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D-FRUCTOSE IN DEFLOCCULATION PROCESS OF NANO-ZrO_2 POWDERS

ZASTOSOWANIE D-FRUKTOZY W PROCESIE UPŁYNNIANIA NANOPROSZKÓW ZrO_2

The purpose of these investigations was to obtain well-dispersed, unviscous ceramic slurries with zirconia nanopowder as solid phase and monosaccharides as dispersants. The as-obtained slurries should have high solid phase concentration and should be of low viscosity, just to be easily processed for example in slip casting process. High concentration of solid phase results in dense, strength products with desirable microstructure.

In the research two different zirconia nanopowders were investigated – the first, with an average particle size of 17nm (CEREL) and the latter, with an average particle size of 44nm (Inframat Advanced Materials). Rheological properties of ceramic slurries were tested.

Celem przeprowadzonych badań było otrzymanie dobrze upłynnionych ceramicznych mas lejnych zawierających nanoproszek dwutlenku cyrkonu jako fazę stałą i wodny roztwór cukru prostego, D-fruktozy, jako substancję upłynniającą. Pożądanymi właściwościami tak uzyskanych mas powinno być m.in. wysokie stężenie fazy stałej i względnie niska lepkość, która ułatwiałaby formowanie elementów z tychże mas. Dzięki wysokiemu stężeniu fazy stałej, możliwe byłoby zaś, otrzymanie dobrze zagęszczonych produktów o odpowiedniej wytrzymałości mechanicznej i pożądanej mikrostrukturze.

W przedstawionych badaniach użyto dwóch nanoproszków ZrO_2 – proszku o średniej wielkości ziarna 17nm, firmy CEREL, (Boguchwała, Polska), i proszku o średniej wielkości ziarna 44nm, firmy Inframat Advanced Materials, (Farmington, USA). Przedmiotem artykułu były badania reologiczne ceramicznych mas lejnych zawierających wymienione proszki oraz dodatek D-fruktozy w postaci wodnego roztworu.

1. Introduction

Apart from alumina, zirconia is the second main ceramic structural material. It is well known for its high /fracture/ hardness, wear and thermal resistance, chemical inertness and ionic electrical conduction [1,2]. Of course, elements made of nano-ZrO_2 would have some more favorable properties then those made of ZrO_2 micropowders – it is commonly known, that "nano-" means not only size, but properties too... [3,4]. It would be very advantageous to master a suitable way of nano-ZrO_2 processing – from powders to sintered pieces. A certain way to get this target is colloidal processing, which requires effective dispersion agents. They make it possible to obtain unviscous slurries with high content of solid phase [5].

A few years ago, it was discovered, that addition of monosaccharides can effectively decrease viscosity of alumina nanosuspensions [6,7]. Explanation of this phenomenon bases on nanopowder, monosaccharide and water interaction (Fig.1.). It was assumed and experimentally proved, that molecules of simple saccharides can adsorb on a surface of "nanograins" and displace adsorbed water molecules. This action increases the amount of free (bulk) water in a slurry and makes an effective nanoparticle radius smaller. Therefore, layers of water surrounding ceramic particles cannot interact, so viscosity of nanosuspensions decreases [6,7].

Monosaccharides, as processing agents, have many advantages:

- they are non-toxic, inexpensive and readily available,
- they dissolve in water, which is non-toxic, inexpensive and readily available also,
- monosaccharides can be easily removed from samples during sintering process,
- they affect on high mechanical strength of "green bodies".

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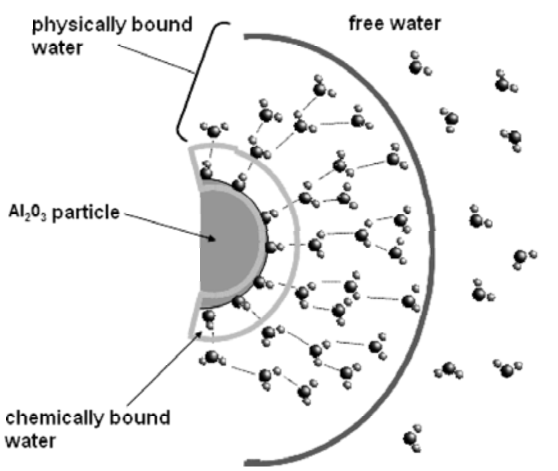

