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Otrzymano (Received) 01.02.2011

APPLICATION OF LIPASE IN SHAPING Al_2O_3 -MULLITE COMPOSITES

The paper presents the method of Direct Coagulation Casting (DCC) which is a recently developed method of near-net-shaping of ceramic components at low costs. The process relies on electrostatic stabilized ceramic suspensions and their desaturation owing to time delayed in situ reactions. In the method, the enzyme-catalyzed reaction is used to shift the pH of the ceramic suspension to the isoelectric point, which causes coagulation of the slurry.

The aim of this work is the research on shaping alumina-mullite composites with the application of a lipase-catalyzed decomposition of glycerin triacetate. Zeta potential measurements in relation to pH were performed and the appropriate substrate and enzyme was chosen to conduct controlled coagulation of ceramic slurry. In the DCC method, the optimal composition of ceramic suspension was experimentally chosen. The slip gaining a high concentration of ceramic powders, small amount of organic additives, good flow properties and the shortest time after which the intensive increase of viscosity, was considered as optimal. The paper also presents the results of the viscosity of slurries with different concentrations of dispersant and lipase. The sintering temperature leading to the best density and mechanical strength parameters was found to be 1600°C. The relative densities of DCC sintered samples were higher than 95%. The Vickers hardness and fracture toughness K_{IC} for DCC sintered samples were measured. The main conclusion is that the DCC method, using the lipase-catalyzed decomposition of glycerin triacetate, can be successfully applied to the formation of complex-shaped alumina-mullite composites. Very good mechanical properties can be achieved due to the low content of binders and other additives.

Keywords: Al_2O_3 -mullite composites, direct coagulation casting, enzymatic reaction, lipase, Vicker's hardness, fracture toughness

ZASTOSOWANIE LIPAZY W FORMOWANIU KOMPOZYTÓW TYPU Al_2O_3 -MULLIT

W ostatnich latach prowadzone są intensywne badania nad zastosowaniem technik formowania elementów ceramicznych opartych na układach koloidalnych. Do jednych z takich metod należy bezpośrednie odlewanie koagulacyjne (Direct Coagulation Casting, DCC), dzięki któremu można formować elementy o skomplikowanej geometrii, stosując ceramiczne masy lejne o wysokim stężeniu fazy stałej i małej ilości dodatków organicznych. Metoda DCC jest alternatywą dla formowania metodą wtrysku, wymagającą stosowania wysokich ciśnień oraz znacznej ilości dodatków organicznych oraz dla tradycyjnego formowania przez odlewanie do porowatych form gipsowych. W artykule przedstawiono wyniki badań nad formowaniem kształtek z kompozytów tlenek glinu-mullit z wykorzystaniem reakcji enzymatycznego rozkładu trójoctanu glicerolu lipazą. Wykonano pomiary potencjału zeta w funkcji pH dla czystych proszków tlenku glinu i mullitu oraz dla kompozytu wraz z pozostałymi składnikami ceramicznej masy lejnej. Na podstawie otrzymanych wyników dobrano substrat oraz enzym, pozwalające na przeprowadzenie kontrolowanej koagulacji masy lejnej. Na drodze eksperymentalnej dobrano optymalny skład masy lejnej tak, aby lepkość układu była stosunkowo niska, a czas koagulacji masy relatywnie krótki. Przedstawiono wyniki pomiarów lepkości ceramicznych mas lejnych w funkcji czasu dla różnych ilości upłynniacza i lipazy w masie. Otrzymane elementy spieczono w temperaturze 1600°C. Uzyskano spieki o gęstości względnej powyżej 95% oraz o wysokich wartościach twardości mierzonej metodą Vickersa i odporności na kruche pękanie K_{IC} mierzonej metodą pomiaru długości pęknięć wykonanych wgłębniakiem diamentowym Vickersa.

