*Journal of the European Ceramic Society* **5** (1989) 3–9

*State of the Art*

# Hexagonal Boron Nitride: Fabrication, Properties and Applications*

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(Received 12 October 1987; revised version received 31 May 1988; accepted 5 June 1988)

**Abstract**

*The production methods for α-BN powders and dense shapes, their physical and chemical properties, industrial uses and potentialities are reviewed.*

*Der Artikel ist ein vergleichender Überblick über α-BN, einschließlich der Herstellung, Eigenschaften und Anwendungen.*

*Les méthodes de production de poudres et de frittés de BN-α, leurs propriétés physiques et chimiques, leurs utilisations industrielles et leurs potentialités sont passées en revue.*

## 1 Introduction

The elements boron and nitrogen, both neighbours to carbon in the periodic table, mutually form 1:1 compounds which are isostructural to the polymorphs of carbon:

α-BN: Hexagonal modification with a layered structure (see Fig. 1) similar to graphite, sometimes called 'white graphite' (theoretical density: 2·27 g cm$^{-3}$);
β-BN: High pressure diamond-like modification with cubic zinc blende structure (theoretical density: 3·48 g cm$^{-3}$);
γ-BN: dense hexagonal modification with wurtzite structure (theoretical density: 3·48 g cm$^{-3}$).

This paper represents a comprehensive review of α-BN including fabrication, properties and uses. For information about the more dense β- and γ-boron nitride modifications the reader is referred to the literature.[1–3]

## 2 Fabrication of α-BN Powder

Hexagonal α-BN was prepared for the first time by Balmain[4,5] in the mid-19th century. It remained a laboratory curiosity until the middle of the current century, when hot-pressed α-BN shapes were made for the first time.[6] Although quite a number of general methods for the preparation of α-BN powder are known,[7,8] three main reactions have found practical application on an industrial scale:

(1) Reaction of boric oxide with ammonia in the presence of a filler material (i.e. tricalcium orthophosphate):

$$B_2O_3 + 2\,NH_3 \xrightarrow{900^\circ C} 2BN + 3H_2O$$

A second heat treatment for purification and crystallization is performed at >1500°C under $N_2$.

(2) Reaction of boric oxide (or borax) with organic nitrogen compounds (i.e. urea, melamine):

$$B_2O_3 + CO(NH_2)_2 \xrightarrow{>1000^\circ C} 2BN + CO_2 + 2H_2O$$

(3) Nitridation of calcium hexaboride in the presence of boric oxide:

$$3CaB_6 + B_2O_3 + 10N_2 \xrightarrow{>1500^\circ C} 20BN + 3\,CaO$$

By the methods (1) and (3) usually crystalline α-BN is obtained in the form of hexagonal-shaped platelets about 0·1–0·5 μm thick and 1–10 μm wide (Fig. 2). However, method (2) can result in the formation of a 'turbostratic' boron nitride, whose hexagonal structure is characterized by a partial or complete absence of three-dimensional order among its lamellae.[9,10]

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* This paper was presented at the *9th International Symposium on Boron, Borides and Related Compounds*, Duisburg, 21–25 Sept. 1987.

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*Journal of the European Ceramic Society* 0955-2219/89/$3.50

