

COLLOID ZIRCONIA BINDER OF IMPROVED WETTING PROPERTIES

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Physicochemical properties of colloid zirconia aqueous sol, used as a binder in the investment casting industry, were thoroughly determined. The size of the particles was determined by dynamic light scattering, and the zeta potential of the particles was measured by microelectrophoresis. The average size of the particles was 13 nm and the zeta potential was positive, equal to 30 mV. The size distribution of particles deposited on mica surface was also determined using AFM measurements. The wetting properties of the binder suspension were determined for the paraffin/air interface using the shape analysis of pendant and sessile drops. The perfluorononanoic acid (PFNA), an anionic surfactant, the non-ionic fluorinated surfactants Zonyl FSO-100 and Rokafenol RN8, and the mixtures of the surfactants were studied. Our investigations showed that the Zonyl-FSO surfactant and its mixture with Rokafenol effectively reduced the dynamic contact angle from the initial value of 94° to the value of 30°. Such low contact angles represent an essential improvement of zirconia binder wettability, thus widen the range of applicability in investment casting of finely shaped details.

INTRODUCTION

Zirconia (zirconium dioxide, ZrO_2) finds many applications in various fields of industry. Its physicochemical properties make it very useful in optical coatings [1, 2], thermal-shield, corrosion resistant coatings, fuel cells, catalyst and advanced ceramics [2, 3]. In some technological processes the addition of nanostructured ZrO_2 improves the resistance to temperature [4], making it useful for the preparation of high-quality titanium casts in the precise investment casting industry [2, 5].

Understanding and quantitative description of rheological behavior of colloidal suspensions is of great importance in the analysis and control of the properties of ceramic materials for the investment casting industry where colloidal sols are used as binders for producing casting forms [6]. Stability of the suspensions, the absence of aggregation processes and high fluidity is vital for producing ceramics of complex geometrical shape with a defect-free microstructure after sintering [7-10]. Rheological measurements are of fundamental interest because of the information that can be derived from them about the structure of the colloid suspension and the specific interaction among particles [11].

The interfacial tension of liquid/liquid or liquid/gas interfaces exerts an essential influence on the kinetics of many technological processes [12]. The decrease of the interfacial tension determines also the wettability of solid substrates by liquids, which has a major practical significance. For example, in the case of fine pattern details, which are the most difficult to be well-wetted by unmodified binders, the efficient wetting of wax patterns by ceramic slurries produced from zirconium binders is critical for the investment casting industry in order to reduce the number of faulty parts. Therefore, various surfactants, especially of a non-ionic character, are added to improve the wetting properties of binders and slurries. The modification of wetting properties of suspensions is not trivial because of a large specific surface area which may lead to a partial removal of surfactants due to the adsorption on solid particles. Despite the major significance of these problems, few systematic studies have been carried out in the literature based on quantitative measurements of surface tension and the contact angles of binders on various interfaces. In our previous work [12] the case of colloid silica modifications using surfactant mixtures was studied.

Therefore, the primary aim of this work was to develop efficient methods for a quantitative charac-

terization of wetting properties of zirconium binders used in the investment casting industry. These methods are based on combined measurements of surface tension and the dynamic contact angles using drop shape analysis. In this way an optimum composition and concentration range of surfactants can be specified, enabling essential improvements of wetting properties of binders. Other methods described in this paper are also of great importance to predict the behavior of colloidal particles, and consequently, the stability of the suspension [13, 14].

EXPERIMENTAL

Materials

In our experimental studies the following surfactants were used:

- perfluorononanoic acid $\text{CF}_3(\text{CF}_2)_7\text{COOH}$, having a purity of 97% (Aldrich), average molecular weight of 464 (hereafter referred to as PFNA, an anionic surfactant),
- ZonylFSO-100 $(\text{C}_2\text{H}_4\text{O})_x(\text{CF}_2)_y\text{C}_2\text{H}_5\text{FO}$ (Aldrich), average molecular weight of 726, a non-ionic surfactant,
- Rokafenol RN8 (produced by Rokita, Dolny Brzeg, Poland), which is a mixture of compounds synthesized by the nonylphenol/ethylene oxide polycondensation reaction with a number of $(-\text{O}-\text{CH}_2-\text{CH}_2-)$ groups ranging from 6 to 9, average molecular weight of 616, a non-ionic surfactant.