Słowa kluczowe: kompozyty Al_2O_3 -mullit, bezpośrednie odlewanie koagulacyjne (DCC), reakcja enzymatyczna, lipaza, twardość Vickersa, odporność na kruche pękanie

INTRODUCTION

In order to fabricate a ceramic element of certain properties, a suitable shaping method must be chosen. Shaping is a very important process which transforms a powder into a ceramic green body in such a way that the geometry of the green body corresponds to the geometry of the final element. A group of shaping methods which rely on colloidal processes and therefore

do not require the application of high pressures or complicated apparatus exist [1, 2]. One of the recently invented methods is direct coagulation casting (DCC) [3, 4]. DCC is a ceramic shaping technique in which the ceramic suspension coagulates in situ due to a time-delayed reaction, leading to highly homogeneous green bodies. In electrostatically stabilized suspensions, this

can be achieved by shifting the pH of the suspensions toward their isoelectric point. It can be done by the use of time-delayed internal chemical reactions which occur homogeneously throughout the system, such as reactions catalyzed by specific enzymes [5]. The greatest advantages of DCC are: the high concentration of ceramic powder in the suspension, very small amounts of organic additives, high homogeneity of green bodies as well as the possibility of utilizing molds from different materials such as metal, plastic, wax etc.

The selection of a suitable chemical reaction leading to homogenous coagulation of the ceramic slurry plays the key role in the whole process. The reactions which fulfill this demand are decomposition reactions with the use of enzymes as biocatalysts. Generally we can divide such reactions into two groups. To the first group belong the reactions where the substrate decomposes into a product that shifts the pH toward higher values, for example the decomposition of urea to ammonia and carbon dioxide with the use of urease as a biocatalyst. To the second group belong reactions where the substrate decomposes into a product that shifts the pH toward lower values for example the decomposition of esters to alcohols and acids with the use of lipase as a biocatalyst. One of the most important properties of the enzyme is its ability to catalyze only one specific reaction, and basically not any other. Their selectivity results from the principle called the principle of the lock and key - the key, a biocatalyst that fits only one lock that is a single substrate.

An important parameter of the DCC process is its duration. If the chemical reaction is too rapid, the suspension coagulates before it can precisely fill the form, whereas when the reaction is too slow, the sample can unmold after a long time up to several hours. By using a properly selected ratio of enzyme to substrate, the pH (or ionic strength) change can be controlled and thus the coagulation time of the ceramic suspension can be adjusted [6]. The entire process proceeds at room temperature and under normal pressure, which is extremely important from a technological point of view.

A great deal of research concentrates on the synthesis and examination of composite materials which have better or new properties than the particular materials themselves. Nevertheless, the received composite material has to pass the stage of shaping in order to become a final product. The authors have chosen the alumina-mullite composite in order to select the appropriate conditions for shaping the composite by the DCC method. The authors described the DCC shaping process of another composite, namely alumina-zirconia in a previous paper [7]. The main advantage of the alumina-mullite composite compared to pure alumina is the increase of wear resistance. Therefore the paper presents the results concerning the shaping of the alumina-mullite composite by the DCC method with the use of lipase.

EXPERIMENTAL PROCEDURE

To prepare the alumina-mullite composite, two ceramic powders were used. The first powder was α -Al₂O₃ A16SG (ALCOA) of an average particle size $D_{50} = 0.5 \mu\text{m}$, density 3.97 g/cm³ and a specific surface area measured by the BET method 8.28 m²/g. The second powder was mullite (Baikalox, USA) of an average particle size $D_{50} = 0.5 \mu\text{m}$, density 3.08 g/cm³ and a specific surface area measured by the BET method 14.97 m²/g.

In order to prepare stable ceramic suspensions, re-distilled water was used as a solvent. Diammonium hydrocitrate (POCh, Poland) and citric acid (Sigma) were used as dispersants in the ceramic slurries. The lipase LIPOZYME CALB L LCN02103 (Novozymes, USA) was used as a biocatalyst for the decomposition reaction. The substance that undergoes decomposition under the influence of lipase was glycerol triacetate (Fluka) of purity > 99% and density 1.16 g/cm³.

The alumina-mullite composite consisting of 90 vol.% of alumina and 10_{vol.}% of mullite was obtained by mixing the powders. The appropriate quantities of ceramic powders were mixed in water using a mill and ceramic grinding media. The weight ratio of the ceramic powders, water, and grinding media was 1:1:1 and the mixing time was 4 hours. Then the obtained suspension was dried at 105°C to a constant weight.

