TECHNICAL REPORT

Preparation of textured B₄C compact with oriented pore-forming agent by slip casting under strong magnetic fieldShota AZUMA¹, Tetsuo UCHIKOSHI¹, Katsumi YOSHIDA² and Tohru. S. SUZUKI^{1,†}¹National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan²Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Control rods are one of the structural components in a nuclear reactor and are required to have a high functionality and reliability to provide a safe nuclear reactor. Random-oriented boron carbide (B₄C) is normally used as the control rods, but cracks are easily generated during the nuclear reaction because of volume swelling due to the accumulation of helium gas and nonhomogeneous thermal stress distribution during the neutron absorption reaction. In this study, we were able to control the crystalline orientation of the B₄C and align the tubal pores for controlling the thermal stress distribution and releasing the helium gas by controlling the dispersion of particles in a slurry and the rotation in a magnetic field.

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1. Introduction

Fast reactors are attracting attention as next-generation nuclear reactors^{1),2)} due to their advantages such as a stable supply of high-density energy, operational safety higher than that of light water reactors and reduction in the amount of radioactive waste. One of the crucial keys for effectively operating the fast reactor is the development of a neutron absorber with higher stability and longer lifespan than the current one, which enables long-term operation along with reducing the cost from the viewpoint of securing the safety of the reactor.

Pelletized boron carbide, B₄C, has many excellent advantages for neutron control rods such as high thermal stability, good mechanical properties, large neutron absorption cross-section, etc.³⁾⁻⁵⁾ It is also used as an applicative material for neutron absorbing in fast reactors.^{6),7)} The problem in prolonging the lifetime of the B₄C pellet material is that the thermal stress of the pellet induced by the enormous heat and alpha rays generated by the neutron absorption reaction, (n, α) reaction of formula (1), resulting in the swelling phenomena leading to its destruction.

In the former case, thermal stress relaxation and improvement in the thermal shock resistance are required by improving the thermal and mechanical properties of the

pellets.^{8),9)} The latter swelling causes internal stress of the pellets, causing not only damage, but also mechanical action to the cladding tube containing the pellets, which also causes cracks in the cladding tube. Pellets of conventional control materials have only a porosity of about 5 to 10%, therefore, those pores are basically closed pores without any directivity and cannot effectively release the helium gas accumulated inside the pellets. Promotion of gas release by making pellets having a higher porosity can be considered as an approach to solve the problem. However, in this method, it is considered that a porosity of 50% or more is required to form connecting holes capable of releasing the helium gas inside the pellet to the outside of the pellet. Such porous pellets inevitably have poor mechanical properties in exchange for their gas releasing ability, as well as the ¹⁰B content decreases, therefore, the neutron absorbing capacity also decreases. In other words, a material having a higher porosity than the conventional material is not preferable as a practical control material from the viewpoint of lowering these properties. Therefore, an ideal B₄C base control material should have good helium gas releasing property, while maintaining high density similar to the conventional material (porosity 5 to 10%) for high neutron absorption capacity, thermal and mechanical properties.

To overcome those apparently conflicting facts as previously mentioned, obtaining a high gas releasing property while maintaining a high density, porosification using the conventional procedure or compounding of different substances should be difficult. It can be achieved by precisely fabricating the microstructures of the dense B₄C matrix and gas permeable pores. We have proposed the following

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Fig. 1. Schematic image of the proposed method in this research for developing a novel type neutron absorber based on B₄C with highly controlled structure.

novel method for fabricating highly structure-ordered materials: Slip casting¹⁰⁾ of a binary suspension containing B₄C as the matrix and fibrous material as a pore-forming agent was done under a strong magnetic field generated by a superconducting magnet. The highly structure-ordered material described in this paper is composed of two different structures, which are open pores for the helium gas release and a dense solid phase composed of B₄C oriented in the *c*-axis direction as shown in Fig. 1. Based on this method, oriented pores for the helium gas release can be introduced in the B₄C matrix by controlling the orientation of the pore former using a strong magnetic field. Therefore, the helium releasing holes can be introduced with the porosity of about 5–10% which is a value similar to the typical materials. Likewise, by uniaxially orienting the crystal axis of the B₄C matrix by a strong magnetic field, not only the thermal and mechanical properties are improved,¹¹⁾ but also the diffusion direction of helium generated in the crystal by the (n, α) reaction can be controlled.^{9),12)} Therefore, the synergistic helium releasing effect, which cannot be realized by a mere Lotus root-structured material,¹³⁾ will be expected. It can significantly contribute to the prolongation of the life of the control material by improving the characteristics and imparting new functions.

