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CERAMIC PROCESSING OF BORON NITRIDE INSULATORS*

C. S. Morgan and R. W. McCulloch

Oak Ridge National Laboratory

Oak Ridge, Tennessee 37830

INTRODUCTION

Fuel pin simulators (FPS), an example of which is shown in Fig. 1, are the prime elements of several test facilities at the Oak Ridge National Laboratory (ORNL). These experimental facilities are used to conduct out-of-reactor thermal-hydraulic and mechanical interaction safety tests for both light-water and breeder reactor programs. The FPS units simulate the geometry, heat flux profiles, and operational capabilities of a reactor core element under steady-state and transient conditions. They are subjected to temperatures as high as 1600°C (2900°F) and power levels as high as 57.5 kW/m (17.5 kW/ft) as well as severe thermal stresses during transient tests.

The insulating material in the narrow annulus between the heating coil and the FPS sheath is subjected to very rigorous conditions. Accuracy of the reactor safety test information and validity of the test data depend on the heat flux uniformity under all test conditions and on the reliable operation of all fuel pin simulators and their internal thermocouples. Boron nitride (BN), because of its high degree of chemical inertness combined with its relatively unique properties of high thermal conductivity and low electrical conductivity, is the most suitable insulating material for FPS. The important BN properties, thermal conductivity and electrical resistance, are strongly influenced by crystallite orientation and by impurities. This article describes new BN powder processing techniques, which optimize these properties. First prior methods of preparing BN-insulated FPS are described.

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Fig. 1. Fuel Pin Simulator, Showing Boron Nitride Insulation.

PRIOR METHOD OF FABRICATING BN INSULATED FPS

The common technique of FPS manufacture involves introducing powder into the annular area, tamping to a predetermined density, and swaging to final density. The final density and annular thermal conductivity are fixed by the initial filling density, the amount of swaging, and the orientation of BN platelets. Nonuniformity in the density of the BN and heating element eccentricity are easily introduced by powder tamping and filling variations, tool tolerances, and possible operator errors. In addition, tool wear introduces metal particles into the BN, often causing failure of a unit by short circuiting when voltage is applied. Further, crystallographic orientation of BN, the importance of which is described below, was found to be very unfavorable in powder filled and swaged FPS.

BORON NITRIDE

The crystal structure of BN, which is shown in Fig. 2, resembles that of graphite except that the hexagonal arrays are directly aligned.¹ In the crystallographic a direction BN has the highest thermal conductivity of any known electrical insulator, while the thermal conductivity in the c direction is only 0.025 of this amount. It is evident, therefore, that crystallite orientation is of great importance. The degree of preferred orientation; that is, a direction parallel to the radial direction in the FPS, can be determined by measurement of the x-ray diffraction intensity from the hexagonal planes and from the (100) planes.

Fig. 2. Crystal Structure of Boron Nitride with Dimensions of the Hexagonal Cell.

Samples of as-received BN powders had a measured intensity ratio close to the ASTM standard value for a randomly oriented BN powder of $I_{0002}/I_{100} = 100/17 = 5.88$. Intensity ratios much greater than 5.88 are desired in order to have more favorable heat transfer properties in FPS. Ratios as unfavorable as $100/57 = 1.75$ were found in FPS prepared by filling with BN powders. Greatly improved orientations, e.g., as high as $100/0.4 = 250$ can be obtained in pressed BN forms.

A number of BN powders are commercially available, but this investigation was centered on two types of BN powders produced by Union Carbide Corporation: HC¹ and TS-1325. The first is a high-purity, hot-pressed and ground powder with a tap density of approximately 1 Mg/m^3 (45% of theoretical density) and a particle size distribution ranging from below $10 \text{ }\mu\text{m}$ to agglomerates of $350 \text{ }\mu\text{m}$. The other is a high-purity powder with a tap density of about 0.65 Mg/m^3 (30% of theoretical density) but with a wider particle size distribution ($\approx 1 \text{ mm}$ to $7 \text{ }\mu\text{m}$) and a higher percentage of small particles. Both powders, as received, had oxygen contents from 0.1 to 0.3 wt % and carbon contents from 0.04 to 0.1 wt %.

