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Fabrication of Si_3N_4–SiC nano-composite ceramics through temperature-induced gelation and liquid phase sintering

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Abstract

This paper describes the fabrication of Si_3N_4–SiC nano-composite ceramics through a novel direct casting method (temperature-induced gelation) followed by liquid-phase sintering. A kind of polyester/polyamine condensation copolymer (hypermer KD1) was used as dispersant and gelling agent. At room temperature (≈20 °C), it plays the role of a steric dispersant, allowing the preparation of stable homogeneous and high concentrated suspension (57.5 vol.% solids) consisting of Si_3N_4, Y_2O_3, Al_2O_3 and 20 wt.% nano-SiC. At low temperature it acts as gelling agent, inducing incipient flocculation due to the collapse of adsorbed layer. The low values of viscosity and elastic modulus at room temperature, increased dramatically within a moderate decrease of temperature from 20 to 5 °C. A completely solidified green body with precise dimensions, smooth surface, high strength and homogeneous density has been obtained, which could be gas-pressure sintered to near theoretical density at 1850 °C.

Keywords: Shaping; Suspensions; Nanocomposites; Si_3N_4; Gelation; Sintering

1. Introduction

Silicon nitride–silicon carbide (Si_3N_4/SiC) nano-composites have received a great deal of attention for high temperature structural applications due to their potentially excellent mechanical properties at both room and elevated temperature.[1–4] However, the commercial applications of these composites are difficult to achieve due to the following reasons: Firstly, when using the conventional mixture of nano-SiC and Si_3N_4, the nanometric SiC powder has the tendency to agglomerate, leading to a degradation in mechanical properties.[5] Secondly, the presence of nano sized SiC makes densification of Si_3N_4–SiC nano-composite ceramics very difficult. Thirdly, high hardness makes post-sintering machining difficult, resulting in high manufacturing cost of components, especially for fabricating parts with complex shapes.

In the present work, we attempted to produce complex shaped Si_3N_4–SiC nano-composites through near-net-shape colloidal forming methods and gas pressure sintering. Colloidal processing approaches have the advantage of reducing the strength limiting defects in green (sintered) bodies, and of increasing the sintering ability of green parts, while using a near-net-shape forming method enables to reduce machining costs, resulting in clear advantages for industrial-scale production of these materials.

Near-net-shape forming techniques have been extensively investigated in recent years.[6–8] They avoid density gradients in the green body and enable to preserve the high degree of homogeneity achieved in the suspensions, leading to accurate dimensional and microstructural control. Among them, the reversible destabilisation of a sterically stabilised suspension could be used as a novel near-net-shape forming method called temperature-induced gelation (TIG).[9]

In sterically stabilised suspensions, the magnitude and range of the interaction forces between polymer layers can be related to the solution properties of the polymer and con-

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Table 1
The specifications of nano-SiC powder as given by the supplier

Crystalline type	Cubic (β-type)
Purity (SiC)	97.0–98.0%
Free silicon (Si_f)	< 0.2%
Free carbon (C_f)	0.6–1.0%
Total oxygen (Σ O)	0.7–1.5%
Chloride (Cl)	< 0.25%
Average diameter range	0.05–0.08 μm
Particle shape	Ball or cubic body
Specific surface area	20–40 m^2/g

formation of the polymer at the solid-liquid interface.[10] Stability is ensured only if the medium is a good solvent for the dispersant;[11] on the contrary, when the solvency decreases to a critical level, incipient flocculation occurs, and when the solids loading of suspension is high enough a network forms, immobilizing all the dispersed particles.

In this work, a high concentrated suspension containing 57.5 vol.% solids (Si_3N_4, Y_2O_3, Al_2O_3 and 20 wt.% nano-SiC powders) has been firstly prepared using hypermer KD1 as dispersant. Then, homogeneous green bodies with high density were consolidated through TIG. The transition from the fluid state at room temperature to the consolidated condition at low temperature was accompanied by rheological measurements (steady shear and oscillation). Finally, the obtained green bodies were gas-pressure sintered to near theoretical density.

2. Experimental procedure

A commercial silicon nitride powder (H.C. Stark, Germany, $d_{50} = 0.38$ μm) and nano-SiC powder (Shijiazhuang High-Tech Ultrafine Powder Products Factory, China) were used in this study. Table 1 summarises the specifications of the nano-SiC powder. Figs. 1 and 2 show the morphology of the starting Si_3N_4 and SiC powders, respectively. The sintering additives chosen were Y_2O_3 (Grade C, H.C. Stark, Germany, $d_{50} = 0.75$ μm) and Al_2O_3 (Alcoa Chemicals, USA, $d_{50} = 0.38$ μm).