Then the obtained alumina-mullite composite was shaped by the direct coagulation method. The mixing of the components in the DCC process was carried out gradually. First, the components of the ceramic slurry were dissolved in redistilled water as follows: the dispersant as the mixture of diammonium hydrocitrate and citric acid and then glycerol triacetate. Then the alumina-mullite powder was added and the slurry was ball-milled in a PM 100 Retsch for 1.5 h to achieve good homogenization. The lipase was added next and the slurry was ball-milled for 15 min.

The pH of the isoelectric point for pure alumina, mullite and the composite with the dispersant was determined by zeta potential measurements vs pH on a Zetasizer 3000 (Malvern Instruments, UK). The concentration of NaCl electrolyte in the solution was 10⁻³ mol/dm³. The solution was ultrasonicated for 5 minutes before the measurements. The pH of the suspension was adjusted using 0.1 mol/dm³ HCl or NaOH solution and varied from 2 to 11.

The measurements of viscosity were conducted on a Brookfield RVDV -II+ PRO Viscometer (Brookfield Engineering Laboratories, Inc., USA). The viscosity in relation to time at a constant shear rate of 0.08 s⁻¹ was measured for the slurry with the addition of lipase in order to fix the appropriate amount of lipase so that the time after which a coagulated specimen is obtained was between 20÷120 min. The measurements were performed for a series of ceramic suspensions with different amounts of dispersant and lipase. The suspension of

the best rheological properties was chosen and the shaping process by the DCC method was carried out. The ceramic suspension was cast into PVC molds of the same dimensions. After a thick coagulated body was observed, the specimens were unmolded and dried at 50°C for 24 hours. Then the properties of the green bodies were examined. The tensile strength of the green bodies was determined by the "Brazilian test" [8] using a Universal Testing Machine Instron 5566. The machine registered the value of the force causing the first cracks in the samples. The tensile strength was calculated as $\sigma = (2P/\pi TD)$, where P is the force, and T and D are the thickness and diameter of the disk. The diameter of the obtained samples was 20.1 ± 0.1 mm and thickness 4.1 ± 0.2 mm. Measurements were carried out for a population of 10 samples. The samples were sintered at 1600°C with a holding time of 1h and with a heating rate of 3.5°C/min.

Then the properties of the sintered bodies were examined. The densities of the sintered specimens were measured by the Archimedes' method in water. The Vickers hardness was measured for sintered and thermally etched samples using a ZHV20 (Zwick, Germany). Hardness was determined by applying a Vickers indenter with a load of 10 kG = 98 N and 20 kG = 196 N. Additionally, the fracture toughness, K_{IC} value, was calculated on the basis of the indentation method for central and Palmquist cracks.

RESULTS AND DISCUSSION

In order to select the suitable substrate and enzyme, the measurements of zeta potential in relation to pH were performed.

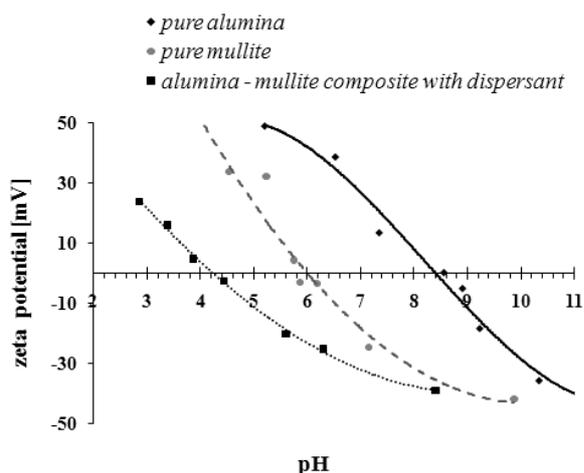


Fig. 1. Zeta potential curves of pure alumina Alcoa, pure mullite BaikaloX and alumina-mullite composite with dispersant

Rys. 1. Krzywe potencjału zeta dla tlenku glinu Alcoa, mullitu BaikaloX oraz kompozytu tlenek glinu - mullit z dodatkiem upłynniacza

