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Gelcasting of silicon carbide based on gelation of sodium alginate

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Abstract

A novel gel-casting process by sodium alginate gelation is presented. Solidified agent and chelator are added into sodium alginate solution simultaneously, thus the gelation between calcium ions and sodium alginate is avoided in this stage due to the chelate complex formed from the chelator and solidified agent (calcium salt). By adding hexanedioic acid, free calcium ions are released from the chelate complexes and react with sodium alginate, forming a three-dimensional network. Therefore, silicon carbide particles are held in this three-dimensional network and the slurry is consolidated. Green body with bending strength of ~3 MPa, perfect surface and homogeneous microstructure has been produced by this process.

Keywords: D. Silicon carbide; Sodium alginate; Chelator; Solidified agent; Gelcasting

1. Introduction

Silicon carbide ceramics have aroused great interest for their use in the field of refractories as well as in the field of high temperature structural applications for a long time. Silicon carbide ceramics are known to possess a variety of virtues, such as high mechanical strength, high chemical stability, high temperature of decomposition, good thermal conductivity, semi-conductivity and so on. They find specific applications in the petrolic, mechanical and aerospace industries [1–3].

Gelcasting, invented by Oak Ridge National Laboratory, is a promising technique for complex shaping of structural ceramics, including silicon carbide products [4]. Compared to slip casting and tape casting [5], the outstanding advantage of the technique is that the slurry can be in situ consolidated, which results in near-net-shape forming. Unfortunately, acrylamide monomer widely used in the process is harmful to health. Therefore, a gelcasting process with low toxicity and without toxicity is paid more attention recently [6–8].

As we know, many natural polymers without toxicity, such as agarose, gelatine and agar, show the gelation property. Some of them have been employed in food and ceramic products. However, both agarose and gelatine are expensive when they are employed in industry. Alginate is a type of gelling polysaccharide, which can be dissolved in water at room temperature and then gelled after reacting with divalent metal ions. Cu^{2+}, for instance, has been used to chelate with sodium alginate. A stronger chelate complex can be formed with calcium ions. The mechanism of cross-linking in alginate gels can be considered in terms of an “egg-box” model involving cooperative binding of calcium ions between aligned polyguluronate ribbons [9–11]. The process has been applied to form ceramic beads, where sodium alginate is dispersed dropwise from a 4-mm opening into a magnetically stirred solution of $CaCl_2{\cdot}4H_2O$ to form rubbery, substantially spherical beads [12]. Calcium iodate has also been applied in gelcasting process because it has low solubility at room temperature and high solubility at increased temperature of 60 °C. Thus, the gelcasting process could be controlled by the heating rate and final temperature. However, the strength of the green body produced by this process is not very high, due to the limited dissolution ability of calcium iodate [6].

In this paper, a novel gelcasting process by alginate gelation is discussed. For this process, solidified agent

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and chelator are added into sodium alginate solution simultaneously, thus the gelation between calcium ions and sodium alginate is avoided in this stage due to chelate complex formed from chelator and sodium alginate. When hexanedioic acid is added into the suspension, free calcium ions are released from the chelate complexes and react with sodium alginate, forming a three-dimensional network. Therefore, ceramic particles are held in this three-dimensional network and the slurry is consolidated.

2. Experimental procedure

2.1. Materials

The starting ceramic powder consisted of coarse silicon carbide and fine silicon carbide powders to reach a high parking density. The mass ratio of coarse powder to fine powder was 70:30. Main impurities of the powders included Fe 520 ppm, O 1.17 wt.%, Si 0.26 wt.% and free carbon 0.35 wt.%. The particle size of mixture containing coarse and fine SiC powders ranged from 0.2 to 350 μm [13].

