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Temperature induced gelation of non–aqueous alumina suspension using oleic acid as dispersant

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ABSTRACT

A novel temperature induced gelation method for alumina suspension using oleic acid as dispersant is reported. Non–aqueous suspension with high solid loading and low viscosity is prepared using normal octane as solvent. Influence of oleic acid on the dispersion of suspension was investigated. There was a well disperse alumina suspension with 1.3 wt% oleic acid. Influence of gelation temperature on the coagulation process and properties of green body was investigated. The sufficiently high viscosity to coagulate the suspension was achieved at −20 °C. The gelation temperature was controlled between the melting point of dispersant and solvent. The gelation mechanism is proposed that alumina suspension is destabilized by dispersant separating out from the solvent and removing from the alumina particles surface. The alumina green body with wet compressive strength of 1.07 MPa can be demolded without deformation by treating 53 vol% alumina suspension at −20 °C for 12 h. After being sintered at 1550 °C for 3 h, dense alumina ceramics with relative density of 98.62% and flexural strength of 371 ± 25 MPa have been obtained by this method.

1. Introduction

The employ of non–aqueous ceramic suspension is essential in the ceramic colloidal forming process. Some special ceramic powders need to be dispersed in organic solvents, such as aluminum nitride which would rapidly hydrolyze in water [1,2]. Non–aqueous ceramic suspension has been employed in many ceramic forming methods such as gelcasting, tape casting, injection molding, temperature induced gelation etc. [3–5]. Also, these methods usually use aqueous suspension [6–8].

Temperature induced gelation is based on the idea of dispersant removing from the ceramic particle surface in a low temperature environment. It is a promising near–net–shaped ceramic forming method for non–aqueous suspension with advantages of convenient process, avoiding the addition of coagulation agent, preventing the solvent evaporation and small linear shrinkage [9,10]. In previous researches, Bergstrom et al. investigated the rheological properties of concentrated ceramic suspension in temperature induced gelation [11]. Xu et al. studied the temperature inducted gelation process of silicon carbide and sialon suspensions which employed the polymer dispersant KD1 as dispersant [12,13]. In these researches, the gelation mechanism was attributed to the decrease of the dispersant solubility in the solvent due to the change of ambient temperature. However, there was no further analysis and direct evidence for the dissolution relationship between the dispersant and solvent. Furthermore, the properties of the sintered ceramics were not systematically characterized.

In the present work, non–aqueous alumina suspension with high solid loading and low viscosity is prepared using oleic acid as dispersant. Influence of gelation temperature on rheological properties of alumina suspension with oleic acid was investigated. Compared with traditional temperature induced gelation method, alumina suspension can be coagulated with shorter time in a low temperature environment. The gelation mechanism can be explained as the oleic acid separating out from the solvent due to the fact that gelation temperature is below the melting point of dispersant. The properties of alumina green body and sintered ceramics were characterized. A novel temperature induced gelation method for non–aqueous alumina suspension is proposed by controlling the dispersant removal at low temperature.

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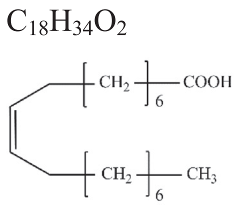
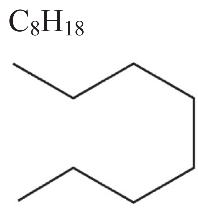
Table 1
Molecular structure and selected physical data of dispersant and solvent.

Name	Oleic acid	Octane
Molecular formula	$C_{18}H_{34}O_2$	C_8H_{18}
Structure		
Molecular weight (g/mol)	282.46	114.23
Density (g/cm^3)	0.891	0.7
Melting point (°C)	13.4	−56.8
Boiling point (°C)	350	125.6
Vapor pressure (kPa)		1.33
Viscosity (mPa s)		0.288

2. Experimental

2.1. Materials

CT3000SG alumina powder (Almatis, Ludwigshafen, Germany) with average particle size of 0.33 µm and specific surface area of 8.08 m^2/g was used. Oleic acid and octane were used as dispersant and solvent to prepare the alumina suspension, respectively. The molecular structure and selected physical data of oleic acid and octane were listed in Table 1. Both of them were produced from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Preparation of alumina ceramics

Fig. 1 shows the flowchart of the low temperature gelation process. Low viscosity alumina suspensions with different solid loading were prepared by tumbling the alumina powder, dispersant and solvent for 24 h. Zirconia balls with diameter of 5–15 mm were used as grinding media. The mass ratio between grinding media and alumina powder was 1:2. Due to the low surface tension of solvent, the suspension can be directly cast into a plastic mold without degassing process. The samples were placed in low temperature environment at different temperatures for a period of time. Then, the coagulated bodies were dried in vacuum for 15–20 min and then demolded. The dried samples were sintered at 1550 °C for 3 h at a heating rate of 5 °C/min.

