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SURFACE PROPERTIES OF NANOCERAMIC POWDERS

WŁAŚCIWOŚCI POWIERZCHNIOWE NANOPROSZKÓW CERAMICZNYCH

The paper focuses on selected fragment of nanopowders surface studies made by author. The studies presented consist of viscosity measurements of ceramic slurries and ionic conductivity and pH determination of supernatants obtained by using of nanozirconia suspensions centrifugation. Three different nanozirconia powders were chosen to compare the influence of D-fructose on the viscosity of nano-ZrO_2 suspensions. Then the powders were centrifuged with water to leach soluble counter-ions. It was proved that the leaching has a SIGNIFICANT effect on the viscosity of nano-ZrO_2 suspension.
Keywords: nanopowder, nanozirconia, deflocculation, surface, viscosity, ionic conductivity, pH

Zaawansowana ceramika stawia coraz wyższe wymagania dotyczące jakości stosowanych materiałów. Poza założonym składem chemicznym i ściśle określonymi parametrami morfologicznymi, syntetyczne proszki ceramiczne powinny charakteryzować się odpowiednimi właściwościami powierzchniowymi, które determinują ich zachowanie na różnych etapach procesu ceramicznego. Powierzchnia proszków różni się zarówno pod względem chemicznym jak i fizycznym od ich *objętościowej charakterystyki*. Szczególnym przypadkiem są tutaj nanoproszki – stan ich rozwiniętej powierzchni ma szczególny wpływ na zachowanie materiału. Właściwości powierzchniowe nanoproszków mają kluczowy wpływ na proces ich formowania, zwłaszcza w metodach wykorzystujących ceramiczne masy lejne. Stan powierzchni znacząco wpływa na oddziaływania międzyziarnowe, oraz na oddziaływania miedzy fazą stałą a fazą ciekłą złożoną z rozpuszczalnika i odpowiednich dodatków. Aby uzyskać stabilną zawiesinę nanoproszku o pożądanych właściwościach reologicznych należy dokładnie poznać powierzchnię materiału, by w razie potrzeby móc zmodyfikować jej niekorzystny wpływ. Jako przykład mogą posłużyć nanoproszki, które zawierają zaadsorbowane na powierzchni resztkowe grupy węglowe będące pozostałością po etapie syntezy. Taka pokryta *węglem* powierzchnia jest bardziej hydrofobowa i kwasowa, co znacząco wpływa na zachowanie proszku w wodnej zawiesinie. W zależności od tego, co znajduje się na powierzchni proszku, możliwa jest odpowiednia manipulacja jego właściwościami i zachowaniem w zawiesinach.

1. Introduction

Previously published papers of the author research team have focused on nanopowders deflocculation by means of saccharides and their derivatives. It was demonstrated that monosaccharides, especially D-fructose and some of monosaccharides derivatives, are effective deflocculation agents of nano-alumina powder [1,2]. It was attempted to carry the promising results on nanozirconia powders in order to obtain time-stable zirconia nanosuspensions of relatively low viscosity and high solid phase loading. The results of the studies were found to be incomprehensible without any deeper examination of nanozirconia properties [3]. The main assumption of the following studies was to correlate these incomprehensible results with nanozirconia surface science and to find any reasonable explanation for the phenomena observed.

Advanced ceramics puts high requirements on the quality of the materials used. Except of the assumed chemical composition and morphological well-defined parameters, synthetic ceramic powders should be of suitable surface properties that determine their behaviour at different stages of the ceramics processing.

Surface science deals with fundamental experimental and theoretical studies in the physics and chemistry of surfaces and interfaces. Surface science covers topics contributing to an understanding of physical and chemical phenomena that occur at the interface of two phases, including solid-liquid interfaces, solid-gas interfaces, solid-vacuum interfaces, and liquid-gas interfaces [4].

