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Rapid coagulation of silicon carbide slurry via direct coagulation casting

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Abstract

Direct coagulation casting via urease-catalyzed hydrolysis of urea in SiC suspension was studied at room temperature. The results demonstrate that high-solids-loaded SiC slurries with low viscosity can be prepared at pH 9.5–10.5. The urease-catalyzed decomposition of urea can be used to shift the pH and to increase the ionic strength of the SiC slurry. The pH value decreased with the increase of coagulation time. The optimal coagulation temperature is 50 °C for 62 vol.% SiC slurry. The strength of wet green body after 1 h of coagulation at room temperature is high enough for demolding and handling without damage in the wet green stage.

Keywords: A. Suspension; A. Shaping; C. Strength; D. SiC

1. Introduction

The list of novel ceramic processing techniques in the technical areas of advanced ceramics is growing ever longer. Recently, great interest has been shown in aqueous near-net-shaping methods, because of not only their economic and environmental benefits but also their ability to manipulate interparticle forces in aqueous slurries, which have proved to play an important role in the performance of the sintered ceramic product [1]. There are basically two groups of wet forming techniques directly from aqueous slurries. One group uses permeable molds, where water is drained out from the slurry until a solid body is formed, for example slip-casting [2]. The other group uses impermeable molds, whereby various physical principles and/or in situ chemical reactions are exploited for increasing the viscosity of the slurry to a certain critical value above which its fluid character is lost and a saturated body is formed. Examples include, gel-casting [3,4], freezing [5], direct coagulating casting (DCC) [6,7]. During gel-casting of water soluble or insoluble, organic or inorganic additives by polycondensation or polymerization, a macromolecular network is created to hold the ceramic particles together. In freeze casting, the dispersion medium is consolidated in mold, kept below the freezing temperature, and is removed after demolding by sublimation.

DCC is one of the novel near-net-shape forming methods. Results for Al_2O_3 and SiC have been published previously [6–9]. These results demonstrated that complex components of high strength and high reliability are possible with this technique. This process is based on the idea of casting a high-solids-loaded stable suspension in a mold and then using a time-delayed chemical reaction in the suspension to either shift the pH toward the isoelectric point (IEP) of the suspension or increase the electrolyte concentration in the suspension [10]. Both reaction paths can be used to minimize the repulsive force between the particles, which transforms a stable suspension from the liquid state to a stiff particle network. This method can result in materials with homogeneous microstructures of high green density. With a high solid concentration, no linear shrinkage occurs during the liquid-solid transition and during the drying of the green body, and accurate sizes of the component can be expected after the sintering stage [8]. DCC is especially suitable for fabricating complex-shaped components with large and small cross sections in the same part. Large and complex Al_2O_3 parts have been successfully shaped using the DCC technique [11].

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SiC is an important ceramic material that is widely used for various structural, electrical and high temperature applications. However, the failure probability, which mainly depends on processing defects, is still one of the most critical issues. Many efforts have been made in recent years to increase the reliability of ceramics by optimizing the process route. It seems that colloidal processing is one of the most promising ways to reduce the flaw size populations and to increase reliability. Wenjie Si [7] developed recipes for the colloidal processing of SiC via the enzyme-catalyzed DCC process, and the resulting compressive strengths of the coagulated wet green bodies were investigated. However, the enzyme must be added and mixed at a temperature lower than 5 °C during the process, and the demolding time is too long, more than 5 h. At the same time, the compressive strength of the coagulated wet green body is too low (the yield stress after 8 h is 0.015 MPa).

The purpose of this work was to demonstrate that the processing, including the addition and mix of enzyme, can be carried out at room temperature, and improve the coagulation strength using the urease-catalyzed hydrolysis of urea casting process DCC in SiC suspension. The composition of high-solids-loaded suspension will be reported, together with their viscosity. The compressive strengths of the coagulated wet green bodies are investigated.

2. Experimental procedure

2.1. Materials

β-SiC powders, manufactured by Grinding Wheel Plant, Shenyang, China, were used in this work. Fig. 1 shows the particle size distribution of SiC powders. SEM observation (Philips SEM 515, Philips Corp. Holland) indicated that the shape of particles was an irregular polyhedron. The specific surface area of the powder was measured by a single point BET method (Masterisizer 2000, Malvern Instrument Ltd., UK) to be 0.39 m^2/g and the $d_{(0.1)}$, $d_{(0.5)}$ and $d_{(0.9)}$ are 9.63, 18.43 and 33.34 mm, respectively. Chemical composition of the powder is given in Table 1. Urease was used to catalyze the urea (Shanghai Chemical Plant, China) decomposition. Tetramethy lammoniuin hydroxides (TMAH Shanghai Chemical Plant, China) were used to adjust to pH value of the suspensions.