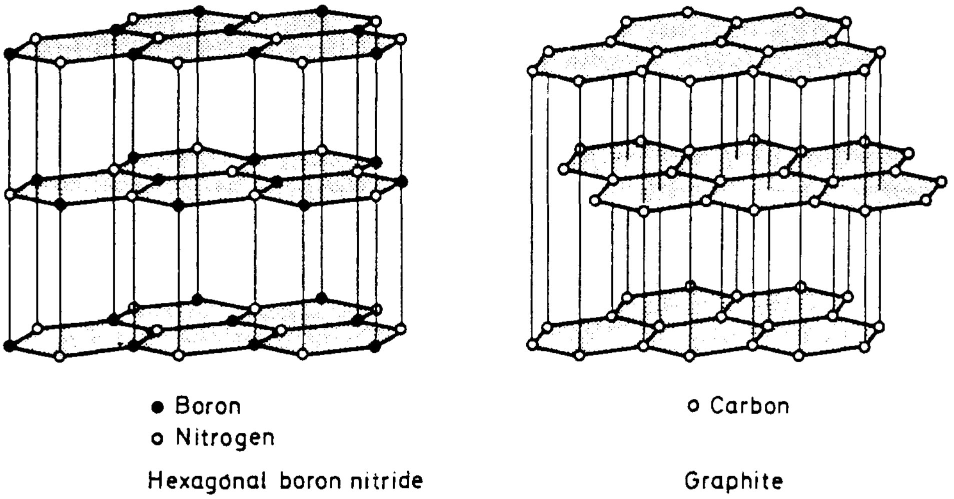

**Fig. 1.** Crystal structures of hexagonal boron nitride (α-BN) and graphite.

## 3 Production of Dense α-BN Shapes

Dense shapes of α-BN are produced by:

(1) Axial hot pressing (HP)[6] or hot isostatic pressing (HIP)[11] of fine powders. The resulting billets can be easily machined with standard tools to various sizes. Depending on the particular process and the purity of the raw BN powder, densities of 2·0–2·2 g cm$^{-3}$, corresponding to 88–97% of the theoretical density, can be obtained. The main impurity in boron nitride powder is boric oxide ($B_2O_3$), which is hygroscopic and is mostly converted into boric acid. Some of the oxygen content also appears as amorphous boron oxynitride. The boron–oxygen compounds act as sintering aids during the hot-pressing process. The hot pressing is done in graphite molds under vertical die pressure at high temperatures up to 2000°C. Because of higher pressure and omnidirectional force, hot isostatic pressing requires less sintering aids ($B_2O_3$) for compression and the fabricated part has a very fine grain structure with isotropic properties. The compression is done at temperatures of approximately 1500°C in metal or glass containment vessels applying gas pressure up to 200 MPa.

(2) Pyrolysis of a boron trichloride–ammonia reaction mixture, $BCl_3 + NH_3 = BN + 3\,HCl$, on a graphite substrate upon which the α-BN is deposited. Pyrolytic BN,

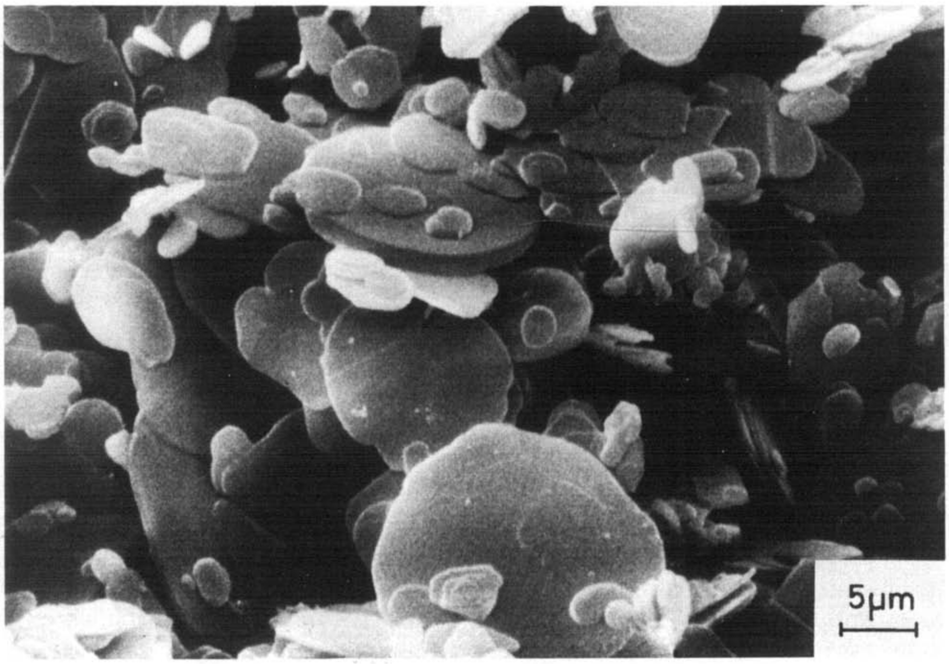

**Fig. 2.** SEM of α-BN powder showing plate-like particles.

although >99% pure, pore-free, dense and impervious to helium, displays a high degree of anisotropy, because the *a*-direction layer planes of the hexagonal structure deposit parallel to the substrate surface.[12] The chemical vapour deposition (CVD) process is very costly and only allows the production of thin-walled parts. A laboratory preparation yielding very pure deposits is effected by pyrolysis of boron trichlorborazine, $B_3N_3H_3Cl_3$.[13]

α-BN had been fabricated in the form of fibres,[14] thin films[15] and multidimensional fibre infiltrated BN–BN composites.[16] However, these products are no longer available today.

