Effect of Y_2O_3 – Al_2O_3 Additive on the Phase Formation and Densification Process of In Situ SiC–BN Composite

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In Situ SiC–BN 複合材料における相生成と緻密化に及ぼす Y_2O_3 – Al_2O_3 助剤添加の影響

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The effect of the addition of Y_2O_3 – Al_2O_3 additive on the phase formation and densification process of in situ SiC–BN composite has been investigated. The in situ reaction started at 1450°C despite the addition of Y_2O_3 – Al_2O_3 additive. However, when Y_2O_3 – Al_2O_3 was added the reaction was much faster and completed after hot pressing at 1700°C. In addition, dense material with well-crystallized SiC and BN grains could be obtained. It was found that denitrification occurred during the reaction process for both specimens with and without Y_2O_3 – Al_2O_3 additive. However, denitrification occurred continuously at temperatures higher than 1700°C for the specimen without Y_2O_3 – Al_2O_3 additive and eventually resulted in decrease of nitrogen content. The above results were explained based on the following mechanism, that is, the Y_2O_3 – Al_2O_3 additive formed a Y–Al–Si–O liquid phase with SiO_2 present in Si_3N_4 raw powder, enhancing diffusion of the elements of the reactants.

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1. Introduction

Sintering additives are usually used to improve the densification of ceramics, especially for non-oxide ceramics due to their strong covalent bonds and low self-diffusion coefficient.^{1)–9)} For SiC ceramics, the commonly used sintering additives are B + C system.^{1),2)} Rare-earth oxides, usually in combination with Al_2O_3 , are also widely used as liquid-phase sintering additives for SiC.^{3),4)} Different sintering additive takes different mechanism on the sintering process. Carbon will reduce the SiO_2 on the particle surface of raw SiC powder and boron will improve the grain boundary diffusivity. Y_2O_3 – Al_2O_3 additive, whereas, will form liquid phase to realize liquid phase sintering.⁴⁾ In the case of BN, the impurity B_2O_3 in the raw BN powder also acts as liquid-phase sintering aids during the hot-pressing process.⁵⁾

Recently the authors proposed the in situ reaction $Si_3N_4 + B_4C + 2C = 3SiC + 4BN$ to prepare SiC–BN composites with fine, isotropic and homogeneous microstructures, high strength, low elastic modulus and excellent strain tolerance.^{10)–12)} These in situ composites would be used as structural parts assembled with parts made of metal materials or as thermal shock resistance materials. For obtaining dense in situ composites, 10 mass% Y_2O_3 – Al_2O_3 additive based on the SiC content was added in our previous works.^{10)–12)} The purpose of this article is to discuss the effect of Y_2O_3 – Al_2O_3 additive on the densification process and phase formation of the in situ SiC–BN composites.

2. Experimental

The starting materials were Si_3N_4 (E–10 grade, oxygen content 1.5 in mass%, Ube Industries), B_4C (F1 grade, particle size 1 μm , main impurities were Fe < 0.8 in mass% and B_2O_3 < 0.3 in mass%, Denki Kagaku Kogyo Co., Ltd.), C (#2600 grade, particle size 13 nm, Mitsubishi Chemical Co.), Al_2O_3 (particle size 0.2 μm , purity 99.99%, main impurities were Si 7 ppm, Fe 4 ppm and Na 2 ppm, Taimei Chemical Co.), Y_2O_3 (particle size 1.06 μm , purity 99.9%, main impurities were Dy_2O_3 < 100 ppm, Yb_2O_3 < 100 ppm,

CaO < 10 ppm and SiO_2 < 50 ppm, Shin-Etsu Chemical Co., Ltd.). Two types of specimens were prepared; one is denoted as specimen AD, for which 7 mass% Y_2O_3 and 3 mass% Al_2O_3 related to the SiC content were added. The other one is specimen NA, for which no sintering additive was added. The stoichiometric reactant powders according to the in situ reaction and the sintering additives were mixed in ethanol with $ZrO_2(Y_2O_3)$ balls for 24 h in a plastic bottle and then dried. The dried mixed powders were hot pressed in graphite die with BN coating on the inner-surface at different temperatures for 60 min under 30 MPa pressure in an argon atmosphere. Below 1100°C the furnace was kept a vacuum of about 10^{-2} Pa. Then Ar gas was inlet into the chamber up to 0.13 MPa and the pressure of hot pressing was gradually increased to 30 MPa.

