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Hydrolysis assisted solidification of silicon carbide ceramics from aqueous suspension

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Abstract

The hydrolysis assisted solidification (HAS) process was used in the slurry forming of SiC green bodies. AlN powder was added to aqueous SiC slurry prior to shaping. The addition of small amount of AlN powder causes a dramatic increase in the suspension viscosity or even solidification in the case of highly loaded suspension. Green bodies were successfully produced. Measurements of the changes in viscosity, the pH and the zeta potential measurements were performed to evaluate the process. Effects of the addition of AlN and solidification temperature on the process and the ceramic suspension were followed.

Keywords: A. Suspension; D. SiC; Hydrolysis assisted solidification

1. Introduction

A well dispersed, highly loaded aqueous ceramic suspension can be solidified in several ways, for example Gelcasting [1], direct coagulation casting (DCC) [2], temperature induced forming (TIF) [3], colloidal isopressing [4] and, etc. Most of these solidification techniques rely on chemical changes within the liquid media resulting from a temperature change. Hydrolysis assisted solidification (HAS) is a novel ceramic wet-forming technique in which a highly loaded aqueous suspension containing a small amount (1–5 wt.%) of well dispersed AlN powder is poured, cast and injected into an impermeable mould, where it solidifies [5]. The HAS process employs the hydrolysis of a small amount of AlN powder that is added to the suspension as a setting agent [6]. When compared with related processes, the HAS process shows several advantages. The process is simple and does not require expensive tools and complex procedures. It is not necessary for the starting suspension to contain a high solids content (above ca. 30 vol.%), and the starting pH may vary from moderate acid to alkaline. The solidification of low-viscosity aqueous suspensions without additional organic binders progresses quickly; however, it can be controlled by means of surface modification of the AlN powder [7]. The disadvantage is that its application is not suitable for high purity ceramics not permitting the existence of alumina since the alumina formed from the hydrolysis of AlN will be remain in the ceramics. Ceramics based on alumina [8], zirconia [9], and silicon nitride [10], have also been prepared by this technique.

In the present paper we report the use of HAS in slurry forming SiC bodies. Alumina, which is formed during thermal decomposition of aluminum hydroxide, later on serves as a sintering additive to promote the densification of SiC. The preparation and properties of suspensions and green parts were described.

2. Experimental procedure

β-SiC powders, manufactured by Grinding Wheel Plant, Shenyang, China, were used in this work. SEM observation (Philips SEM 515, Philips Corp. Holland) indicated that the shape of particles was irregular polyhedron. The specific surface area of the powder measured by a single point BET

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method (Masterisizer 2000, Malvern Instrument Ltd., UK) is 2.494 m^2/g and the $d(0.1)$, $d(0.5)$ and $d(0.9)$ are 8.93, 14.16 and 19.85 μm, respectively. AlN powder used throughout the experimental work was supplied by Fujian, China. The specific surface area of the powder was measured to be 3.587 m^2/g and the $d(0.1)$, $d(0.5)$ and $d(0.9)$ are 1.48, 7.68 and 21.82 μm, respectively. Tetramethyl ammonium hydroxide (TMAH, Shanghai Chemical Plant, China) were used as dispersant.

A series of suspensions containing a certain amount of SiC powders, deionized water and TMAH dispersant were mixed. The suspensions were then blended thoroughly by ball milling for 8 h using SiC spherical grinding media. In the last 10 min of the homogenization, AlN powder was added to the suspension. These suspensions were then cast.

The progress of the hydrolysis process and the solidification were estimated by the following methods: (a) by periodic visual inspection of the consistencies; (b) by measuring viscosity or (c) by measuring pH. The time or temperature related viscosity was measured using a strain-controlled rheometer (4ARES-9a, Rheometric Scientific, USA). Couette (cup diameter: 36.8 mm, bob diameter: 35.0 mm, bob length: 37.37 mm) was used for all these measurements. The samples were protected from drying by adding a thin layer of paraffin oil on top. To avoid undesired influence from different mechanical histories, fresh samples were homogenized by pre-shearing at an identical rate of 100 s^{-1} for 1 min. Steady rate sweep measurement was used to characterize the general flow behavior with shear rates ranging from 10^{-2} to 500 s^{-1}. Dynamic time sweep test was used to characterize the solidification of suspension.

