MODERN APPROACH TO STUDY SUSPENSIONS FOR THE CREATION OF POROUS ZIRCONIA NANOCERAMICS

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Abstract

The presented work deals with the analysis of suspensions from two types of zirconium oxide nanopowder and two types of reagents (Disperbyk and Dolapix) suitable for the creation of porous ceramics. In the work, a secondary material - micro methyl cellulose (MMC) was used as a combustion additive, and the stability and rheological behaviour of suspensions with increasing MMC content were observed. The stability analysis proved a fast analysis, complementary to conventional rheological measurements. It enabled predicting the behaviour of the suspensions after forming the ceramic body, particularly for the case of slip casting. The microstructure analysis confirmed the influence of MMC on the pore content as well as the applicability of a unique stability analysis for predicting the formation of porous ceramic bodies.

Keywords: Kinetic stability, rheology, viscosity, microstructure

1. INTRODUCTION

Porous ceramics are three-dimensional structures that are sintered at high temperature and present large numbers of pores, traditionally between 20 % and 90 % [1,2]. Porous zirconia ceramics can be utilized in a wide range of applications, including artificial cortical bones [3], zirconia filters for hot gas filtration [4], and supporting materials for catalysts [5]. Additionally, zirconia is one of the best-known thermal insulators due to its low thermal conductivity. Furthermore, the presence of porosity further decreases thermal conductivity, as air in the pores also contributes to this effect [6,7].

Nowadays, ecological methods that contribute to the sustainability of research and production of ceramic (and generally silicate) bodies are gaining popularity. Secondary raw materials or biological substances are used precisely for sustainability and ecological reasons, and the preparation of porous ceramics is no exception. For example, Mustafa et al. [8] used waste coffee ground with contents 1 – 15 wt. % to create porous alumina ceramics, while number of pores increased with increasing content of coffee waste. The research [8] assumed that the combustion of waste coffee grounds formed pores during sintering. Shakir et al. [9] used tapioca starch for the manufacturing of porous zirconia bodies and, similar to research [8], reported that starch creates porosity during high-temperature processing, and as the starch content increases, the porosity content and ceramic shrinkage increased. Other substances used as foaming agents include paper waste [10], rice husk [11] or eggshells [12].

Before the actual analysis of the properties of sintered ceramics take place, such as the analysis of microstructure, pore content, thermal conductivity, etc. it is important to know the properties of the prepared suspension itself. As reported by [8,13], ceramic suspensions exhibit non-Newtonian behaviour; their dynamic viscosity changes with the shear rate. The value of dynamic viscosity should serve as a quick tool to consider the suitability of the forming method [14]. An equally important factor is the stability of the prepared suspension. For the case of rapid sedimentation, separation of the ceramic powder from the matrix may occur, resulting in a defective-shaped body or defects manifesting during high-temperature processing.

The presented work aims to introduce a new method for characterizing ZrO_2 suspensions in the preparation of porous ceramics, utilizing different mass contents of environmental pore-forming additives, and to confirm the viability of the stability analysis using actual rheological results.

2. EXPERIMENTAL PROCEDURE

The dispersion medium for suspensions was prepared by dissolving 2 wt. % of carboxymethyl cellulose with M_w = 700,000 (Sigma Aldrich) in distilled water for 1.5 hours on a magnetic stirrer at an increased temperature of 60 °C. Zirconia suspensions were created following this procedure: 25 g of dispersion medium was placed into the agate bowl, and 4 wt.% % of dispersing agent (agent Disperbyk – 103 from BYK GmbH or agent Dolapix CE64 from Zschimmer & Schwarz GmbH Co.) was added to the bowl. Subsequently, one-third of the selected zirconia powder (CY3Z-RS with d50 = 300 nm from ZirPro or 3Y–ZrO_2 d_{50} = 25 nm from SkySpring Nanomaterials, Inc.) was added. Then, the selected amount (see **Table 1**) of ecological combustible additive micro methylcellulose (MMC), which arose as a secondary synthesis product, was added. Consequently, approximately 30 wt.% of zirconia milling balls and suspension were added to reach 50 wt.% of solid content. The mixture was mixed on the planetary mill Pulverisette (Fritsch) for 10 minutes at 650 RPM. This procedure was repeated twice until all remaining powder was homogenized in suspension. This procedure was repeated twice to ensure the homogeneity of the defined amount of zirconium powder.