As a binder the following colloidal zircon-based product was used:

- Zircon IV oxide, ZrO_2 - 20 %, a colloidal dispersion (Nyacol).

Data given by the manufacturer:

- solid content in stock solution 20% [w/v], pH = 3.5, density $\rho = 1.26 \text{ g cm}^{-3}$.

Other materials:

- as a model wax pattern substrate, the parafilm of "M", Laboratory Film, American National Can™ was used.
- as a substrate for zirconia colloidal particles deposition, ruby mica sheets supplied by Continental Trade Ltd. Poland were used. Thin mica sheets were freshly cleaved and used in experiments without any pre-treatment.

Experimental methods and procedures

The surface tension and contact angle measurements

The surface tension and contact angle measurements were carried out using the drop shape analysis method presented schematically in Figure 1. The home-made

apparatus exploits the video image processing system of a pendant drop for surface tension measurements, and the sessile drop for contact angle measurements. This method enables one to perform non-stationary (dynamic) surface tension measurements of surfactants over long periods of time, sometimes hours, which is especially vital in the case of diluted surfactant solution, where the surface tension varies slowly with time due to the diffusion of surfactants to the liquid/air interface. This set-up enables one to perform direct measurements of the dynamic surface tension of binders modified by surfactants and, simultaneously, the dynamic contact angle under the same temperature and humidity conditions. In order to determine contact angles, the stalagmometer was placed over the paraffin surface. The only change in the set-up is the substitution of the container with the examined solution onto the table covered with a wax film. A pendant drop, which was detached from the capillary and formed a sessile drop at the paraffin surface, is characterized by the advancing contact angle θ . The volume of sessile drops was constant, equal to 20 μl . The computer software allowed one to determine the contact angle every 5 sec. In order to increase the precision of measurements, the whole set-up was situated on an anti-vibration table. In this work at least five kinetic measurements of contact angles and surface tension were done for each experimental condition. The relative error for contact angle measurements was $\pm 2^\circ$. The surface tension and contact angle measurements were carried out at 295 K.

The principle of this method described in detail in previous works [15-17], is based on producing the drop and determining its shape on the basis of computer image analysis. Images of the drop are taken by a video camera equipped with a macro lens. The images are digitized in real time by a Matrox Meteor frame grabber card installed in a personal computer. The image processing is done in C++ using the commercial software library Mil-Lite 4.0 by Matrox.

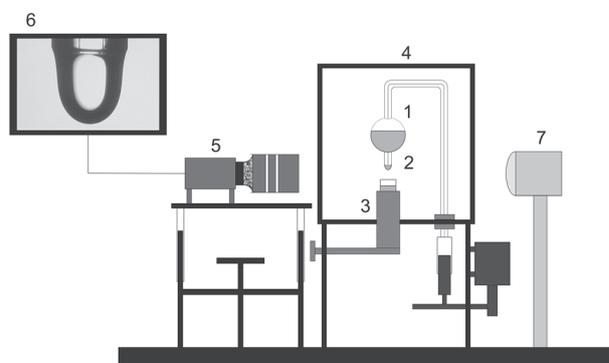


Figure 1. The scheme of the experimental apparatus used for simultaneous surface tension and contact angle measurements (1 - stalagmometer, 2 - quartz capillary, 3 - investigated solution, 4 - thermostatic chamber, 5 - camera, 6 - computer, 7 - light source).

The density and dynamic viscosity measurements

The zirconia concentration in the suspension was determined by the densitometer, providing relatively precise measurements of 5×10^{-6} . The measurements were carried out using the Anton Paar densitometer. This method is based on an oscillating U-shaped capillary and may be used for measurements of density and concentration.

The density of the stock zirconia suspension ρ_s and the supernatant solution ρ_e were measured using this device. Then, the weight fraction of zirconia in the suspension was determined from the formula [7, 11].

$$w_p = \frac{\rho_p (\rho_s - \rho_e)}{\rho_s (\rho_p - \rho_e)} \quad (1)$$

where $\rho_p = 2.0 \text{ g cm}^{-3}$ is the specific density of zirconia particles for the weight fraction equal to 0.33.

The density of the zirconia powder after roasting was determined by a pycnometer. The dynamic viscosity measurements were carried out using the commercial Schott ViscoClack device, thermostated at a temperature of 293 K. The stock sample of the zirconia binder was diluted by acetic acid solutions keeping a fixed pH value. The volume fraction of the solid was calculated from the formula $\Phi_v = (w_p \cdot \rho_{\text{sus}}) / \rho_c$ where w_p is the weight fraction solid in the diluted binder determined from the mass balance, ρ_{sus} is the suspension density determined by the densitometer and ρ_c is the solid zirconia particle density.