The changes in pH were monitored with a PHB-1 pH-meter (San-Xin Instrumentation, Inc. Shanghai, China). The suspensions were hold in a gutter with constant temperature and were gently mixed during pH measurements to prevent sedimentation. 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. After solidification, the wet solid parts were removed from the molds and dried in an oven at 100 °C for 24 h. The microstructure of the green body was characterized using a s-450 scanning electron microscope (Hitachi Corporation, Japan).

3. Results and discussion

3.1. Preparation of SiC slurry

In the HAS process, a highly loaded aqueous suspension of well-dispersed ceramic powder is prepared prior to the addition of AlN. In order to disperse powders in water, the surface charge properties of the powder have to be controlled. Fig. 1 shows the effect of TMAH on the zeta potential of SiC powder. The IEP of SiC powder is 2.5, which agrees with that reported in ref. [11]. The absolute value of zeta potential reaches maximum at the pH value of about [10].

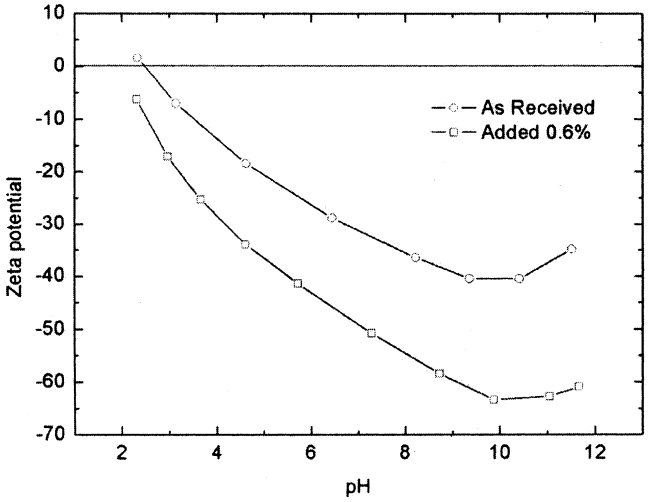

Fig. 1. Zeta potential of SiC powder.

When TMAH is added, the IEP is displaced towards acidic direction, the absolute value of maximum increased with 22 mV. The shifting of the curves in the acidic direction indicates that the organic cations (TMA^+) dispersant have been adsorbed onto the particles' surface [12]. The adsorption of the bulky TMA^+ leads to the thickening of the stern layer which results in the increase of the electrostatic repulsion potential. Therefore, TMAH can efficiently improve the dispensability of SiC powder and the fluidity of the suspension. According to our previous work [13], a homogenous SiC suspension can be obtained when 0.6 wt.% TMAH (based on the weight of SiC powder) was added at pH 10.

3.2. Hydrolysis assisted solidification

Ammonia formation will cause a pH change and a subsequent zeta potential change that leads to electrostatic destabilization in the HAS process [14]. Fig. 2 shows the pH changes with time at different temperature in aqueous SiC suspension that containing 1 wt.% of AlN. According to our results, the pH decreases from the beginning without an incubation period. The steep pH decrease appears after approximately 3 min at 25 °C (Fig. 2a) and 1 min at 60 °C (Fig. 2b). After approximately 7 min at 60 °C and 3 h at 25 °C the pH reaches the minimum following a increasing of pH. Similar results were also observed by other authors [15]. The TMAH is a strong organic base. The aluminum on the surface of AlN was dissolved in basic solutions as Al^{3+} and AlO_2^- based on the potential-pH equilibrium diagram [15]. Therefore, the hydrolysis of AlN powder was promoted on the TMAH aq. The decrease of zeta potential with the decrease of pH (Fig. 1) reduces the repulsive forces among the suspended particles, which would increase the probability of flocculation [16]. At the same time, the viscosity of SiC suspension will be affected with the change of pH.

