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Si_3N_4–BN Composites obtained from Aminoboranes as BN Precursors and Sintering Aids

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Abstract

The Si_3N_4–BN composite ceramic has been elaborated by combining Si_3N_4 fine powder with boron nitride provided by the thermolysis of a molecular precursor. The properties of this new type of sample has been compared with those of composite ceramics obtained by the classical hot-pressing method using Si_3N_4–BN powders and sintering aids (Y_2O_3, Al_2O_3). Giving the best ceramic yield, tris(methylamino)borane (TMB) has been used as BN precursor and sintering aid. Boron nitride formed from TMB thermolysis was poorly crystallized when the hot-pressing was run up to a temperature lower than 1800°C. The density of the composite ceramic samples obtained from molecular precursors was higher than expected, this could be related to the sintering activation properties of the precursor. Moreover the problems due to the BN platelets orientations were removed. The Vickers hardness was clearly improved for samples without BN platelets, however the bending strength was not increased. The precursor improved some properties of the composite and could be considered as a sintering activator avoiding oxide addition as sintering aid. © 1997 Elsevier Science Limited.

1 Introduction

Boron nitride addition to silicon nitride, Si_3N_4, led to composite ceramics which combined the properties of Si_3N_4 and the superior resistance of BN to thermal shocks and to erosion by molten metals.[1] Beside the classical hot-pressing methods leading to composite ceramics, a new synthetic route to SiC-Si_3N_4 composites has been successfully developed using a molecular precursor of silicon carbide converted into ceramic[2] by pyrolysis. More recently, nanostructured B–Si–N composite materials have been obtained directly from mixtures of BN and Si_3N_4 molecular precursors.[3] To obtain BN coatings or fibers, various BN precursors have been synthesised and studied.[4–7] Most of them were prepared from borazine $(HNBH)_3$ or trichloroborazine $(HNBCl)_3$ whose structure was based on the graphite-like $(BN)_3$ framework. Many attempts to obtain BN fibers, coatings or matrix have been made leading to amorphous, turbostratic, hexagonal or cubic boron nitride according to the experimental conditions used.[4,8–16]. Due to the difficult synthesis and the high cost of borazine derivatives, these boron nitride precursors were not favourable to industrial development. The well-known[17,18] aminoboranes, $B(RNH)_3$, used in this study, could be easily obtained in a very high yield from boron trichloride, BCl_3, and a primary amine, RNH_2 in a one-step reaction. Due to the reactivity of the amino group, a polymerization of the aminoborane could be performed following two different methods.[17–20] The first, classical method was a simple thermolysis under low pressure, leading to the aminoborazine, N, N′, N″-trisalkyl-B, B′, B″-trisalkylaminoborazine, which transformed into polymers easily pyrolysed into BN. The second way to obtain boron nitride from aminoborane precursors was an exchange reaction of the aminogroups of the precursor for ammonia followed by a pyrolysis of the residue. This technique led to carbon-free boron nitride but the amine–ammonia exchange control was difficult. In fact, to keep the precursor wetting properties, a proportion of hydrocarbon chains remaining from the amino part of the aminoborane was needed. A carbon-free precursor would exhibit low wetting properties.[8,12] In a previous work[16] the ability of tris(methylamino) borane (TMB) to convert into boron nitride has been studied in order to obtain BN coatings on graphite or BN matrix-carbon fibers micro-composites. The precursor and graphite or carbon fibers were simply heated under an ammonia flow and a polymerization occurred leading to amorphous BN when the pyrolysis was run up to 1000°C. In this study, in order to obtain Si_3N_4–BN composite ceramic, Si_3N_4 powder alone or Si_3N_4 powder and BN platelets have been mixed with a TMB-aminoborazine mixture. The obtained paste was then pyrolysed yielding to a preceramic which was hot-pressed leading to the composite ceramic. Several attempts were made in order to assess the efficiency of TMB as boron nitride source and sintering agent. A comparison was made with classically prepared samples.