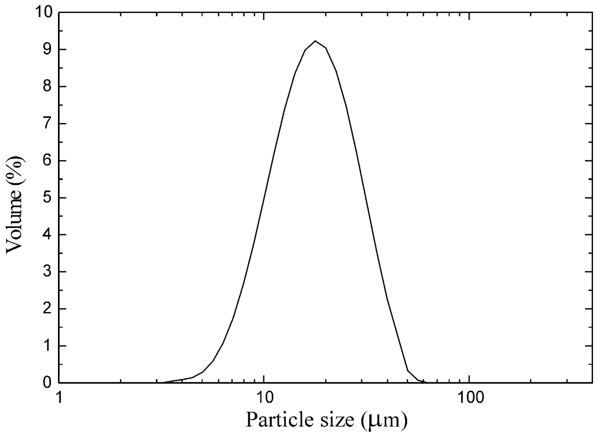

Fig. 1. Grain size distribution of SiC.

2.2. Processing

The DCC flow chart is shown in Fig. 2. The suspensions were first mixed with high-purity deionized water. The pH value of the suspensions was adjusted to 11 with TMAH, followed by ball milling for 8 h using SiC

Table 1
Chemical composition (wt.%) of SiC powder[a]

SiC	Free carbon	Oxygen	Calcium	Aluminum	Magnesium	Iron	Sodium
98	0.2	0.9	0.05	0.05	0.04	0.04	0.03

[a] As given by the supplier.

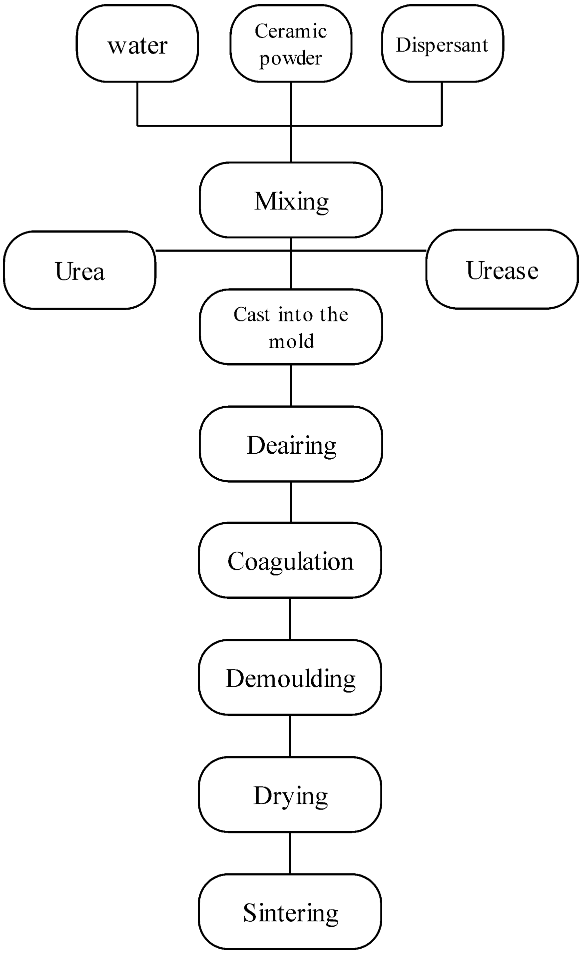

Fig. 2. Flow chart off the forming process.

spherical grinding media. The urea was added after the suspensions were milled. Before casting, the suspension was degassed in a vacuum evaporator for 20 min. The coagulation resulted in a green body with sufficient strength for being removed from the mold. The demolded parts were dried naturally. The green density was calculated according to the weight and the dimension of the cylindrical green body. All processes were performed at room temperature.

2.3. Measurements

A strain-controlled rheometer (4ARES-9a, Rheometric Scientific Inc. USA) was used to measure the rheological properties of the SiC suspensions at room temperature. Zeta potential measurements were performed on BI-ZetaPlus (Brookhaven Instruments Corp., USA) which uses the Doppler shift resulting from laser light scatter from the particles to obtain a mobility spectrum. Samples 25 mm in diameter and 20 mm in thickness for compressive strength measurement were cast into a plastic molds. The measurements were performed on BTC-FR020TN.A50 (Zwick Corp., Germany). The strain rate of compressive test is 0.5 mm/min.

