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PROPERTIES OF WATER-BASED SLURRIES FOR FABRICATION OF CERAMIC-METAL COMPOSITES BY SLIP CASTING METHOD

WŁAŚCIWOŚCI WODNYCH ZAWIESIN DO OTRZYMYWANIA KOMPOZYTÓW CERAMIKA-METAL METODĄ ODLEWANIA Z MAS LEJNYCH

The main advantage of ceramic-metal composites is the increase of fracture toughness of the brittle ceramic matrix. The slip casting method gives the possibility to obtain products of complicated shapes without green machining.

In the work results concerning colloidal and rheological aspects of ceramic-metal composite fabrication via the slip casting method are presented. Slurry consisted of ceramic (α-Al_2O_3) and nickel powder suspended in water with addition of deflocculants composition (citric acid and diammonium citrate), surface-active agents and binder. Ceramic and metallic powders show great differences in electrokinetic behavior, which cause that the heteroflocculation effect in the suspension can take place. In order to investigate the particles interaction characteristics, the zeta potential of each powder was examined. The zeta potential measurements were performed for diluted suspensions as a function of pH. Rheological measurements of the slurries were performed. Although surface of alumina was modified, so that the electrokinetic behavior resembled one of nickel, it turned out that the presence of nickel particles has great influence on the slurry properties. The change of rheological properties for slurries containing nickel particles results probably from strong interaction between alumina and nickel particles.
Keywords: alumina, ceramic-metal composite, nickel, slip casting, zeta potential

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.

Przedstawiono wyniki badań właściwości mas lejnych do otrzymywania kompozytów o osnowie z tlenku glinu z rozproszonymi cząstkami niklu metodą odlewania z mas lejnych na bazie proszków metalicznego i ceramicznego. W skład mas lejnych wchodziła mieszanina proszku tlenku glinu i niklu oraz układ upłynniaczy, środek powierzchniowoczynny i spoiwo. Materiały wykorzystane w badaniach charakteryzują się dużą różnicą ich właściwości elektrokinetycznych, przez co w ich mieszaninie może dochodzić do efektu heteroflokulacji (przyciągania się elektrostatycznego cząstek o różnego rodzaju i o różnym ładunku).

W niniejszej pracy przedstawiono opis zjawisk elektrokinetycznych występujących w układzie tlenek glinu i nikiel na podstawie pomiarów potencjału zeta zarówno w wodzie, jak i w roztworze upłynniaczy stosowanych w masie lejnej. Ponadto przeprowadzono badania właściwości reologicznych w celu określenia wpływu obecności cząstek metalicznych w masie lejnej na właściwości zawiesiny. Wprowadzane do masy lejnej środki upłynniające modyfikują powierzchnię tlenku glinu minimalizując aglomerację cząstek związaną z efektem heteroflokulacji. Pomimo to zaobserwowano znaczny wpływ obecności cząstek niklu na właściwości reologiczne mas lejnych.

1. Introduction

Ceramic-matrix composites due to their unique properties find application in diverse fields. Presence of ductile metal phase hinder propagation of cracks in ceramic matrix originating from strain exhibiting in the material. This results in, among others, an increase of fracture toughness and thermal shock resistance in comparison with ceramic material [1-3].

Lately, much interest has been devoted to design the fabrication method of ceramic-metal composites by colloidal route [1, 4-8]. Slip casting molding method is widely used in ceramic industry. In this method powders are formed from slurries – dispersions of particles

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in liquid medium. Slurry after being poured into porous mould is filtrated so that solidified material settles at mould surface replicating its shape. Slip casting method gives possibility of product shape control without green machining step. It also guarantees high quality and homogeneity of powder consolidation. Uniform densification in the green state is crucial in ceramic and ceramic matrix composites fabrication rout as it influences the properties of the material [9].

