczne oraz wybrane parametry mechaniczne spieków z Al_2O_3 i Al_2O_3-3% obj. Ni**

			Nickel content, vol%			
			0		3	
Properties of sintered samples						
linear shrinkage	S_l	%	14.2%	± 1.0%	14.8%	± 0.4%
relative density	d_{rel}	%	97.6%	± 0.7%	97.3%	± 0.4%
Mechanical properties						
bending strength	W	MPa	475	± 141	308	± 125
Vickers hardness	H_{V20kg}	GPa	15.27	± 0.58	14.84	± 0.37
fracture toughness	K_{IC}	MPa·m^{½}	4.88	± 0.48	6.09	± 0.66

The distribution of nickel particles proved to be very homogenous (Fig. 4).

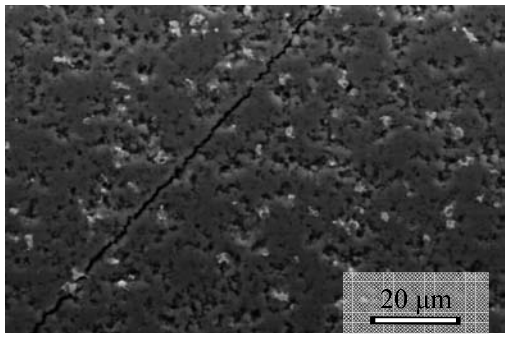

Fig. 4. Typical microstructure of Al_2O_3-Ni composites (light areas represent nickel and dark - alumina)

Rys. 4. Typowa mikrostruktura kompozytu Al_2O_3-Ni (jasne obszary odpowiadają fazie metalicznej, natomiast ciemny obszar odpowiada tlenkowi glinu)

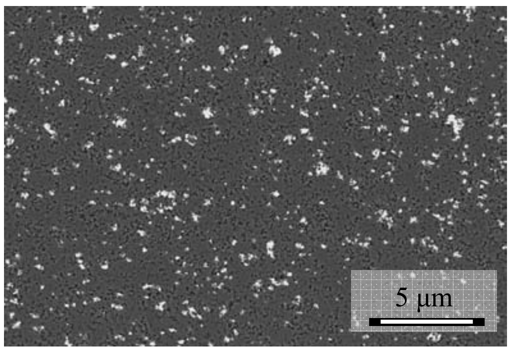

Fig. 5. Deflection of crack path (originating from Vicker's indentation) by nickel particle

Rys. 5. Ugięcie pęknięcia wychodzącego z naroża odcisku po wgłębniku Vickersa

Increase in fracture toughness is observed for in composites in comparison to alumina samples. On the other hand, the bending strength is lower for the composites. In ceramic matrix composites reinforced by ductile metal particles, an increase of fracture toughness results from the inhibition of propagating cracks due to a few mechanisms, i.e.: crack bridging, crack path deflection by particles and crack relaxation via local plastic flow [14].

In dispersive composites, in which particles of different phases are dispersed in the matrix, the presence of particles imposes a specific distribution of residual thermal stresses. In composites in which the dispersed particles are characterized by a higher thermal expansion coefficient than the matrix, there are regions where compressive stresses resulting from thermal expansion coefficients mismatch between the particles and matrix exhibit [15]. In those regions it is less probable for a crack to propagate [15]. Thus the energy of propagating cracks is dispersed by means of its crack path deflection (Fig. 5). This kind of distribution of residual thermal stresses resulting from this kind of thermal coefficient mismatch causes an increase in fracture toughness, which was observed for the obtained Al_2O_3-Ni composites, without a significant change in bending strength. In this case, however, a drop in bending strength was observed.

CONCLUSIONS

The zeta potential curve of a powders mixture does not show the intermediate characteristic of those obtained separately for alumina and nickel, but it resembles the one of alumina. This can indicate that due to the great colloidal incompatibility of alumina and nickel particles, they interact with each other - heteroflocculation effect takes place. Thanks to this interaction, nickel particles that are more than twice as heavy as alumina (d_{Al2O3} = 3.8 g/cm^3, d_{Ni} = 8.9 g/cm^3) do not sediment. The presence of nickel particles influences the rheological stability of slurries. Slurries containing nickel particles have a higher viscosity. Pressureless sintering was applied. Both composite and ceramic sintered samples showed high relative density. The presence of metallic particles in the ceramic matrix caused an increase in fracture toughness with only a slight decrease of hardness.

Acknowledgments

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REFERENCES

[1] Aldridge M., Yeomans J.A., The thermal shock behavior of ductile particle toughened alumina composites, Journal of European Ceramic Society, 1998, 19, 1769-1775.

[2] Konopka K., Oziębło A., Microstructure and the fracture toughness of the Al2O3-Fe composites, Materials Characterization 2001, 46, 125-129.

[3] Moya J.S., Lopez-Esteban S., Pecharroman C., The challenge of ceramic/metal microcomposites and nanocomposites, Progress in Materials Science 2007, 52, 1017-1090.

[4] Tomsia A.P., Saiz E., Ishibashi H., Diaz M., Requena J., Moya J.S., Powder processing of mullite/mo functionally graded materials, Journal of European Ceramic Society 1998, 18, 1365-1371.

[5] Hernandez N., Sanchez-Herencia A.J., Moreno R., Forming of nickel compacts by a colloidal filtration route, Acta Materialia 2005, 53, 919-925.

[6] Szafran M., Konopka K., Bobryk E., Kurzydłowski K.J., Ceramic matrix composite with gradient concentration of metal particles, Journal of European Ceramic Society 2007, 27, 651-654.

[7] Gizowska M., Szafran M., Konopka K., Bobryk E., Wasilewski Ł., Kompozyty ceramika-metal otrzymywane z wykorzystaniem ceramicznych mas lejnych, Kompozyty (Composites) 2008, 1, 53-58.

[8] Konsztowicz K.J., Wpływ heteroflokulacji zawiesin koloidalnych Al_2O_3-ZrO_2 na mikrostruktury i właściwości mechaniczne ich kompozytów, Polskie Towarzystwo Ceramiczne, Kraków 2004.

[9] De Faria L.A., Trasatti S., Physical versus chemical mixtures of oxides: the point of zero charge of Ni-Co mixed oxides, Journal of Electroanalitycal Chemistry 2003, 355--359.

[10] Shetty D.K., Rosenfield A.R., McGuire P., Bansal G.K., Duckworth W.H., Biaxial flexure tests for ceramics, Ceramic Bulletin 1980, 59(12).

[11] Gijsbertus de With, H.M. Wagemans, Ball-on-ring test revisited, Journal of American Ceramic Society 1989, 72(8).

[12] Niihara K., Morena R., Hasselmann D.P.H., Evaluation of K_{IC} of brittle solids by indentation method with low crack-to-indent ratios, Journal of Materials Science Letters 1982, 1, 13-16.

[13] Hidber P.C., Graule T.J., Gauckler L.J., Citric acid: A dispersant for aqueous alumina suspensions, Journal of American Ceramic Society 1996, 79 1857-1867.

[14] Konopka K., Maj M., Kurzydłowski K.J., Studies of the effect of metal particles on the fracture toughness of ceramic matrix composites, Materials Characterisation 2003, 51, 335-340.

[15] Pampuch R., Kompozyty ceramiczne, Kompozyty (Composite) 2003, 2 3-15.