3. Results and discussion

3.1. Viscosity of slurries

The stability and flow behavior of slurries were characterized using viscosity and zeta-potential measurement. For pressureless casting, it is necessary to prepare slurries of low viscosity, <5 Pas. [5]. Fig. 3 shows the viscosity of slurries with 34 vol.% solids loading as a function of shear rates at different pH value 3.4, 7.3 and 9.8, respectively. The viscosity decreases with increasing of pH value at different share rates. A maximum of viscosity (60 Pas at 0.1 s^{-1}) is obvious at a pH of 3.4 and a minimum of viscosity (2.6 Pas at 0.1 s^{-1}) at a pH of 9.8.

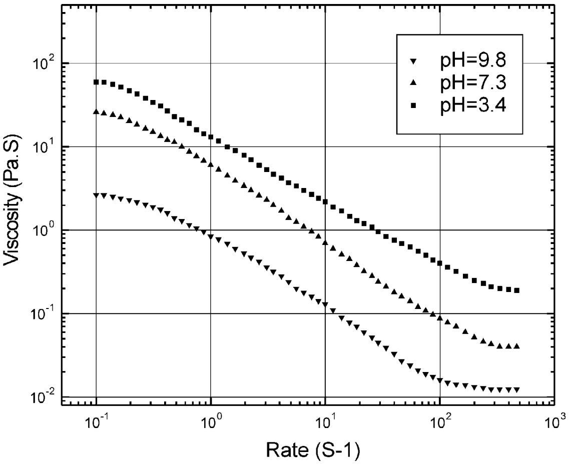

Fig. 3. Viscosity of SiC slurry vs pH value.

Fig. 4 shows the zeta-potential of SiC powder as a function of pH. The zeta-potential of particles in the slurry correlates with the surface charge of the particles and directly influences the interparticale forces [12]. For a pH below 3.6, the particles are positively charged. The isoelectric point (IEP) is at a pH of 3.6. Above this neutral point the slurry shows a negative zeta-potential. Between the IEP and a pH of 10, a steep decrease is observed for the zeta-potential. In the region of pH from 9.5 to 10.5, the negative zeta-potential reaches the max. (−40 mV) which means the repulsive force in interparticles is strong. So the viscosity of SiC slurry in this region is better than other regions. According to the results that are presented in Figs. 3 and 4, the larger the zeta-potential and the pH value, the less the viscosity. So high-solids-loaded slurries with low viscosity can be prepared at pH 9.5–10.5.

In addition, viscosity was also dependent on many other factors. Qiang Huang and co-workers [13] have demonstrated that the viscosity of electrostatically stabilized SiC slurries was dependent on the solids content and powder characteristics such as surface modification, calcination, pretreatment and blend ratio.

3.2. Influence of urease catalyzed urea on viscosity of SiC slurries

When urease, as a kind of catalyst, was added into the SiC slurry, urea could be decomposed through the following steps:

$$\mathrm{CO(NH_2)_2{+}2H_2}O \xrightarrow{\text{urease}} \mathrm{2NH_3 + H_2CO_3}$$

$$\mathrm{NH_3 + H_2}O \longrightarrow \mathrm{NH_4^+ + OH^-}$$

$$\mathrm{H_2CO_3} \longrightarrow \mathrm{HCO_3^- + H^+}$$

$$\mathrm{HCO_3^-} \longrightarrow \mathrm{CO_3^{2-} + H^+}$$

The reaction rate mainly depends on the pH and temperature. These reactions can be used to shift the pH and increase the ionic strength of the SiC slurry. The most effective in situ coagulation mechanism for SiC is based on electric double-layer compression. This procedure can be achieved via the above reactions, which increase the concentrations of NH_4^+ and HCO_3^-, which shields the surface charge on the particle surfaces on a short distance. The resulting pH shifts versus time at room temperature are shown in Fig. 5. It is shown that the pH decreased with increase of coagulation time. Fig. 6 shows the G' change with the coagulation time after adding urease. The viscosity increased rapidly at the initial stage. After 1 h, the slurry lost fluidity and coagulated due to the formation of a three dimensional network through attraction among particles. The urease

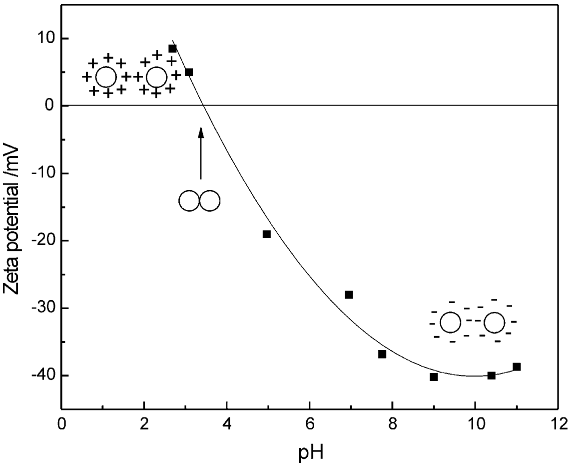

Fig. 4. Zeta potential vs pH os SiC.

