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UTILISATION OF ENZYMATIC REACTIONS IN Al_2O_3 POWDER MOULDING PROCESS

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Abstract

Direct Coagulation Casting (DCC) method was applied for an alumina powder molding. In the paper the results of studies on the application of the reaction of acetic acid generation from glycerol triacetate catalyzed by lipase PPL for the flocculation of ceramic slips are presented. The ceramic samples obtained according this method were homogenous of a low content of organic binder (below 0.5 mass%), high tensile strength in the green state (>1 MPa) and high uniformity of thickening and a uniform structure.

Keywords: alumina, enzyme, slip casting, viscosity

Introduction

In recent years extensive investigations have been carried out on new methods of molding of ceramic materials. The known methods of molding of complex shape profiles comprise the injection molding of a ceramic powder mixed with an appropriate binder and the gel casting, in which a suitable monomer is mixed with a ceramic powder and polymerized in a mould. The above-mentioned methods use considerable amounts of organic substances. The removal of the organic material results in a decrease of density and increase of porosity of the ceramic products. The high content of organic material has both an economic and ecological impact. The higher is the content of a compound of organic origin, the higher the costs of production and the higher emission of pollutants.

From among the new methods of molding of complex shape ceramic materials one should mention the Direct Coagulation Casting (DCC) [1–6]. This process consists in a change of the double dielectric layer around the powder particles suspended in the ceramic casting slip. A slow change in pH around each individual particle of the ceramic powder, thus leading to a decrease of electrostatic repulsion between the double electric layers and as a result slip concentration takes place. A rapid coagulation of the ceramic slip, occurring in the isoelectric point, enables the formation of a highly homogeneous product of low content of an organic binder.

The change in pH of a ceramic slip may be achieved by the use of an enzyme catalyzing the decomposition of an appropriately selected substrate. In this method of

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molding, depending on the isoelectric point of the ceramic powder, a chemical compound and enzyme are selected to adjust the pH value of the casting slip. As a result, a suitable chemical compound, causing a required pH change, is slowly released throughout the whole volume of the system. For example, during the decomposition of urea, in the presence of urease, ammonium ions are released, and the decomposition of glycerol triacetate by means of esterase liberates glycerol and acetic acid. Sometimes this process consists in the formation of a salt modifying the double electric layer of the ceramic powder.

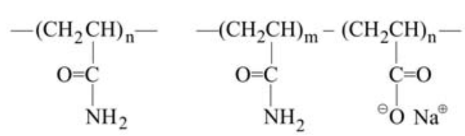
In order to achieve good mechanical strength of the green body it is necessary to add a certain amount of a polymeric binder into the ceramic slurry [7]. Usually, water-soluble binders such as poly(vinyl alcohol), methylcellulose, poly(oxyethylene) glycol, as well as water dispersible binders (styrene-acrylic copolymer, polyurethane, poly(vinyl acetate) emulsions) are used for this purpose [8–13]. Such polymers play the role of both the binder and the flocculant of the casting slip. Depending on the polymeric flocculant used, both the suitable substrate and enzyme should be selected. The enzyme responsible for the slow decomposition of the given substrate should cause a change in the nature of interactions between the random coils of the polymer and a change of their conformations into a dense net of entangled chain structures. Thus, the ceramic slip of low viscosity is transformed into a rigid solid, additionally reinforced with the interactions between the ceramic powder particles and the binder, which is the polymer used in the enzymatic flocculation of the ceramic slip.

This paper presents the results of studies on the use of selected polymeric flocculants in the process of forming ceramic profiles by means of enzymatic decomposition of glycerol triacetate with lipase.

Experimental

Materials and sample preparation

Ceramic slips were obtained from an aluminum oxide powder produced by ALCOA (A16SG) of 0.5 μm diameter grain size, specific surface (BET) of 8.28 $m^2\ g^{-1}$ and density of 3.968 g cm^{-3}. A mixture of diammonium citrate (DAC) (p.a., of POCh Gliwice Poland) with citric acid (p.a., of POCh Gliwice Poland) was used as the dispersing agent, and redistilled water of specific conductivity $\kappa=2.71\cdot10^{-5}\ \Omega^{-1}\ m^{-1}$ was used as a solvent. Lipase PPL (Sigma, Type II, Crude, from Porcine Pancreas) was used as the biocatalyst for the decomposition of glycerol triacetate (Fluka, >99.5% purity). The chemical structure of nonionic and anionic flocculants used are shown properly below:



The degree of ionicity of these copolymers can vary between 0% (homopolymer of acrylamide) to 100% (homopolymer of acrylic acid) depending on the ratio of the comonomers involved, and is expressed in mol%.