## 4 Properties of α-BN

Hexagonal α-BN is being used increasingly because of its unique combination of properties which include a low density ($2·27\,g\,cm^{-3}$ theoretical density), high temperature stability (melting point near 2600°C), chemical inertness (corrosion resistance against acids and molten metals), stability in air up to 1000°C (in argon gas atmosphere up to 2200°C and in $N_2$ up to 2400°C), stability to thermal shock, easy workability of hot-pressed shapes, excellent electrical insulating character as well as very high thermal conductivity. As a thermal conductor, BN ranks with stainless steel at cryogenic temperatures and with beryllium oxide, BeO, at elevated conditions; above 700°C, the thermal conductivity of α-BN exceeds that of toxic BeO.

Of particular interest are its good dielectric properties (dielectric constant is 4, i.e. half of that of α-$Al_2O_3$, also high dielectric strength; see Table 1) and its ability to lubricate over a wide range of temperatures. Its small coefficient of friction is retained up to 900°C, whereas other solid lubricants like graphite and molybdenum disulphide are burnt away at lower temperatures.[17] Because of its high temperature stability and inertness against carbon and carbon monoxide up to 1800°C it is as a refractory ceramic superior to the nitride ceramics $Si_3N_4$ and AlN, and the oxide ceramics MgO, CaO, $ZrO_2$. Due to its non-wetting properties it is stable to attack by molten glass, molten silicon, boron, nonoxidizing slags, molten salts (borax, cryolite) and reactive metal melts (e.g. Al, Fe, Cu, Zn). Because of its poor sinterability, dense shapes of α-BN are obtained almost exclusively by hot pressing; typical properties of axial and isostatic hot-pressed BN are summarized in Table 1.

It must be recognized that most chemical and physical properties of axial hot-pressed BN shapes depend on the nature and the amount of additives used for densification (up to 6 wt% $B_2O_3$, metal borates or $SiO_2$).[2] Further, some thermal (coefficient of expansion, thermal conductivity) and mechanical (flexural strength, Young's modulus) property values vary according to the direction of hot pressing, BN being similar to graphite in respect of anisotropy. By hot pressing isostatic of canned BN-powder, theoretically dense and pure α-BN shapes without texture (isotropic) and with improved properties (see Table 1) can nowadays be obtained.[11]

The high content of $B_2O_3$, the axial pressure and the high temperature are responsible for the orientation of the hexagonal crystals and the grain growth during the hot-pressing process (Fig. 3). Owing to isostatic pressure during hot isostatic pressing (hipping), no orientation of the BN crystals occurs and, at the same time, because of the lower

**Table 1.** Physical properties of hot-pressed α-BN

| *Property* | | *HP-BN* *(6·0 wt% $B_2O_3$)* | *HP-BN* *(1·7 wt% $B_2O_3$)* | *HIP-BN* *(0·1 wt% $B_2O_3$)* |
|---|---|---|---|---|
| Sintered density, $g\,cm^{-3}$ | | 2·1 | 2·0 | 2·2 |
| Flexural strength, MPa (4-point bend) | 25°C | $115 \perp 50 \parallel$ | $95 \perp 70 \parallel$ | 60 |
| | 1000°C | $20 \perp 10 \parallel$ | $35 \perp 20 \parallel$ | 45 |
| Young's modulus, GPa | 25°C | $68 \perp 44 \parallel$ | $72 \perp 35 \parallel$ | 32 |
| Thermal conductivity, $Wm^{-1}\,K^{-1}$ | 25°C | $55 \perp 50 \parallel$ | $48 \perp 43 \parallel$ | 50 |
| | 1000°C | $28 \perp 24 \parallel$ | $28 \perp 24 \parallel$ | 20 |
| Coefficient of linear expansion, $K^{-1}$ | 20–1000°C | $1·1 \times 10^{-6} \perp$<br>$8·6 \times 10^{-6} \parallel$ | $1 \times 10^{-6} \perp$<br>$8·4 \times 10^{-6} \parallel$ | $4·4 \times 10^{-6}$ |
| Electrical resistivity, Ω cm | 25°C | $9·3 \times 10^{10}$ | $4·9 \times 10^{12}$ | $6·3 \times 10^{13}$ |
| | 1000°C | | $10^7$ | $10^8$ |
| Dielectric constant | 25°C | 4·6 | 4·0 | 5·4 |
| Loss factor, tan δ (100 kHz, 1 V) | 25°C | $3 \times 10^{-4}$ | $3 \times 10^{-4}$ | $3 \times 10^{-4}$ |