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Surface characterization of powders is a leading tool to exclude some specific phenomena occurring, particularly, during colloidal processing of ceramic powders –it concerns especially nanopowders, which are of highly developed surface. Surface significantly affects intergranular interaction and interaction between solid and liquid phase consisting of solvent and some additives. To obtain a stable nanosuspension of desired rheological properties, surface properties should be studied in detail.

Researchers increasingly study ceramic powders surface – especially on the stage of synthesis [5-7] or during colloidal processing [8-11]. The surface studies are more and more advanced and extended [12]. The author of the paper examines nanozirconia powders, which are in focus of attention of advanced structural ceramics [13,14].

Xie *et al.* [10] proved that soluble ionic compounds that contaminate ZrO_2 nanopowders can significantly disturbance deflocculation process, leading to some incomprehensible rheological behaviour of ceramic suspensions. The more ions are leached from powder, the more differences between *as-received* and leached powder could be observable. Ions, like Na^+, K^+, Mg^{2+}, can deflocculate nanopowders by means of electrostatic repulsion, but they can also cause some *disturbances* in interaction between powder grains and suspension additives [10].

2. Materials and experimental procedure

Three different nanozirconia powders were chosen for rheological and surface studies:

- **TOSOH** – nano-ZrO_2 stabilized by 3 mol.% of Y_2O_3 (*Tosoh Corporation*, Japan),
- **3IAM** – nano-ZrO_2 stabilized by 3 mol.% of Y_2O_3 (*Inframat Advanced Materials*, USA),
- **IAM** – non-stabilized nano-ZrO_2 (*Inframat Advanced Materials*, USA).

All of the powders used were of an average primary particle size of 40-50 nm. TOSOH powder was granulated; the granules were of diameter of about 50-100 μm.

Nanozirconia suspensions were obtained on the basis of deionized water, which was purified by *MilliQ* (*Millipore*) water purification system. The water ionic conductivity was 41.2 $\mu S \cdot cm^{-1}$ and its pH value was 6.17.

Water nanozirconia suspensions containing 35 vol.% of solid phase loading were prepared to carry on viscosity measurements. The powders were added to deionized water with an adequate amount of D-fructose (*POCh*, Poland). The slurries were mixed in a planetary ball mill *PM100* (*Retsch*) for 90 minutes with a speed of 300 RPM.

Viscous properties of ceramic nanosuspensions were studied by using *Kinexus Pro* (*Malvern*) rotational rheometer attached with *C25 SC002 SS* spindle and *PC25 C0027 AL* cylinder. The viscosity measurements were performed at 25.00°C.

In order to conduct ionic conductivity and pH measurements, the nanozirconia powders were dispersed in deionized water with a mass ratio of 1:4. The suspensions obtained were stirred intensively for 60 minutes and then kept at room temperature for 24 h to approach ionic equilibrium in suspensions bulk. Afterwards, the nanosuspensions were stirred for 15 minutes and centrifuged at a rate of 13000 rotations per minute for 30 minutes (*MPW – 350R, High Speed Brushless Centrifuge, MPW Med. Instruments*, Poland). The supernatants (denoted as **first leaching**) were decanted and then used to measure ionic conductivity and pH. The centrifuged powders were removed from test-tubes and dried at 105°C for 24 h and then the procedure was repeated in order to obtain successive, second supernatants (denoted as **second leaching**).

The measurements of ionic conductivity and pH were conducted by using of multifunctional measuring device (*HI 2550, Hanna Instruments*, USA). All the measurements were taken at 25.0°C.