In this study, preparation of a binary slurry for slip casting and the optimum conditions of the magnetic field applied during molding were investigated for preparing the B₄C control material with the ordered structure control by the above-mentioned strong magnetic field-assisted colloid process.

2. Experimental

Reagents used in this study were B₄C (HC STRCK, GRADE HS) as the base particles, Nylon 66 (N66, manufactured by Chubu Pile Industries, Ltd., nominal shape

Fig. 2. Response of N66 fiber dispersed in epoxy-resin to a rotating magnetic field (12T, 30 rpm); Inserted image in the figure shows as-received nylon66 fiber particle. The below scheme indicates relation between the direction of magnet field, sedimentation and rotation.

ϕ 10 $\times$ 300 μ m) as a pore former, polyethylene Imine (PEI, M_w : 10,000, Wako Pure Chemical Industries, Ltd.) and acetic acid (special grade, Nacalai Tesque) as the pH adjusting agent. A two-component slurry used for slip casting was prepared by the following two different described procedures: [Procedure 1] N66 powder (1 vol.%) of fiber was added to distilled water to which PEI (2 wt % versus the B₄C powder) and acetic acid were added, then irradiated with an ultrasonic homogenizer for 5 minutes to obtain a nylon slurry. Thereafter, B₄C powder (20 or 30 vol.%) was gradually added over 10 minutes while homogenizing with strong ultrasounds. [Procedure 2] 1 vol.% N66 powder was added to distilled water to which PEI (2 wt % vs. B₄C) was added, then mixed using a planetary mixer at 2,000 rpm for 5 minutes to obtain a nylon slurry. Thereafter, the B₄C powder (20 vol.%) was added and dispersed using the planetary mixer again. Finally, the slurry was irradiated using an ultrasonic homogenizer for 10 minutes. The pH of the obtained binary slurries was adjusted to 6 by adding acetic acid.

The viscosity of the formulated slurries was characterized by a rotational viscometer (Model R215, TOKI Sangyo). Consolidation of the slurries was performed by slip casting on a turntable placed at the center of a horizontally-placed 12 T magnetic field. After the slurry was poured into a porous alumina mold, the stage was kept turning at various conditions until a consolidated cake was formed.¹¹⁾

3. Results and discussion

Figure 2 shows the response of the N66 fiber substances to a rotating magnetic field. The short fibers are

Fig. 3. Relationship between viscosity and time for the slurries with B₄C and nylon fabricated via ultrasonication (U.S.) and planetary mixing (P.M.); temperature is 30°C and speed of corn rotator is 0.5 rpm.

oriented in the vertical direction in the rotating magnetic field. This result suggests that orientation of the pore-forming agents with a high aspect ratio should be advantageous for introducing connecting pores. Application of a rotating magnetic field also produces a *c*-axis orientation of the B₄C. This result suggests that a *c*-axis oriented B₄C green body in which vertically-oriented nylon fibers are uniformly distributed can be obtained using a rotating magnetic field.

Figure 3 shows the relationship between the viscosity and time for the blended slurries containing B₄C and N 66. In the slurry prepared by Procedure 1 and having a 30 vol.% solid concentration, the drastic increase in the viscosity with time, the so-called thixotropic property, is observed, suggesting quick occurrence of a strong aggregation of the particles. This tendency was observed for a slurry containing only B₄C; therefore, we thought that this phenomenon might be useful for the quick fixing of the oriented nylon fibers in the B₄C matrix. In the slurry prepared by Procedure 1 and having a 20 vol.% solids concentration, the thixotropic property was not observed. The viscosity of the slurries prepared by Procedure 2 is much lower than that of the slurries prepared by Procedure 1, the so-called Newtonian property, as shown in Fig. 3.

