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Nonoxide–boron nitride composites: in situ synthesis, microstructure and properties

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Abstract

Hexagonal graphitic boron nitride (h-BN) composites show excellent corrosion and thermal shock resistance, good mechanical tolerance and machinability, especially Si_3N_4–BN and Sialon–BN composites; they have already been used as break rings for horizontal continuous casting of steel. However, the strength of the conventionally processed BN composites were remarkably degraded by the addition of BN due to the poor densification behavior and the existence of large BN flakes or agglomerates of BN flakes that acted as fracture flaws. This means that BN dispersoids with fine particle size and homogeneous distribution are the key factors to obtain high strength composites. By in situ process, such microstructural features can be realized. In this work, by using the proposed in situ reactions, synthesis, microstructures and properties of various in situ nonoxide-boron nitride (Nobn) composites including SiC–BN, Si_3N_4–BN, AlN–BN, Sialon–BN and Alon–BN composites were investigated. For some Nobn composite systems, due to the large volume expansion during the reaction processes, near-net shape sintering can be realized. For example, the sintering shrinkage of AlN-30 vol.% BN was 3.1% and that of Alon-21 vol.% BN was 4.2%. This will be an advantage for the fabrication of large and complicated products.

Keywords: Boron nitride; Ceramic composite; In situ synthesis; Mechanical properties; Microstructure

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1. Introduction

In situ synthesis of ceramic composites is an attractive and effective way to obtain advanced materials with excellent properties.[1–5] For example, one can obtain composites with finer and more homogeneous microstructures, higher chemical and microstructural stability at high temperatures, and better mechanical properties than the conventionally processed ones. Also, composites with special microstructures such as in situ formed whiskers,[6] platelets[7] and disks/flakes are obtainable. In the conventional process, the reinforcements are directly added to the matrix and in general the size and shape of the reinforcements do not change during the processing. Thus the final microstructures of the obtained composites are closely related to the raw materials. In addition, distribution process for the reinforcements shows direct effect on the microstructure homogeneity, especially for reinforcements with shapes of whisker or flake or with very fine particle size (nanoparticles) homogeneous distribution is difficult to obtain. If hot pressing is used to produce composites with whisker or flake/disc reinforcements, in general the obtained materials will show anisotropy in microstructure and properties. On the other hand, in the in situ synthesis process, due to the reinforcements are formed in situ during the synthesis of composite powders or sintering process, the effect of the shape and size of the starting materials on the final microstructure of composite is not direct.[1,2,8] Accordingly, even by using common starting materials with large particle size, nanoparticles, whiskers or disks/flakes reinforced composites are obtainable.

BN composite family is an important one in the field of advanced ceramics. In general they demonstrate excellent thermal shock resistance and machinability. Some systems show excellent corrosion resistance to

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molten-metal, such as Si_3N_4–BN,[9–11] Sialon–BN[12] and BN–AlN–BN[13] composites. AlN–BN[14–17] composites demonstrate excellent properties such as high thermal conductivity, high electrical insulation, good dielectric behavior, and high corrosion resistance, which are expected to be used as corrosion resistant parts, electromagnetic window material and as a high thermal conductive element. Alon–BN composites[18] are considered as break ring materials used in steel industry for substituting for Sialon–BN or Si_3N_4–BN materials due to the decomposition of Sialon or Si_3N_4 by the dissolution of silicon into molten steel. SiC–BN composites[19–23] are expected to be structural material candidates used in high temperature and thermal/mechanical shock environments.

BN composites can be produced either by directly adding or by in situ synthesizing BN particles in ceramic matrices. By conventional process, however, BN agglomerates or large BN flakes which are difficult to avoid in starting powders may act as fracture flaws due to the easy cleavage perpendicular to the *c*-axis of BN flakes. In addition, due to the poor densification behavior of BN, hot pressing is usually used to prepare BN composites. However, such hot pressed BN composites generally demonstrate remarkable property anisotropy because of the flake structure of BN component. In our recent work, various nonoxide–boron nitride (Nobn) composites were prepared by the proposed in situ reactions. In this article, we will introduce these in situ reactions and discuss the microstructural feature and the mechanical properties of the obtained Nobn composites.