Fig. 3 shows the viscosity change of SiC suspension containing 32 vol.% solids after AlN is added. The viscosity

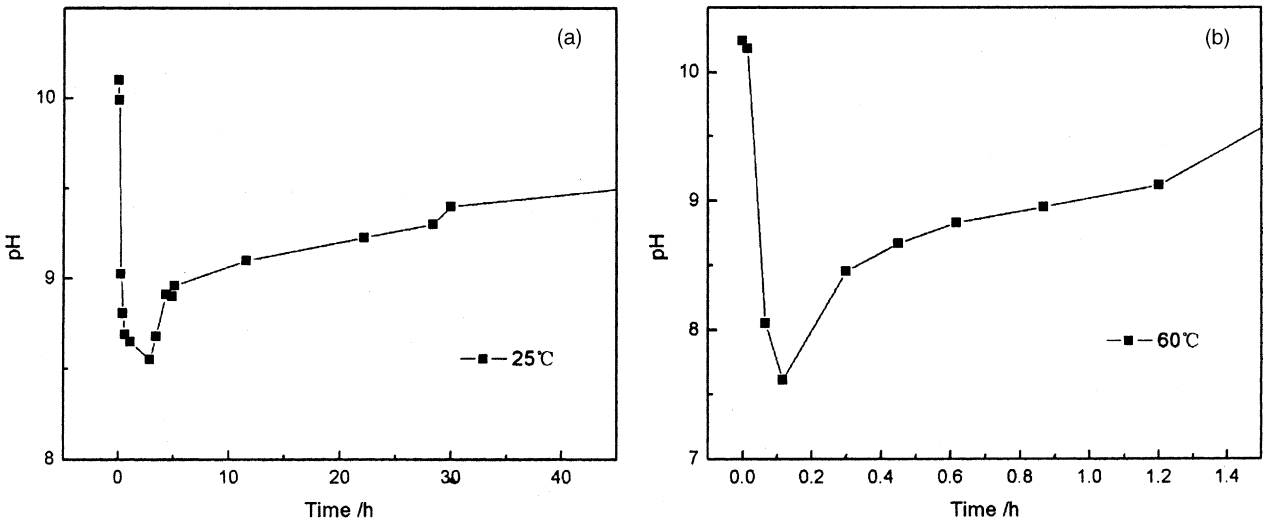

Fig. 2. pH change in aqueous SiC suspension containing 1 wt.% AIN.

increased obviously after the addition of AlN for 30 and 60 min, and the suspensions show obvious shear-thickening behavior at shear rates between 100 and 400 s^{-1}. The critical shear rate for the onset of shear-thickening changed from 100 s^{-1} for the suspension after the addition of AlN for 30 min to 200 s^{-1} for the suspension after the addition of AlN for 60 min.

Fig. 4 shows the variation of G′ with the solidification time of the SiC suspension containing 62 vol.% solids with the addition of 1 wt.% AlN powder at different temperatures. The viscosity increased rapidly at the initial stage. After 9 min at 75 °C, the slurry lost fluidity and coagulated. In the presence of water AlN will hydrolyze following the reaction scheme introduced by Bowen et al. [17]:

$$AlN + 2H_2O \rightarrow AlOOH_{amorph} + NH_3$$
$$AlOOH_{amorph} + H_2O \rightarrow Al(OH)_{3gel}$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

The hydrolysis of AlN is accompanied by a dramatic increase in viscosity which ultimately leads to solidification. This is due to:

(1) flocculating/coagulating induced by the pH change of the suspension to the IEP of the ceramic powder;
(2) gelling of $Al(OH)_3$ reaction product and forming a stiff network;
(3) consuming of water during the formation of AlOOH and $Al(OH)_3$.