Fig. 1. Three types of water around alumina nanoparticle

2. Experimental

Materials. For these investigations, two different zirconia nanopowders were used. Both of them were 3mol.% yttria stabilized; the first one, with an average particle size of 17nm, was purchased from CEREL (Boguchwała, Poland) and the latter, with an average particle size of 44nm, was purchased from Inframat Advanced Materials (IAM) (Farmington, USA). Both of the particle size values bases on specific surface area BET, which is given in the Table 1. X-ray diffraction method revealed, that the two powders are cubic (Fig.2.), but they differ significantly in terms of their morphology. ZrO_2 CEREL forms packed, large agglomerates, while ZrO_2 IAM structure seems to be more dispersed; instead of agglomerates, many aggregates are clearly visible (Fig.3.).

TABLE 1

Characteristics of the used nanozirconia powders

Manufacture	Chemical form of powder	Pycnometric density [$g \cdot cm^{-3}$]	S_{BET} [$m^2 \cdot g^{-1}$]	d_{BET} [nm]
CEREL, Boguchwała (Poland)	3mol.% YSZ	5,33	64,63	17
Inframat Advanced Materials, Farmington (USA)	3mol.% YSZ	5,56	24,41	44

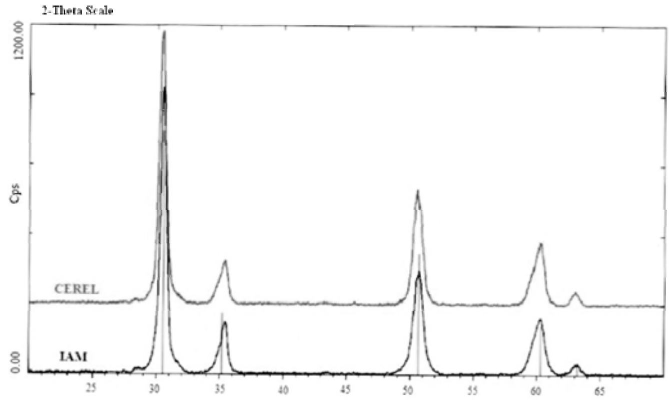

Fig. 2. X-rays diffraction patterns of both the used ZrO_2 nanopowders

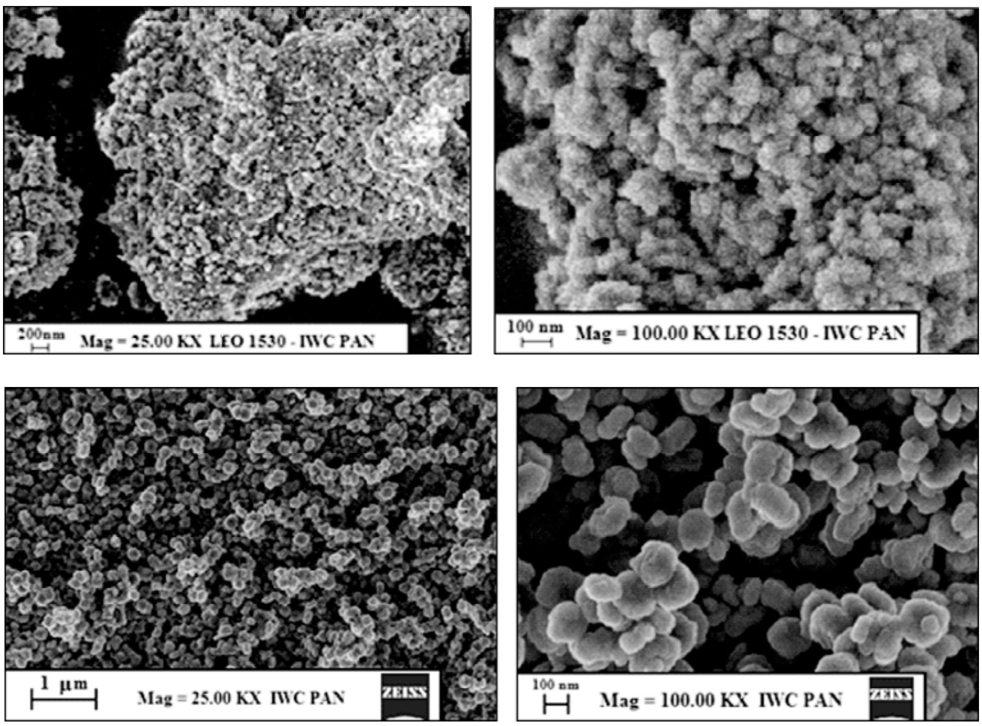

Fig. 3. SEM micrographs of nano-ZrO_2 powders – above – CEREL, below – IAM

To investigate some powder – water interactions, measurements of dzeta potential were performed. Isoelectric Point (IEP) of ZrO_2 CEREL was found to lie at pH = 6,55 and IEP of the latter powder was found at pH = 9,45 (Fig.4.). These two different values of pH in IEP suggest that the powders behave differently in water suspensions, what certainly influences powder – monosaccharide interactions.