2. Reactions

Boron-bearing components are considered to use as the boron source. These components can be B_4C and various metal borides such as AlB_2, SiB_4, SiB_6 or boron–metal alloys.[24] Together with the reaction of carbon reduction, boron oxide (B_2O_3 or H_3BO_3) can also be used as a boron source. As for the nitrogen source, nitrogen gas or solid state nitrogen-bearing metal nitrides such as Si_3N_4, AlN, and TiN can be used. Some examples of the in situ reactions are listed as follows:

$$Si_3N_4 + 3B_2O_3 + 9C = 3SiC + 4BN + 6CO \quad (1)$$

$$Si_3N_4 + B_4C + 2C = 3SiC + 4BN \quad (2)$$

$$(1 + x)Si_3N_4 + B_4C + 2C = xSi_3N_4 + 3SiC + 4BN \quad (3)$$

$$AlB_2 + 1.5N_2 \rightarrow AlN + 2BN \quad (4)$$

$$9Al_2O_3 + 5AlB_2 + 7.5N_2 \rightarrow Alon(9Al_2O_3{\cdot}5AlN) + 10BN \quad (5)$$

$$Si_3N_4 + Al_2O_3 + AlB_2 + N_2 \rightarrow Sialon + BN \quad (6)$$

$$SiB_6 + C + 3N_2 \rightarrow SiC + 6BN \quad (7)$$

$$3SiB_6 + 11N_2 \rightarrow Si_3N_4 + 18BN \quad (8)$$

$$3SiB_4 + 8N_2 \rightarrow Si_3N_4 + 12BN \quad (9)$$

$$SiB_6 + Al_2O_3 + AlN + N_2 \rightarrow Sialon + BN \quad (10)$$

$$SiB_6 + AlB_2 + Al_2O_3 + N_2 \rightarrow Sialon + BN \quad (11)$$

$$4TiN + B_4C + 3C = 4TiC + 4BN \quad (12)$$

The above in situ reaction examples are thermodynamically possible. Accordingly, if proper processing conditions are adopted, the corresponding in situ Nobn composites are obtainable. Owing to the by-product of CO in reaction (1), the pressure of hot pressing should be applied after the reaction has completed. For example, a feasible program for the fabrication of the composite is keeping at 1700 °C for 60 min without applied pressure in vacuum, then increasing the applied stress to 30 MPa, Ar atmosphere to 1 atm and temperature to 2000 °C. If the pressure of hot pressing is applied too early, the reaction will be apparently retarded and the desired final phase composition can not be obtained. Solid state nitrogen-bearing metal nitrides are used in reactions (2), (3) and (12), so usual hot pressing can be used. For reactions (4)–(11), pressureless sintering in nitrogen atmosphere should be adopted to prepare these composites due to the nitrogen source is from the atmosphere.

3. Experimental procedures

In this work SiC–BN, AlN–BN and Alon–BN composites were prepared according to the proposed in situ reactions (2), (4) and (5). SiC or AlN powder was added into reaction (2) or (4) to change the phase composition in the obtained composite, respectively. Al_2O_3–Y_2O_3 for SiC–BN, and Y_2O_3 for AlN–BN and Alon–BN, were used as sintering additives. The starting powders were Si_3N_4 (E-10 grade, particle size 0.5 μm, Ube Industries, Yamaguchi, Japan), B_4C (F1 grade, particle size 1 μm, Denki Kagaku Kogyo, Ltd., Tokyo, Japan), C (2600# grade, particle 13 nm, Mitsubishi Chemical, Tokyo, Japan), AlB_2 (particle size <10 μm, High Purity Chemicals Laboratory, Saitama, Japan), Al_2O_3 (particle size 0.2 μm, Daimei Chemical Co., Nagano, Japan), Y_2O_3 (particle size 1.06 μm, Shin-etsu Chemical, Tokyo, Japan), SiC (A2 grade, particle size 0.63 μm, Showa Denko, Tokyo, Japan) and AlN (F type, particle size 1.23 μm, Tokuyama Chemical, Tokyo, Japan). Hot pressing was used to prepare the SiC–BN composite and