Suspension of powders is a very complex system. In order to predict slurry quality it is indispensable to investigate the phenomena taking place at solid-liquid interface. Certain phenomena and reactions taking place at the material surface immersed in water cause that surface of the material is charged. Potential drop between charged particle surface and bulk solvent constitutes an opposite force to van der Waals attraction between particles. One of the method of colloid stabilization uses this effect. The surface of dispersed phase is modified (e.g. by ionization of surface groups, ion adsorption) so that the potential drop overwhelms the tendency to agglomeration [10].

In case of ceramic matrix composite dispersion, where ceramic phase is dominating, it must be taken care that surface charge of ceramic particles is high enough, so that particles do not agglomerate in the suspension. High polarizability of metal causes that metallic particles are much more difficult to stabilize in water, as van der Waals attraction governs their interaction characteristic. Thus metallic particles are prone to agglomerate.

The charge value depends (among others) on electrolyte pH. Each material is characterized by pH_{pzc} (*point of zero charge*) in which pH the total charge on a surface equals zero. While designing a slurry consisting of two kinds of powders it is crucial to examine their electrokinetic characteristics. Suspension of mixed powders which show certain degree of incompatibility in surface charge may interact with each other – heteroflocculation takes place [11-13]. In such a suspension, in certain range of pH particles show opposite surface charge, which causes that particles attract each other and undergo agglomeration, which is schematically shown in Fig. 1.

This phenomena have both positive and negative results. High agglomeration caused by heteroflocculation effect in the slurry may lead to deformation and fluctuation of density in green body [11] or even slurry flocculation. Whereas, heteroflocculation may be desirable in case of slurries containing mixture of powders of different density [6]. Interaction between particles prevents from segregation of heavier material.

Materials used in experiments are characterized by their electrokinetic properties and basing on these results the characteristics of particle interaction are given. Furthermore, the influence of metallic particles presence on slurry properties is described.

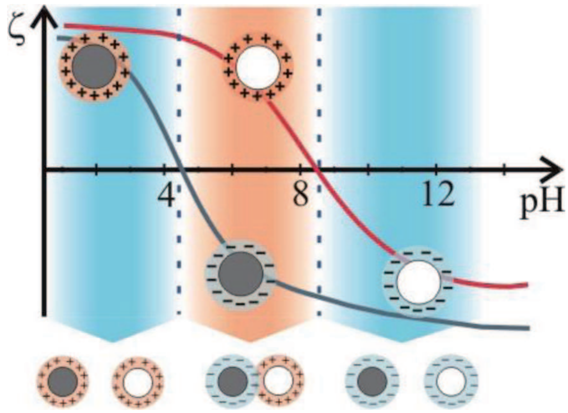

Fig. 1. Scheme of possible interactions in dispersion of powders mixture that show great colloidal incompatibility depending on pH value

2. Experimental

Experiments were performed using following materials: 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 initial average particle size D_{50} = 0.53 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, 0.5, 3 and 5 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^{TM} B-1000, Rohm and Haas). 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 measurements were conducted by means of a zeta potential analyzer (Zetasizer Nano ZS, Malvern Instruments) for diluted suspensions, which underwent ultrasonication (BioLogics Inc., Ultrasonic 3000) for 10 min prior 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 Brookfield DV II pro rheometer. The tests were carried out by an increasing and decreasing shear rate.

Further investigations concerning rheological properties were carried out for alumina slurry and alumina slurry containing 3 vol.% of nickel powder. Rheological characterization was conducted by means of Kinexus Pro (Malvern) rotational rheometer with attached C25 SC002 SS spindle and PC25 C0027 AL cylinder. The flow behavior was measured under shear stress controlled regime. The curves obtained by increasing shear rate were fitted to Moore model. Moore model is a simplified version of the Cross model [14, 15]:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 - K\dot{\gamma}} \tag{1}$$

where: η – viscosity [Pa·s], $\dot{\gamma}$ – shear rate [s^{-1}], K – coefficient of consistency, inversely proportional to shear rate of the onset of shear thinning [s], η_0 – extrapolation of viscosity to the zero shear rate, η_∞ – limiting value of viscosity at shear rates $\dot{\gamma} \to \infty$ [15].