Controllable casting and consolidation are possible through the use of sodium alginate (Na-alginate), sodium hexametaphosphate ($(NaPO_3)_6$), tertiary calcium phosphate ($Ca_3(PO_4)_2$) and hexanedioic acid ($C_6H_{10}O_4$). Sodium alginate is used as a gelation reagent, which dissolves in deionized water at room temperature. When the sodium alginate and calcium ions react, the molecular chains attract each other to form a three-dimensional network; sodium hexametaphosphate, a vitriform solid, is used here as a chelator and tertiary calcium phosphate as a solidified agent. Three dispersants TMAH, DOLARPIX PC33 (PC33) and tri-ammonium citrate are employed.

2.2. Procedures

The forming process flow chart is shown in Fig. 1. Sodium alginate was dissolved in the deionized water to form a solution, which had been decomposed at 70° C for 48 h to reduce solution viscosity. And then silicon carbide powder, dispersant, solidified agent and chelator were added into the solution, the resulting slurry was then ball milled for 24 h. After degassing in a rotary evaporator under vacuum, hexanedioic acid was added

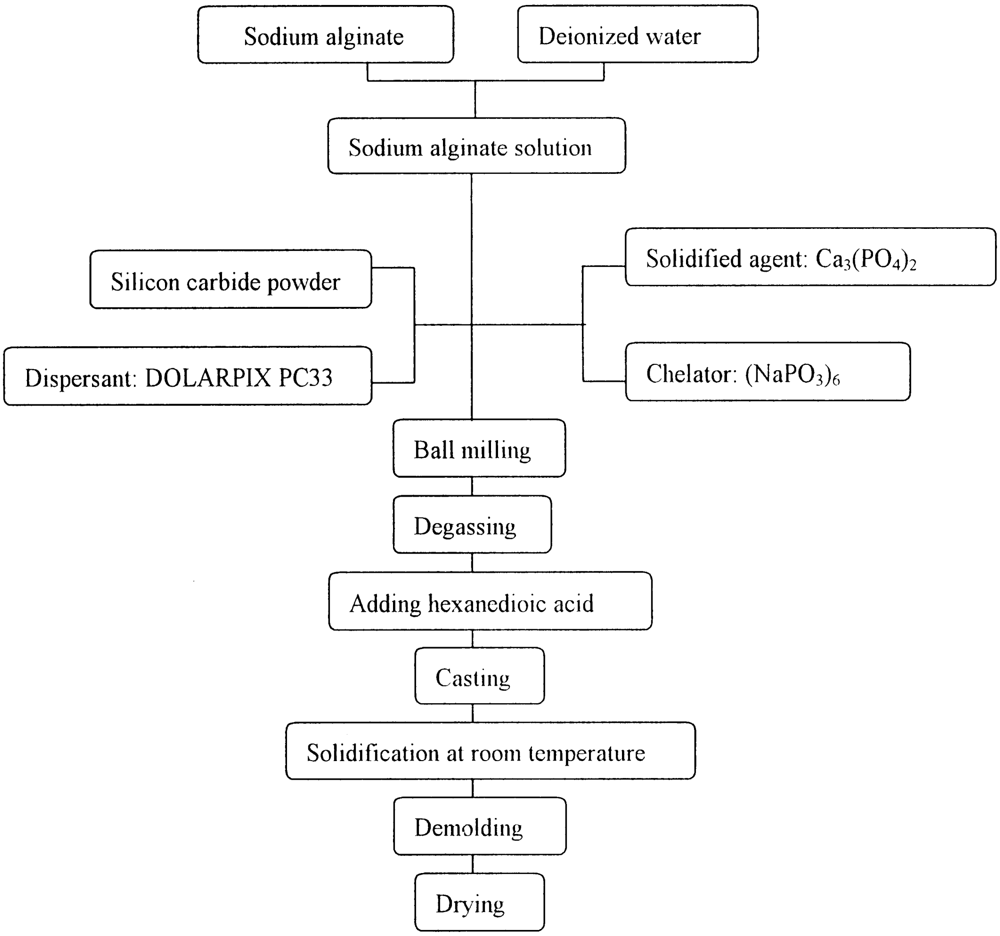

Fig. 1. Flow chart of the forming process.

into this slurry before the slurry was cast into a nonporous mould, and consolidation occurred. After several hours, the wet green body was demoulded and dried at room temperature.