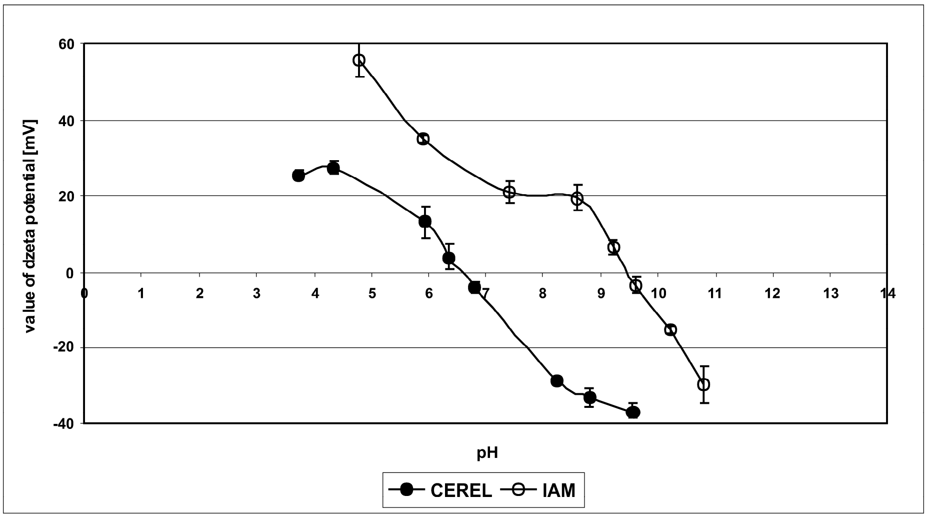

Fig. 4. Dzeta potential curves of the ZrO_2 nanopowders. Measurements of dzeta potential were performed using Zetasizer 3000 by Malvern Instruments

In the paper some results concerning **D-fructose** (POCh, Poland) will be given, because it has been found to be "most representative" for monosaccharides group – its interaction with nanometric alumina suspensions was studied in details [6,7]. It had been experimentally proved before, that the other monosaccharides have had quite similar influence on nano-ZrO_2 slurries. The structure of this commonly known monosaccharide is presented on Fig.5.

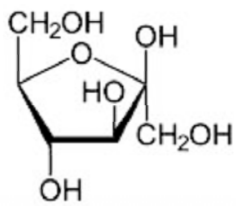

Fig. 5. The structure of D-fructose

Method. Studied ceramic slurries were composed in turn with:

★ redistilled water,

★ D-fructose,

★ ZrO_2 nanopowder.

As-obtained slurries were mixed in a planetary ball mill PM100 (Retsch) for 90minutes with a speed of 300r.p.m. Subsequently, some of the slurries were ultrasonificated (Ultrasonic Homogenizer, Biologics, Inc., Model 3000) and mixed once again for 15minutes in a planetary ball (300r.p.m.). The second mixing was applied to eliminate some effects of superficial coagulation of the slurries, which was created by ultrasonic treatment. Rheological properties were investigated by means of DV+II-Brookfield Rheometer (Brookfield Engineering Laboratories Inc., Massachusetts, USA).

3. Results and discussion

Some rheological properties of as-obtained slurries were tested in details. Viscosity and thixotropic properties of two slurries with no addition of deflocculation agent were compared (Fig.6.).