Even though the received powders were purer than 99.5%, both contained small amounts of metal and other electrically conducting impurities dispersed as small particles. These impurity particles are potentially detrimental to FPS operation since they can provide shorting paths in the insulated gap between the heating element and sheath wall. This distance is small, being about 0.5 mm over lengths as long as 2.15 m. The metallic particle content of the powders was reduced by about 90% by magnetic separation performed by Magnetic Engineering Associates, Inc., Cambridge, Massachusetts. The TS-1325 powder was further cleaned before use by sieving out larger particle aggregates and separating visibly contaminated particles.

ORIENTATION IMPROVEMENT

The basic improvement in crystallite orientation is obtained in the preform pressing step, as platelets tend to become oriented with the hexagonal plane perpendicular to the pressing direction. Further improved preferred orientation during pressing was obtained by reducing the particle size of the BN powder. The as-received powder, after being cleaned to remove metallic particles, was ball-milled overnight in hexane in a ceramic mill using alumina balls. The ball milling served primarily to break up aggregates. For instance, in the case of TS-1325 powder, which had a smaller initial particle size than the HCM powder, the average particle size after milling overnight was reduced only about 1 to 7 μm , as determined with a Coulter Counter.* However, the fraction of this powder passing a 100-mesh screen (149- μm openings) increased from 35% to essentially 100%. Diffraction data obtained on preforms pressed from this ball-milled powder showed intensity ratios of $100/0.4 = 250$ compared with $100/1.1 = 91$ on preforms pressed from as-received TS-1325 powder and $100/4 = 25$ from as-received HCM powder.

Thermal conductivity measurements on the cold-pressed preforms have not yet been obtained, but enhanced radial thermal conductivity due to the preferred orientation is evident by qualitative room-temperature measurements. Since BN purity is of such paramount concern, great care was taken to keep fibers and lint out of the powder during handling. Use of ball-milling suspension agents such as ethyl alcohol was avoided because traces of water in these liquids resulted in unacceptable oxidation of the BN powders.

APPLICATION OF LUBRICANTS AND PREPRESSING

Although BN preforms can be pressed without lubricating additives, die life, initial preform density, and density uniformity are much improved by use of a lubricant because of the reduced friction. In addition, automatic production, needed to produce the required thousands of pellets for FPS production, is not possible without lubricants. Lubricants can be added either into the powder or on the die surface. Both methods have been used successfully, with the latter method preferred because it attains higher density in the finished preform. However, only the former technique has been fully developed, so the discussion will be limited to the use of lubricants in the powder.

Lubricants, dissolved in hexane, are added to a thick hexane slurry of the BN powder. The mixture is allowed to evaporate, with occasional stirring to ensure that the lubricant is distributed

*Registered trademark of Coulter Electronics, Inc., Hialeah, Florida.

homogeneously on the particle surfaces. Many organic compounds were tested, and nearly all gave some improvement in powder pressability. However, two additional factors must be considered. The final strength after lubricants have been removed must be adequate for preform handling during loading of FPS, and the preform density, which is usually reduced as the lubricant is removed, must be as high as possible for good thermal conductivity. The most suitable lubricant was determined to be a composite consisting of 0.5 wt % (based on the weight of BN) dodecane plus 0.5 wt % dodecanol. Amyl alcohol at a concentration of 4 wt % was also an effective lubricant but was more difficult to work with because of its higher volatility. Camphor, although not an optimum lubricant for die operation, produced preforms with the highest final density and strength.

BN powders were prepressed and sieved to obtain a particle size range that would flow into the die and to obtain higher powder density in the die. Prepressing was carried out in 100-g batches at a pressure of 34.5 MPa (5000 psi). After granulation the powders were sieved to obtain a -30 +100 mesh fraction. The presence of lubricants in the powder facilitated preparation of sized powder with desirable flow characteristics by strengthening prepressed aggregates.