Methods

The ceramic slips used contained 20, 48 or 59 vol% of aluminum oxide. The ceramic slips were prepared by mixing for 1 h in a ball mill appropriate amounts of aluminum oxide, a dispersing agent, flocculant, enzyme and water. In the next step the substrate - glycerol triacetate was added. After ca. 20 min the viscosity of the obtained mass was measured using a DV-I+ Brookfield viscometer for a shear rate of 0.3 s^{-1}. Then, the casting slip was poured into PVC moulds and dried for 24 h at room temperature. The green bodies were removed from the mould and dried at 333 K for 24 h.

Thermal analysis was performed by means of Derivatograph C (MOM, Hungary). The thermogravimetric investigation was carried out in air atmosphere, to temperature 1273 K at heating rate 5 K min^{-1}.

After determination of the apparent density, green bodies were sintered at 1823 K for 1 h. For the sintered ceramic profiles the linear shrinkage, apparent density and open porosity were measured. The porosimetric measurement was carried out with the use of a mercury porosimeter (AUTOPORE II 9215 V300 produced by Micromeritics, USA). Scanning electron microscope studies of both green and sintered samples were performed with the use of an instrument LEO 1530.

Results and discussion

The initial stage of studies on the use of enzymatic reactions in the process of polymeric flocculation of ceramic slips was devoted to the selection of an enzyme and of a substance to be decomposed by the enzyme in order to change the pH of the slip. The ceramic slips based on Al_2O_3, dispersed with a mixture of citric acid with diammonium citrate exhibit pH within 8.0–8.5. Thermal analysis of ceramic body (50 mass% alumina and 50 mass% diammonium citrate, citric acid and other organic substances) is shown in Fig. 1. The curves reveal that the dehydration process occurs

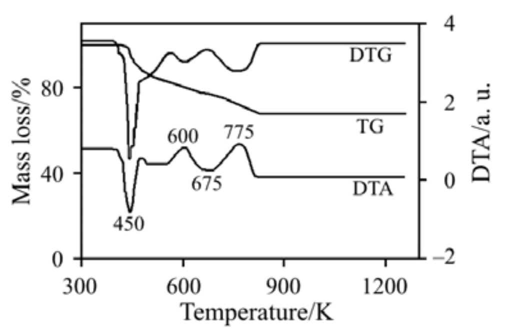


Fig. 1 Thermoanalytical curves of the sample obtained by the DCC methods

in one step (at about 450 K). In temperature range from 450 to 800 K the decomposition of organic substances are observed.

An addition of a very small amount of an anionic flocculant (0.004 mass% with respect to alumina) to the ceramic slurry leads to a slight increase of viscosity in time (curve A, Fig. 2). No viscosity changes of the ceramic slurry in time were observed without the addition of the flocculant (curve B, Fig. 2).

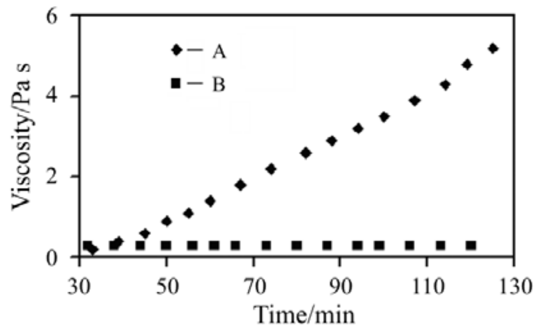


Fig. 2 Changes in viscosity of the ceramic casting slip in time. A – ceramic casting slip containing the polymeric flocculant, B – ceramic casting slip without polymeric flocculant. Composition: Al_2O_3 – 48 vol%, lipase and ester – 0.08 mass%, flocculant – 0.004 mass%

The studies on the kinetics of decomposition of glycerol triacetate were carried out using PPL lipase as an enzyme. Glycerol triacetate decomposes to acetic acid. One molecule of this compound produces on decomposition three molecules of acetic acid, which enables the reduction of pH to 4.0 value.