The mechanical and thermal properties of hot-pressed BN (HP-BN) are anisotropic—they differ when measured perpendicular (⊥) and parallel (∥) to the pressing axis. On the other hand, these same properties are isotropic for hot isostatic pressed BN (HIP-BN).

**Fig. 3.** Microstructure of HP–BN.

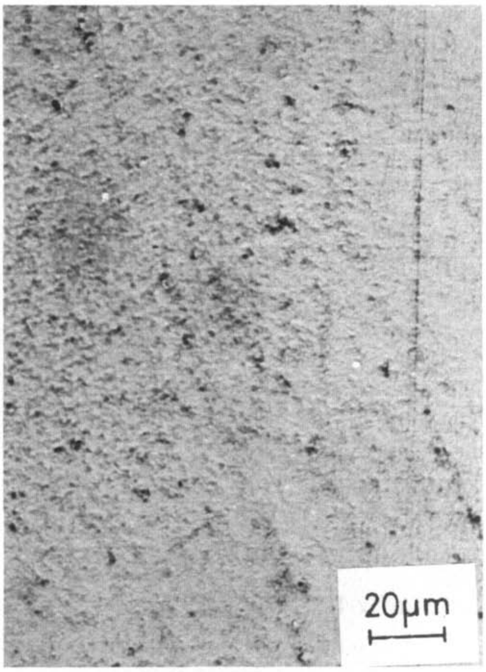

**Fig. 4.** Microstructure of HIP–BN.

temperatures and the lower proportion of liquid phase ($<0{\cdot}5$ wt% $B_2O_3$), grain growth is suppressed and a fine-grained microstructure results (Fig. 4).

Boron nitride is inert to reaction with most other ceramic materials, and it is possible to produce mixed ceramic composites (O–BN, SC–BN and A–BN compositions, see Table 2) to obtain special properties. Materials that are harder, more wear and/or corrosion resistant, and with other unique mechanical and electrical properties can be tailor-made for many applications.

In Table 2 the mechanical and thermal properties for various hot-pressed BN-based ceramic composites are compared with those of dense single-phase HIP-BN. These materials have been developed for use in horizontal continuous casting of steels.

## 5 Applications

The many uses for α-BN powder and hot-pressed shapes are summarized in Table 3, which includes a classification on specific properties. The increasing application of α-BN hot-pressed shapes is due to the unique combination of the following properties:

High temperature refractoriness;
chemical inertness and non-wetting property;
high thermal conductivity;
excellent thermal shock resistance;
insulator of electricity;
ease of machining.

As can be seen from Table 3, α-BN has established itself in the various fields of chemistry, metallurgy, high-temperature technology, electrotechnology and electronics. Granulated α-BN powders[18] of high bulk density (up to 0·8 g cm$^{-3}$) are applied as a filler for silicone rubber, insulation medium for heating wires (immersion tube heaters) and separators for high temperature lithium–sulphur batteries. α-BN powder is also available in the form of aqueous coating suspensions and as a handy aerosol spray. In the following, a few examples of the uses for α-BN hot-pressed shapes are described in detail.