The particle size and zeta potential measurements

Diffusion coefficients and the electrophoretic mobility of zirconia nanoparticles were determined using a Zetasizer Nano ZS Malvern instrument (measurement range of 3 nm to 10 μm for zeta potential and 0.6 nm to 6 μm for particle size). The size of colloidal particles was determined by the dynamic light scattering (DLS) method. From the autocorrelation function, the diffusion coefficient D of zirconia nanoparticles can be easily calculated, and knowing D one can calculate the hydrodynamic radius of particles R_H from the Stokes-Einstein relationship [18, 19]:

$$R_H = \frac{kT}{6\pi\eta D} \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solution, and R_H is the hydrodynamic radius of particles.

It is important to mention that in the case of nearly spherical particles, the hydrodynamic radius corresponds to the geometrical radius of the particle a .

On the other hand, the zeta potential of zirconia particles ζ was measured in the same device exploiting

laser Doppler velocimetry (LDV). The principle of this method consists in the fact that charged particles are attracted to the oppositely charged electrode and their velocity is measured and expressed per unit field strength as the electrophoretic mobility μ_e . Knowing the mobility, one can calculate the zeta potential of particles using the Henry-Smoluchowski equation [20,21]:

$$\zeta = \frac{3\eta}{2\varepsilon F(\kappa a)} \mu_e \quad (3)$$

where ε is the dielectric constant of the zirconia dispersion, $F(\kappa a)$ is the function of the dimensionless κa parameter, $\kappa^{-1} = (\varepsilon kT / 2e^2 I)^{1/2}$ is the double-layer thickness, e the elementary charge, $I = 1/2(\sum_i c_i z_i^2)$ is the ionic strength of the electrolyte, c_i are the ion concentrations in the bulk, and z_i are the ion valences.

Additionally, the zirconia binder size distribution was determined by depositing the particles on a mica substrate under diffusion-controlled conditions. Then, the atomic force microscopy (AFM) method was applied using the NT MDT Integra device to acquire particle monolayer topology. Using image analysis software, the average horizontal diameter of the deposited particles was determined for approx. 100 particles and the average particle size was determined.

RESULTS AND DISCUSSION

The zeta potential and the particle size measurements

One of the most important characteristics of colloidal binders is the zeta potential and particle size, which were determined via microelectro-phoretic and DLS measurements. Zeta potential, which is strictly correlated with the uncompensated surface charge of particles [20, 21], determines the stability of colloid suspensions and interaction of particles with surfaces leading to deposition phenomena. Knowing the zeta potential of suspensions, one can quantitatively predict their stability, i.e., their tendency to form aggregates [18, 22], which usually diminishes the techno-logical properties of colloidal binders. It was determined that the zeta potential of the zirconia binder was positive, varying between 33 and 26 mV for the ionic strength of $10^{-4} \text{ M} - 10^{-2} \text{ M}$ (pH = 4.1).

On the other hand, the particle size in the suspension was determined by measuring the diffusion coefficient using DLS. From these measurements, using Eq.(2) it was found that the average size of the particles, assumed equal to $2 R_H$, was 13 nm +/- 3nm (see Table 1). This is above the value given by the manufacturer, equal to 5-10 nm. In order to clarify this discrepancy, zirconia particle size was also determined via AFM measurements of particles deposited on mica. The use of mica is advantageous because molecularly smooth sheets can be easily cleaved having a macroscopic dimension. Mica is also negatively charged for all pH

values above 3 [25], thus the positively charged zirconia binder particles can be readily deposited. In order to produce zirconia particle monolayers on mica a diluted sample of the binder (weight content ca 0.0001 %) was used. The deposition experiments were carried out under the diffusion-controlled condition in a thermostatted cell (for the ionic strength of 10^{-2} M NaCl). The mica sheets were placed vertically in order to avoid deposition of larger aggregates. After a desired time the sheets were dried and inspected under AFM. A micrograph of the zirconia particle monolayer obtained in these measurements is shown in Figure 2. The particle size distribution was determined as described above by counting the diameters of approx. 100 particles. The average particle size determined in these experiments was 14 nm. As can be deduced the agreement with the previous value obtained from DLS is quite satisfactory. This unequivocally suggests that the real size of particles in the suspension was much larger than the postulated