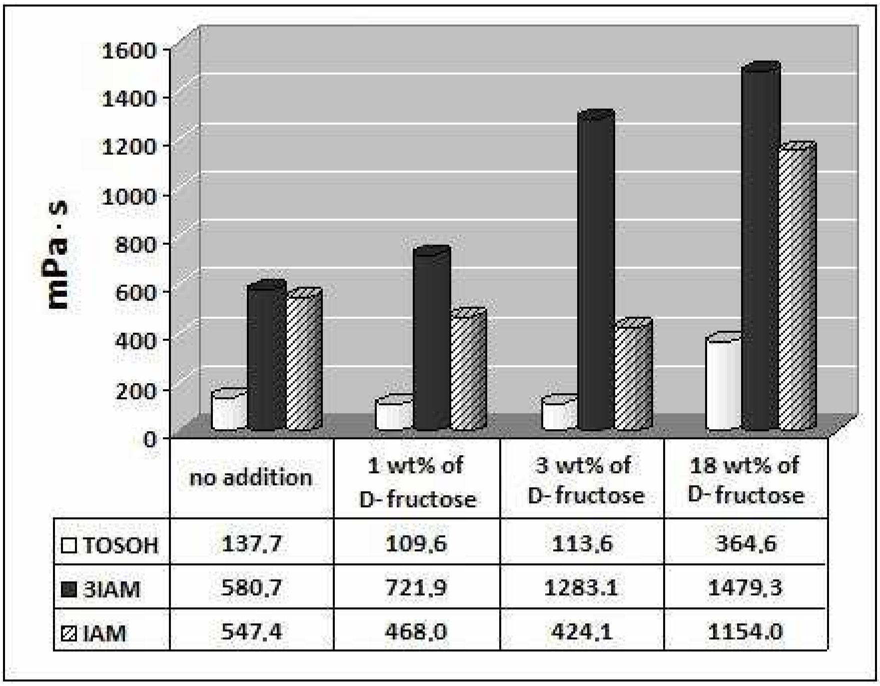
3IAM nanozirconia powder was chosen to study the influence of the water leaching on rheological properties of its suspension.

3. Results and discussion

The results of D-fructose influence on three different nanozirconia suspensions are demonstrated in Fig. 1. The solid phase loading in each of the suspensions was 35 vol.%, the viscosity measurements were taken at 100/s shear rate.

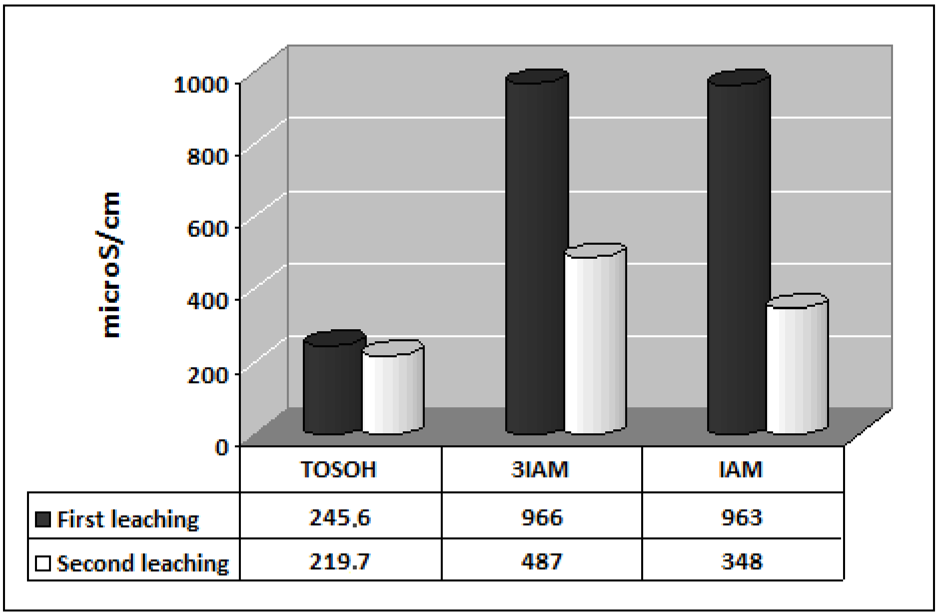
1 and 3 wt% of D-fructose slightly decrease the viscosity of TOSOH and IAM slurries in comparison to the suspensions with no monosaccharide addition. 18 wt% of D-fructose increases strongly the viscosity of TOSOH, IAM and 3IAM slurries – the latter ones are of definitely increasing viscosity whenever any D-fructose addition is given. The results are discordant – they prove that D-fructose is not a universal deflocculant, even within nanozirconia powders group.