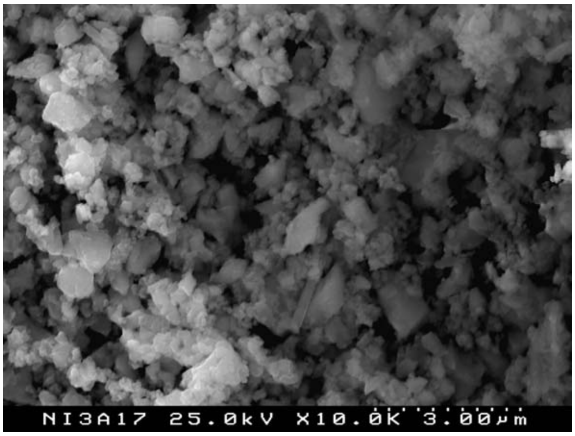

Fig. 1. Morphology of the raw Si_3N_4 powder.

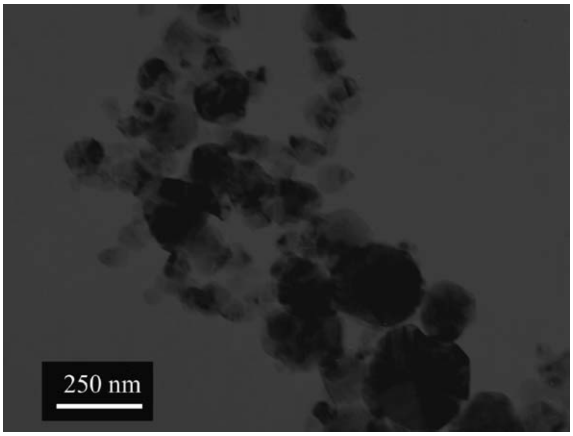

Fig. 2. Morphology of the raw nano-SiC powder.

The solvent selected was an azeotropic mixture of 60 vol.% methyl ethyl keton (MEK) (Riedel-de Haën, Germany) and 40 vol.% ethanol (E) (Merck, Germany). The dispersant used was the Hypermer KD1 (Imperial Chemical Industries PLC, England), which is a polyester/polyamine copolymer with an estimated MW of about 10,000 g/mol. The dispersant has proved its efficiency in dispersing a wide range of ceramic powders.[12,13] The solubility of KD1 in MEK/E solvent changed dramatically with temperature.[14]

The suspensions were prepared through planetary ball milling of the powders in the solvent in the presence of 3 wt.% dispersant, using an Al_2O_3 jar and Si_3N_4 balls for 4 h. The composition of starting powders was 75.83 wt.% Si_3N_4, 2.5 wt.% Al_2O_3, 5 wt.% Y_2O_3, 16.67 wt.% nano-SiC. Steady shear measurements were preformed with a rheometer (C-VOR 150, Bohlin Instruments, UK) under controlled shear rate condition with a core and plate geometry. A solvent trap was used to avoid the evaporation of solvent. Viscoelastic measurements were performed using the same rheometer by applying a sinusoidal strain and measuring the stress and phase shift between the stress and strain. The selected amplitude (0.1%) was sufficiently small to be in the linear viscoelastic range (LVR) where the viscoelastic response is independent of strain.

A plastic ring was used as a mould. The obtained suspension was moved into the mould and cooled down to 4 °C. The mould was sealed during cooling process to avoid evaporation of solvent. The gelled body was removed from the mould after 48 h, and left at gelling temperature for additional 48 h for partial drying, followed by complete drying at 40 °C for 48 h. The obtained green bodies were then placed inside a powder bed composed of about 30 wt.% BN + 70 wt.% starting powders and sintered in a graphite furnace under N_2 atmosphere. Sintering was performed first at 1750 °C for 1 h under a nitrogen pressure of 0.1 MPa, and then at 1850 °C for 2 h under nitrogen pressure of 0.6 MPa.

The compressive strength of green bodies was evaluated in a universal testing machine (Instron 5565, Japan) using a crosshead displacement speed of 0.5 mm/min. The size of specimen was 4 mm × 4 mm × 6 mm. For green density measurements according to the Archimedes method, the as-prepared green samples were heat treated in air at 600 °C for 0.5 h to remove the dispersant, and then immersed in mercury. The theoretical density was calculated from the theoretical densities of individual constituents. The fracture surfaces of green and sintered bodies were observed by SEM (Hitachi S-4100, Japan).

3. Results and discussion

3.1. Preparation and rheological characterization of the suspensions

The preparation of a well-dispersed, uniform and high concentrated suspension is considered a critical step for temperature-induced gelation. In a suspension containing a mixture of powders with different surface chemistry properties (Si_3N_4, nano-SiC, Y_2O_3 and Al_2O_3), coagulation may easily occur between the different powder particles. On the other hand, different particle sizes and specific gravities might lead to particles' segregation. The dispersing properties of Si_3N_4, Y_2O_3 and Al_2O_3 using KD1 have been proved to be suitable elsewhere.[15] Here, the efficiency of KD1 in dispersing nano-SiC powder was studied.