Figure 2. A micrograph of zirconia particle monolayer deposited on mica surface (AFM, semi-contact mode, scan size 5×5 micrometers).

size, probably because of the formation of a shell on particles, composed of gel layer, which stabilizes the particle. This hypothesis is supported by the fact that the binder suspensions were stable over a month period, which was checked by systematic hydrodynamic radius measurements carried out as a function of time. This would be not the case if the particles were charge stabilized, because of their small size. It can be easily shown using the classical colloid stability DLVO theory [19] that for this relatively low zeta potential value and high concentration, the binder suspension should aggregate rapidly.

The density and dynamic viscosity measurements

In order to study the structure of the particles in the suspension, additional experiments aimed at determining their density were carried out in addition to the dynamic viscosity measurements. As shown in Ref. 11, dynamic viscosity measurements can be utilized to determine the effective hydrodynamic volume of particles in the suspension and to reveal the presence of a gel shell and its porosity.

The first step in these measurements involved determining the suspension and particle density. The density of the stock binder suspension ρ_{sus} was routinely determined by the densitometer and was equal to 1.26 g cm^{-3} which was in accordance with the manufacturer's data. However, determining the particle density in the suspension was more complicated. Here, we effectively applied the suspension dilution method which was used before [11] in the case of colloid silica binders. The application of this procedure requires the knowledge of the solid weight content in the binder suspension. This was done in the usual way by roasting the sample under a programmed temperature. It was found that for the drying temperature of 473 K the solid residue after 24 hours was $w_p = 0.33$ of the initial mass of the sample. For increased temperature above 573 K, the weight loss was much higher, so the solid residue was $w_c = 0.2$,

Table 1. Physicochemical data for the zirconia binder.

Property	Volume and Unit	Remarks
Average particle size in suspension	13 (+/-3) (nm)	Malvern DLS by Intensity ($I = 10^{-2}$ M NaCl, $pH = 4.1$)
Zeta potential ζ	26 (+/-2) (mV)	Microelectroforesis, ($I = 10^{-2}$ M NaCl, $pH = 4.1$)
Density	1.26 g cm^{-3}	stock suspension $pH = 3.5$
Dynamic viscosity	4.87 (mPas)	stock suspension $pH = 3.5$, $T = 293 \text{ K}$
Surface tension	55 mN m^{-1}	stock suspension, pendant drop method, $T = 293 \text{ K}$
Contact angle	94°	stock suspension, paraffin/air, sessile drop method, $T = 293 \text{ K}$
Apparent particle density ρ_a^*	2.0 g cm^{-3}	dilution method
Particle density ρ_c	5.1 g cm^{-3}	roasting $T > 573 \text{ K}$
Residue solid weight w_c	0.2	$T > 573 \text{ K}$
Solid weight content w_p	0.33	$T < 473 \text{ K}$

which agrees with the manufacturer data for the zirconia binder. Thus, the latter value describes the true content of the solid zirconia in the sample forming the particle core whereas the former value characterizes the content of organic complexes forming the shell layer. The ratio of the two weight contents equals to 1.65.

The density of the solid zirconia core was determined by the pycnometer using the powder roasted at a temperature above 573 K. In this way, it was measured that $\rho_c = 5.1 \text{ g cm}^{-3}$, which is slightly smaller than the crystalline zirconia equal to 5.79 g cm^{-3} [7], indicating that there was some degree of porosity in the solid zirconia core.

Additionally, knowing the solid weight content w_p and applying the dilution method [11] the apparent density of particles in the suspension ρ_a^* was determined to be 2.0 g cm^{-3} , which is much smaller than the density of the crystalline zirconia. This indicates that a shell of low density was present on the particle core. The extent of the shell layer was further studied using dynamic viscosity measurements carried out for various dilution degree. The results of these measurements are collected in Table 2 and shown graphically in Figure 3 as the dependence of the reduced viscosity $\bar{\eta} = (\eta/\eta_s) - 1$ on the volume fraction of the core particles [11] $\Phi_v = (w_c \cdot \rho_{sus})/\rho_c$,