Results of ionic conductivity of supernatants after first and second water leaching are demonstrated in Fig. 2.



	no addition	1 wt% of D-fructose	3 wt% of D-fructose	18 wt% of D-fructose
☐ TOSOH	137.7	109.6	113.6	364.6
■ 3IAM	580.7	721.9	1283.1	1479.3
▨ IAM	547.4	468.0	424.1	1154.0

Fig. 1. Influence of D-fructose additive on viscosity of nanozirconia suspensions made of three different nano-ZrO_2 powders



	TOSOH	3IAM	IAM
■ First leaching	245.6	966	963
☐ Second leaching	219.7	487	348

Fig. 2. Ionic conductivity of supernatants after first and second water leaching

The results indicate that IAM and 3IAM powders are abundant of soluble ionic compounds – the more ions in supernatant, the higher ionic conductivity. The ions are easy to leach during centrifugation process, therefore ionic conductivity of IAM and 3IAM samples decreases significantly after leaching step. The parameter is of similar value and of similar change trend in the case of IAM and 3IAM sample, what can be caused by analogical preparation route of the powders purchased from the same manufacturer. TOSOH powder contains much less ionic compounds, then IAM and 3IAM ones, what can be interpreted as higher purity of the powder. Changes of pH values of the supernatants are illustrated in Fig. 3.

The supernatants are of slightly acidic pH, the changes after second leaching are not of significant rate, only pH of IAM supernatant is decreasing from ca. 4.8 to 3.2. These changes can be correlated with ionic conductivity, but their detailed interpretation is difficult without any further research of nanozirconia surface.

