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Effect of hexagonal-BN on phase transformation of additive-free Si₃N₄/SiC nanocomposites prepared from amorphous precursor

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Abstract: Si₃N₄/SiC nanocomposites are well known and attractive for advanced ceramic applications due to excellent mechanical and thermal properties, which make them suitable for use in turbine engines, heat exchangers, and other sophisticated applications. However, without the presence of additives, the fabrication of Si₃N₄/SiC composites is difficult. The additives form a liquid phase during sintering and facilitate the densification of the composite. However, the additives present a drawback at high temperatures since they decrease the mechanical properties of the composites. Recently, Si₃N₄/SiC composites were fabricated via the polymer precursor route without any additives, using electric field assisted sintering (EFAS). In this study, fully densified Si₃N₄/SiC nanocomposites incorporating hexagonal-BN were successfully fabricated by hot pressing without any additives at 1700 °C for 2 h under vacuum at a pressure of 50 MPa (via the amorphous precursor route). Moreover, the incorporation of additives and h-BN is found to decrease the content of SiC. The phase transformation, densification, microstructure, and mechanical properties were discussed and presented.

Key words: Si₃N₄/SiC; hot pressing; hexagonal-BN; additives; sintering

1 Introduction

As advanced ceramics, Si₃N₄/SiC composites are attractive due to excellent mechanical and thermal properties [1,2], which make them suitable for use in turbine engines, heat exchangers, and other sophisticated applications. With the high covalence and low diffusivity of the Si-based ceramics, it is very difficult to sinter to high density without any additives. For example, pure SiC at near theoretical density could only be achieved by hot pressing at 2500 °C and 50 MPa [3]. The addition of sintering additives is therefore necessary to obtain high-density Si-based ceramics at a lower temperature. The additives form a liquid phase during sintering and densified Si-based ceramic from the liquid phase sintering mechanism. The additive used for the enhancement of densification becomes a glassy phase in the final ceramic, which usually reduces its mechanical properties at high temperatures [4]. Moreover, the liquid

at the grain boundary produces grain growth, which occurs easily due to high boundary mobility. Not only densification, but also grain growth, occurs significantly [5]. This has led to the omission or minimized use of sintering additives in Si-based ceramics.

Recently, a polymer precursor has been used to fabricate Si_3N_4/SiC nanocomposites [6–9] by two steps. First, the polymer precursor is pyrolyzed to obtain an amorphous powder. The second step is the sintering of the amorphous powder, prepared by hot pressing (HP) or electric field assisted sintering (EFAS). By adopting the EFAS route, a fine grain size can be achieved at a relatively low temperature without the addition of sintering additives [8,9].

Hexagonal BN (h-BN), known for its white graphite structure with low hardness, is an important additive to the field of advanced ceramics due to its excellent thermal shock resistance and machinability [10].

 Si_3N_4 -BN composites have exhibited exceptional corrosion resistance [11]. Additionally, SiC–BN

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composites are expected to be structural material candidates used in high-temperature and thermal/mechanical shock environments [10]. Unfortunately, thus far, there are no reports on the effects of h-BN on the phase transformation of Si_3N_4/SiC composite synthesized by the precursor route.

The goal of this study is to investigate the effects of h-BN addition in Si_3N_4/SiC on phase transformation via the polymer precursor route. The results on phase composition, densification, and microstructure are discussed.

2 Experimental

The polymer precursor used in this work was a commercially available polyureasilazane, Ceraset SN (Commodore Polymer Technologies, Columbus, OH). Hexagonal BN (Sonderkeramik) had an average particle size of 1 µm. Al₂O₃ (D_m=150 nm, 99.9% purity, Baikowski, Japan) and Y₂O₃ (D_m=220 nm, 99.99% purity, Acros Organics, USA) were used as sintering additives in a mass ratio of 60:40, respectively. The details of sample composition and nomenclature are given in Table 1. Liquid polymer was cross-linked at 200 °C for 90 min. A mortar and pestle were used to grind the cross-linked infusible polymer to a 75 µm powder, which was then pyrolyzed under N₂ atmosphere for 4 h. In order to reduce the particle size, the amorphous powder was milled in a high energy milling system (MiniCer, Netzch, Germany) for 1 h using 0.45 mm ZrO₂ beads at 3000 r/min. The mean particle size after milling was about 1 µm. The amorphous powder, h-BN, and sintering additive were mixed in ethanol and subjected to ball milling for 24 h using SiC balls (5 mm diameter) to minimize contamination, followed by drying in a rotary evaporator. Hot pressing was then carried out at 1700 °C for 2 h under vacuum at a pressure of 50 MPa. For comparison, EFAS was performed at 1700 °C for 10 min under vacuum at a pressure of 50 MPa.