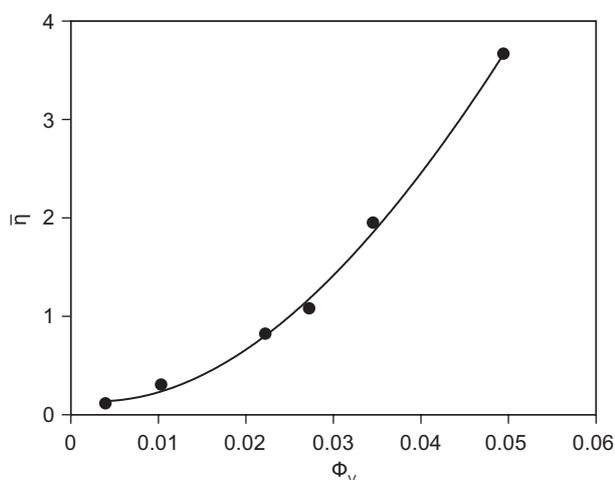


Figure 3. The dependence of reduced dynamic viscosity $\bar{\eta} = \eta/\eta_s - 1$ on the volume fraction of the zirconia binder suspension determined at $T = 293 \text{ K}$.

Table 2. Dynamic viscosity of ZrO_2 suspensions $T = 293 \text{ K}$, $\rho_p = 5.1 \text{ g cm}^{-3}$, intrinsic viscosity.

Nominal weight fraction w_p	Density ρ_s (g cm^{-3})	Volume fraction Φ_v	Dynamic viscosity η_s (mPas)	$\frac{\eta}{\eta_s}$	$[\eta] = \frac{(\eta/\eta_s) - 1}{\Phi_v}$
0.00	1.0001	0	1.04	1	0
0.02	1.0269	0.00403	1.15	1.108	27
0.05	1.0587	0.0104	1.35	1.299	29
0.1	1.1373	0.0223	1.89	1.816	37
0.12	1.1597	0.0273	2.16	2.073	39
0.15	1.1780	0.0346	3.07	2.943	56
0.20	1.2616	0.0495	4.87	4.660	74

where η is the viscosity of the electrolyte and η_s is the viscosity of the suspension. Using these data, the intrinsic viscosity of the suspension can be calculated as $[\eta] = \bar{\eta}/\Phi_v$. As can be noticed (see Table 2) the value of $[\eta]$ in the limit of very diluted suspension equals 27. Thus, the ratio of this value to the Einstein value, pertinent to solid spherical particles, equals V_p/V_c , where V_p is the hydrodynamic particle volume, V_c is the core volume, equals to $27/2.5 = 10.8$. As discussed in Ref. 11 this ratio characterizes the effective hydrodynamic volume of the composite core/shell particle to the core volume. Accordingly, the hydrodynamic volume of the shell is 9.8 times larger than the solid zirconia core.

Knowing the V_p/V_c parameter and the size of the particle d_p , one can easily determine the diameter of the solid zirconia core from the formula:

$$d_c = d_p \cdot \left(\frac{V_c}{V_p} \right)^{\frac{1}{3}} \quad (4)$$

Using our data, i.e. $d_p = 13 \text{ nm}$ one can calculate that $d_c = 5.9 \text{ nm}$ and the hydrodynamic thickness of the shell to be $d_s = 3.5 \text{ nm}$. Additionally, knowing the w_p/w_c ratio determined as above one can calculate that the apparent density of the shell layer ρ_s^* equal to 0.34 g cm^{-3} . Using this value one can further calculate the porosity of this layer p from the formula:

$$p = 1 - \frac{\rho_s^*}{\rho_s} \quad (5)$$

where ρ_s is the density of the shell forming complexes.

Using our data and assuming $\rho_s = 1.1 \text{ g cm}^{-3}$ one obtains $p = 0.69$. It should be noted that very similar values were previously obtained for the colloid silica binder [11].

Knowing the porosity one can calculate the apparent density of the composite particle in the solution form the formula:

$$\rho_a^* = \frac{\rho_p + \rho_s^* \frac{V_s}{V_p}}{1 + \frac{V_s}{V_p} (1 - p)} \quad (6)$$

Thus, in our case one obtains from Equation (6) $\rho_a^* = 2.09 \text{ g cm}^{-3}$, which is in agreement with the previously

mentioned value of 2.0 g cm^{-3} determined by the dilution method. Exploiting these experimental findings the composite zirconia binder particles having the core/shell structure can be schematically represented as shown in Figure 4. Such a model is in agreement with all the above reported experimental measurements, explaining also the high stability of the zirconia binder as due to the steric repulsion of the shell layers.