The large surface area of nano-SiC makes the powders susceptible to agglomeration, which results in difficulty in achieving a homogeneous distribution of the nanophase. The agglomerates must be broken down and prevented from reforming again with the assistance of the dispersant. Fig. 3 shows the flow curves of nano-SiC suspensions at different solids loadings. The optimal addition of KD1 for dispersing other powders was 3 wt.%,[11–13] so the KD1 addition here was also set at 3 wt.% based on the weight of nano-SiC powders. Although the small particle size limits the maximum solids loading of nano-SiC suspensions, the dispersant KD1 has good dispersing power. This could also be confirmed by conducting ageing tests, where the flow curve of a 10 vol.% suspension shows little change after 4-h ageing. The excellent dispersing results for all powders could be attributed to the structure of KD1. The oligomeric nature of the anchoring groups makes that there will be always one or more anchors attached to the surface of different particles, and a polymeric chain with a chemical structure designed to give optimum steric stabilisation to the dispersion. The good dispersing efficiency of KD1 for all powders with the same addition of 3 wt.% makes it possible to prepare stable suspension of the starting powders.

The use of high solids loaded suspensions with high stability and acceptable viscosity is a key point to achieve good quality of the ultimate products, especially when consolidated by near-net-shape forming techniques that do not involve liquid removal.[15] The steady shear viscosity curves of Si_3N_4–SiC nano-composite suspensions at various solids loadings are shown in Fig. 4. All the curves are smooth, featuring good stability of the suspensions. Viscosity always increases with increasing solids loading, as expected. This is noticeable especially at high solids loading, where a small increase of solids content leads to sharp increase of viscosity. The suspensions exhibit a shear-thinning behaviour, which was due to the perturbation of the suspension structure under shear.[16] A high solids loading of 57.5 vol.% has been achieved.

3.2. Setting of the suspensions by temperature-induced gelation

The 57.5 vol.% suspension exhibits enough stability and fluidity, which make it acceptable for direct casting at room temperature. Fig. 5 shows the evolution of viscosity (shear rate = 1.37 s^{-1}) and elastic modulus (frequency = 1 Hz) with temperature for 57.5 vol.% suspensions. The viscosity increases slowly with temperature decreasing from 20 to 15 °C. However, within the temperature range of 15–10 °C, viscosity sharply increases more than two orders of magnitude. In good agreement with the results of viscosity, the elastic modulus also increases about 3 orders of magnitude from 15 to 10 °C. The most possible explanation for the sharp increase in viscosity and elastic modulus is temperature-induced gelation

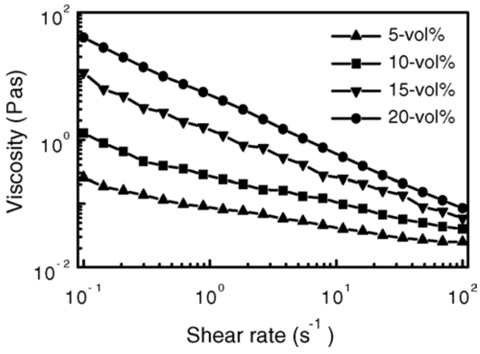

Fig. 3. Flow curves of nano-SiC suspensions at different solids loadings.

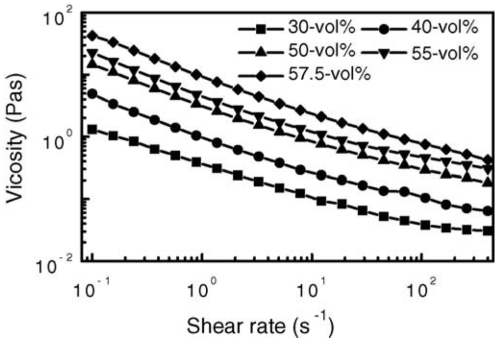

Fig. 4. Flow curves of Si_3N_4–SiC nano-composite suspensions at different solids loadings.

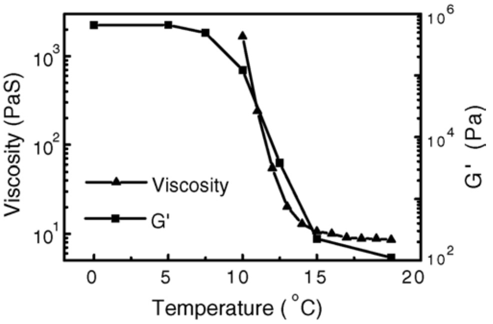

Fig. 5. Evolution of viscosity (shear rate = 1.37 s^{-1}) and elastic modulus (frequency = 1 Hz) with temperature for 57.5 vol.% suspensions.

causing network formation, where the structure of the suspension changes from a stable fluid to a volume filling gel within this temperature range.