**Table 2.** Mechanical and thermal properties of HIP-BN and boron nitride composites

| *Property* | *HIP-BN* | *O-BN* | *SC-BN* | *A-BN* |
|---|---|---|---|---|
| Flexural strength, MPa (4-point bend) 25°C | 60 | 77 | 142 | 48 |
| Knoop hardness (HK-0·1) 25°C | 29 | 410 | 330 | 230 |
| Young's modulus, GPa 25°C | 32 | 54 | 83 | 36 |
| Thermal conductivity, W m$^{-1}$ K$^{-1}$ 25°C | 50 | 50 | 25 | 55 |
| 1 000°C | 20 | 18 | 13 | 18 |
| Coefficient of linear expansion, 10$^{-6}$ K$^{-1}$ 20–1000°C | 4·1 | 5·0 | 1·2 | 5·0 |

Grades O–BN, SC–BN and A–BN are composites that contain 30 wt% $ZrO_2$, SiC and AlN, respectively.

**Table 3.** Uses and potential uses of α-boron nitride

| *Use* | *Property desired* | | | | | |
|---|---|---|---|---|---|---|
| | *R* | *T* | *E* | *I* | *L* | *M* |
| α-BN powder | | | | | | |
| Solid lubricant for high-temperature bearings | + | | | | + | |
| Mould release for die casting of glass and metals | + | | | + | + | |
| Active filler for rubber, resin and plastics | + | + | + | + | + | |
| Additive to oils and high-temperature grease | | | | + | + | |
| Ultrahigh-pressure transmitting agent | + | | | + | + | |
| Coatings for evaporation plants, as parting agent for deposited metal films | + | | | + | | |
| Coating for graphite hot-pressing moulds | + | | | + | + | |
| Embedding medium for heating wires | + | | + | + | | |
| Boron source for preparation of other boron compounds | + | | | | | |
| α-BN hot-pressed shapes | | | | | | |
| Crucibles for melting glass and metals | + | + | | + | | + |
| Break rings for horizontal continuous castings | + | | | + | + | + |
| Components for high-temperature electric furnaces | + | + | + | + | | + |
| Structural parts for magnetohydrodynamic devices | + | | + | + | | + |
| Dielectric for radar antennas and windows | | | + | | | + |
| Insulators for low- and high-frequency equipment | + | | + | | | + |
| Insulators for plasma-jet furnaces, arc pulse generators and ion engines | + | | + | | | + |
| Holders, mounting plates, substrates and heat sinks in valve and transistor circuits | | + | + | | | + |
| Pump components, pipes and nozzles for handling liquid metals | + | | | + | | + |
| Protective tubes and insulating sleeves for thermocouples | + | + | + | + | | + |
| Protective sleeves for electrodes in automatic welding | + | | + | + | | + |
| Wafers for boron-doping of semiconductors | + | | | | | + |
| Moulds for hot-pressing of ceramics like $B_6O$ or $B_{6.5}C$ | + | + | | + | + | + |
| Neutron absorbers and shields for nuclear reactors | + | + | | + | | + |

R, High-temperature refractoriness; T, thermal conductivity; E, electrical insulator; I, chemical inertness, nonwetting; L, lubricity; M, machining ease.

### 5.1 Insulators for high-temperature furnaces

The heating elements of resistance-heated electric furnaces, like graphite, molybdenum- or tungsten-tube high temperature furnaces, require fixing devices made from ceramic insulating materials. Today, due to frequent breakdown of oxide ceramic insulators at temperatures >2000°C, α-BN insulators are almost exclusively in use. Therefore the BN material should contain only minimum amounts of boric oxide, since $B_2O_3$ exudes at high temperatures and finally forms a conductive surface layer.

### 5.2 Protective tubes and insulating sleeves for thermocouples

The high-temperature refractoriness, high thermal conductivity, and high electrical resistivity of dense α-BN material are utilized as thermocouple protection tubes and insulating sleeves (Fig. 5). Preferably for the new $B_4C/C$ thermocouple,[19] which can be used up to 2200°C, α-BN insulating sleeves are used. The $B_4C/C$ couple consists of a graphite tube and a $B_4C$ rod connected to each other by a conical fitting. This end is exposed to the heated area. Along its entire length the $B_4C$ rod is insulated from the graphite tube by a α-BN sleeve of segmented construction. Typical fields of application are sintering furnaces, hot presses and hot isostatic pressing equipment working in the temperature range 1800–2200°C. The thermocouple should only be used in a rare gas atmosphere or under vacuum. If the inert gas used contains oxidizing gases or nitrogen, reaction with the graphite tube and the $B_4C$ rod will occur, which can strongly influence the life of the thermocouple.