2.3. Properties measurement

Zeta potentials of the powder were measured by zeta potential analyzer (Zetaplus Brookhaven company, USA). The rheological properties of the solution and SiC slurries were measured by a control-rate rotary rheometer (MCR300, Physica, Germany) and a concentric cylinder measurement device with a 1.13 mm gap was employed. The sample volume was 23 ml. The measurements were performed within the shear rate range of 0.1–250 s^{-1} at a constant temperature of 25 °C. The gel strength from alginate was examined by a simple device, which was usually used in the gums industry [10,12]. The room temperature bending strength of the dried green body samples was determined by the three-point bending method, with a cross-head speed of 0.2 mm/min and a span of 30 mm. The bars of green samples were usually $5\times6\times36$ mm^3. Cross-section surfaces of the samples were examined with a scanning electric microscope (SEM) and the density of the green body was measured by the Hg immersion based on Archimedes Principle.

3. Results and discussion

3.1. Effect of dispersant on the colloidal behaviors of the SiC suspension

The variations of zeta potential versus pH for as received silicon carbide and the suspension containing TMAH, DOLARPIX PC33 and tri-ammonium citrate as dispersants respectively are plotted in Fig. 2. The addition of sodium alginate produced a pronounced effect on SiC electrokinetic behaviors, in which isoelectric point (IEP) of the SiC suspension changed from pH 3.02 to 2.36. This is caused by the absorption of carboxyl negative charge on the alginate chains onto the surface of SiC particles. At the range of pH 7–9, a negative Zeta potential about $-10\sim15$ mV was observed. This may be resulted from the fact that the electrostatic layer was compressed by ions with a high value in sodium alginate [14,15].

TMAH is an organic alkali, PC33 is a kind of polyelectrolyte, and tri-ammonium citrate is an inorganic salt. TMAH and PC33 are alkaline, which result in better dispersion of the SiC powder since SiC powder is suitable for being suspended in basic solution, larger repulsion between ceramic particles and more stable suspension are achieved with zeta potential increase, as shown in Fig. 2. In contrast, tri-ammonium citrate is an acid, it does not provide good dispersion [1,13]. DOLARPIX PC33 is best among the three kinds of dispersants due to its high absolute zeta potential value (about 40 mV at pH 7–9) and poly-electrolyte stabilization, which is helpful for the more stable suspension [11]. In this case, DOLARPIX PC33 is a proper dispersant to the sodium alginate solution compared to the other two.

3.2. Rheological property of SiC suspension

A suspension with 50 vol.% SiC and 1.5 wt.% sodium alginate (based on water) was prepared, as shown in Fig. 1. The influence of the amount of dispersant (DOLARPIX PC33) on the rheological property of SiC suspension is illustrated in Fig. 3, which indicates that the dispersant PC33 (curve B, C, D) increase the fluidity of the suspensions compared to suspension without dispersant (curve A). When the shear rate is 100 s^{-1}, the apparent viscosity of the slurry with volume ratio of 10 μl:1 ml (PC 33 to sodium alginate solution) system (B) was lower than 1 Pa·s, the empirical value below which

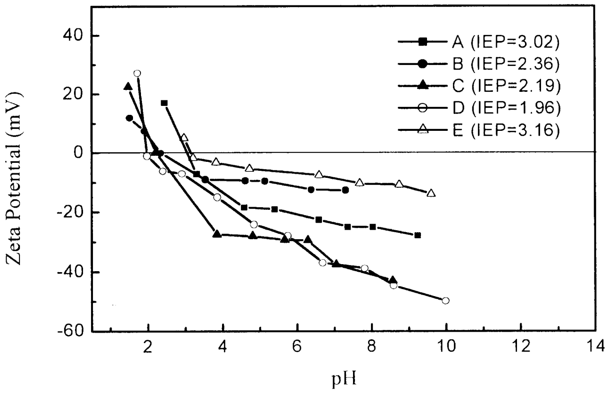

Fig. 2. Zeta potential versus pH value of SiC suspension in deionized water (A), in Na-alginate solution (B), in Na-alginate solution with dispersant TMAH (C), PC 33 (D) and tri-ammonium citrate (E) respectively.