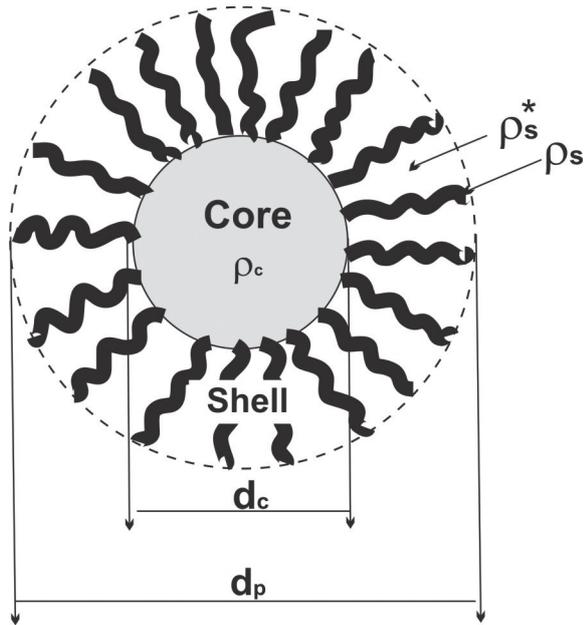


Figure 4. The schematic representation of the composite core/shell zirconia particle.

Modifications of zirconia dispersion
- the surface tension measurements

The surface tension and contact angles for the unmodified zirconia sol were measured. The stock colloidal zirconia exhibited the surface tension of 55 mN m^{-1} (dyn cm^{-1}). This indicates that the zirconia dispersion contained surfactants, producing a reduction in the surface tension in comparison to distilled water, which exhibits a surface tension of 72.4 mN m^{-1} .

The contact angle of the colloidal zirconia drop on the paraffin surface was 94° (see Table 1). This high value indicates poor wetting of hydrophobic surfaces being, therefore, unacceptable from the point of view of the investment casting industry.

These facts indicate unequivocally that modifications of zirconia suspension, by the addition of surfactants, are needed in order to produce a binder suitable for practical applications.

Therefore, surface tension measurements were performed for the surfactants used in this work with the aim of determining the range of their concentrations

which would be suitable for practical applications. First, surface tension of pure surfactant solutions was determined. In order to increase the precision of these measurements, the surface tension dependence on time was determined for each surfactant solution. Then, these results were extrapolated to infinite time as was done in Ref. 17, in order to produce equilibrium values of the surface tension.

As can be deduced from the results shown in Figure 5, the fluorinated surfactants studied in this work effectively reduce the surface tension of zirconia dispersions. In order to verify this hypothesis, the surface tension γ of zirconia dispersion in the presence of the surfactants and their mixtures was determined as a function of surfactant concentration c .

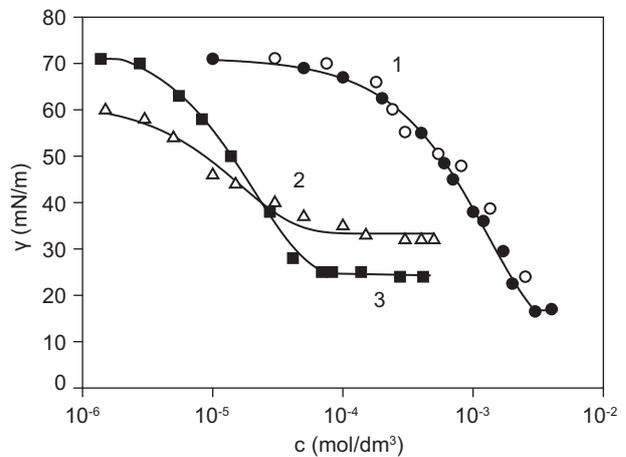


Figure 5. The dependence of the surface tension γ on the molar concentration of aqueous solutions of various surfactants: 1 - PFNA (drop shape and the ring method), 2 - Rokafenol N8, 3 - Zonyl FSO.