Figure 4 shows the fracture surface parallel to the magnetic field and X-ray diffraction (XRD) patterns for the top (RT) and side (RS) surfaces of the B₄C green body obtained by slip casting of a binary slurry prepared by Procedure 1 and having a 30 vol.% solids concentration under a rotating magnetic field (12 T, 30 rpm). The distribution of N66 in the green body was uniform; however, the N66 orientation was not obviously observed and the orientation index f_{L003} , calculated using formula (2), of the B₄C matrix phase was 0.30.

$$f_{L003} = \frac{P - P_0}{1 - P_0} \quad (2)$$

where the values of P were calculated from the intensities of the surface perpendicular to the rotating plane, and the

Fig. 4. XRD patterns for the top (RT) and side (RS) surfaces of B₄C green body obtained by slip casting of binary slurry prepared by Procedure 1 and having a 30 vol.% solids concentration under a rotating magnetic field (12 T, 30 rpm). The diffraction intensity reported for typical B₄C is also shown as a reference. f_{L003} was calculated by formula (2). The inserted image is the fracture cross-section of the specimen.

value of P_0 was calculated from the ICDD No. 00-035-0798 by the formula (3).

$$P = \frac{\sum I(00l)}{\sum I(hkl)} \quad (3)$$

Since f_{L003} was 0.58 in the oriented compacts of B₄C without any nylon addition, the uniaxial orientation of the B₄C matrix also obviously decreased. This result is probably due to the higher solids concentration, i.e., the higher slurry viscosity, the lower the magnetic field responsiveness of each component.

Figure 5 shows the fracture surfaces of the B₄C green body with nylon obtained by slip casting of the binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T 30 rpm). The vertical orientation of the fiber was observed, however, the distribution of the fiber was nonuniform due to segregation. The density of Nylon is 1.12 which is slightly higher than that of water, and the vertically-oriented nylon could go down into the mix; however, a lot of nylon fibers were segregated at the top of the green cake.

Figure 6 shows the fracture surface parallel to the magnetic field in the B₄C green body with nylon obtained by slip casting on a turntable (30 rpm) of the binary slurry prepared by Procedure 1 having a 20 vol.% solids concentration without a magnetic field. It was revealed that the segregation of N66 is independent of the magnetic field application and occurs by rotation of the sample.

Fig. 5. Fracture surface parallel to the magnetic field in the B_4C green body with nylon obtained by slip casting of binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12T 30 rpm); (b) is magnified image of nylon fiber particle deposited on top surface of the B_4C green body in (a).

The segregation is known as a phenomenon in which the components in the powder mixture are separated by applying a mechanical force, such as vibration, etc., to the mixture powder including a different ratio of particle size and specific gravity.¹⁴⁾ This phenomenon could be observed in a binary slurry employed as slip-casted media.

Figure 7 shows the fracture surface parallel to the magnetic field and XRD patterns for the top (RT) and side (RS) surfaces of the B_4C green body obtained by slip casting of the binary slurry prepared by Procedure 1 and having a 20 vol.% solid concentration under a rotating magnetic field (12 T, 30 rpm) for 30 minutes followed by a static magnetic field (12 T, 0 rpm). The time of 30 minutes was selected that was confirmed to be a sufficient time to ensure the particles' orientation in our previous experi-

Fig. 6. (a) Fracture surface parallel to the magnetic field in the B_4C green body with nylon obtained by slip casting on a turntable (30 rpm) of binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration without magnetic field; (b) the fracture surface of the B_4C green body without rotation outside of a magnetic field (0 T, 0 rpm).

Fig. 7. XRD patterns for the top (RT) and side (RS) surfaces of B_4C green body obtained by slip casting of binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 30 rpm) for 30 minutes followed by static magnetic field (12 T, 0 rpm). The inserted image is the fracture surface parallel to the magnetic field.

Fig. 8. XRD patterns for the top (RT) and side (RS) surfaces of B₄C green body obtained by slip casting of binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 20 rpm) for 15 minutes followed by rotation at 1 rpm in the horizontal magnetic field (12 T). The inserted image is the fracture surface parallel to the magnetic field.

Fig. 9. XRD patterns for the top (RT) and side (RS) surfaces of B₄C green body obtained by slip casting of binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The inserted image is the fracture surface parallel to the magnetic field.

ences. The N66 distribution was uniform; however, the degree of orientation of the matrix phase was lower ($f_{L003} = 0.48$) than that of B₄C without N66.