The results presented in Figure 1. show that the pH of the isoelectric point (IEP) for pure alumina is 8.4, while for pure mullite it is 6.0. A significant shift of

pH_{IEP} is observed for the alumina-mullite composite with dispersants and equals 4.1. This shift of pH is caused by the addition of the dispersant (the mixture of diammonium hydrocitrate and citric acid) which modifies the electrical double layer around the ceramic particles in an aqueous solution. The zeta potential measurements also show that the ceramic slurry with the alumina-mullite composite is very stable in an alkali and slightly acidic pH. At pH equal to 8.0, the zeta potential is around -40 mV. The stability of the suspension increases with an absolute value of the zeta potential. It is assumed that the colloidal suspension is stable if the absolute value of the zeta potential is greater than 20 mV [9]. The pH of the ceramic suspension with dispersant was measured and equals 8.9. Therefore the zeta potential measurements allowed us to determine the pH changes necessary to generate a spontaneous coagulation process. On the basis of these results, it was found that the pH value should be shifted toward the acidic by over 4 pH units. Changes in pH from alkaline to acidic are possible during the hydrolysis of esters. Among many esters in use, glycerol di- and triacetates are employed in order to induce internal pH changes. The hydrolysis of these compounds is a three-stage reaction, during which the acetic acid is released as shown in Figure 2. One of the enzymes which assists the hydrolysis of esters is a lipase. Lipases are water-soluble enzymes acting on water-insoluble substrates. There is a large family of lipases that exhibit the same structure.

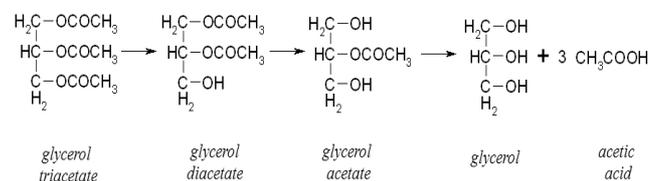


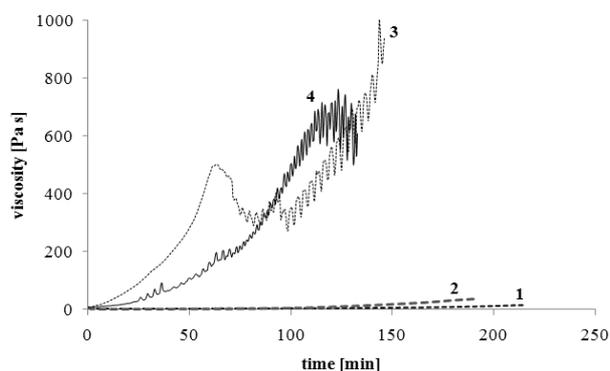
Fig. 2. Stages of glycerol triacetate hydrolysis with use of lipase as biocatalyst

Rys. 2. Etapy hydrolyzy trójoctanu glicerolu z zastosowaniem lipazy jako biokatalizatora

A series of rheological measurements with different amounts of ceramic powder and other additives was performed in order to determine the appropriate quantity of each component of the suspension to maintain the high solid loading. The viscosity measurements were carried out in relation to time. The factors affecting the coagulation time are components that change the pH (or ionic strength) of the ceramic slurries i.e. the quantity of dispersant, enzyme and substrate. As shown in Figure 3, the addition of 0.45 wt.% of lipase based on the powder content results in rapid coagulation of the entire system. The lower the quantity of lipase, the longer time before the coagulation process begins. The optimum composition of ceramic suspension is that corresponding to curve 3, where the ceramic powder concentration is 83 wt.% (55,7vol.%), the quantity of

dispersant is 0.01 wt.% of DAC and 0.07 wt.% of CA, the amount of glycerol triacetate is 3.0 wt.% and the amount of lipase is about 0.45 wt.%. This amount of glycerol triacetate and lipase assures at least 20 minutes before the slurry starts to quickly coagulate.

