Improved crystallisation of polysilazane-derived Si₃N₄/SiC nanocomposites with Fe₂O₃ catalyst

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Abstract

In the present study, the use of a 3 wt% Fe₂O₃ catalyst improved the crystallisation of polysilazane PSN2. Crystallisation peaks of higher intensity were observed for Si₃N₄ and SiC at 1250 °C by using a 3 wt% Fe₂O₃ catalyst than at 1500 °C without Fe₂O₃. Besides, the effects of temperature on the morphology of the samples were determined through scanning electron microscopy. Porous structures were observed at 1250 °C and these structures were transformed to flaky and near-spherical nanoparticles as the temperatures were increased to 1350 and 1450 °C, respectively. Finally, the mechanism of Fe origination from Fe₂O₃ reduction, the production of a supersaturated liquid alloy, and the release and diffusion of N₂ were proposed for Si₃N₄ formation.

1 | INTRODUCTION

Si₃N₄/SiC composite ceramics have attracted increasing attention for many engineering applications, such as turbine engines, garbage incineration boilers, and rocket nozzle, because of their outstanding mechanical properties, excellent thermal shock resistance, and corrosion resistance [1, 2]. Polysilazane, a class of inorganic polymers with silicon nitrogen bonds as a repeating unit in the main chain of the molecule, could be an appropriate precursor for Si₃N₄/SiC synthesis [3].

In recent years, the processing of polymer-derived ceramics (PDCs) has gained a remarkable interest because of its unique advantages compared with conventional ceramic processes, such as low ceramization temperature, simple processing technology, outstanding performance at high temperature, and excellent uniformity of the composition [4]. Polysilazane polymers are precursors to amorphous SiCN when they are pyrolysed at a lower temperature (≈1100 °C). Afterwards, they continue to crystallise into Si₃N₄/SiC as the treatment temperature is increased. Numerous studies have investigated the crystallisation behaviour and phase evolution of polysilazane under different conditions such as annealing temperature, atmosphere, and dwell time [4–9]. Polysilazane-derived SiCN ceramics are basically amorphous and do not crystallise up to 1400 °C or even higher [4, 8]. Strong et al. [7] showed that a novel NH₃-controlled pyrolysis approach can be used to tailor the C:N content of SiCN powders for Si₃N₄/SiC-based nanocomposites obtained at 1650 °C. Golczewski et al. [8] reported that polysilazane could be transformed into Si₃N₄ and SiC with free carbon by a carbothermal reaction (Equation (1)) at a temperature of more than 1484 °C. PDC processing is known to be associated with several disadvantages, including (i) Si₃N₄/SiC cannot be prepared efficiently at lower temperatures and (ii) at a temperature higher than 1484 °C, a low Si₃N₄/SiC ceramic yield is obtained, wasting energy and increasing the production costs.

\[
\text{Si}_3\text{N}_4 + 3\text{C} \rightarrow 3\text{SiC} + 2\text{N}_2 (g)
\]  

The introduced transition metals and their compounds are known to effectively accelerate the formation of Si₃N₄ and SiC at a reduced temperature (1300 °C) [10–12]. In several studies, catalysts were used to synthesise nano-scaled Si₃N₄ and SiC by the PDC route. Yang et al. [13–15] reported the synthesis of Si₃N₄ nanobelts, Si₃N₄ nanowires, and SiC nanorods with the addition of FeCl₃ into the cross-linked polysilazane powder, and this mixture is subsequently pyrolysed at the elevated temperatures in N₂ atmosphere. Vakifahmetoglu et al. [16] produced Si₃N₄ and SiC nanowires on the cell walls of polymer-derived ceramic foams through catalyst-assisted pyrolysis in the presence of FeCl₃. Other researchers mainly focused on the synthesis of Fe-containing Si–C–N magnetic ceramic by adding various Fe compounds [17–20]. However, no study has reported the synthesis of highly crystallised Si₃N₄/SiC...
nanocomposites derived from polysilazane in the presence of a Fe-based catalyst.

In this study, we investigated a more convenient pathway of synthesising highly crystallised Si₃N₄/SiC nanocomposites from the polysilazane PSN2 by adding 3 wt% Fe₂O₃ additives at a relatively low temperature (1250 °C) and under an inert (N₂) atmosphere. The influence of temperature on the microstructures and phase compositions of the prepared materials was studied systematically, and the growth mechanism was discussed in detail.

2 EXPERIMENTAL

In this study, a commercially available polysilazane (PSN2, Institute of Chemistry, Chinese Academy of Science) was used as the precursor. Iron oxide powder (Fe₂O₃, analytical-grade purity, Tianjin Yuanli Chem. Co. Ltd., Tianjin, China) was used as the catalyst. In the first instance, 3 wt% Fe₂O₃ was mixed with liquid PSN-2 by ultrasonication for 1 h and then by electromagnetic stirring for 1 h more. Afterwards, the as-obtained mixtures were cross-linked at 130 °C for 2 h in a vacuum. The cross-linked solid was put into an alumina crucible and subsequently pyrolysed at different temperatures (i.e. 1100, 1250, 1350, and 1450 °C) for 4 h in an oven with purging in N₂ atmosphere. The experiments were also performed on the sample without Fe₂O₃ annealed at 1100–1500 °C for 4 h.