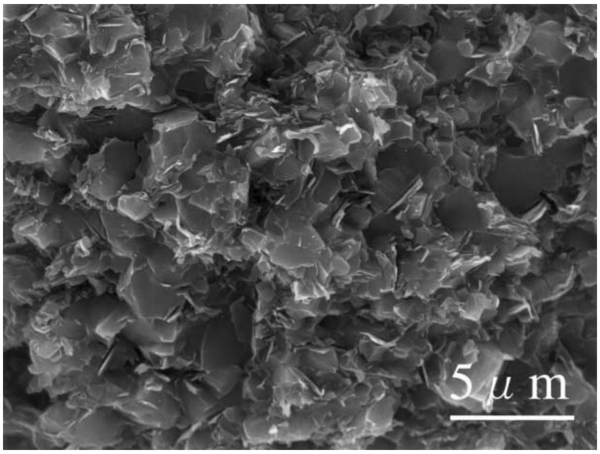

Fig. 1. SEM microstructure of in situ SiC–25 vol.% BN composite.

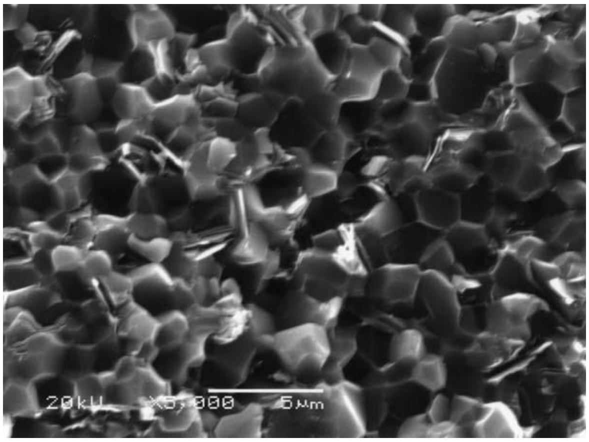

Fig. 2. SEM microstructure of in situ AlN–15 vol.% BN composite.

pressureless sintering for the AlN–BN and Alon–BN composites. X-ray diffraction (XRD) was used to determine the phase composition. Scanning electron microscopy (SEM) observations of the fracture surfaces were carried out at 20 kV in a Jeol JSM-5600. Three-point bending strength was measured on samples of 2.5 × 3 × 20 mm (for SiC–BN) or 3 × 4 × 20 mm (for AlN–BN and Alon–BN) with 16 mm span and a cross-head speed of 0.5 mm/min. The strength data were an average of five measurements for SiC–BN and 3 measurements for AlN–BN and Alon–BN.

4. Results and discussion

Our results showed that using solid state nitrogen-bearing components excellent Nobn composites with fine and homogeneously distributed BN flakes in the matrixes by hot pressing process was obtainable. For example, by the addition of SiC to change the BN content and 7 wt.% $Al_2O_3 + 3$ wt.% Y_2O_3 to promote densification, an SiC-25 vol.% BN composite was prepared according to reaction (2) by hot pressing under the pressure of 30 MPa at 2000C for 60 min in an argon atmosphere. XRD analysis shows that the main phases in the obtained composite are β-SiC and h-BN. This composite demonstrates very fine isotropic microstructures as showing in Fig. 1. The SiC phase is a quasi-spherical shape of about 1 μm and h-BN is a flake shape with 0.1–0.2 μm in thickness and about 1 μm in diameter. The bending strength of this composite is very high, showing a data of 588±32 MPa which is about 95% of that of the monolithic SiC material. The Al_2O_3–Y_2O_3 aids not only to increase the reaction rate, but also effectively promoted the crystallization of the in situ formed h-BN phase.

