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Investigation of alumina samples cast from concentrated polymer suspensions

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Abstract. In this research we investigated a new ceramic forming process. The technology is based on a concentrated ceramic suspension with ethylene acrylic acid copolymer binder system. After the forming procedure to get the final products, the samples were dried, debinded and sintered on high temperature. The samples were studied by different ways during the process: rheological studies, surface properties (optical and scanning electron microscopy), mercury porosimetry.

1. Introduction

Various ceramic processing technologies utilize concentrated ceramic suspensions to produce shaped ceramic final products (e.g. slip casting, tape casting, gel casting, low pressure injection molding etc.). In these technologies the "green body" is obtained by drying the suspension followed by debinding (thermal decomposition of the polymer component) and finally by sintering of the "brown body". The advantage of these techniques over powder injection molding (PIM) is that they usually require less organic binder, thus they are cheaper and more environmentally friendly.

The aim of the research was to invent a new technology for making various shape of alumina products. The most important requirements for the technique are the simplicity, the cost-effectiveness, the size limitation and the good mechanical properties of the products. To reach these requirements the proper composition of the suspension is needed.

2. Materials and methods

In this research we investigated a special system containing alumina filler and ethylene-ethyl acrylate (EEA) solutions as liquid phase. As EEA dissolves in water only under high pH conditions, we have tried to use both NaOH and concentrated aqueous ammonia solution to produce the polymer solution. It has to be noted, that not all EEA grades dissolve in water even under such conditions, therefore first we had to select the proper polymer grade. When preparing the samples we varied the following parameters: NaOH or NH_4OH for dissolving the polymer, the concentration of the polymer solution (the relative amount of the filler and of the liquid phase was kept constant), and the composition of the filler: in some samples we replaced a part of Al_2O_3 by $Al(OH)_3$. It is expected that in the case of $Al(OH)_3$ the greater concentration of surface Al-OH groups as compared to alumina (where such groups are formed only by partial hydration) produces stronger physical network. The potential advantage of using ammonia instead of NaOH is that the ammonium salts decompose and evaporate at

high temperature, not causing further contamination in the pure Al_2O_3 product to be prepared. It is more important in the case of high purity alumina samples [1-6].

The details of the examined samples are shown in the table 1. There were two outstanding samples which are containing only alumina powder with low polymer concentration and NaOH base.

During the research different measurement methods were used to study the samples. These were the reological studies, optical and scanning electron micrography, and mercury porosimetry.

3. Rheological properties of the EEA suspensions

The rheological properties of the EEA solutions and the suspensions made of them were studied by rotation viscometry as a function of frequency and shear rate respectively. Nonlinearities as function of shear rate were observed which is called dilatancy [7].

The following table contents the data of the measured samples:

Table 1. The details of the examined samples

Samples:	**1**	**4**	**6**	**9**	**11**
EEA solution concentration (with NaOH basis)	5%	5%	10%	10%	15%
Powder	Al_2O_3	$Al_2O_3 + Al(OH)_3$	Al_2O_3	$Al_2O_3 + Al(OH)_3$	Al_2O_3

The diagram on the figure 1. shows that the top of the processability window is at 10% polymer content. If the polymer solution is more concentrated the viscosity is too high for easy handling.