Table 1	Samples	and their	composition
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Sample	w(Amorphous	w(h-BN)/	w(Additives)/	
	100	/0	/0	
UBN	100	0	0	
0BNEFAS	100	0	0	
0BNAdd	95	0	5	
5BN	95	5	0	
5BNEFAS	95	5	0	
5BNAdd	90	5	5	

Densities of the sintered specimens were measured using the Archimedes method. The phases observed after sintering were later identified by X-ray diffraction (XRD, X'Pert-PRO MPD, PANalytical), using the Cu K_{α} line, 40 kV, and 30 mA. The microstructures of various specimens were examined by scanning electron microscopy (SEM, Hitachi S–4800), using 15 kV and 10 μ A. The hardness of the sintered samples was measured with a Vickers hardness indenter (MVK-H1, Akashi, Japan), with a 9.8N (1 kg) load for 10 s. Tabulated data of Gibbs free energies for thermodynamic calculations were obtained from BARIN [12] and CHASE [13].

3 Results and discussion

Figure 1 shows the XRD patterns of the pyrolyzed polymer precursor at different temperatures. Depending on the temperature, different phases were observed during pyrolysis. At 1450 °C, only α -Si₃N₄ and free C were observed in the XRD spectra, while at 1650 °C, β -Si₃N₄ and β -SiC were observed. Phase formation during pyrolysis can be estimated by the Gibbs free energy analysis, as shown in Fig. 2, whereby β -SiC is more stable than α -Si₃N₄ at t>1427 °C. However, α -Si₃N₄ was formed during pyrolysis at both 1450 and 1650 °C



Fig. 1 XRD patterns of pyrolyzed polymer powders at 1450 °C and 1650 °C



Fig. 2 Standard Gibbs formation free energy vs temperature for β -SiC and α -Si₃N₄ formation

because pyrolysis under a nitrogen atmosphere prevented the decomposition of Si_3N_4 at high temperatures [14]. As proven by the Gibbs free energy analysis shown in Fig. 2, a small amount of free carbon can react with α -Si₃N₄, which then forms SiC at 1650 °C. Since an amorphous powder is much preferred in the sintering process, the powder was pyrolyzed at 1450 °C rather than at 1650 °C. Figure 3 presents the XRD pattern of the Si₃N₄/SiC composite sintered at 1700 °C under a pressure of 50 MPa.



Fig. 3 XRD pattern of Si_3N_4/SiC composites after sintering at 1700 °C under pressure of 50 MPa in vacuum using hot press and EFAS

amorphous The powder has already been crystallized into the main phases: α - and β -SiC, β -Si₃N₄, ZrO₂, ZrSi₂, Si and h-BN. Although the sintering additives were added in the samples (i.e., 0BNAdd and 5BNAdd), peaks for additives were not detected in the XRD patterns due to the small amount of addition. The other peaks observed in the XRD were from ZrO₂, presenting as an impurity from the high energy ball milling with ZrO_2 media. α - and β -SiC were observed, even though β -SiC was initially formed, as shown in Fig. 1. However, at the sintering temperature, a portion of β -SiC was transformed into α -SiC, where β - to α -SiC transformation is common at high temperatures [15]. β -Si₃N₄ peaks were also observed without any trace of α -Si₃N₄. According to TANAKA [16], α - to β -Si₃N₄ transformation occurs at 1750 °C. However, α-Si₃N₄ was already completely transformed to β -Si₃N₄ at 1700 °C in this study, which is lower than TANAKA's result [16]. This may be due to the different sintering conditions. In contrast, for the EFAS sample, OBNEFAS, a highly crystalline β -SiC peak was observed along with free Si and ZrSi₂, without peaks for Si₃N₄. It appears that under the high temperature EFAS conditions, all the Si₃N₄ had already transformed to SiC, leaving the excess Si due to the insufficient amount of carbon in the amorphous powder.

This indicates that the kinetics of phase transformation in the EFAS is faster than that in the hot pressing. This phenomenon is also observed in the sintering of Ta [17], where the formation of TaC in the EFAS is higher than that in the hot pressing. Moreover, no β - to α -SiC transformation was observed in the hot pressed samples, since the holding time for EFAS was only 10 min. ZrSi₂ was observed in the EFAS samples instead of ZrO₂. The formation of ZrSi₂ is due to the reaction between ZrO₂ and free Si in the EFAS samples, as previously observed in the deposition of ZrO₂ on a silicon wafer [18].

The phase composition of Si₃N₄/SiC composites after hot pressing based on the Rietveld refinement method is shown in Table 2. The amount of SiC decreased with the addition of additives and h-BN. At 1700 °C, SiC is more stable than Si_3N_4 (Fig. 2), and therefore, the amount of SiC is higher than that of Si₃N₄, as shown in the 0BN sample. The amount of SiC decreased with the incorporation of additives, as shown in the 0BNAdd sample. The additives form a liquid phase at high temperatures, acting as a mass transport medium to help densification, and locate finally in the grain boundary. Since Si₃N₄ is formed initially, the additives at the grain boundary of the Si₃N₄ probably hinder the transformation of Si₃N₄ to SiC. In the case of h-BN, chemical inertness hinders the transformation of Si₃N₄ to SiC. The addition of h-BN was also found to restrain the growth of β - Si₃N₄ [19].