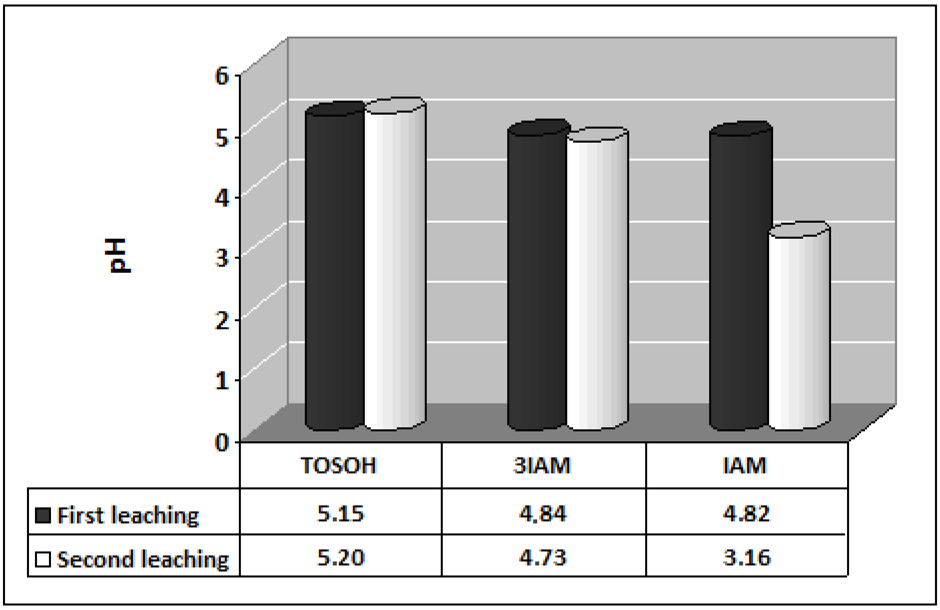


Fig. 3. Values of pH of supernatants after first and second water leaching

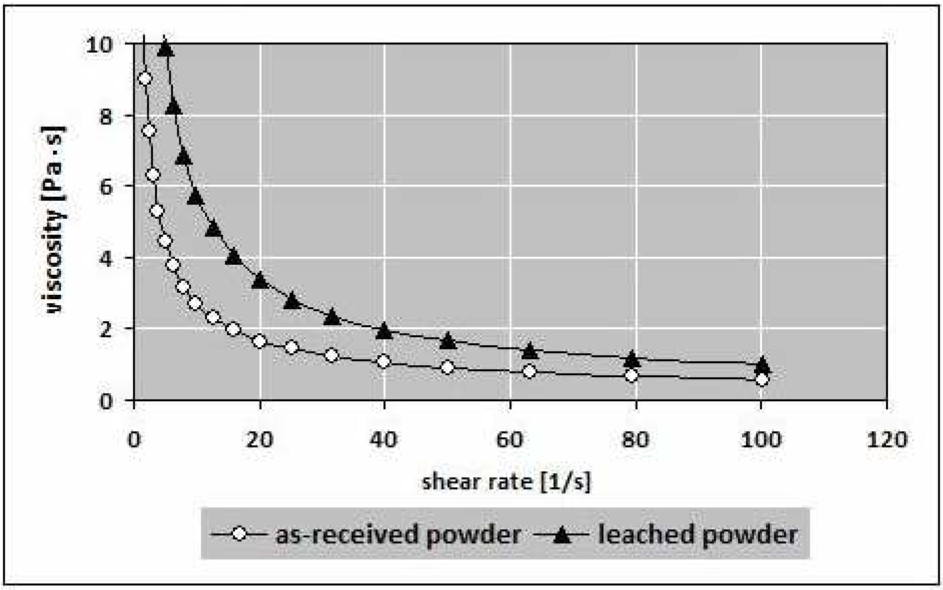


Fig. 4. Viscosity curves of 3IAM suspensions – the powder used in as-received state and after single water leaching

3IAM nanozirconia powder was found to be most difficult to deflocculate (see Fig. 1. and [3]) and its water leaching provided some interesting results (Fig. 2.). The mentioned reasons were crucial to check how 3IAM nanozirconia powder behaves after water leaching in comparison with *as-received* powder. The results are presented in Fig. 4.

The viscosity of the leached powder suspension is slightly higher then the viscosity of *as-received* one. It can be assumed that soluble ionic compounds contamination deflocculates 3IAM nanosuspension by means of electrostatic repulsive interactions. With the ions leached, the viscosity is increasing.

This kind of studies, where soluble counter ions are leached from powders, is worth to repeat for TOSOH and IAM powders, as well as for nanozirconia suspensions with D-fructose addition. Most likely the ions *mask* the surface of the powders and preserve it from deflocculating influence of D-fructose.

4. Conclusions

The studies revealed that different nanozirconia powders interact in a different way with D-fructose additive what results in specific rheological behaviour of nanozirconia suspensions. D-fructose, which was found to be an efficient deflocculant of nano-alumina, is not a universal deflocculation agent of nanopowders; it was proved that even within the group of nano-ZrO_2 powders, the results are of various characters. The main reason of the differences observed is thought to lie in surface properties of the powders.

Centrifugation of water nanosuspensions allowed obtaining clear supernatants which were examined in terms of their ionic conductivity and pH. For most samples, it was revealed that after the second water leaching, pH and ionic conductivity of the supernatants change in comparison to the values obtained after the first leaching. This variability points out on the problem of nanopowders impurity caused by soluble ionic compounds. Their contamination modifies widely understood *surface properties* of ceramic nanopowders, what is easy to prove by comparing rheological behaviour of leached and *as-received* powder.

The studies proved that soluble counter-ions influence rheological behaviour of 3IAM nano-ZrO_2 suspension. The ions leached from the powder deflocculate its suspension by electrostatic repulsion, therefore the visocity of the slurry increases, when the ions are leached.

The results presented are just a fragment of complex surface studies of ceramic nanopowders made by author. The studies are going to be extented to some deeper correlations between surface properties and rheological behaviour of nanopowders.

Acknowledgements

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