Table 1 Composition of prepared zirconia suspensions and their designations

Amount of MMC (wt. %)	Particle size of zirconia powder (nm)	Agent used	Suspension designation	Amount of MMC (wt. %)	Particle size of zirconia powder (nm)	Agent used	Suspension designation
0	300	Dolapix	Dol300(0)	0	25	Dolapix	Dol25(0)
1.0	300	Dolapix	Dol300(1)	1.0	25	Dolapix	Dol25(1)
2.5	300	Dolapix	Dol300(2.5)	2.5	25	Dolapix	Dol25(2.5)
5.0	300	Dolapix	Dol300(5)	5.0	25	Dolapix	Dol25(5)
0	300	Disperbyk	Dis300(0)	0	25	Disperbyk	Dis25(0)
1.0	300	Disperbyk	Dis300(1)	1.0	25	Disperbyk	Dis25(1)
2.5	300	Disperbyk	Dis300(2.5)	2.5	25	Disperbyk	Dis25(2.5)
5.0	300	Disperbyk	Dis300(5)	5.0	25	Disperbyk	Dis25(5)

Rheological properties were measured using a rheometer (Discovery HR–2, TA Instruments). The conditioning was set to 5 minutes at a temperature of 25 °C, and preheat was set for a duration of 1 minute at a shear rate of 100 s^{-1}. The flow curves measurements were carried out from 100 s^{-1} to 0.01 s^{-1} in a logarithmic sweep. The stability of the suspensions was observed using a LUMiSizer analytical centrifuge (LUM GmbH). Samples were dosed in polyamide cuvettes and analyzed at a centrifugal speed of 1000 RPM, with 200 sedimentation profiles performed. Temperature measurement was set at 25 °C, and the laser had a wavelength of 865 nm.

Part of the freshly prepared samples was put to a gypsum mold and removed to high-temperature processing after one day. Samples were sintered in a muffle furnace following the next steps – a process started with a heating rate of 3 °C up to 600 °C and it was held for 45 minutes. Then, the heat rate was again set to 3 °C and held up to 1500 °C for 2 hours, followed by free cooling to room temperature. The porosity of the samples was determined by the Archimedes' method, following the norm [15]. An electron microscope, JSM 7600F (JEOL), was used to observe the microstructure of sintered zirconia bodies.

3. RESULTS AND DISCUSSION

3.1 Stability of suspensions and rheological properties

As can be seen in **Figure 1**, all measured suspensions exhibited pseudoplastic behaviour (as most ceramic suspensions do [16]); the dynamic viscosity decreased with increasing shear rate. All square Pearson´s correlation coefficient achieved values in the interval 99.97 – 100 % by fitting with the Cross model. In all four types of suspension, viscosity increased with increasing volume filling of micro methylcellulose, which should be caused by the underlying bimodal distribution character, which, according to Del Gaudio [17], should increase viscosity. The dispersing agent Disperbyk provided higher values of dynamic viscosity, and subsequently, the mobility of the particles could be influenced.