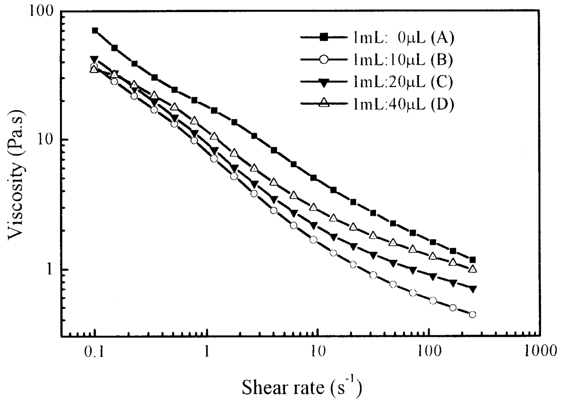

Fig. 3. Effect of the dispersant (DOLARPIX PC33) amount on the viscosity of the slurry of 50 vol.% SiC suspension (volume ratio of PC33 to 1.5 wt.% Na-alginate solution).

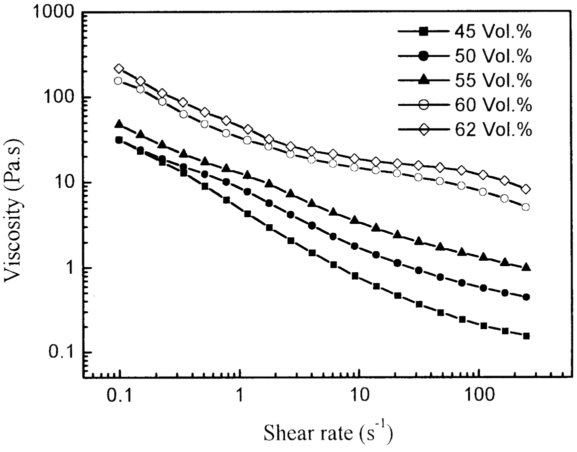

Fig. 4. Rheological property of the slurry with various solids loading (based on 1.5 wt.% Na-alginate).

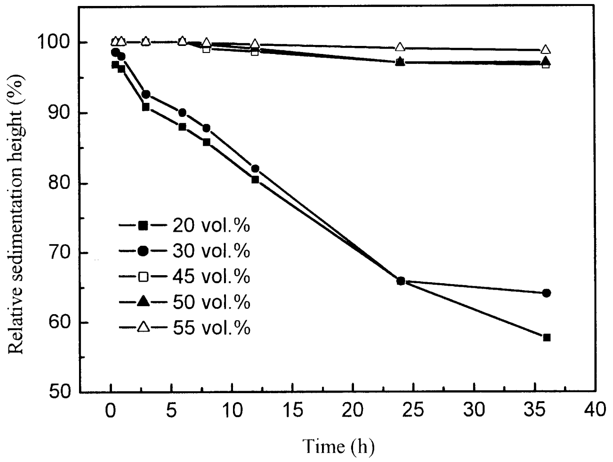

Fig. 5. Sedimentation of the SiC slurry with various solids loading.

casting process was allowed. While the viscosity of the slurry with volume ratio of 20 μl:1 ml system is about 1 Pa·s and that of even higher than 1 Pa·s was observed in the slurry with volume ratio of 40 μl:1 ml, which implies that the excessive polyelectrolyte (DOLARPIX PC33) is not absorbed on the SiC particles, therefore, the viscosity of the suspension increases.