The obtained billets were ground by SiC sandpaper to remove the surface layer. The density was calculated by measuring the specimen size and weight. Theoretical densities were calculated using density values (g/cm^3) of 3.22 for SiC, 2.27 for BN, 3.96 for Al_2O_3 and 5.031 for Y_2O_3 . Relative density was calculated from the measured density divided by the theoretical density even though for the specimens in those the reaction has not yet finished. X-ray diffraction (XRD) was conducted to determine the phase composition of the obtained specimens using Cu K α radiation. The chemical compositions of the obtained specimens were analyzed to see whether there was any change in composition after reaction at certain temperature and any difference between the specimens AD and NA. The used analysis methods for each composition are: C: infrared radiation (IR) absorption method; N: thermal conductivity method; B: ICP emission spectroscopy (ICP–ES); Si: gravimetric method. Scanning electron microscopy (SEM) was used to observe the microstructure.

3. Results

The XRD patterns of the specimens AD and NA hot pressed at different temperatures are shown in Fig. 1. It can

Fig. 1. XRD patterns of the specimens hot pressed at different temperatures.

be seen from Fig. 1 that the reaction did not take place when the temperature was below 1200°C despite the addition of $Y_2O_3-Al_2O_3$. If the hot pressing temperature was increased to 1450°C, the reaction took place gradually. However, according to the peak intensities of the formed phases SiC and BN, the reaction rates for the specimens AD and NA were obviously different. The reaction rate of the specimen AD was much faster than that of the specimen NA. The reaction had completed for the specimen AD when the temperature was increased to 1700°C, whereas that for the specimen NA had not yet completed and the peak intensities of the reactants remained strong. This result suggests that the addition of $Y_2O_3-Al_2O_3$ has paid an important role in the reaction process. At 2000°C the obvious difference between the XRD patterns of these two specimens is the peak intensity of the reaction-formed BN. It seems that the addition of $Y_2O_3-Al_2O_3$ additives also improved the crystallization of the reaction-formed BN. The other difference of these two XRD patterns is that there are numbers of small peaks for the specimen AD and the determination of these small peaks is difficult. However, these small peaks should be related to the $Y_2O_3-Al_2O_3$ additives and most probably they belong to a crystallized phase formed from $Y_2O_3-Al_2O_3-SiO_2$ (existing in the starting powder of Si_3N_4) during cooling down from the hot pressing temperature.

Figure 2 illustrates the relationships between relative densities and hot pressing temperatures for the specimens AD and NA. With the increase of the hot pressing temperature, the relative density increased steeply for the specimen AD and reached 95T.D.% at 2000°C. On the other hand, for the specimen NA the relative density increased slowly with the hot pressing temperature and only reached 70T.D.% at 2000°C. It means that for this in situ reaction system, sintering additives are necessary for obtaining a dense material.

The results of the chemical composition analysis are listed in Table 1. The content change ratio of each element be-

Fig. 2. Relative density of the specimens as a function of hot pressing temperature.

(a)

(b)

Fig. 3. Content change ratio of each element as a function of hot pressing temperature (a) nitrogen, (b) other elements.

fore and after hot pressing is listed in parenthesis. Figures 3 (a) and (b) show the content change ratios of the elements as a function of hot pressing temperature. It can be seen that the decrease of nitrogen content occurred for all the specimens; on the other hand there was a relative increase of content for other elements despite the addition of $Y_2O_3-Al_2O_3$ except for the B content for the specimen NA hot pressed at

Table 1. Chemical Composition of the Specimens Hot Pressed at Different Temperatures

Specimen	C	N	B	Si	Total
1450 °C-ad	15.2 (1.03)	23.5 (0.97)	17.6 (1.01)	37.2 (1.02)	93.5
1450 °C-na	16.1 (1.03)	25.4 (0.98)	18.7 (1.01)	39 (1.01)	99.2
1550 °C-ad	14.8 (1.01)	22.9 (0.94)	17.3 (0.99)	36.5 (1.01)	91.5
1550 °C-na	15.7 (1.01)	25.5 (0.99)	17.5 (0.94)	38.1 (0.99)	96.8
1700 °C-ad	15.4 (1.05)	21.6 (0.89)	17.5 (1.00)	36.8 (1.01)	91.3
1700 °C-na	15.6 (1.00)	25 (0.97)	17.4 (0.94)	39.6 (1.03)	97.6
2000 °C-ad	15.1 (1.03)	22.3 (0.92)	17.7 (1.01)	37.1 (1.02)	92.2
2000 °C-na	16.7 (1.07)	22.2 (0.86)	19.8 (1.07)	41.2 (1.07)	99.9
Calculated-ad	15.47	24.06	18.57	36.16	94.26
Mixed	14.7	24.3	17.5	36.3	92.8
Powder-ad	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)

1550 and 1700°C.

Figure 4 shows the microstructures of the specimens hot pressed at 1700 and 2000°C. It can be seen that for the specimen NA, reaction has not been completed yet and reactants still remains at 1700°C (Fig. 4(a)). For the specimen AD

hot pressed at 2000°C, well-grown BN flakes can be easily distinguished, compared to the undistinguishable spherical fine SiC and BN particles of the specimen NA obtained at the same condition.