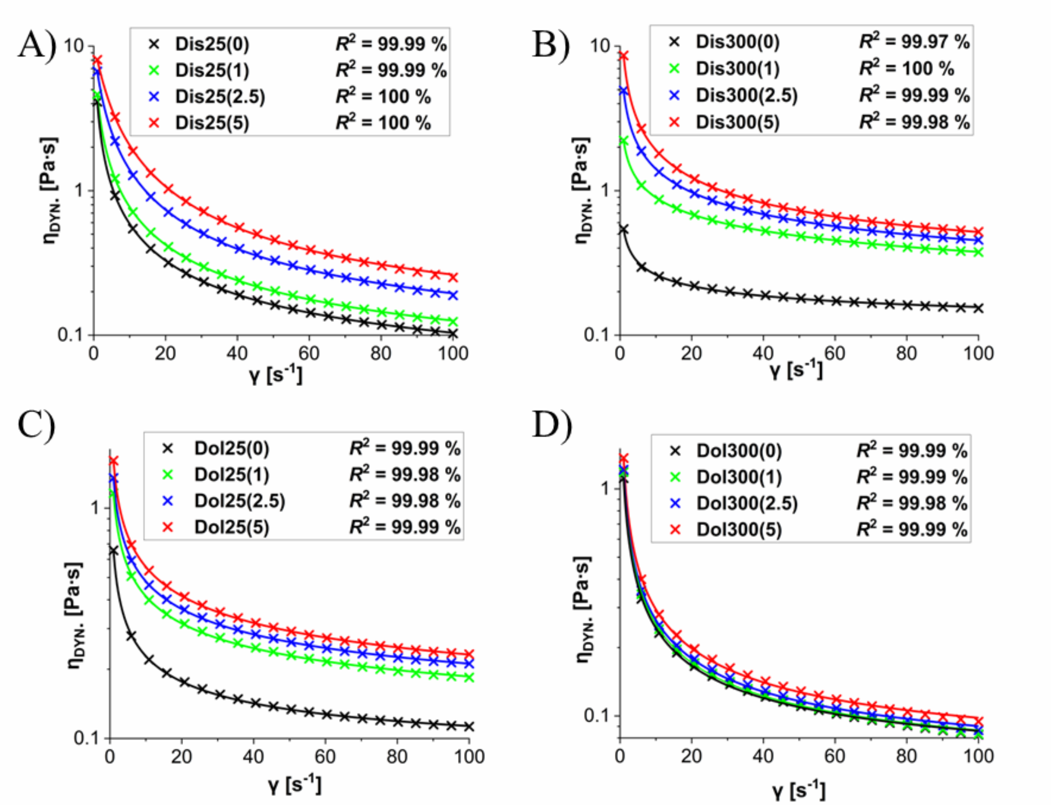

Figure 1 Graph of the dependence of dynamic viscosity on shear rates for a) Dis25, b) Dis300, c) Dol25, d) Dol300 and their MMC derivates

Stability analysis on the LUMiSizer analytical centrifuge is a unique approach to determining the stability of a suspension and assessing the sedimentation or agglomeration of particles, thanks to the scanning of transmission profiles during the setup time [18]. As shown in the exemplary **Figure 2** for a system with a Dolapix agent and powder with a d_{50} of 300 nm, the transmission profiles change with increasing MMC content. Without any content of MMC (see **Figure 2a**), a peak illustrating separation in the cuvette occurred. The red colour represents the oldest profiles, while the green colour represents the newest profiles – solid content was moving from left to right in the cuvette (representing centrifugal movement in the cuvette) along the *y*-axis. With an increasing content of MMC, the peak became smaller and smaller with every addition of MMC. The presented phenomenon could be caused by steric stabilization because of a bimodal distribution [19].

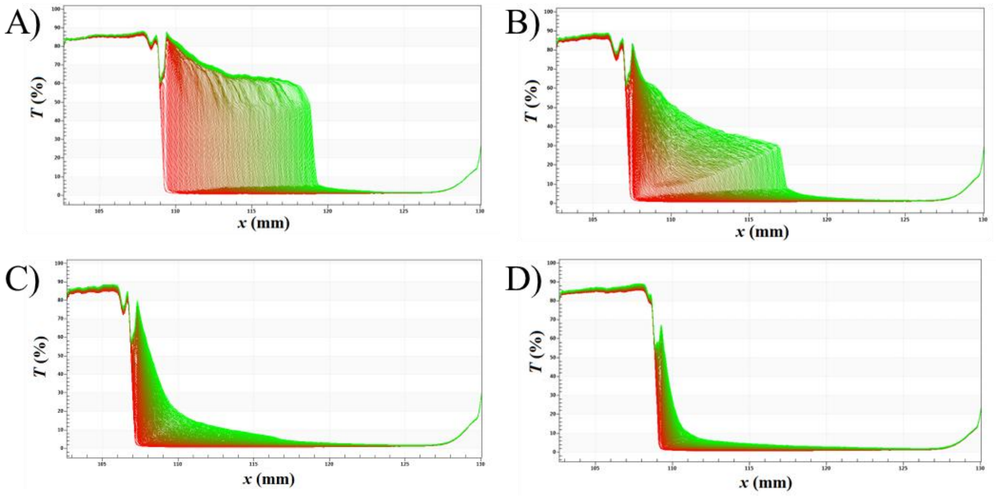

Figure 2 Graph of the dependence of transmittance on cuvette position for a) Dol300(0), b) Dol300(1), c) Dol300(2.5), d) Dol300(5)

LUMiSizer analytical centrifuge also provides so–called instability indexes. The instability index is a dimensionless number between 0 and 1, where 0 represents zero separation of phases and 1 represents complete separation of solid from the matrix [18]. **Table 2** represents instability indexes averaged from 3 measurements, along with their standard deviation. As can be seen, when using the agent Disperbyk, the instability index reached much higher values for suspensions with particles of a diameter of 300 nm, which was caused by a more substantial effect of centrifugation on particles with a larger radius, in agreement with Stokes' law [20]. Additionally, the trend of decreasing instability index with increasing MMC content aligns with rheological measurements, where the dynamic viscosity increases with increasing MMC content. Firstly, the particles exhibit greater resistance to flow, and secondly, this result corresponds to the aforementioned steric stability.