It is on the one hand beneficial to obtain a solids loading as high as possible in order to better control the final geometry of the part, and to achieve higher dimensional tolerances by minimizing the possible complex distortion during drying and sintering shrinkage. On the other hand, the shaping of intricate parts requires the slurry to easily fill moulds of possible complex geometry. This in turn means that the viscosity of the slurry has to be kept below some acceptable level. The two-boundary conditions necessitate a well controlled tailoring of the suspension that can meet both of the requirements. Fig. 4 demonstrates that the suspension has relatively low viscosity and pseudoplastic property when solids loading are below 55 vol.%. When solids loading increased up to 60 vol.%, viscosity is 7.79 Pa·s under the shear rate of 100 s^{-1}. For the slurry of 62 vol.%, viscosity even reaches the value of 12.46 Pa·s, which does not fit for gel-casting. Therefore, the suspension with solids loading of 45–55 vol.% is suitable for this process.

3.3. Sedimentation behavior of the SiC suspension

When ceramic powder is dispersed in a liquid medium, the particles are influenced by a variety of forces such as force of gravity, drag force from the medium and Brownian motion of particles, etc. Assuming that the other forces are negligible or non-varying type, the ceramic particles tend to settle under the force of gravity. The state of dispersion and its stability is measured by the particle settle rate (manifested in terms of an increase of sediment height or sediment volume) versus time [14,16]. The particle settling rate manifested in terms of an increase of sediment height or sediment volume as a function of time gives a measure of the state of dispersion and its stability. Relative sedimentation height here refers to the ratio of the mixed suspension height (including the stable suspension and the sedimentation layer) to the whole height of the suspension. The sedimentation height is inversely related to the dispersion of the powder; the more dispersed the powder, the smaller the sediment height.

Sedimentation behavior was conducted in test tubes that had a capacity of 50 ml. A control sample with solids loading of 20,30,45,50,55 vol.% is included to provide a basis for contrast. Fig. 5 shows the sedimentation of suspensions of low solids loading, such as 20 vol.%, 30 vol.%, is obvious; while that of high solids loading, such as 45, 50 and 55 vol.% cannot even be observed [16].

3.4. Gelation principle and process of the alginate solution

The mechanism of cross-linking in alginate gels can be considered in terms of an "egg-box" model involving cooperative bonding of calcium ions between aligned polyguluronate ribbons [9–11]. However, it is generally difficult to control the reaction rate, which makes it impossible to complete the casting process at a certain period. Therefore, the calcium salts at a controlled reaction rate with alginate are considered in this study. The calcium ions concentration released from the salt can be adjusted by the formation and decomposition of the chelate complexes, the principle sketch of the process is shown in Fig. 6. Tertiary calcium phosphate (the solidified agent) and sodium hexametaphosphate (the chelator) were added into the alginate solution, forming chelate complexes. Therefore, calcium ions were chelated

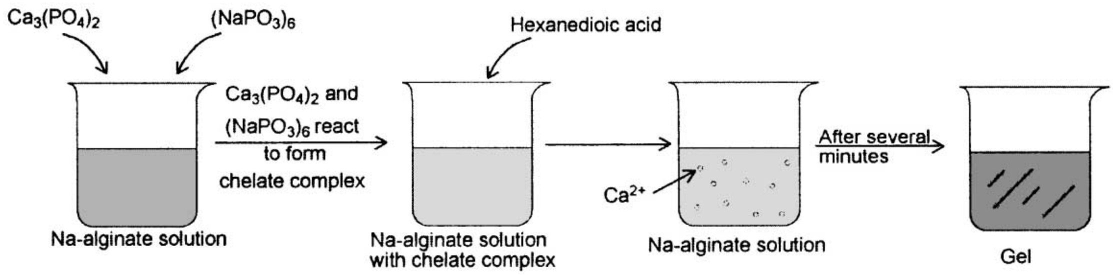

Fig. 6. The principle sketch of the gelation process.

in the chelate complexes and could not react with alginate and the gelation between calcium ions and alginate was avoided in this stage before ceramic slurry casting. Then hexanedioic acid was added into the solution, chelate complexes decompose and release the calcium ions slowly. The time delayed release of cross-linking calcium ions allowed the Ca-alginate suspension to be molded into complex geometry before gelation occurred. Thus, gelation rate control was realized.