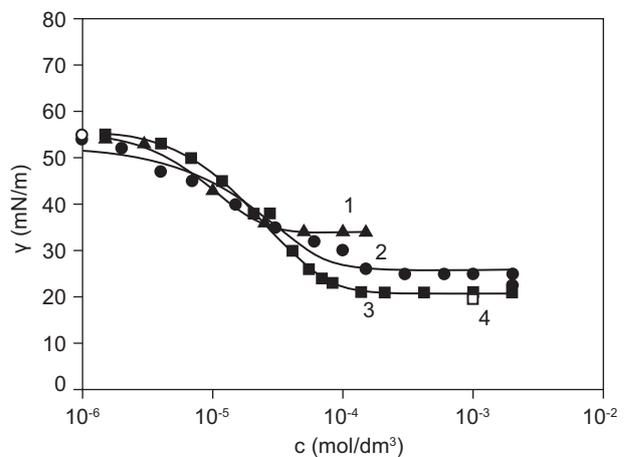


Figure 6. The dependence of the surface tension of zirconia binder suspensions on the molar concentration of various surfactants: 1 - Rokafenol N8, 2 - PFNA, 3 - Zonyl FSO, 4 - mixture (Zonyl FSO + Rokafenol 1:1).

The results of these measurements are shown in Figure 6 in the form of the dependence of the equilibrium surface tension on the surfactant concentration varied within the range 10^{-6} to 10^{-2} M. As can be noticed, all three surfactants used in the research exhibited a similar trend in lowering the surface tension in the presence of colloidal zirconia. The significant difference in the surface activity of the surfactants occurred at the surfactant concentration above 3×10^{-5} M. At the surfactant concentration ranging from 10^{-6} M – 3×10^{-5} M, all three surfactants lowered the surface tension from 55 mN m^{-1} to the value of 35 mN m^{-1} . Starting from the concentration of 3×10^{-5} M the adsorption of the surfactants at the liquid/air interface exhibits differences in activity of the surfactants. In the case of the nonionic surfactant, Rokafenol, for a higher concentration than 3×10^{-5} M, the surface tension remains practically constant, reaching the value of 34 mN m^{-1} . The concentration at which this transition occurs is referred to in the literature as the critical micelle concentration (c.m.c.) [23,24]. As can be noticed, the PFNA exhibited the higher surface activity than Rokafenol. The PFNA lowered the surface tension to the value of 32 mN m^{-1} – 26 mN m^{-1} at the surfactant concentration of 6×10^{-5} M – 1.5×10^{-4} M respectively, achieving the c.m.c. values for $c = 3 \times 10^{-4}$ M and lowering the surface tension to the value of 25 mN m^{-1} . The most significant results were obtained for the nonionic surfactant Zonyl-FSO. In this case the surface tension attained the values of 30 mN/m – 23 mN/m for the concentration range of 4×10^{-5} M – 8×10^{-5} M. Even more significant is the appearance of the c.m.c. for bulk Zonyl concentration as low as 1.4×10^{-4} M above which the equilibrium surface tension of colloid zirconia attained the value of 21 mN m^{-1} .

It is interesting to mention that the surface activity of the Zonyl FSO and Rokafenol mixture was also investigated. The mixture was prepared for the same

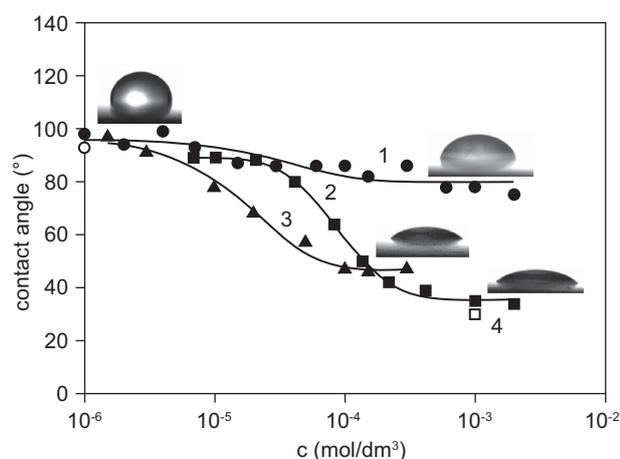


Figure 7. The dependence of the contact angle of the zirconia binder of the paraffin/air interface on the concentration of various surfactants: 1 - PFNA, 2 - Zonyl FSO, 3 - Rokafenol N8, 4 - mixture (Zonyl + Rokafenol N8 1:1).

molar concentration of surfactants $c = 1 \times 10^{-3}$ M. However no significant changes in decreased the surface tension were noticed (see Figure 6).