PREFORM PRESSING AND PURIFICATION

The prepared BN powder was pressed into tubular shapes that fit the annular gap of fuel pin simulators. Solid cylindrical pellets were also pressed to fill the volume inside the coiled FPS heating elements (Fig. 1). Typical length to wall thickness ratio of tubular preforms was about 12.5 and the length to diameter ratio of solid and tubular preforms was about 4.0. Density, before purification, was about 1.91 Mg/m³ for pressing pressures of 310 MPa (45 ksi). Axial density variation was less than 2% with suitably prepared powders.

After pressing, preforms were put in a vacuum oven for several days with the temperature slowly raised to 200°C to remove the bulk of lubricating additives. Purification was completed by treating the preforms in anhydrous ammonia at 930°C for a minimum of 8 hr. For example the anhydrous ammonia treatment reduced the oxygen content from 810 to 225 ppm and carbon from 471 to 100 ppm. The final oxygen and carbon levels were equivalent to or lower than the initial values of magnetically cleaned BN powder. High-temperature electrical conductivity tests of FPS have yielded typical values of 10⁴ Ω-m at 1200°C.

Figure 3 shows a group of as-pressed preforms. Purified preforms were weaker than as-pressed preforms but were sufficiently strong for fabrication of FPS. Removal of lubricating additives

Fig. 3. Boron Nitride Preforms Prepared for Installation in an FPS.

tended to reduce the density of preforms, apparently by allowing or causing the particle structure to relax. Typically the density decreased 8 to 10% for preforms in which the additives were 0.5 wt % dodecane plus 0.5 wt % dodecanol or amyl alcohol. The density loss was much greater with use of some additives, such as stearic acid, and was less for camphor. Outside diameter increases of about 3% accompanied the 8 to 10% density decrease. Crystallographic orientation of preforms was not significantly affected by lubricants or by their removal.

PREFORMED FPS FABRICATION

The BN preforms are grooved, if necessary to accommodate thermocouples, and are individually inserted and crushed to assure complete filling of the FPS annular volume. Crushing moderately reduces the degree of preferred orientation. For example, in one test the I_{0002}/I_{100} value changed from $100/1 = 100$ to $100/3 = 33$. Swaging of the assembled FPS, which is needed to improve thermal contact of the BN with the FPS sheath and heating element, results in further reduction of preferred orientation. With respect to thermal conductivity, this is offset by the density increase due to swaging. The overall effect of density increase accompanied by reduction in preferred orientation on thermal conductivity has not yet been determined. However, since initial orientation is higher with preforms than with powder and the amount of swaging required is reduced significantly because of higher initial BN density of preforms, better orientation and increased thermal conductivity should result.

The use of preforms affords several advantages in production of FPS units in addition to preferred crystallographic orientation. Typical preform lengths are about 10 mm, so that preform filling is much simpler and quicker than powder filling. In addition, metal spalling from tamping tools is practically eliminated, the chance of introducing other fabrication impurities is reduced, and heating element eccentricity (now determined by preform dimensions) is typically too small to measure by standard gaging. The reduced swaging required results in less heating element and thermocouple distortion and improved dimensional tolerances.

Infrared scans were used to evaluate the effect of annular BN density uniformity and thermal conductivity on the uniformity of the heat flux profile of FPS. Figure 4 shows infrared scans after transient power application to the cladding for two FPS, where one is powder filled and one is preform filled. Since the heat generation in the sheath is uniform, infrared readings vary axially only as a result of thermal conductivity and density variations across the insulation (including conductivity of interfaces). The nearly flat temperature profile of the scan of the preform-filled FPS attests to the uniformity of the insulation. By comparison the insulation uniformity afforded by powder packing is distinctly inferior.

Fig. 4. Infrared Scans of Two FPS After a Transient Cladding Current. (a) Preform filled. (b) Powder filled.

CONCLUSION

The use of boron nitride preforms with preferred crystallite orientation, while relatively new, promises better control of FPS fabrication and critical properties affecting FPS operation. The

increased accuracy and reliability needed of FPS units operating under severe test conditions can more realistically be met by this boron nitride fabrication method.

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