With the decrease of temperature, the solubility of hypermer KD1 significant decreases leading to low steric repulsive forces. Incipient flocculation occurs when the steric repulsive forces could not counterbalance van der Waals forces,[17] leading to a sudden jump of viscosity and elastic modulus, as shown in Fig. 5. The continuous increase of elastic modulus along the temperature range of 10–5 °C could be attributed to the separation of KD1, which increases the bonding strength of neighbour particles.

3.3. *Preparation and characterization of green and sintered bodies*

The 57.5 vol.% solids loaded suspension was cast into plastic moulds at 20 °C, and then the temperature was decreased to about 4 °C to induce gelification. Strong gelled bodies could thus be obtained. No sedimentation, phase separation or cracking were observed during gelation, drying or preheating processes. After removal of dispersant KD1, the density of green body was 1.96 g/cm^3 or 58.6% of the theoretical density, which is a relatively high value. A small total linear shrinkage of about 0.7% occurred during the gelation step and during drying and preheating processes. The obtained green bodies exhibited precise dimensions, smooth surfaces, homogeneous density and a compressive strength of about 1.2 MPa. This measured value of compressive strength might be underestimated, since it is very difficult to prepare sample with parallel surfaces.

The SEM image of a fracture surface of obtained green body is shown in Fig. 6, revealing the uniform microstructure without large pores.

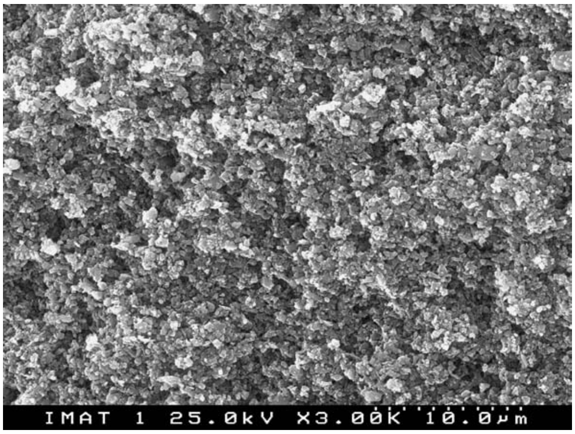

Fig. 6. Micrograph of fracture surface of green Si_3N_4/SiC nano-composite body after removal of KD1.

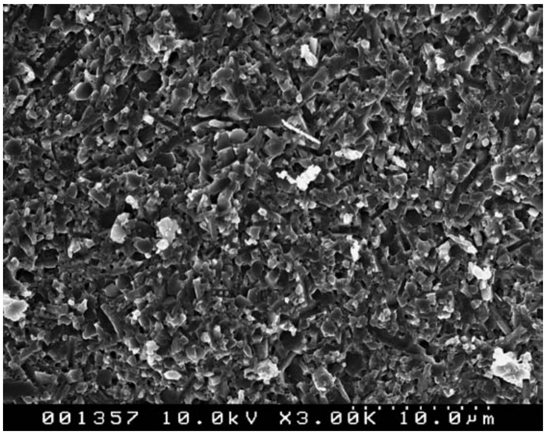

Fig. 7. Micrograph of fracture surface of Si_3N_4/SiC nano-composite ceramics.

Thanks to low organic compound addition, the gelled green body could be sintered directly without separate binder burning out process. The sintered sample had a 98.1% theoretical density. No cracks and a homogeneous microstructure could be appreciated in sintered samples, as shown in Fig. 7. The micrograph shows that the composite has a distinctly small grain size. It is believed that SiC particles limited the Si_3N_4 grain growth by pinning and slowing down the grain boundary movement. Achieving well-dispersed SiC particles in the sintered Si_3N_4 matrix can be attributed to the uniform distribution of the nano-sized component and of the density in the green state.

4. Conclusions

Temperature-induced gelation and liquid phase sintering of Si_3N_4/SiC nano-composite have been investigated in this paper. Hypermer KD1 proved to be an effective dispersant to disperse all starting powders (Si_3N_4, Y_2O_3, Al_2O_3, SiC). A high solids loading of 57.5 vol.% could be achieved using 3 wt.% hypermer KD1 as dispersant for Si_3N_4 composite powders. Green bodies with a high particle net-work strength ($G' = 7 \times 10^5$ Pa) were prepared from 57.5 vol.% suspension through temperature-induced gelation in a narrow temperature range (from 20 to 5 °C). The obtained homogeneous green body could be gas pressure sintered to 98.1% theoretical density. The proposed method offers the possibility of cost-effective production of complex shaped Si_3N_4-nano SiC composite ceramics.

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