3.5. *Gelation of the SiC suspension with alginate*

To study the influence of various Na-alginate concentration, the amount of solidified agent ($Ca_3(PO_4)_2$) and chelator ($(NaPO_3)_6$) on consolidation and property of the green body, several groups of samples have been fabricated, as shown in Table 1.

At the same content of solidified agent ($Ca_3(PO_4)_2$) and chelator ($(NaPO_3)_6$), sample Nos. 1, 2 and 3 were made from 45 vol.% SiC and 1.0, 1.5 and 2.0 wt.% Na-alginate solutions, respectively. Accordingly, the consolidation time increased from 2 to 5 h, as Na-alginate concentration increased from 1.0 to 2.0 wt.%. These results exhibited decreasing consolidation rate with increasing polymer (sodium alginate) concentration, which may be an indication that the conformational rearrangement of the polymer chains was important for cross-linking formation. A higher polymer concentration likely resulted in higher viscosity, leading to slower rearrangement of the polymer chain conformations to form the effective cross-linked structure. On the other hand, the resulting bending strength and relative green density increased with the greater alginate concentration, which indicated that the strength of the green body was mainly determined by the three-dimensional network. It could be concluded that the stronger network and higher strength of the green body was achieved when the alginate concentration increased. However, the consolidation rate also increased with the increase of alginate concentration, and some agglomerates were observed in the consolidation process of the slurry dispersed in 2.0 wt.% Na-alginate solution, which probably results in ununiform structure. In this case, 1.5 wt.% Na-alginate solution was employed in the following experiment.

Further characterization of mechanical properties of the green bodies of samples 4, 2 and 5 were studied, which were fabricated from suspensions with decreasing content of 6, 4, 1.2 g $Ca_3(PO_4)_2$ (with 45 vol.% SiC and 20 ml 1.5 wt.% Na-alginate solution). Comparing samples 5 (2.54 MPa) with 2 (2.85 MPa) and 4 (3.47 MPa), it was found that the strength of the green body increased with the calcium content, presumably due to increased cross-linking density. The sodium ions on the Na-alginate molecules would be further replaced when more calcium salt was added into the slurry. In this case, the overall contribution of the effective ionic interactions between calcium ions and Na-alginate

Table 1
Properties and gelation of the suspension with 45 vol.% SiC (400 μl DOLARPIX PC33 in 20 ml Na-alginate solution) at various conditions

No.	Na-alginate concentration (wt.%)	$Ca_3(PO_4)_2$ (g)	$(NaPO_3)_6$ (ml)[a]	PH	Consolidation time (h)[b]	Bending strength (MPa)	Relative green density (%)[c]
1	1.0	4	1.0	8.18	2	2.49	47.86
2	1.5	4	1.0	8.36	3	2.85	52.41
3	2.0	4	1.0	8.66	5	3.09	50.57
4	1.5	6	1.0	8.71	1	3.47	52.16
5	1.5	1.2	1.0	8.04	4	2.54	51.57
6	1.5	4	2.0	8.30	5	3.26	53.99
7	1.5	4	0.4	8.95	0.5	2.67	51.74

[a] Concentration of $(NaPO_3)_6$ is 20 wt.% (based on deionised water).

[b] Consolidation time refers to the time of change from slurry to wet green body.

[c] The theoretical density of SiC is 3.217 g/cm^3.