The effect of the amount of glycerol triacetate on the viscosity of the ceramic slurry in the absence of the flocculant is shown in Fig. 3. The relatively small increase in viscosity of the slurry can be explained by the formation of positive charges on the alumina particles leading to disintegration of alumina agglomerates. The increase in viscosity is preceded by a short initiation time, the length of which depends on the amount of the ester in the ceramic slurry. The length of the initiation period is inversely proportional to the concentration of glycerol triacetate.

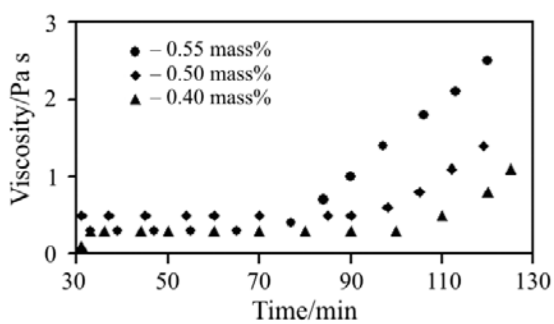


Fig. 3 Influence of the amount of glycerol triacetate on the viscosity of ceramic casting slip. Composition: Al_2O_3 – 20 vol%, lipase – 0.05 mass%

While planning the application of polymeric flocculants for the coagulation of ceramic casting slips it is necessary to choose an appropriate flocculant to be used (cationic, anionic or nonionic one). An analysis of the phenomena occurring at the interface between the ceramic particle and the electrolyte solution shows that the particle charge changes from negative or neutral to positive (adsorption of H_3O^+ ions) when pH was changed from the values ≥pH isoelectric point to the values $<pH_{IEP}$ ones. For this reason the efficiency of the performance of anionic flocculants in a ceramic casting slip of $pH<pH_{IEP}$ is high due to the possibility of association of positively charged aluminum oxide particles to the polymeric anions.

The influence of pH of the ceramic casting slip on its viscosity in time is showed in Fig. 4. As can be seen, the lower the pH (higher degree of the adsorption of hydronium ions on the alumina particle surface) the higher effectiveness of the anionic flocculant. The very high viscosity (higher than 100 Pa s) was observed for a ceramic slurry containing 0.004 mass% of an anionic flocculant when pH decreased to 4. For this pH characteristic fluctuations of viscosity were also observed. The amplitude of these changes increases with increasing viscosity of the casting slip. A possible explanation of these fluctuations is, that during the growth of the flocs the individual particles contact each other. The shearing forces occurring result in partial disintegration of the flocs, hence a decrease of viscosity of the system. A further adsorption of the polymer chains on the alumina particles restores the increase of viscosity.

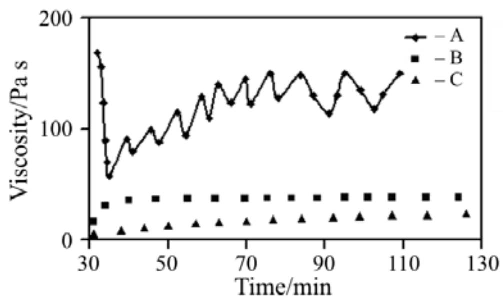


Fig. 4 Influence of pH on the viscosity of ceramic casting slip. A – pH=4, B – pH=5, C – pH=6. Composition: Al_2O_3 – 48 vol%, ester and lipase – 0.08 mass%, flocculant – 0.004 mass%

The measurements of mechanical properties of green bodies prepared using an anionic flocculant were performed for cylindrical samples. The effect of the degree of anionicity of the flocculant on the tensile strength of the green ceramic samples is shown in Fig. 5. As can be seen, the highest strength was achieved when anionic flocculants of very low degree of anionicity were used.

It was shown that the sintering shrinkage, open porosity, and density of sintered ceramic samples practically do not depend on the degree of the flocculant anionicity used in the molding process (Table 1).

Table 1 Effect of the degree of anionicity of the flocculant on selected physical parameters of alumina samples (solid phase concentration 59 vol%) sintered at 1823 K/1 h

Theoretical ionicity/mol%	S_L/%	P_0/%	d_r/%
0	12.1	0.36	96.0
3	13.4	0.39	94.6
30	12.8	0.68	95.2
40	11.7	0.70	93.3
50	12.6	0.70	95.1

S_L – linear shrinkage after sintering; P_0 – open porosity of sintered body; d_r – relative density after sintering

The ceramic samples obtained from casting slips applying different methods of molding were subjected to porosimetric studies and using a scanning electron microscope. The results of porosimetric measurements are shown in Table 2.