4. Discussion

According to the thermodynamic calculation and XRD analysis in our previous study, it has been suggested that the reaction sequence in the Si_3N_4 - B_4C -C system would be as follows:¹²⁾

However, the decomposition of Si_3N_4 :

will become intense with temperature rising, and at above 1488°C the reaction:

will also occur thermodynamically.

In Al_2O_3 - Y_2O_3 - SiO_2 system, the lowest eutectic temperature is 1380°C.¹³⁾ Further, the oxide phase composition, calculated from the Y_2O_3 - Al_2O_3 additive content and the oxygen content in Si_3N_4 is located in the sub-triangle of $\text{Y}_2\text{Si}_2\text{O}_7$ - Al_2O_3 - $\text{Al}_6\text{Si}_2\text{O}_{13}$ in the phase diagram of Al_2O_3 - Y_2O_3 - SiO_2 system and the eutectic temperature is 1450°C. As it can be seen from Fig. 1, there is no difference in the XRD patterns between the specimens AD and NA when the temperature is below 1200°C. However, at above 1450°C the phase formation rates of BN and SiC are much fast in the case of the specimen AD. Thus, a possible mechanism was proposed to explain this phenomenon. That is, it was suggested that the

Fig. 4. SEM fracture micrographs of the specimens hot pressed at 1700 and 2000°C (a) specimen NA at 1700°C, (b) specimen AD at 1700°C, (c) specimen NA at 2000°C, (d) specimen AD at 2000°C.

Fig. 5. Reaction sequences of the specimens with and without $Y_2O_3-Al_2O_3$ addition (specimens AD and NA).

formation of liquid phase based on $Al_2O_3-Y_2O_3-SiO_2$ system improved the reaction rate by enhancing the element diffusion rates of reactants. The schematic illustration of the reaction sequences is shown in Fig. 5. In the case of the specimen NA, the reaction and formation of SiC and BN could occur only at the contact points of the reactants because of the low diffusion of elements. However for the specimen AD, the elements of reactants could diffuse through the Y-Al-Si-O liquid phase and formed SiC and BN in a wide region and resulted in a rapid reaction rate. This liquid phase also improved the densification process (Fig. 2) and further reduced the diffusion distance at the same time. At higher temperatures than 1700°C, the re-crystallization and grain growth of the in situ formed fine SiC and BN particles at low temperatures have also been improved by the rapid diffusion through the liquid phase.

On the other hand, the formation of Y-Al-Si-O liquid phase seems to have enhanced the Reaction (4) at the same time and resulted in higher denitrication below 1700°C as can be seen from Fig. 3(a). For the specimen NA, however, because the reaction occurred mainly at higher temperatures than 1700°C and at this moment the decomposition of Si_3N_4 (Reaction (3)) became much intense, inversely higher denitrication than that of the specimen AD has been shown when hot pressed at 2000°C. Concerning the change of other elements after hot pressing, it is suggested that the main reason is that with the decrease of nitrogen content, content increase at some extent has been shown.

About the state of the Y-Al-Si-O liquid phase after cooling down from the hot pressing temperature, it is believed that part of this has crystallized to form a phase corresponding to the un-identified small peaks in the XRD pattern. Another part of this liquid phase may remain as amorphous phase located at the grain boundaries or triple junctions of the in situ composite.

According to the above results and discussion, it can be stated that the addition of $Y_2O_3-Al_2O_3$ additive has taken an important role in the phase formation, densification process and recrystallization of the in situ SiC-BN composites produced by the reaction between Si_3N_4 , B_4C and C. In addition, it is expected that by adjusting the amount of $Y_2O_3-Al_2O_3$ additive, or even by adding other additives, in situ SiC-BN composites can be fabricated by pressureless sintering process.

5. Conclusion

Addition of $Y_2O_3-Al_2O_3$ accelerated the reaction rate of the reaction among Si_3N_4 , B_4C and C for preparing SiC-BN composite. The reaction with $Y_2O_3-Al_2O_3$ addition (specimen AD) was completed after hot pressing at 1700°C and a dense material with well-crystallized SiC and flake-shaped BN grains was obtained when hot pressed at 2000°C. For the specimen without $Y_2O_3-Al_2O_3$ addition (NA), larger decrease in nitrogen content was shown because the reaction mainly occurred at higher temperatures than 1700°C at which Si_3N_4 became easy to decompose. The effects of the $Y_2O_3-Al_2O_3$ addition were attributed to the formation of Y-Al-Si-O liquid phase at temperatures higher than about 1450°C and the enhanced diffusion of elements of the reactants.

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