According to reaction (4), with the addition of AlN powder an AlN-15 vol.% BN composite was produced by pressureless sintering at 1900C for 120 min in 8 atm nitrogen atmosphere. The relative density of the obtained composite was 92.8%. The shrinkage of the composite during the sintering process was small (3.1%) due to the large volume expansion of reaction (4) during the nitridation process of AlB_2 which partly compensated the shrinkage by densification. With the increase of BN content in the composite, the shrinkage will decrease to near zero, even positive "shrinkage" will appear for specimens with BN content higher than 40 vol.%. The microstructure of the obtained composite is showed in Fig. 2. It can obviously be seen that the microstructure is very fine, homogeneous and isotropic. This material shows a bending strength of 217±12 MPa which is relatively higher than that (155 MPa) of a conventionally hot pressed AlN-15 wt.% BN composite with 96.5% relative density.[14]

By the addition of Al_2O_3, Alon-21 vol.% BN composite was manufactured according to reaction (5) by pressureless sintering at 1900C for 120 min in 8 atm nitrogen atmosphere. The relative density of the obtained composite was 82.4%. Due to the same reason as for reaction (4), the shrinkage of the composite during the sintering process is also small (4.2%). Such low-shrinkage behavior is beneficial to the production of large specimen. Fig. 3 shows the microstructure of the obtained composite. The material has a bending strength of 178±16 MPa which is relatively higher than that (about 80 MPa) of a conventionally hot pressed Alon-10 vol.% BN composite with about 87% relative density.[18]

The above results demonstrate that in situ synthesis is an effective process to prepare BN composites with fine particle size, homogeneous and isotropic microstructures. Liquid-phase-forming additives take an important role in the processes of reaction, densification and crystallization of the in situ formed BN phase. Although the in situ process is complicated due to the reaction and densification simultaneously or successively taking place, desired composites can be obtained

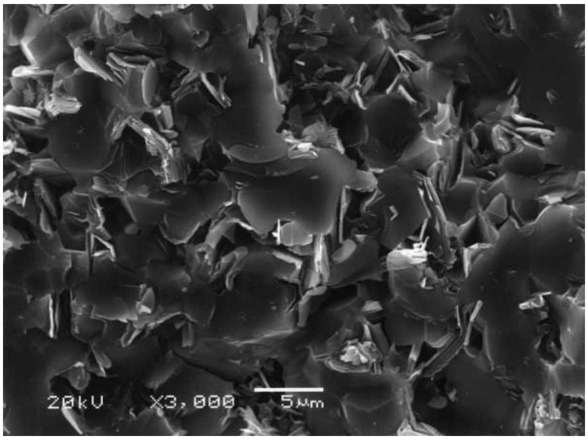

Fig. 3. SEM microstructure of in situ Alon–21 vol.% BN composite.

by designing the temperature and pressure rising program and controlling the reaction process to occur before or after the densification process.

5. Conclusion

Various Nobn composites including SiC–BN, Si_3N_4–BN, AlN–BN, Sialon–BN and Alon–BN composites can be produced by the proposed in situ reactions. Boron-bearing components such as B_4C and various metal borides such as AlB_2, SiB_4 and SiB_6 can be used as boron sources. Together with the reaction of carbon reduction, boron oxide (B_2O_3 or H_3BO_3) can also be used as a boron source. For reaction systems with solid state nitrogen-bearing components, hot pressing can be used to prepare the composites. For reaction systems having nitrogen gas reactants, pressureless sintering was used to prepare the specimens and low-shrinkage behavior during the sintering process can be realized. These Nobn composites demonstrate very fine, homogeneous and isotropic microstructures and high bending strength.

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