2 Results

The aminoboranes were obtained when an excess of a primary amine, RNH_2, was reacted with boron trichloride at low temperature. This reaction led to a mixture of aminoborane and aminoborazine in proportion depending on the amine used.[17–20] When the amine is not too bulky, the aminoborazine yield is high. When the aminoborane was heated, a polymerization generally occurred, yielding an N substituted aminoborazine. Most of the polymerizations were run under an ammonia flow, to lower the carbon content of the BN matrix. Several amino boranes were prepared and tested in order to determine the best conditions for the thermolysis. An exchange of the amino group of the aminoborane for ammonia took place leading to an unstable ammoniaborane, $B(NH_2)_3$, whose polymerization immediately occurred. In a first step, an uncharacterized ammonia-substituted borazine $(HNBNH_2)_3$ was obtained which transformed very rapidly into a polymer with borazine cycles bonded through –NH– bridges.[17] The aminoborane reactivity towards ammonia was related to the nature of the amine. The exchange of phenyl- or isopropyl-amino group for ammonia occurred at room temperature with a 50% yield whereas a 50°C temperature was the minimum needed to allow the methylamino group to be exchanged. An example of TGA curves obtained is shown in Fig. 1. With TMB, the difference between the weight loss observed with (plain curve (a)) and without ammonia (plain curve (b)) corresponded to the amount of carbon remaining in the final material. The elemental analysis confirmed the lowering carbon ratio effect of ammonia during the pyrolysis (BN obtained from TMB under N_2: B, 34; N, 36; C, 18 and under NH_3: B, 40; N, 58; C, 0·5 wt%). Unfortunately, the more complete the amino-ammonia conversion, the more unstable were the obtained compounds. Furthermore the interaction between the precursor and the reinforcing phase became more difficult. In fact, when a pyrolysis was performed, the precursor remained under a waxy form up to high temperature (400°C) that allowed the gas evolution coming from the polymerization and a good interaction with the solid adducts. The ammonia effect in the aminoborane polymerization was more evident using a bulky aminoborane: the trisisopropylaminoborane, $B(Pr^iNH)_3$. The TGA curves (Fig. 1) showed a very different behavior when heating without ammonia (dotted line curve (c)) and with ammonia (dotted line curve (d)). No thermal polymerization of $B(Pr^iNH)_3$ occurred and the aminoborane was stripped off even though low carbon content BN could be obtained with a good yield when the thermolysis was performed under ammonia (BN obtained from $B(Pr^iNH)_3$ with NH_3: B, 38; N, 53; C, 0·7 wt%). After several attempts, trismethyl aminoborane (TMB) was chosen for a precursor and was used as obtained from the synthesis (it contained 15% of aminoborazine). This precursor is a liquid which easily wets a large number of substrates. The preceramics were obtained by mixing the crude precursor with Si_3N_4 fine powders in various conditions according to the procedure described in the literature.[21,24] An homogeneous paste-like mixture was obtained whose viscosity depended on the powder/precursor ratio. Several samples have been prepared overviewing the experimental conditions in order to estimate the ability of the system. Samples II, III and IV were obtained from the mixture of molecular precursor and Si_3N_4 powder. Two pyrolysis temperatures (700°C in III and 1050°C in II and IV) were used

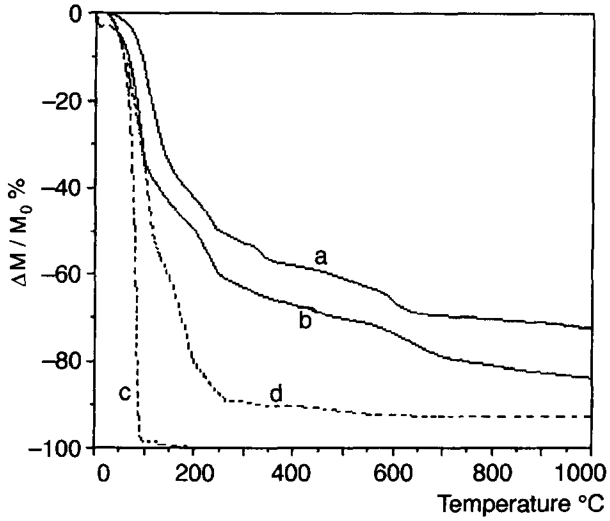


Fig. 1. TGA of aminoboranes (a) $B(MeNH)_3$ under N_2; (b) $B(MeNH)_3$ under NH_3 (c) $B(Pr^iNH)_3$ under N_2; (d) $B(Pr^iNH)_3$ under NH_3.