Each of these mechanisms is capable of transforming a concentrated slurry into a saturated body. The solidification time for the suspension with 62 vol.% solid loading was shown in Fig. 5. At a particular solidification temperature the solidification time was found to be slightly shortly for a suspension containing 3 wt% AlN than that for the suspension containing 1 wt.% AlN. More experiments have shown that the concentration of the added AlN in the whole

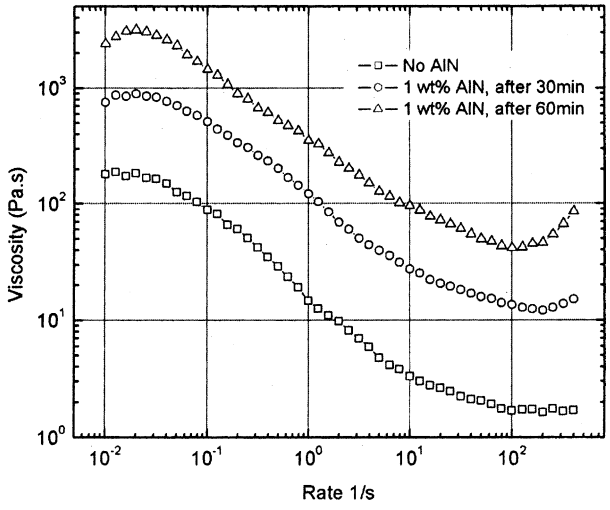

Fig. 3. Viscosity change of SiC suspension.

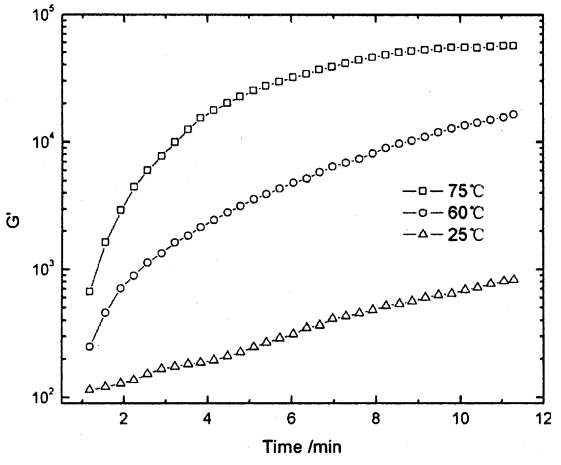

Fig. 4. G′ change of SiC suspension with the solidification time.

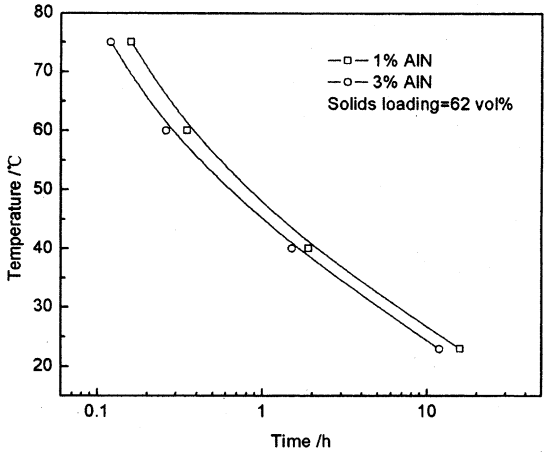

Fig. 5. Solidification time for SiC suspension as a function of temperature.

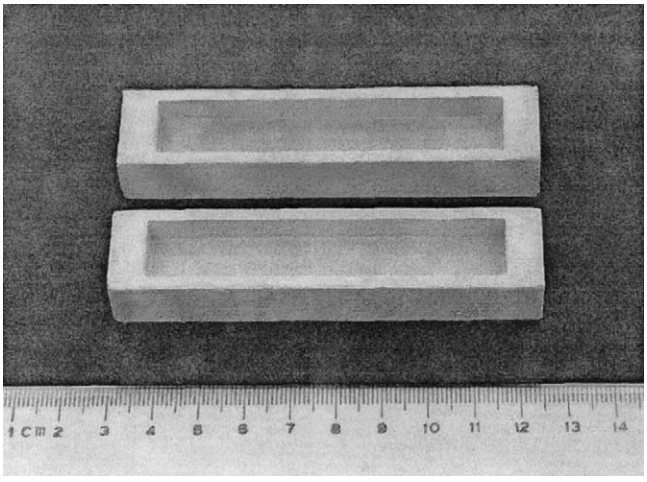

Fig. 7. SiC parts with thin wall formed by HAS.

analyzed region (1–5 wt.% AlN) all affect the solidification time only slightly.