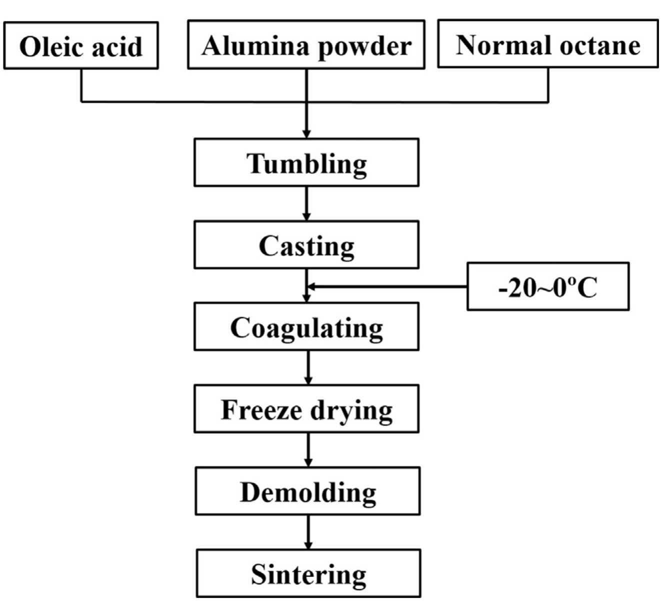


Fig. 1. Flowchart of the gelation process.

2.3. Characterization

Zeta potential of the non–aqueous alumina suspension was measured by a Zeta Potential Analyzer (CD–7020, Colloidal Dynamics Co., Ltd., Ponte Vedra Beach, FL, USA) with a stirring speed of 300 r/min. In zeta potential measurement, 10 vol% alumina suspension was employed. Acetic acid and triethylenediamine were used to adjust the pH value of the suspension. Both of them are analytical reagent. Rheometer (KINEXUS PRO, Malvern Instruments, Worcestershire, UK) attached with C25 R0634 SS spindle and PC25 C0138 AL cylinder was employed to measure the rheological properties of the suspension. After gelation and drying process, the samples were demolded, and their compressive strength was measured in an AG–IC20KN (Shimadzu, Tokyo, Japan) testing machine with a cross head speed of 0.5 mm/min. Cylindrical bodies with 25.5 mm in diameter and a height between 25 and 30 mm were prepared for compressive strength measurement. Using the same mechanical testing machine, the flexural strength of the ceramic specimens with dimension of 3 mm × 4 mm × 36 mm were measured via the three–point bending test. The pressure side of the samples was polished before measurement. The density of the sintered ceramics was measured using the water displacement technique. The microstructure of green bodies and sintered ceramics was observed by a field emission scanning electron microscope (MERLIN VP Compact; Carl Zeiss, Jena, Germany). For observing the microstructure of alumina ceramics after sintering, the samples were thermal etching at 1500 °C for 30 min.

3. Results and discussion

Generally, stability mechanism of ceramic suspension includes electrostatic stabilization, steric stabilization and electrosteric stabilization [14]. In addition, there is another unusual stability mechanism of ceramic suspension which is called semisteric stabilization [15]. The semisterically stability ceramic suspensions use organic solvent as the dispersion medium. The dispersion mechanism can be considered as the facts that the ceramic particles change to lipophilicity in nonpolar solvent (wetting) and the modification of Hamaker constant decreases the Van der Waals' attractive potential energy due to the effect of dispersant [16].

As we know, oleic acid is one of the fatty acids which are commonly used as a dispersant for ceramic powder in tape casting technology [17,18]. It is not a long chain molecule (see Table 1) dispersant and cannot achieve steric stabilization of suspension. In previous studies, there are many reviews which have shown that oleic acid dispersed ceramic suspension is due to the semisteric stabilization [17–21].

To investigate the effect of oleic acid on dispersion of alumina powder, Fig. 2 shows the effect of oleic acid concentration on viscosity of 53 vol% alumina suspension. Due to the high viscosity of the suspension, the data of the oleic acid content lower than 0.5 wt% cannot be measured. It can be seen in Fig. 2 the viscosity of alumina suspension decreases gradually with the addition of oleic acid. The lowest viscosity of 0.73 Pa s appears when the content of oleic acid reaches 1.3 wt%. It indicates that the alumina suspension can achieve sufficient stability with 1.3 wt% oleic acid in octane. Furthermore, it can be also seen in Fig. 2 that excess additives of oleic acid result in the increase of viscosity. It can be explained by dispersant–dispersant and/or dispersant–solvent interactions due to the free–floating dispersant molecules [21]. The alumina particles are easy to reunite and aggregate which leads the increase of the viscosity. The minimum value of the viscosity appears when the concentration of oleic acid at 1.3 wt%.