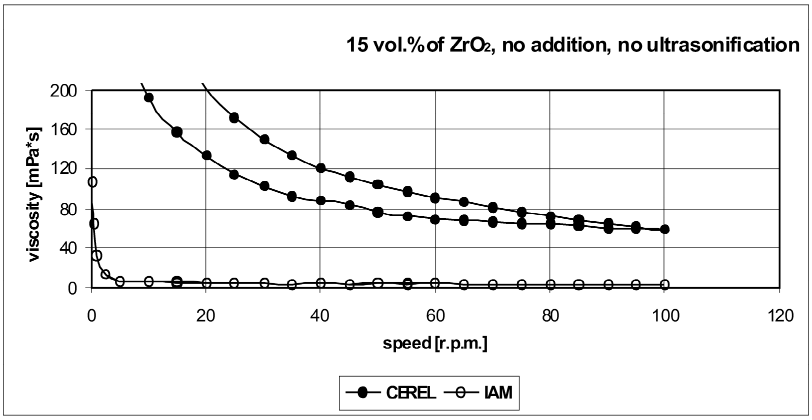

Fig. 6. Rheological properties of slurries made of the ZrO_2 nanopowders with no dispersant

The slurry made of ZrO_2 CEREL is viscous and has significant thixotropic properties. 15vol.% of this nanopowder is close to its maximal concentration in a slurry with no disperse agent. Then again, the slurry made of ZrO_2 IAM can be characterized by low viscosity and no thixotropic structure. The concentration of solid phase is over two times higher in the first case. Just described, very different rheological properties, follows with quite disparate size and morphology of used nanopowders (Fig.3.).

The investigations conducted revealed, that addition of D-fructose decreases viscosity of slurries with content of CEREL ZrO_2 (17nm). It was tested that the most profitable amount of D-fructose comes to 3wt% – this value is found to lie in the minimum of "viscosity curve" (Fig.7.). Besides, it is convenient from economical point of view. When more D-fructose is added, the curve obtains *plateau* – probably no more saccharide can be adsorbed on a surface of nanopowder. In general, D-fructose does not seem to be highly effective as deflocculation agent of used nanopowder, but it was proved, that it decreases viscosity of the slurries.

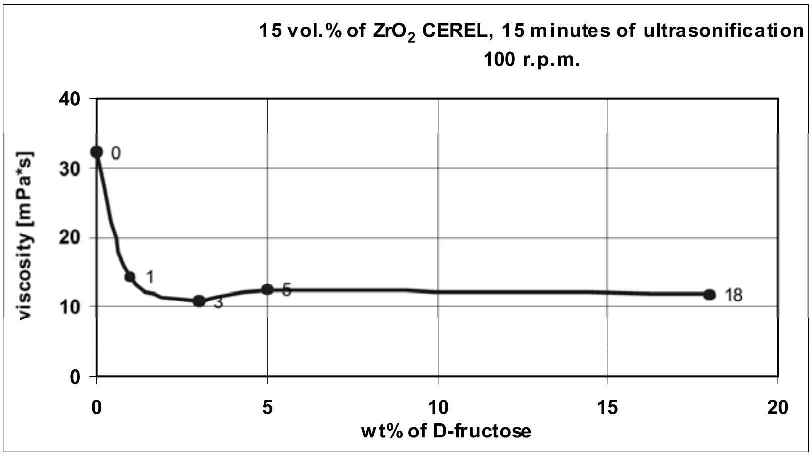

Fig. 7. Influence of D-fructose on rheological properties of ZrO_2 CEREL slurries

On the other hand, addition of D-fructose increases viscosity of slurries with content of Inframat Advanced Materials ZrO_2 (44nm). The viscosity growth is most significant for 3wt% of addition (Fig.8.). Generally, the more D-fructose in slurry, the lower viscosity. The slurry with content of 18wt% of addition has a similar viscosity like the slurry with no D-fructose. Therefore, D-fructose does not act as effective disperse agent of ZrO_2 IAM nanopowder.

The cases presented suggest, that for the tested powders, there are two different mechanisms of nano-ZrO_2 – water – D-fructose interaction, which probably results from distinct morphology of the nanopowders.