The curves were also fitted to Ostwald-de Waele model:

$$\tau = k\dot{\gamma}^n \tag{2}$$

where: k – flow consistency index [$N \cdot s^n/m^2$], n – the flow behaviour index (dimensionless).

Viscoelastic properties of ceramic suspensions were studied by frequency sweep in stress controlled mode. Before the measurement was carried out, linear viscoelastic range was determined.

Time dependency on rheological properties were estimated by single shear stress rate (10 s^{-1}) viscosity measurement. All measurements were performed at 25°C.

3. Results and discussion

Pure alumina powder in water shows a point of zero charge at a pH of 9.3 and nickel – 4.6 (Fig. 2). Thus in pH range of 4.6-9.3 particles are oppositely charged and dispersion flocculates. The interaction is very strong and in this range it is impossible to disperse mixture of alumina and nickel powder and to obtain a slurry of good quality without any additives.

On the other side, it is recommended to keep nickel powder in water suspensions in pH range of 6-10, because of its chemical stability [16]. In order to obtain a well stabilized slurry all particles in the dispersion must show the same charge in this pH range. The zeta potential characteristic of alumina can be easily modified by applying some additives that decrease pH of point of zero charge (pH where ζ=0) and cause that its electrokinetic characteristics resembles one of nickel. An affective additive that shifts alumina isoelectric point 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 [17,18]. which decreases total charge of alumina surface.

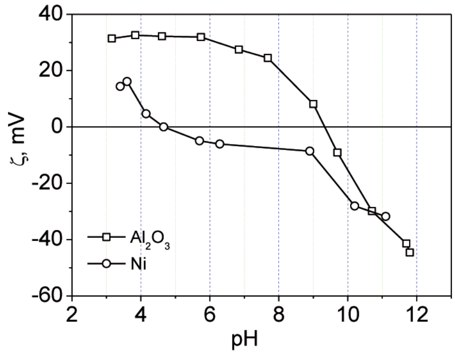

Fig. 2. Zeta potentials of Al_2O_3 and Ni powders in water as a function of pH

In presence of applied composition of deflocculants alumina pH_{pzc} (*point of zero charge*) drops to about 6,5, whereas there is no significant influence for nickel powder observed (pH_{pzc}(Ni)=4.2) (Fig. 3).

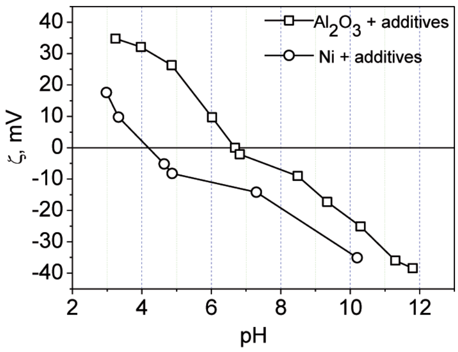

Fig. 3. Zeta potential as a function of pH of Al_2O_3 and Ni powders with additives

The rheological measurement (Fig. 4) showed that the presence of nickel particles in the slurry cause a significant increase of 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.

All slurries were prepared with the same volume content of powders. The variable was the nickel content in the dispersion.

The size of nickel particles was over two times greater than those of alumina powder. The bigger the particles, the fewer the possible number of particle-particle contact points. On the contrary, with decreasing particle size in a slurry containing the same volume fraction of solids, the agglomeration of particles would more probable because of the greater number of contact spots between particles. Thus the increase of viscosity cannot be a result of the increase of the number of grain-grain contact as with addition of nickel powder, the average particle size diameter increases.