Table 2 Phase composition of Si_3N_4/SiC composites after hotpressing based on Rietveld refinement method

Sample	w(SiC)*/%	$w(\beta-\mathrm{Si}_3\mathrm{N}_4)/\%$	w(h-BN)**/%	w(ZrO ₂)/%
0BN	67.3	32.3	0	0.4
0BNAdd	54.1	45.4	0	0.5
5BN	42.7	51.8	5	0.5
5BNAdd	30.8	63.7	5	0.5

*including α -SiC and β -SiC; **based on initial mass of h-BN

Figure 4 shows the bulk density and relative density of the Si₃N₄/SiC composites after sintering. The density of the sintered sample was not found to significantly increase in the presence of additives. In other words, the amorphous powders were easily densified and formed SiC and Si₃N₄ without any additives. This result is different from the conventional crystalline powder because at least 8% of additive was needed to aid the densification of SiC [20–26]. The addition of h-BN decreased the bulk density of the sintered samples, as shown in Fig. 4. The sintering temperature of h-BN was found to be higher than 1800 °C [19]. Hence, the porosity increased with the addition of h-BN, which decreased the relative density of the sintered sample. The same behavior was also observed in the EFAS samples: the addition of BN simply decreased the density. However, the overall density of the EFAS samples was lower than that of the hot-pressed samples due to the formation of free Si, which has a lower density than SiC or Si_3N_4 .



Fig. 4 Bulk density and relative density of Si_3N_4/SiC composites after sintering

Figure 5 shows SEM images of the polished surfaces of Si₃N₄/SiC after sintering. Three different colors were observed in the SEM images of samples 0BN, 0BNAdd, 5BN, and 5BNAdd—black, grey, and white.

Electron dispersive spectroscopy (EDS) revealed that the black, grey, and white phases were β -Si₃N₄, SiC, and ZrO₂, respectively. The ZrO₂ impurity was located at the grain boundary of SiC. With irregular shape, the grain size of SiC varied between 50 and 300 nm. Moreover, the β -Si₃N₄ content increased in the presence of additives and h-BN, as shown in Fig. 5. The EFAS samples show that grain sizes are three times larger (approximately >1 µm) than the hot-pressed samples. The EFAS samples contain two different forms of SiC: stoichiometric SiC with a bright color, and nonstoichiometric one with a dark color. In the EFAS samples, EDS also revealed the ZrSi₂ impurity and a free Si phase.

Figure 6 shows the hardness of the Si_3N_4/SiC composites after sintering. The highest hardness (24.1 GPa) was achieved in 0BN sample, and the hardness decreased with the incorporation of additives, as shown in the 0BNAdd sample. The decreasing



Fig. 5 SEM images of polished surfaces of Si_3N_4 /SiC composites after sintering: (a) 0BN; (b) 5BN; (c) 0BNAdd; (d) 5BNAdd; (e) 0BNEFAS; (f) 5BNEFAS



Fig. 6 Hardness of Si₃N₄/SiC composites after sintering

hardness is a function of the SiC content, since the amount of SiC decreased with the incorporation of additives and h-BN. The hardness of the EFAS samples was lower than that of the hot-pressed samples because of the formation of the ductile Si phase. Moreover, the hardness of the EFAS samples was also low due to the large grain size of the samples.

4 Conclusions

The influence of h-BN addition on the phase transformation, microstructure, and mechanical properties of Si₃N₄/SiC ceramics were investigated. The incorporation of additives and h-BN simply decreases the densification. Furthermore, both the additives and h-BN hinder the transformation of Si₃N₄ to SiC, due to the liquid phase of the additives and the chemical inertness of h-BN. From these results, it is possible to fabricate h-BN Si₃N₄/SiC nanocomposites using the polymer precursor without any additives. The bulk density of the sintered samples reaches 95.5%, consisting of SiC grains of 50-300 nm. The SiC in the sample appears to play a significant role with respect to hardness.

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六方-BN 对非晶前驱体制备不含添加剂的 Si₃N₄/SiC 复合材料相变的影响

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摘 要: Si₄N₄/SiC 纳米复合材料由于具有优良的力学和热性能,广泛应用于涡轮发动机、热交换器和其他复杂情 况中。然而,不添加添加剂很难制备出 Si₃N₄/SiC 复合材料。添加剂在烧结过程形成液相从而促进复合材料的致密 化。然而,添加剂的存在降低了复合材料的高温力学性能。通常在不添加添加剂的情况下,采用电场辅助烧结,利 用聚合物前体路线制备 Si₁N₄/SiC 复合材料。本研究中,在无添加剂、温度 1700 °C、真空 50 MPa 条件下,热压 烧结2h,利用非晶前体路线成功制备了六方-BN 致密化的 Si₃N₄/SiC 复合材料。聚合物前驱体和 BN 的作用减少 了的 SiC 含量。并对相变、致密化、微观组织和力学性能进行了讨论。 关键词: Si₃N₄/SiC; 热压烧结; 六方-BN; 添加剂; 烧结

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