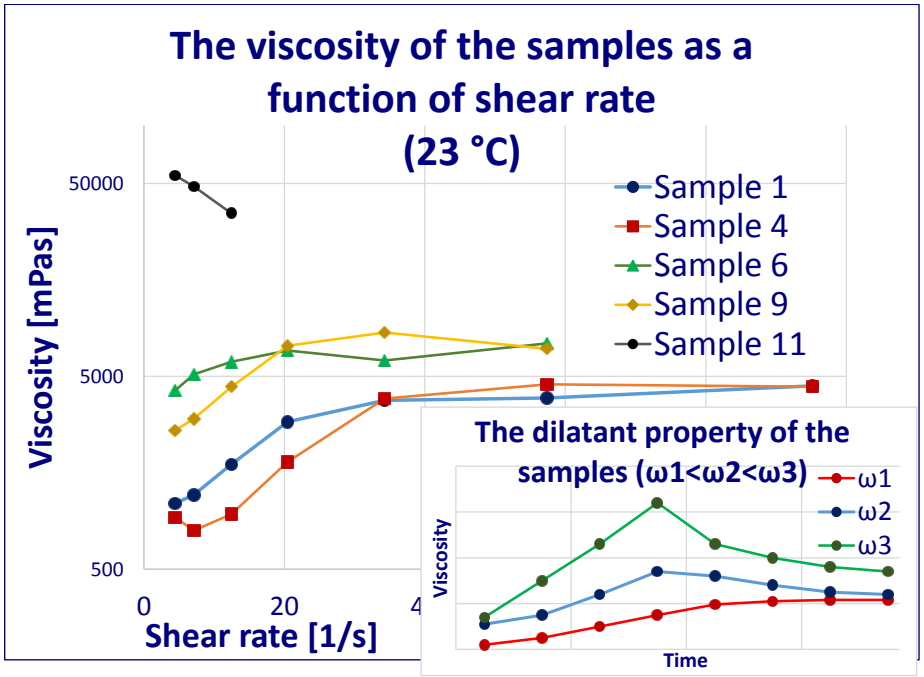

Figure 1. The reological studies

4. Surface study

For the optical studies a Keyence VHX-2000 digital optical microscope was used. During the test different surface defects were detected (Figure 2., 3.). The samples with higher $Al(OH)_3$ content had this kind of defect and these samples also had surface deformation after sintering e.g. bubbles, meniscus, deflection of the sample.

A few samples showed outstanding surface properties. The scanning electron micrograph (Hitachi TM-1000) of sample 1 is shown on figure 4. Both sample 1 (containing 98,83% Al_2O_3 powder and 1,17% EEA with equimolar NaOH) and sample 6 (containing 97,64% Al2O3 and 2,36% EEA with equimolar NaOH) has almost the same surface properties.

Figure 2. Surface defects – bubbles – on optical microscope

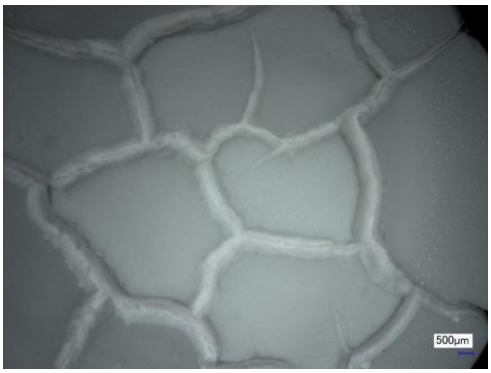

Figure 3. Surface defects – cracks – on optical microscope

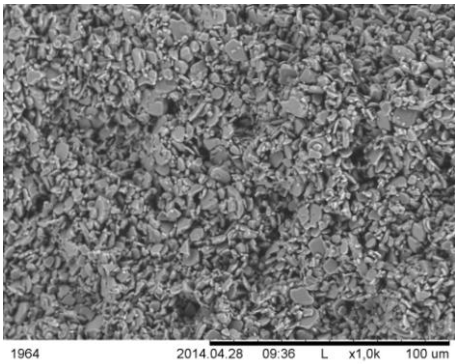

Figure 4. The surface of an outstanding sample (SEM micrograph)

5. Mercury porosimetry

3 chosen samples were studied by mercury porosimetry. From the results of this measurement the distribution of the pores can be calculated.

During the measurement, the height of the mercury level in the capillary was recorded. While the pressure is increasing the mercury penetrates more and more into the pores of the sample and this causes the decrease of the mercury level in the capillary. [8]

The following table (table 2.) shows that the sample 1 has the smallest distribution of pore size. Moreover we can see that the increase of the sintering temperature causes a quite big decrease in the pore volume.

Table 2. The results of the porosimetry studies

Measurement data	Sample 1	Sample 6	Sample 6 (sintered at 1650°C)
Range of pore diameter [µm]	0,088-26	0,035-37,5	0,035-48
Most frequent pore size range [µm]	0,65-2,5	0,6-3,4	0,7-3,4
Cumulative pore volume [cm^3/g]	0,096	0,119	0,078
Pore volume [%]	19,4	22,6	16,3

6. Conclusions

Negative results: The green bodies which were made with NH_3 solution were too fragile to place into the furnace and these samples got relevant deformity during the drying. The density of the sintered samples were significantly lower than the theoretical density of the Al_2O_3 which points to major closed porosity.

The samples which contain both Al_2O_3 and $Al(OH)_3$ powders also became fragile after the drying or the debinding process. Moreover several surface defects were observed after the heat treatment.

Positive results: The sample 1 and sample 6 showed the best properties in every study. These contain only Al_2O_3 powder. The difference between them is in the concentration of the EEA solution. Both of them had outstanding surface properties and the SEM micrograph proves the homogenous structure. There wasn't any surface deformation after the drying or the sintering and both of them had proper stability after the debinding.

Overall the sample 1 showed better results in almost every test e.g. viscosity of the suspension, density, porosity, and mechanical properties. This sample has similar mechanical properties as in other researches.

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