while the slow heating rate and the ammonia flow were kept constant for all the samples' thermolysis. Samples I, III and IV were prepared without sintering aids (5% Y_2O_3, 2%Al_2O_3) and without BN platelets. With the samples obtained from the BN precursor, after the pyrolysis under ammonia, a preceramic white residue was obtained. These products were then introduced, under a controlled atmosphere, into graphite dies to be subjected to an uniaxial hot-pressing up to 40 MPa and 1800°C under a nitrogen atmosphere. The other reference samples were obtained using classical sintering material and methods.[22–24] The composition and properties of the different samples are given in the Table 1.

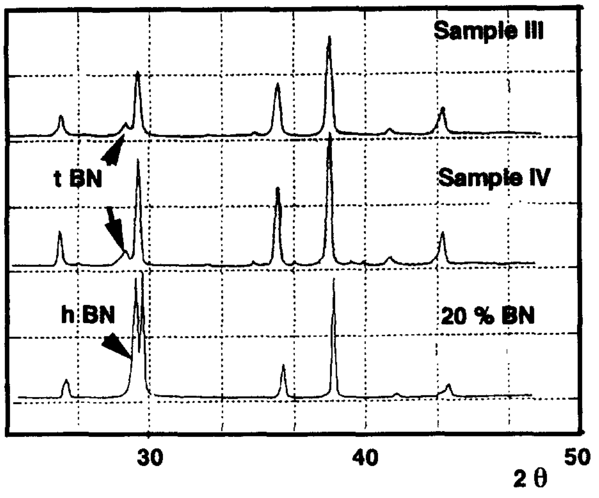


Fig. 2. XRD of the hot-pressed samples III and IV obtained from precursor and of the classical 20% BN platelets one. t = turbostratic BN; h = hexagonal BN. The other diffraction lines are from Si_3N_4.

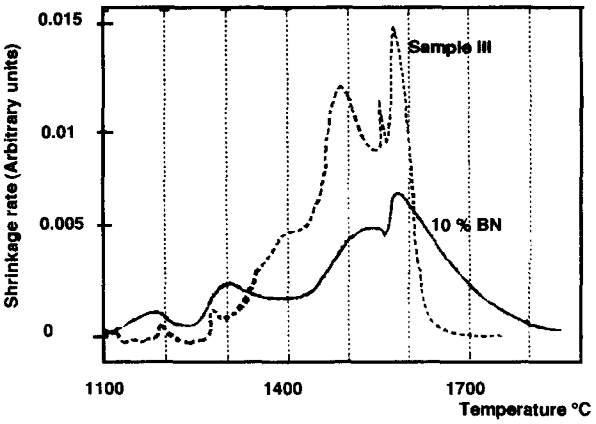
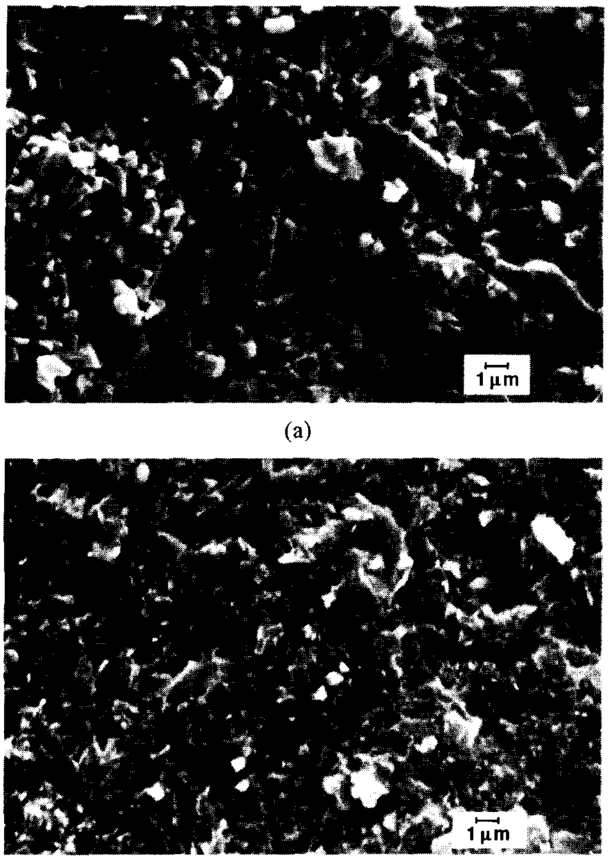