Table 2 Comparison of the pore sizes of samples pressed with the addition of 2 mass% of a *A* – polyacrylic binder, *B* – samples obtained by the DCC method and *C* – samples obtained by the DCC method with the use of 0.004 mass% of an anionic flocculant

Measurement	Die pressing/*A*	DCC process/*B*	DCC process with the use flocculant/*C*
Volume/μm	0.086	0.080	0.063
Area/μm	0.081	0.074	0.058
Total pore area/m^2 g^{-1}	9.590	9.760	11.090

The results collected in Table 2 indicate that the mean pore size of green bodies, related both to the surface and to the volume, was higher in the case of the *A* and *B* samples and lower in the case of sample *C*. This means that the samples obtained by DCC method with the use of a flocculant exhibit higher uniformity and a more regular structure. For all samples comparison of the pore sizes obtained in single peak form.

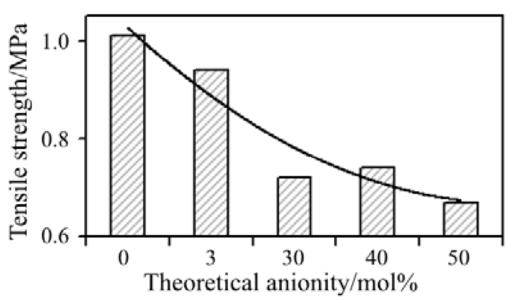


Fig. 5 Influence of the degree of the flocculant anionicity on the tensile strength of the green ceramic samples

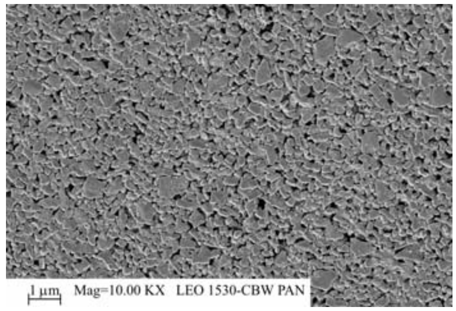


Fig. 6 SEM micrograph of the surface of the green body obtained by the DCC method from the casting slip of 59 vol% of alumina with 0.004 mass% of an anionic flocculant. Magnification 10000×

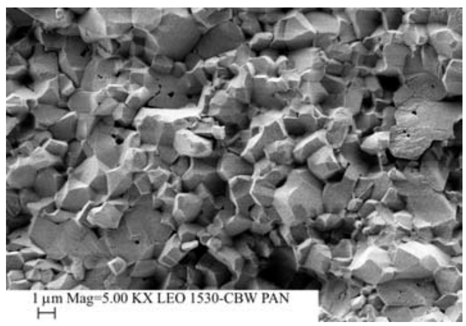


Fig. 7 SEM micrograph of the sintered samples (1 h at 1823 K), obtained by the DCC method from the casting slip of 59 vol% of alumina with 0.004 mass% of an anionic flocculant. Magnification 5000×

Moreover, it should be pointed out, that in the case of the die pressing method the addition of organic substances exceeded 2 mass%, whereas in the case of the DCC method the content of organic substances was lower than 0.5 mass%.

Scanning electron microscope studies of the structure of the ceramic profiles have shown that the use of enzymes and flocculants in the process of molding ceramic materials makes it possible to obtain highly homogeneous green (Fig. 6) as well as sintered samples (Fig. 7).

Conclusions

The use of polymeric flocculants of an anionic type in the DCC molding method together with enzymatic decomposition of glycerol triacetate enables the obtaining of ceramic samples of high uniformity of thickening and of a uniform structure.

The reducing of pH of the ceramic slurry below 5 in the presence of an anionic flocculant leads to flocculation and formation of rigid, viscoelastic green bodies.

The kinetics of the increase of viscosity of ceramic casting slips may be controlled by changing the amount of the flocculant added, as well as by changing the degree of the flocculant ionicity.

Polymeric flocculants present in the ceramic casting slips act as coagulants of the slip and serve as binders of the ceramic powder.

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