The phase composition was characterised through X-ray diffractometry (XRD, Bruker D8 Advanced, Germany) by using a Cu Kα radiation source (λ_CuKα = 0.15406 nm) at voltage–current settings of 40 kV and 40 mA in the 2θ = 20°–65° (2θ) regime. The micro/nanostructures were characterised through scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM and EDS, S4800, Hitachi, Tokyo, Japan).

3 RESULTS AND DISCUSSION

First, we investigated the crystallisation of polysilazane PSN2-derived samples without Fe₂O₃. Figure 1 presents the XRD patterns of the PSN2-derived samples at various temperatures without an additive after a thermal treatment of 4 h. The PSN2 pyrolysed at 1100 °C was completely amorphous. The sample obtained at 1300 °C gave two large diffuse peaks at approximately 2θ = 36° and 2θ = 61°, revealing that its amorphous network was starting to become ordered. As the temperature of thermal treatment increased from 1300 to 1500 °C, the decrease in the full-width at half maximum and the increase in the intensity of the two broad peaks suggested a slightly increase in the crystallisation degree. However, the PSN2-derived Si₃N₄/SiC was poorly crystallised without the catalyst Fe₂O₃ even at 1500 °C.

Figure 2(a) shows the XRD patterns of samples derived from polysilazane by using 3 wt% Fe₂O₃ as a catalyst at different temperatures and a holding time of 4 h in N₂. Compared with Figure 1, the XRD patterns of the samples in Figure 2(a) showed visible changes, indicating that the addition of Fe₂O₃ promotes the crystallisation of Si₃N₄/SiC samples derived from PSN2. As shown in Figure 2(a), the sample pyrolysed at 1100 °C consists of only two phases: C (PDF#89-8487) and C-Fe-Si (PDF#47-1293). When the temperature increased to 1250 °C, more diffraction peaks were detected; these peaks were attributable to α-Si₃N₄ (PDF #41-0360), SiC (PDF #49-1430), C, and C–Fe–Si. With a further increase in temperature, the intensity of
FIGURE 3 SEM micrographs of samples pyrolysed at 1100 °C (a) without Fe₂O₃ and (b) with 3 wt% Fe₂O₃ for 4 h in N₂. (c) SEM micrographs of Fe₂O₃ particles

TABLE 1 The average crystal size (\(d\)) and microstrain (\(\varepsilon\)) for Si₃N₄ and SiC of samples pyrolyzed at 1250, 1350, and 1450 °C.

| Sample     | \(<d>\) SiC [Å] | \(\varepsilon \times 10^3\), SiC | \(<d>\), Si₃N₄ [Å] | \(\varepsilon \times 10^3\), Si₃N₄ |
|------------|-----------------|----------------------------------|---------------------|----------------------------------|
| 1250 °C    | —               | —                                | —                   | —                                |
| 1350 °C    | 25 ± 2          | 1.6 ± 0.4                         | 174 ± 14            | 3.1 ± 0.4                        |
| 1450 °C    | 41 ± 3          | 1.8 ± 0.2                         | 220 ± 15            | 1.8 ± 0.3                        |

The diffraction peaks corresponding to Si₃N₄ and SiC became more intensive and narrower, suggesting that the degree of crystallisation of the prepared Si₃N₄/SiC composites was further increased. Similar results could also be confirmed by estimating the crystallite size from XRD patterns according to the Williamson–Hall equation. As described in Table 1, at the pyrolysis temperature of 1250 °C, the crystal sizes of Si₃N₄ and SiC were hard calculated, mainly owing to their rare production. With increasing pyrolysis temperature, the crystal size could be clearly determined. Furthermore, as the pyrolysis temperature was increased from 1350 to 1450 °C, the average crystal size of Si₃N₄ increased from 174 to 220 Å, and this was accompanied by the change in SiC crystal size from 25 to 41 Å. Samples investigated show microstrain of about \(\varepsilon \approx 0.0015–0.003\) at different temperatures. These results demonstrated that the beneficial forms of Si₃N₄ and SiC were developed at high pyrolysis temperatures.

The Williamson–Hall equation:

\[
\frac{FW(\delta) \cos \theta}{\lambda} = \frac{1}{d} + \varepsilon \frac{4 \sin \theta}{\lambda} \tag{1}
\]

\(FW(\delta)\) is the width among two or more diffraction peaks with half height; \(2\theta\) is the Brag angle (rad); \(d\) is the average crystal size (Å); \(\varepsilon\) is the microstrain; and \(\lambda_{\text{CuKα}} = 0.15406\) nm.