Modifications of zirconia dispersion - the contact angle measurement

Surface tension measurements discussed above provide one with general information, enabling pre-selection of the most favorable conditions for promoting an efficient wetting of surfaces by silica dispersions. However, a precise selection of these parameters becomes feasible only upon determining the contact angles of colloidal zirconia drops on the paraffin surface.

In Figure 7 the dependence of the equilibrium contact angle of the zirconia dispersion is plotted vs. the surfactant concentration. Taking into account the ability to decrease contact angles by a pure surfactant, it can be noticed that for the low concentration range 10^{-6} M till 10^{-4} M, the Rokafenol surfactant was the most efficient in the reduction of the contact angle to the limiting value of about 45° .

For this concentration range the PFNA and Zonyl were less effective, probably because of their significant adsorption on the paraffin surface. The PFNA also was not efficient in lowering the value of contact angles which attained 75° for the $c_b = 2 \times 10^{-3}$ M. However, the Zonyl surfactant at higher concentrations, exceeding 10^{-4} M, induced a more significant decrease in the contact angle than Rokafenol, down to a value of about 33° .

Similarly as in the case of surface tension, the contact angle of the mixture of Zonyl + Rokafenol was investigated. However, the reduction in the contact angle was not more efficient than in the case of pure Zonyl surfactant (see Figure 7).

In such wetting studies, an interesting question of practical significance is the kinetics of the contact angle variations as a function of the time. Experiments of this type, involving zirconia binders, have not been done before in the literature.

In Figure 8 the dependencies of the contact angle of the zirconia dispersion modified by addition of Zonyl, for concentrations 1×10^{-4} M, 4×10^{-4} M and 1×10^{-3} M, on the time are plotted. As can be noticed, the initial contact angles were relatively high, equal to 62° , 55° and 53° . However, they decreased with time, attaining quasi-stationary values equal to 39° and 35° for the $c = 10^{-4}$ M and 4×10^{-4} M, for a time of 600 seconds. In the case of the highest concentration $c = 10^{-3}$ M, the quasi-stationary value was 33° for a time of 300 seconds.

Hence, these measurements proved unequivocally that the surfactants studied in our work and their mixtures can be used for major improvements of wetting properties of colloid zirconia binder used in investment casting.

CONCLUSIONS

An efficient method for quantitatively characterizing wetting properties of zirconia binders was developed, based on precise measurements of surface tension and the dynamic contact angles using the drop shape analysis. In this way an optimum composition and concentration range of surfactants were specified, enabling essential improvements of wetting properties of binders used in investment casting.

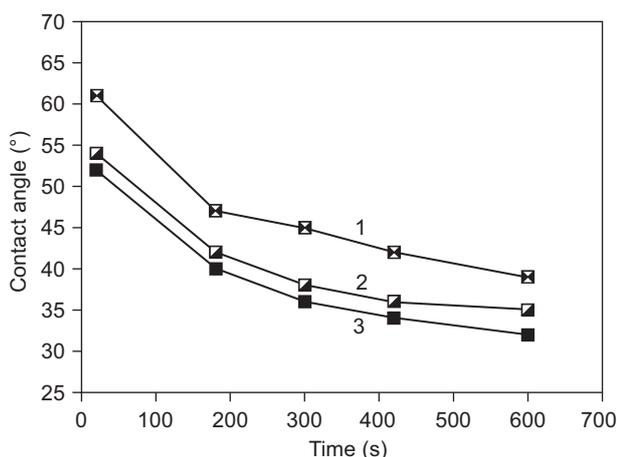


Figure 8. The kinetics of contact angle changes of the zirconia binder on the paraffin/air interface: 1 - ZrO_2 + Zonyl at the concentration of 1×10^{-4} M, 2 - ZrO_2 + Zonyl at the concentration of 4×10^{-4} M, 3 - ZrO_2 + Zonyl at the concentration of 1×10^{-3} M

Our investigations showed that the fluorinated nonionic surfactant Zonyl-FSO and its mixture with Rokafenol effectively reduced the surface tension of colloid zirconia used as a binder in investment casting to the low value of 20 mN m^{-1} . Because of surfactant adsorption, the dynamic contact angle of binders on paraffin films was decreased, attaining the minimum value of 30° at the bulk surfactant concentration of about 10^{-3} M (0.07%). Such low contact angles represent an essential improvement in comparison with ordinary binders commonly used for producing casting forms in the investment casting industry.

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