Table 2
The influence of hexanedioic acid on consolidation

Hexanedioic acid (g)	<0.3	0.5	0.6	0.8	1.0	1.2	>1.5
Consolidation time	>24 h	50 min	50 min	35 min	35 min	20 min	18 min
Consolidating degree	Not consolidated	Fair	Good	Good	Good	Good	Good
The morphology of the green body	Poor	Fair	Good	Good	Good	Good	Good

became greater at higher calcium contents, leading to better mechanical properties of the green body. Therefore, at low content of $Ca_3(PO_4)_2$ (1.2 g), the sodium ions on the Na-alginate molecules would inevitably be replaced incompletely, thus the resulting network was not strong, and the density and strength of the green body were reduced. It should also be noted that the suspenion with high content of $Ca_3(PO_4)_2$ (6 g), on the other hand, consolidated too quickly, which might have resulted in structural heterogeneity, leading to lower relative density. Therefore, the appropriate content of $Ca_3(PO_4)_2$ was 4 g in this study.

Samples 6, 2 and 7 were produced from 45 vol.% SiC slurries and 1.5 wt.% Na-alginate solution with different content of 2, 1, 0.4 ml $(NaPO_3)_6$ (20 wt.%) and the corresponding green bars were also made. When the chelator ($(NaPO_3)_6$) addition is not enough, calcium ions will be chelated incompletely and the redundant calcium ions will react with sodium alginate to form partially gelation, which is detrimental to the fluidity of the slurry. Furthermore, it has negative effect on the uniformity and density of the green body, as shown in sample 7. So high content of $(NaPO_3)_6$ is helpful to the fluidity of the slurry and the ultimate strength of the green body. With the increasing content of $(NaPO_3)_6$, however, the consolidation rate decrease promptly due to the time-delayed calcium releasing period. Considering the effect of the chelator addition to both the consolidation rate and the strength of the green body, 1 ml $(NaPO_3)_6$ seems to be appropriate in this study.

Hexanedioic acid addition plays a critical role in this process, which can release the calcium ions from the chelate complex and initiates the consolidation. To study the effect of hexanedioic acid on the consolidation, 45 vol.% slurry was made, which was composed of 52.4 g SiC powder, 20 ml 1.5 wt.% Na-alginate solution, 1 ml 20 wt.% $(NaPO_3)_6$, 1.2 g $Ca_3(PO_4)_2$ and 1 ml PC33. Disc shaped green bodies with different hexanedioic acid addition were fabricated. Calcium ions will be released incompletely because of the small amount of hexanedioic acid (<3 g), therefore consolidation will not be available. It seems that a threshold amount of hexanedioc acid is needed to form a fixed shaped green body; below this threshold amount, consolidation is impossible. Table 2 demonstrates that the consolidation rate increases with the increasing amount of hexanedioic acid and only when the amount of hexanedioic acid reaches 0.6 g/20 ml Na-alginate solution complete consolidation will occur.

Green parts with the strength of ~3 MPa and perfect surface are obtained in this process. The microstructure of the cross-section of the green body (from the slurry composition of No. 2) is studied by the scanning electron microscope (SEM), which shows that the structure of the green body is homogeneous and dense.

4. Conclusions

Silicon carbide is suitable for being suspended in basic solution. The dispersant DOLARPIX PC33 is better, compared to the other two dispersants of TMAH and tri-ammonium citrate. Sedimentation experiment shows that the sedimentation of the slurry with solids loading over 45 vol.% does not clearly occur within 6 h, which indicates that the structure of the green body consolidated within 6 h is homogeneous. The suitable content of sodium alginate for suspensions of 45–55 vol.% silicon carbide powder is 1.5 wt.%, since such slurries have apparent viscosities lower than 1 Pa·s and are pseudoplastic in rheological property, which is helpful for casting.

The consolidation rate increases with the decreasing concentration of Na-alginate solution, the increasing addition of the solidified agent and hexanedioic acid, and the decreasing content of the chelator as well. The green strength enhances with the increasing content of the chelator. To obtain the optimal property of the green body, appropriate concentration of the sodium alginate and content of solidified agent should be paid attention, the green strength is mainly determined by the three-dimensional network, which is formed by cross-linking between sodium alginate and calcium ions. Considering both the consolidation rate and the green strength, gelation process of sample No. 2 is proper for gel-casting. Green bodies of silicon carbide with the strength of ~3 MPa, perfect surface and homogeneous microstructure have been produced by this process.

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