3.3. Microstructure of green body

Fig. 6 shows the microstructure of green body prepared with HAS and DCC. It is obviously observed that the green body obtained by HAS has a more compact packaging than that obtained by DCC. As a consequence, a higher strength and a higher density of the HAS samples can be obtained. Fig. 7 shows the SiC parts with thin wall formed by the HAS process.

4. Conclusions

The present paper summarized the processing parameters on the behavior of an aqueous SiC suspension solidified by hydrolysis assisted solidification. A homogenous SiC suspension can be obtained when 0.6 wt.% TMAH (based on the weight of SiC powder) was added at pH 10. In this strong basic solution, the hydrolysis of AlN powder can be accelerated, which is reflected in a rapid decrease of the suspension pH and consequently, in its viscosity. The pH decreases from the beginning without an incubation period.

The addition of small amount of AlN powder to an aqueous SiC suspension causes a dramatic increase in the suspension viscosity or even solidification in the case of highly loaded suspension. The change of pH, gelling of $Al(OH)_3$ reaction product and the consuming of water contributed to the solidification of SiC suspension. The SiC suspension containing 62 vol.% solids with the addition of 1 wt.% AlN powder can coagulate within 9 min at 75 °C. Temperature plays a much more important role in the solidification kinetics than the AlN content. The green body obtained by HAS has a more compact packaging than that obtained by conventional shaping methods.

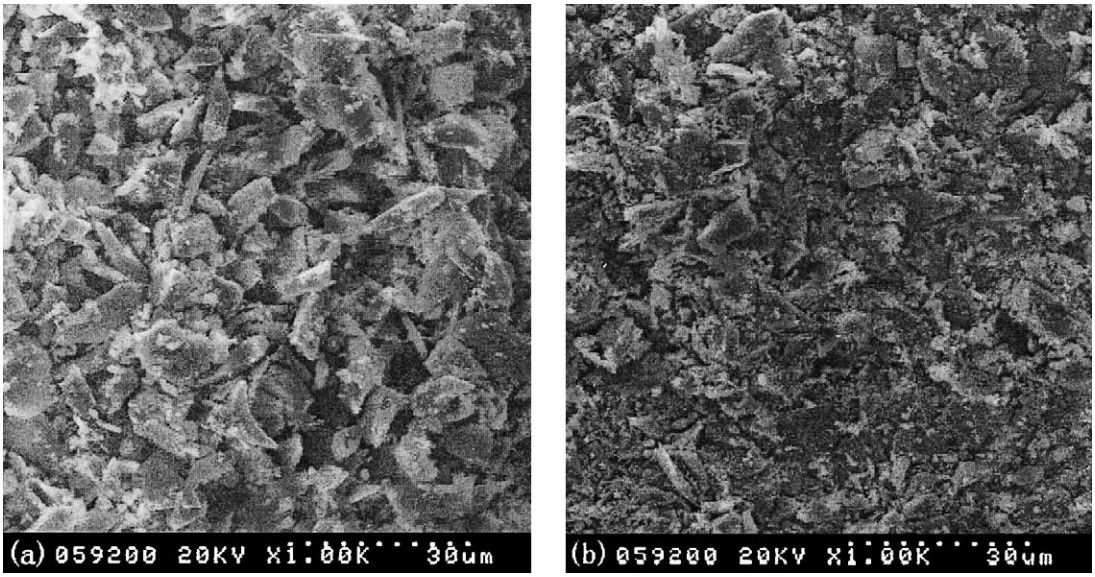

Fig. 6. Microstructure of green body formed by (a) DCC, (b) HAS.

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