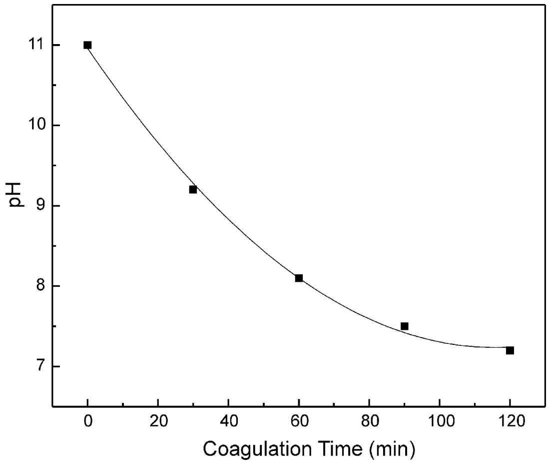

Fig. 5. Change of pH vs coagulation time.

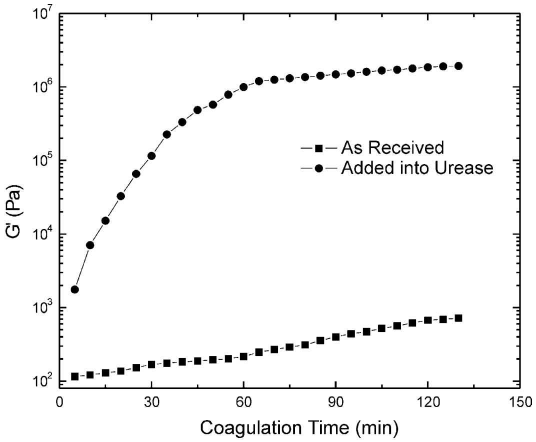

Fig. 6. Evolution of G′ vs coagulation time.

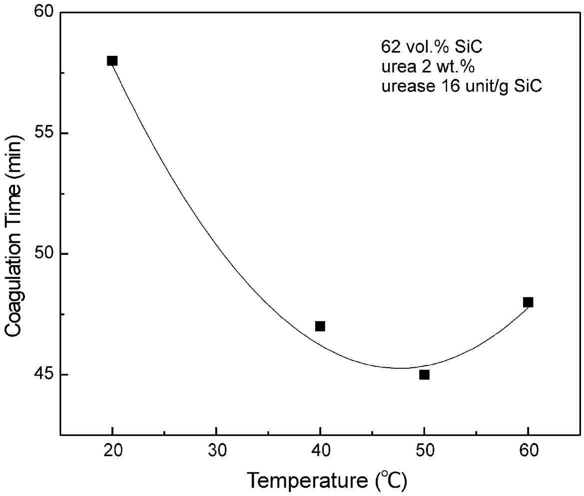

Fig. 7. Effect of temperature on coagulation time.

activity is related to temperature which can be suppressed at a temperature lower than 5 °C. With the increase of temperature, the urease activity is enhanced. When above 50 °C, the enzymes are damaged irreversibility leading to prolonged reaction times for higher temperature. At a temperature around 80 °C, the spontaneous decomposition of urease occurs [11]. The time to reach coagulation was clearly influenced by temperature. From Fig. 7, it can be seen that the least coagulation time occurs at about 50 °C.

3.3. Compressive strength

Fig. 8 shows the stress–strain curves of coagulated bodies with 62 vol.% SiC, for different coagulation times. After 60 min of coagulation at room temperature, the wet green body started to show a solidlike behavior. Fig. 9 shows the coagulation strength (yield stress) that has been obtained after different coagulation times. The elastic modulus of green body is 0.02 GPa for all samples. The coagulation strength increases with increase of coagulation time. The demolding experiments showed that a coagulation strength of >0.01 MPa was sufficient for coagulated bodies to be demolded without damage [7]. The results shown in Figs. 8 and 9 indicate that the wet SiC green bodied are rigid enough after 1 h of coagulation at room temperature for demolding and further handling. Before reaching the highest, the stress increases steeply followed a slight increase. After the highest, the stress decreases steeply until cracks were produced around samples. According to DLVO theory, the total interaction potential of a particle in a suspension is the sum of the attractive potential and the electrostatic repulsion potential. Ceramic particles that are noncharged will strongly attract each other, because of their large Hamsker constant [10], and form a stiff network at high solids loadings. We can imagine that the particle network