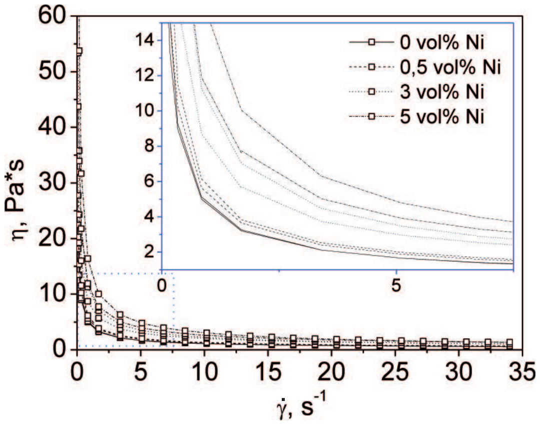

Fig. 4. Viscosity as a function of increasing (γ) and decreasing (ϕ) shear rate of Al_2O_3 and Al_2O_3-Ni slurries

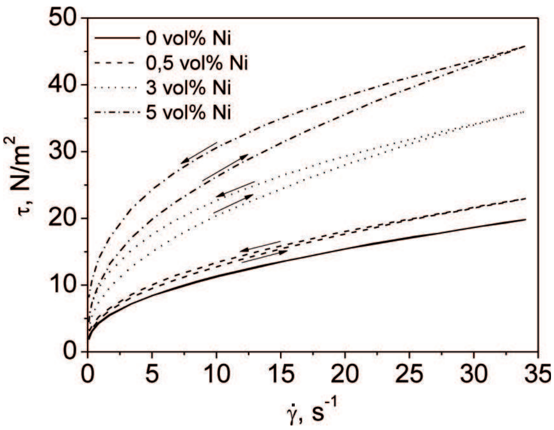

Fig. 5. Shear stress as a function of increasing (γ) and decreasing (ϕ) shear rate of Al_2O_3 and Al_2O_3-Ni slurries

Both alumina based and composite slurries exhibit shear thinning properties. Dispersions containing nickel particles exhibit time dependency (Fig. 4 and 5). Additionally, the higher the nickel content, the more distinct the loop in the flow curve occurs (Fig. 4).

Both the observed increase of viscosity and more distinct time dependency of slurries containing nickel particles indicate that some structure is formed in the slurry. Increase of viscosity may be the result of certain agglomeration. Although the alumina surface was modified and in the pH of the slurry show the same surface charge as nickel, some interaction between alumina and nickel particles may occur. Consequently, the surface modification appeared to be insufficient in preventing from heterofloculation effect. Alumina-nickel agglomerates cause greater shear friction in liquid "layer" movement along each other. The alumina-nickel interaction imposes the formation of internal slurry structure.

In Fig. 6 flow curves for alumina slurry and alumina slurry containing 3 vol.% of nickel for high shear rate is presented (up curves). These measurements served for estimation of rheological parameters that are presented in Table 1.

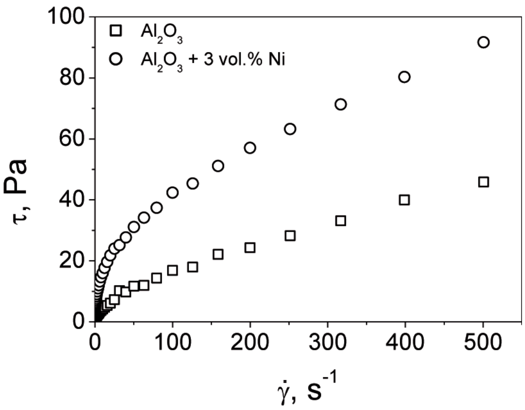

Fig. 6. Flow curves of alumina and alumina-nickel (3 vol.%) suspensions obtained in shear stress controlled mode. Only up-curves are presented

TABLE 1
Rheological parameters of alumina and alumina-nickel suspensions

	n*	G', G" crossover frequency	η_0	η_∞
Slurry composition	–	Hz	Pa·s	Pa·s
Al_2O_3	0.57	0.63	12.00	0.049
Al_2O_3+ 3 vol.% Ni	0.39	–	33.20	0.176

* flow behavior index from Ostwald-de Waele model

On the basis of the rheological parameters listed in table 1 few conclusions can be drawn. The flow consistency index for both slurries is n<1 which proves shear thinning behaviour. The coefficient value for alumina slurry is higher. This means that although composite slurries show higher viscosity, it has greater tendency for thinning when shear stress is applied. On the other hand, infinit viscosity value for composite slurry is three times higher than the one of alumina slurry. This can indicate, that the structure in the slurry is complex. Alumina-nickel agglomerates, formed as a result of colloidal incompatibility of the materials, are very stable. Agglomerates may interact with each other, whereas the agglomerate-agglomerate interaction is much weaker than these occurring between alumina-nickel and even alumina-alumina particles. The agglomerate-agglomerate structure undergoes destruction already by applying low shear stress – which is observed as shear thinning behavior, which is more distinct than one observed for alumina slurry.