Fig. 3. Shrinkage rate evolution during the thermal treatment.

X-ray diffraction patterns recorded on several samples given in Fig. 2 showed the very low crystallinity of the obtained BN. These results were consistent with the conditions required to transform turbostratic BN into the hexagonal phase. A temperature higher than 1800°C was required in the solid state.[25] Only the 002 diffraction line was clearly present and no graphitization index according to the usual method[15,25] could be determined. During the sintering, the efficiency of the molecular precursor and of the boron nitride obtained was evident. Figure 3 shows the densification increase versus temperature. The sample III compaction was clearly faster than for the 10% BN sample in spite of the sintering aids. The efficiency of the precursor could be explained by the low crystallinity of the boron nitride which removed the problems due to the orientation of the BN platelets. However the oxygen presence during the precursor pyrolysis could lead to the formation of borosilicates in a low concentration. Such compounds, molten in the hot-pressing conditions, are well known to favour sintering by their viscosity and could lead to more dense samples. Although boron nitride could be considered as a sintering inhibitor, the porosity of the samples obtained from Si_3N_4 and organic precursor was lower than expected with regard to the classic Si_3N_4–BN samples. In the composites obtained from powder mixtures, the flexural strength decreased when the boron nitride content increased. The composites obtained from precursors (samples III and IV) had a comparable strength to composites obtained from powder mixtures, for the same BN content (about wt 20%). The Vickers hardness of the samples obtained from precursor (III, IV) was higher than that of the hardness measured in the samples obtained from powder mixtures. SEM fractographic observations performed in 10% BN (A) and Sample IV (B) are shown in Fig. 4. Under the same experimental conditions the grain morphology in (A) was very much larger than in (B). The small needle-like particles of Si_3N_4 were completely embedded in the fine BN grains and the general texture of the samples obtained using BN precursor was clearly more isotropic.

Table 1. Experimental results (contents wt%)

Sample	*I*	*II*	*III*	*IV*	*BN 10%*	*BN 20%*	*BN 30%*
Sintering Temp. °C	1780	1770	1765	1780	1800	1850	1830
BN content wt%	0	27·7	21·3	21·3	10	20	30
Measured density	3·11	2·92	3·04	3·03	3·08	2·95	2·74
Theoretical density	3·18	3·02	3·09	3·09	3·20	3·10	3·00
Porosity %	2·2	3·6	1·6	1·9	3·7	4·8	2·87
Flexible Strength (MPa)	630	405	515	530	835	530	370
Hardness (GPa)	15·6		14	13·7	9·6		



(a)

(b)

Fig. 4. SEM micrographies of the two types of samples. (a) classical hot-pressed sample obtained with sintering aids and 10% of BN platelets; (b) sample IV obtained from BN molecular precursor pyrolysis.

3 Conclusion

Boron nitride provided from molecular precursors could be easily hot-pressed with Si_3N_4 in order to obtain composite ceramics. Although the ceramic yield of aminoboranes was very low, a partial conversion of these compounds by ammonia led to low carbon content BN. The elaboration of the composite ceramic following an impregnation-like method with Si_3N_4 powder and TMB led to ceramic samples exhibiting interesting properties. BN obtained from TMB, under the experimental conditions was poorly crystallized, nevertheless the precursor could be considered as a boron nitride source for Si_3N_4–BN composites and as a sintering activator increasing the density of the samples. The Vickers hardness of the samples was also clearly improved using this synthesis approach.

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