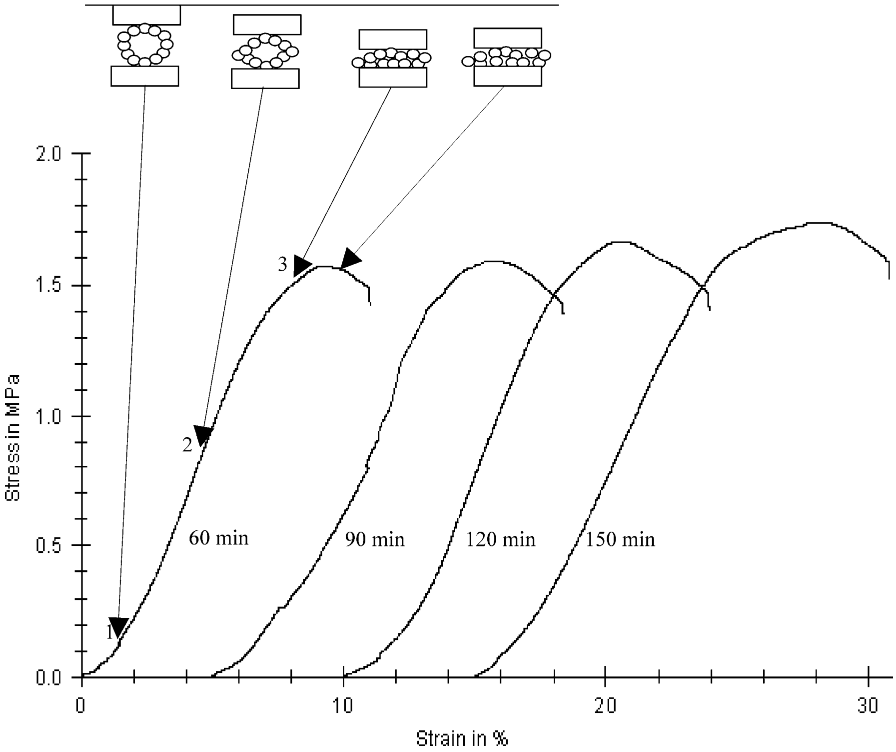

Fig. 8. Stress–strain curves of wet coagulated SiC green bodies after different coagulation times.

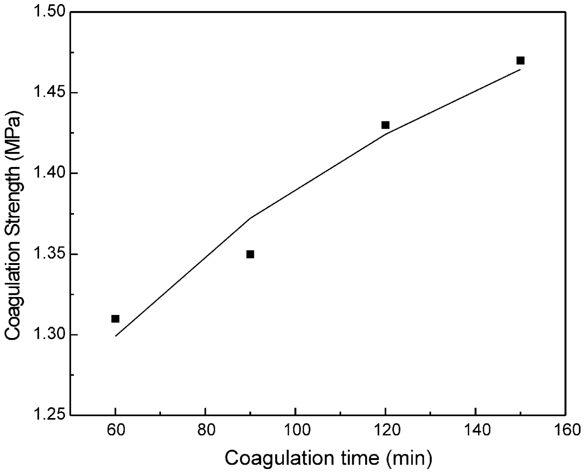

Fig. 9. Coagulation strength vs coagulation time.

is built up by columns of particles touching each other. After the elastic regime, the particle network is damaged irreversibly by sliding processes. The attractive forces between the particles are overcome by shear forces introduced by the outer compression force and the particles slide. In regime 2, new particle–particle contacts are formed. The high compressive force can be carried by the new columns, as already described and discussed in [14]. Further compression results in formation of microcracks at the surface of the cylinder in regime 3, which might be explained by kink formation in the particle columns, as proposed already by Gauckler [11] earlier.

4. Conclusions

DCC via urease-catalyzed hydrolysis of urea in SiC suspension was studied at room temperature. The viscosity results demonstrate that high-solids-loaded SiC slurries with low viscosity can be prepared at pH 9.5∼10.5. The viscosity increases with decreasing pH value. The pH decreased with the increase of coagulation time. The urease-catalyzed urea decomposition has been used to coagulate the SiC suspensions. The time to reach coagulation was clearly influenced by temperature. The optimal temperature for 62 vol.% SiC is 50 °C. The coagulation time will be increased whatever above or under 50 °C. The coagulation strength of wet green body after 1 h of coagulation at room temperature is high enough for demolding and handling without damage in the wet green stage. Because of the shaping capability of very complex components, this casting process is very attractive for commercial applications.

Acknowledgements

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