The curves presented in Figure 3 exhibit the fluctuation of viscosity. This phenomenon can be explained by the coagulation mechanism occurring during measurements. When the slurry coagulates, the number of aggregates increases, they touch each other, which causes an increase in viscosity. An increasing shear rate causes partial disintegration and reduction of the aggregate size, resulting in a decrease in viscosity. Subsequent re-joining of the powder particles leads to a renewed increase in viscosity.



ceramic suspension	concentration of alumina-mullite composite		diammonium hydrocitrate DAC [wt %]	citric acid CA [wt %]	glycerol triacetate [wt %]	lipase [wt %]
	[wt %]	[vol %]				
----- 1	83,0	55,7	0,14	0,10	2,50	0,33
--- 2	82,0	55,4	0,12	0,08	2,00	0,27
..... 3	83,0	55,7	0,10	0,07	3,00	0,45
— 4	83,0	55,7	0,11	0,08	3,00	0,05

Fig. 3. Viscosity vs time for selected ceramic slurries of alumina-mullite composite

Rys. 3. Zależność lepkości od czasu dla wybranych mas lejnych kompozytu tlenku glinu z mullitem

The green samples shaped by the DCC method were obtained from a ceramic slurry of the composition described above, which was selected as the optimal. They were then sintered at 1600°C. The properties of the sintered samples are presented in Table 1. The relative density of the green bodies was about 57% of the theoretical density which can be found as a high value. The relative density of the sintered bodies was over 95% which is a good result, but some separate experiments focused only on the sintering process would be useful for developing the DCC process. The linear shrinkage was 14% which can be considered as typical shrinkage for ceramics if the densification in the green and sintered stage is high. It corresponds to the fact that the density of the obtained green bodies was high, thus the distances between the grains were shorter and linear shrinkage below 15%.

On polished and thermally etched samples, the Vickers hardness and fracture toughness K_{IC} were measured. The Vickers hardness was about 14 GPa, which is a result typical for alumina ceramics.

TABLE 1. Properties of samples sintered at 1600°C
TABELA 1. Właściwości kształtek spieczonych w 1600°C

Relative density of green bodies, %	56.9
Apparent density of sintered bodies, g/cm ³	3.5
Relative density of sintered bodies, %	95.6
Linear shrinkage, %	14.0
Volumetric shrinkage, %	36.8
Vickers hardness at 98 N, GPa	14.4
Vickers hardness at 196 N, GPa	14.2
Fracture toughness K_{IC} at 98 N for central cracks, MPa·m ^{0.5}	4.1
Fracture toughness K_{IC} at 98 N for Palmquist cracks, MPa·m ^{0.5}	8.5
Fracture toughness K_{IC} at 196 N for central cracks, MPa·m ^{0.5}	3.1
Fracture toughness K_{IC} at 196 N for Palmquist cracks, MPa·m ^{0.5}	13.2

In the calculations of K_{IC} , the obtained value of the elastic modulus was $E = 380$ GPa, a typical value for alumina. The central cracks predominated at load 196 N, while at load 98 N the number of central and Palmquist cracks was comparable. It should be noted that the values of K_{IC} for the pure sintered Al₂O₃ are located generally in the range of 3÷5 MPa·m^{0.5} [10]. The prepared alumina-mullite composite contains 10 vol.% of mullite therefore the properties for the obtained ceramics are similar to those for pure alumina. Nevertheless, the values of fracture toughness are in the upper range for pure Al₂O₃. For example the K_{IC} for alumina ceramics of grain size 0.5 μm under a load of 196 N equals 3.9 MPa·m^{0.5} and for ceramics of grain size 3÷5 μm, equals 3.3 MPa·m^{0.5} [11].

CONCLUSIONS

Lipase is a promising biocatalyst which can be applied in shaping the alumina-mullite composite. Direct coagulation casting (DCC) is a convenient, low-cost shaping method which allows one to obtain ceramic samples of high density in the green state. The zeta potential measurements showed that in order to realize the controlled coagulation of ceramic suspension with alumina-mullite composite (90:10 vol.%), the pH value should be shifted toward the acidic by over 4 pH units. It was possibly due to the hydrolysis of glycerol triacetate in the presence of lipase as a biocatalyst. The rheological measurements showed that the ceramic slurry can contain a high concentration of ceramic powder equal to 55,7 vol.% and the optimal amounts of glycerol triacetate and lipase are 3 and 0.45wt.% respectively for the examined system. The green bodies obtained in the performed DCC shaping method had a high density equal to ca 57%. The sintered samples had relative density amounting to over 95%. The values of Vickers hardness and fracture toughness for the obtained ceramics were in the upper range for pure alumina ceramics.

Acknowledgements

This work has been partially supported by the Ministry of Science and Higher Education of Poland (Grant No. N R05 001506) and by the Warsaw University of Technology.

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