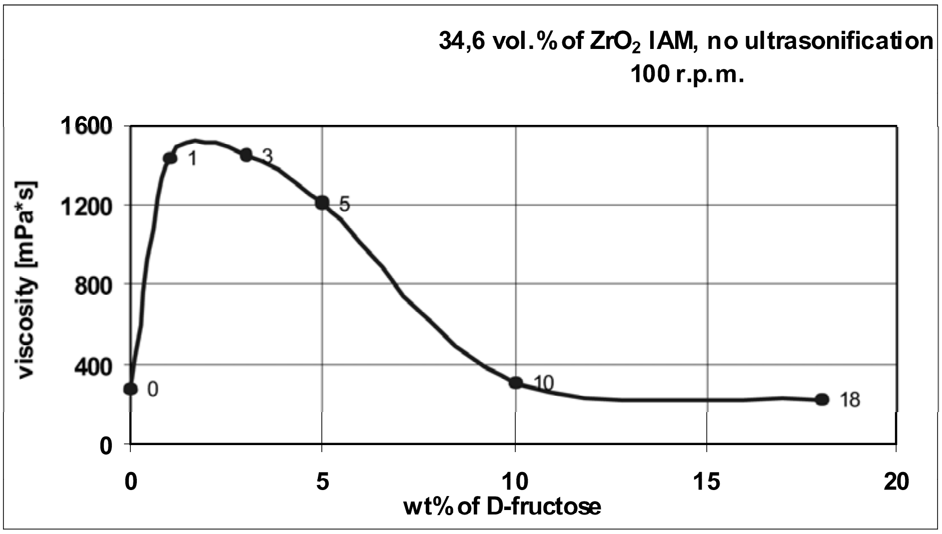

Fig. 8. Influence of D-fructose on rheological properties of ZrO_2 IAM slurries

Besides, it was studied, how ultrasonification process influences rheological properties of the slurries. The research shows that ultrasound usage decreases viscosity of slurries (Fig.9. and Fig.10) – the same phenomenon was observed in the case of deflocculation of nano-Al_2O_3 slurries [7].

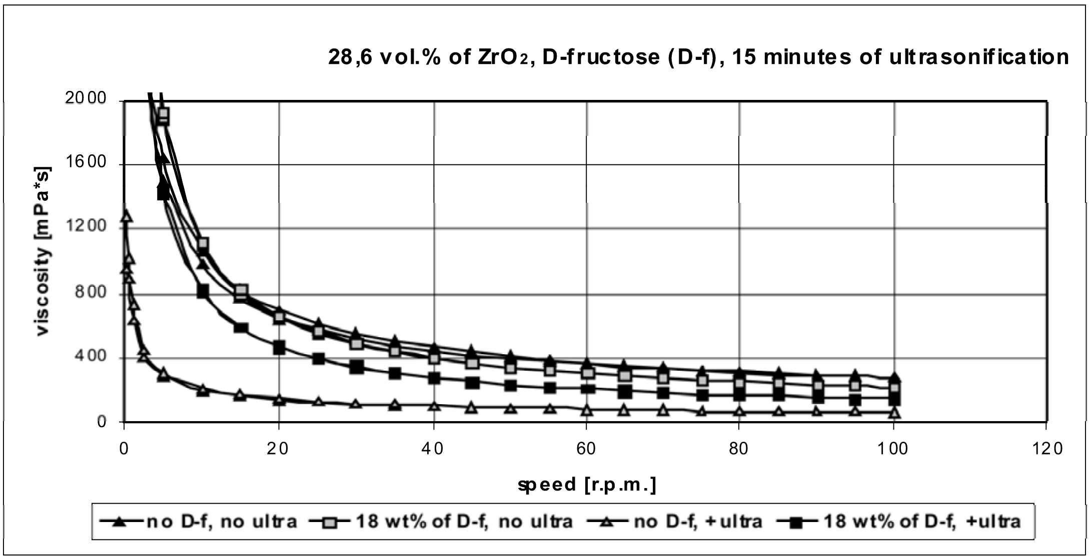

Fig. 9. Influence of ultrasonification on rheological properties of ZrO_2 IAM slurries