The effect of the Fe₂O₃ catalyst on Si₃N₄ crystallisation was determined. As displayed in Figure 2(b), 1 wt% Fe₂O₃ induced the formation of Si₃N₄ at 1250 °C. However, the crystallisation was low. With an increase in the Fe₂O₃ dosage to 3 wt%, a high degree of crystallisation was observed for Si₃N₄, and it remained unchanged with a further increase in the Fe₂O₃ dosage to 5 wt%. Therefore, 3 wt% Fe₂O₃ was chosen in the present study.

SEM was performed on samples pyrolysed at 1100, 1250, 1350, and 1450 °C with 3 wt% Fe₂O₃ and on the sample pyrolysed at 1100 °C without Fe₂O₃, used as a reference for comparison. Figure 3(a) shows that the sample obtained without the catalyst was amorphous SiCN, and this is consistent with XRD analysis results. Compared with Figure 2(a), 1 wt% Fe₂O₃ induced the formation of Si₃N₄ at 1250 °C. However, the crystallisation was low. With an increase in the Fe₂O₃ dosage to 3 wt%, a high degree of crystallisation was observed for Si₃N₄, and it remained unchanged with a further increase in the Fe₂O₃ dosage to 5 wt%. Therefore, 3 wt% Fe₂O₃ was chosen in the present study.

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treatment was increased further (1350 and 1450 °C), the amorphous materials observed in Figure 3(b) entirely transformed into large amounts of Si₃N₄ or SiC nano-scaled particles with flaky and near-spherical shapes (Figure 4(b–d)) of diameters 20–100 nm. Meanwhile, as displayed in Figure 3(c), Fe₂O₃ particles of sizes 50–200 nm could be obtained. Upon ceasing heating, the particle size increased significantly to 250 nm, as shown in Figure 3(b), hinting that Fe₂O₃ particles facilitate the formation of Si₃N₄/SiC nanocomposites.

Moreover, the elementary compositions of the prepared nanocomposites were analysed, as shown in Figure 5. The weight percentages of C, N, Si, and Fe were 7.30%, 37.04%, 55.02%, and 0.65%, respectively. The corresponding atom percentages were 11.63%, 50.64%, 37.51%, and 0.22%. The atom ratio was 1:4.35:3.22 for C:N:Si. These compositions further led to the production of Si₃N₄/SiC nanocomposites.

Based on the aforementioned results of XRD and SEM investigations, the synthesis mechanism of Si₃N₄/SiC nanocomposites can be proposed as shown in Figure 6. Our studies revealed that the growth mechanism of Si₃N₄/SiC nanocomposites involves dissolution, reaction, and precipitation. As shown in Figure 6(a), Fe₂O₃ is first reduced by pyrolysis products CH₄ and H₂ into Fe, and PSN2 is decomposed thermally into SiCN at approximately 1000 °C. As shown in Figure 6(b), the amorphous SiCN reacts with Fe to form a liquid C–Fe–Si alloy at a high temperature and N₂ gas is released, which leads to the formation of pores. The further reaction between SiCN and C–Fe–Si leads to the formation of a supersaturated liquid alloy, which is rich in Si and C and then precipitates. Under the N₂ atmosphere, the silicon nitride has the most...
stable phase. The external N$_2$ (Figure 6(c)) diffuses into the bulk through the previously formed pores and reacts with the Si elements in the liquid C–Fe–Si alloy (Figure 6(d)) to form Si$_3$N$_4$. Meanwhile, a small amount of SiC is precipitated.

The EDS results (Figure 7) showed the difference in the distribution of the N element at 1250 and 1450 °C. The difference between the two temperatures could be explained with the introduction of the nitrogen element from the N$_2$ atmosphere, instead of being generated by the SiCN matrix. Moreover, temperature is an essential factor affecting the formation of Si$_3$N$_4$/SiC nanomaterials, as the energy at 1100 °C is not sufficient for the reaction between N$_2$ and Si in the liquid C–Fe–Si alloy. However, on the other hand, the reaction occurred and Si$_3$N$_4$ and SiC started to precipitate and grow subsequently with the increased temperature (Figure 2(b–d)).

4 | CONCLUSION

In this work, crystallised Si$_3$N$_4$/SiC nanocomposites were successfully synthesised from the polysilazane PSN2. The 3 wt% Fe$_2$O$_3$ catalyst lowered down the crystallisation temperature from 1500 to 1250 °C. As the pyrolysis temperature was elevated from 1250 to 1350 °C and 1450 °C, the porous structure transformed into flaky and near-spherical nanoparticles on Si$_3$N$_4$/SiC nanocomposites. Furthermore, the production of Fe from Fe$_2$O$_3$ reduction by CH$_4$ and H$_2$ caused the transformation of amorphous SiCN to a liquid C–Fe–Si alloy. Afterwards, the reaction of SiCN with C–Fe–Si led to the formation of a Si- and C-rich supersaturated liquid alloy, which then precipitated. Besides, the N$_2$ that diffused through the pores facilitated the formation of Si$_3$N$_4$ through its reaction with Si in the liquid C–Fe–Si alloy.

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