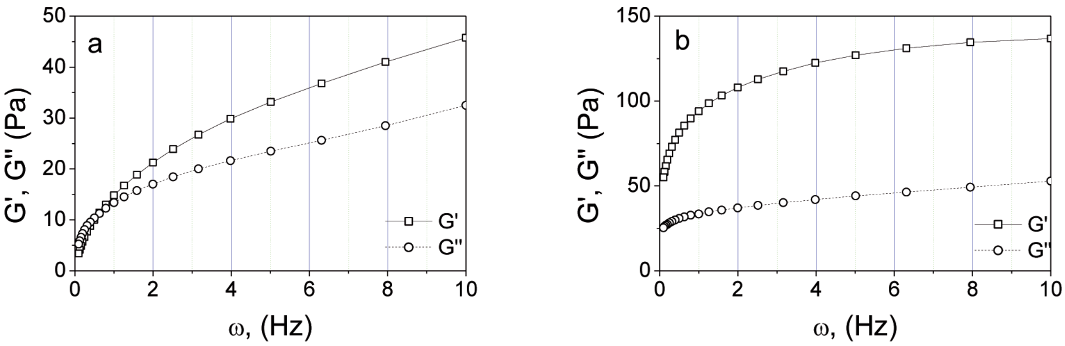

Fig. 7. Elastic (G') and viscous (G") modulus as a function of oscillation frequency for alumina (a) and composite (alumina + 3 vol.% nickel) slurry (b)

High η_∞ of composite slurry is caused by the presence of "hard" agglomerates, that are formed as a result of strong interaction between ceramic and metallic particles. The stability of agglomerates is caused by colloidal incompatibility and the interaction is still exhibiting even by applying high shear rates.

More thorough analysis – conducted for slurry containing 3 vol.% of nickel – showed that the presence of second phase (nickel) causes changes also in viscoelastic characteristics of alumina slurry. In stress controlled frequency sweep analysis alumina slurry shows dependency in viscous and elastic properties in regard to oscillation frequency (Fig. 7a). For frequencies below 0,6 the viscous modulus (G") has higher value than elastic modulus (G'), which means that in this range slurry response to the applied stress is more viscous. Slurry containing 3 vol.% of nickel powder in the whole range of investigated oscillation frequency show predominating elastic characteristics (Fig. 7b).

4. Conclusions

- In order to obtain alumina-nickel slurry for composite moulding by slip casting method it is indispensable to apply deflocculants that will decrease pH of point of zero charge of alumina to make its elektrokinetic characteristics resemble the one of nickel. In this case polycarboxylic acids can be applied.
- Great influence of presence of nickel particles on the rheological stability of slurries was observed. Slurries containing nickel particles have higher viscosity. Furthermore, alumina slurry viscoelastic characteristics undergo significant alteration when slurry contains nickel particles.
- Obtained results indicate that interaction between alumina and nickel particles occurs. Modification of alumina surface with citrate anions, which are relatively small molecules, may constitute barrier not high enough to prevent alumina and nickel particles to agglomerate. However, the agglomeration is minor and does not lead to slurry flocculation.
- The interaction of alumina and nickel particles prevent heavier nickel particles from sedimentation. Metal is usually heavier than ceramic particles and it is prone to sediment in slurry. However, metallic particles surrounded by ceramic particles in an agglomerate remains suspended in dispersion. Such agglomerates cause greater friction during sedimentation process and composites with homogenous distribution of metallic particles can easily be obtained even from slurries containing low concentration of powders.

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