Table 2 Instability indexes for measured suspensions and their standard deviations

Suspension designation	**$I_I \pm \sigma$**	**Suspension designation**	**$I_I \pm \sigma$**	**Suspension designation**	**$I_I \pm \sigma$**	**Suspension designation**	**$I_I \pm \sigma$**
Dol300(0)	0.422 ± 0.031	Dol25(0)	0.010 ± 0.001	Dis300(0)	0.365 ± 0.027	Dis25(0)	0.102 ± 0.008
Dol300(1)	0.271 ± 0.018	Dol25(1)	0.003 ± 0.000	Dis300(1)	0.339 ± 0.011	Dis25(1)	0.075 ± 0.007
Dol300(2.5)	0.145 ± 0.009	Dol25(2.5)	0.002 ± 0.000	Dis300(2.5)	0.326 ± 0.014	Dis25(2.5)	0.035 ± 0.003
Dol300(5)	0.074 ± 0.004	Dol25(5)	0.002 ± 0.000	Dis300(5)	0.292 ± 0.014	Dis25(5)	0.014 ± 0.001

3.2 Structure of sintered bodies

The percentage representation of open porosity was determined by the Archimedes method [15], and all investigated bodies, which could be successfully sintered, contain open porosity above 20% and therefore meet the definition of porous ceramics [1,2], as shown in **Table 3**. Suspensions, which instability index was higher than 0.27, and thus there was a significant separation of the solid phase from the matrix, either could not be entirely removed from the gypsum mould or disintegrated during high-temperature processing. The open porosity increased with the weight percentage of MMC combustion additive. **Figure 3** shows a representative picture of porosity for sample Dol25(5).

Table 3 Open porosity found out by Archimedes method

Suspension designation	*P* ± *σ* (% ± %)	Suspension designation	*P* ± *σ* (% ± %)	Suspension designation	*P* ± *σ* (% ± %)	Suspension designation	*P* ± *σ* (% ± %)
Dol300(0)	-	Dol25(0)	22.73 ± 0.64	Dis300(0)	-	Dis25(0)	23.16 ± 0.51
Dol300(1)	-	Dol25(1)	23.98 ± 0.49	Dis300(1)	-	Dis25(1)	24.27 ± 0.47
Dol300(2.5)	21.54 ± 0.69	Dol25(2.5)	26.35 ± 0.44	Dis300(2.5)	-	Dis25(2.5)	26.09 ± 0.63
Dol300(5)	24.78 ± 0.53	Dol25(5)	28.75 ± 0.72	Dis300(5)	-	Dis25(5)	28.38 ± 0.53

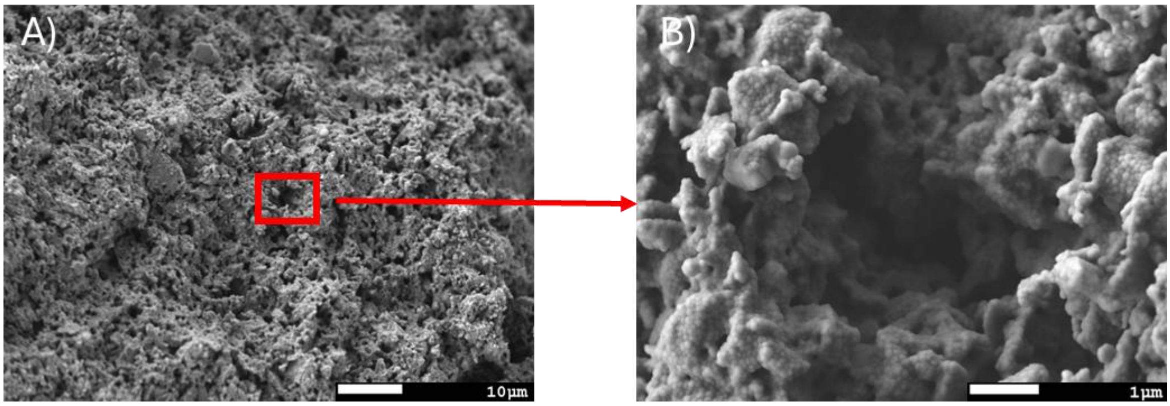

Figure 3 SEM images of sample Dol25(5) with magnification a) 1000 ×, b) 3500 × from the bulk

4. CONCLUSION

In the presented work, 16 types of ceramic suspensions were investigated using two different dispersing agents and two types of zirconia nano-powders. It was found that the innovative approach of analysing the stability of ceramic suspensions is suitable for assessing the formation of ceramic bodies. If the instability index is too high, phases will separate during the molding process, and the ceramic body will not be molded successfully. Furthermore, the stability analysis corresponds with conventional rheological measurements. As the content of the combustible environmental additive, micro methyl cellulose, increases, the viscosity of the system also increases, thereby enhancing the stability of the system. Naturally, the open porosity content of the sintered bodies also increased as the amount increased.

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