Figure 8 shows the fracture surface parallel to the magnetic field and XRD patterns for the top (RT) and side (RS) surfaces of the B₄C green body obtained by slip casting of the binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 20 rpm) for 15 minutes followed by rotation at 1 rpm in the horizontal magnetic field (12 T). The N66 distribution was uniform, and the degree of orientation in the B₄C matrix was higher ($f_{L003} = 0.73$).

Figure 9 shows the fracture surface parallel to the magnetic field and XRD patterns for the top (RT) and side (RS) surfaces of the B₄C green body obtained by slip casting of the binary slurry prepared by Procedure 1 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The N66 distribution was uniform, and the degree of orientation in the B₄C matrix was the highest ($f_{L003} = 0.77$).

For Figs. 7–9, the *c*-axis orientation of B₄C was achieved, however, the degree of orientation of the N66 fibers was insufficient. In order to increase the degree of the N66 fiber alignment, enhancement of the N66 dispersion in a slurry was considered to be necessary.

Figure 10 shows the fracture surface and XRD patterns for the top (RT) and side (RS) surfaces of the B₄C green

Fig. 10. XRD patterns for the top (RT) and side (RS) surfaces of B₄C green body obtained by slip-casting of binary slurry prepared by Procedure 2 and having a 30 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The inserted image is the fracture surface parallel to the magnetic field.

Fig. 11. XRD patterns for the top (RT) and side (RS) surfaces of B_4C green body obtained by slip casting of binary slurry prepared by Procedure 2 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The inserted image is the fracture surface parallel to the magnetic field.

body obtained by slip-casting of the binary slurry prepared by Procedure 2 and having a 30 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The degrees of orientation of both B_4C and N66 were lower than that of the sample with the 20 vol.% of solids content prepared by Procedure 1.

Figure 11 shows the fracture surface parallel to the magnetic field and XRD patterns for the top (RT) and side (RS) surfaces of the B_4C green body obtained by slip casting of the binary slurry prepared by Procedure 2 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm). The orientation of B_4C $f_{L003} = 0.77$ was sufficient compared to the sample prepared by Procedure 1, but a strong segregation of the nylon fibers was observed. In order to suppress this segregation, the period of the rotating magnetic field was restricted, but the static horizontal magnetic field was still continuously applied.

Figure 12 shows the fracture surface parallel to the magnetic field and XRD patterns for the top (RT) and side (RS) surfaces of the B_4C green body obtained by slip casting of the binary slurry prepared by Procedure 2 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm) for 30 minutes followed by placement in the static magnetic field without rotation. A uniform dispersion of N66 and excellent alignment were observed. This result indicated that the planetary cen-

Fig. 12. XRD patterns for the top (RT) and side (RS) surfaces of B_4C green body obtained by slip casting of binary slurry prepared by Procedure 2 and having a 20 vol.% solids concentration under a rotating magnetic field (12 T, 1 rpm) for 30 minutes followed by applying in the horizontal static magnetic field (12 T). The inserted image is the fracture surface parallel to the magnetic field.

trifugal mixer is efficiently utilized for the dispersion of both the B_4C particles and N66 short fiber to enhance the degree of orientation. For introducing tubal pores into the B_4C body with the porosity of about 5 to 10%, the co-oriented green body as shown in Fig. 12 could be expected due to the alignment of the fiber particles with a high aspect ratio compared with a green body with a random orientation, such as shown Fig. 6, prepared via conventional colloidal processing. A sintered B_4C material can be obtained from a green body via burnout of the N66 followed by sintering. The highly structure-ordered materials described in the introduction could be achieved from the co-oriented compact obtained by the suggested process in this study.

4. Conclusions

A significant difference in the slurry viscosity occurs depending on the preparation method and the conditions of the binary dispersion slurry used for slip casting, particularly the solid concentration of the slurry. By adjusting the solid content concentration to about 20 vol.%, using a planetary centrifugal mixer and the 1 rpm rotation speed of the sample for 30 minutes followed by placement in a under 12 T magnetic field, co-orientation of the B_4C matrix particles and the Nylon pore former can be achieved.

Separation of each component becomes significant by slip casting under the application of a rotating magnetic field depending on the components of the slurry.

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