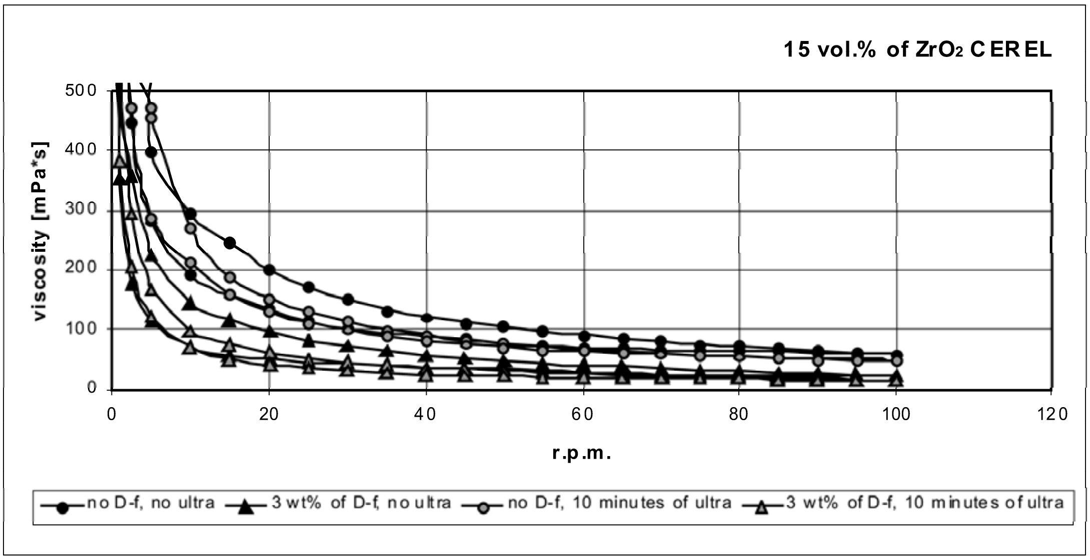

Fig. 10. Influence of ultrasonification on rheological properties of ZrO_2 CEREL slurries

4. Conclusions

At this stage of investigations, it has to be concluded, that D-fructose addition has not proved as an efficient nano-ZrO_2 dispersant. D-fructose disperses slurries with a content of CEREL ZrO_2, but their viscosity is just a little lower then with no addition of this saccharide (Fig.7.). On the other hand, viscosity of slurries with a content of IAM ZrO_2 increases, when D-fructose is added (Fig.8.). These phenomena allow assuming, that monosaccharides are not efficient dispersants for all the nanopowders regardless of their physiochemical and surface properties. Probably, the main factor inducing mentioned differences in influence of monosaccharides on rheological properties of nanosuspensions is morphology of used nanometric powders. Fig.3. shows how different are the studied powders in terms of their morphology. Is it a sufficient explanation? According to our current knowledge – yes, but some further investigations are clearly needed to find what and how exactly influence such different nano-ZrO_2 – monosaccharides interactions.

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REFERENCES

[1] H. L e d a, Współczesne materiały konstrukcyjne i narzędziowe. Wydawnictwo Politechniki Poznańskiej, Poznań 1996.

[2] M. A n d r z e j c z u k, M. L e w a n d o w s k a, T. K o s m a č, J. K. K u r z y d ł o w s k i, The Structural Stability of Zirconia Ceramics in Water and Acid Solutions. Archives of Metallurgy and Materials **51**, 4, 659-663 (2006).

[3] A. N a v r o t s k y, Materials and Nanotechnology. Journal of the Franklin Institute **340**, 263-268 (2003).

[4] . M. J u r c z y k, J. Jakubowicz, Nanomateriały Ceramiczne, Wydawnictwo Politechniki Poznańskiej, Poznań 2004.

[5] M. J. M a y o, Processing nanocrystalline ceramics from ultrafine particles. International Materials Reviews **41**, 85-120 (1996).

[6] C. L i, M. A k i n c, Role of Bound Water on the Viscosity of Nanometric Alumina Suspensions. (Department of Materials Science and Engineering and Ames Laboratory Iowa State University, Ames, IA 50011, USA).

[7] M. S z a f r a n, P. F a l k o w s k i, T. M i z e r s k i, Effect of chemical structure of saccharides on the rheological properties of nanometric alumina powders. Berlin Conference 2007.