### 5.3 Break rings for horizontal continuous casting of steel

The high chemical and thermal stability combined with the non-wetting property makes α-BN a useful crucible and structural material in metallurgical applications.[20] For horizontal continuous casting of nonferrous metals, graphite can be used as mould. However, the higher melting temperatures of steel alloys and their aggressiveness towards graphite and other conventional refractory materials results in the need for special materials at the point of connection between the tundish and the mould.[21] This connection consists of a casting nozzle made of a high quality refractory such as zirconium oxide and a

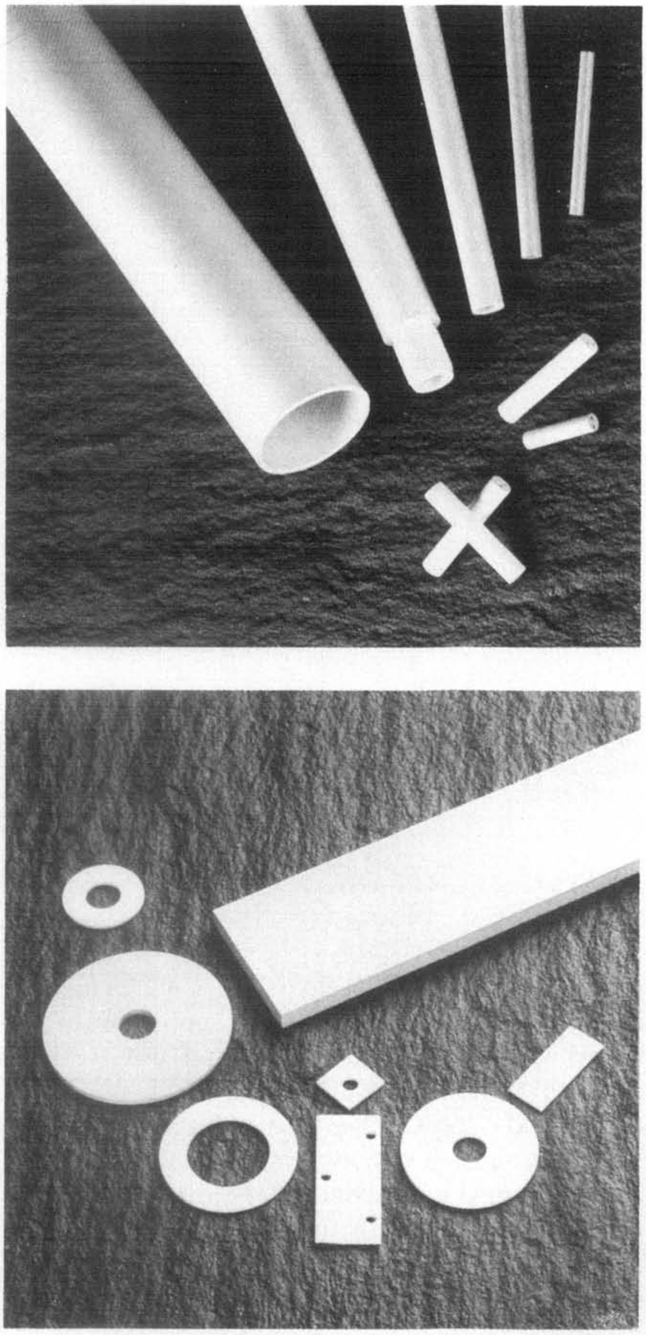

**Fig. 5.** Thermocouple protection tubes and insulation components.

break ring made of boron nitride or a BN-composite ceramic as depicted in Fig. 6. Several sizes and shapes of these BN break rings are shown in Fig. 7. The sizes and shapes of the break rings and geometry are generally dependent on the type of equipment and type of steel (high or low alloy steels).

Cross-sections of 50–250 mm diameters are now in use. The break ring determines the zone in which the liquid steel forms a solid. In addition the break ring must act as a seal or gasket with the tundish and the mould itself. The reaction of the ceramic boron nitride ring with steel alloying agents such as nickel, chromium, tungsten, manganese, sulphur, etc., can cause breakdown of the BN material during service life. Therefore particular emphasis has been placed upon BN-composite materials to prevent this corrosive attack.

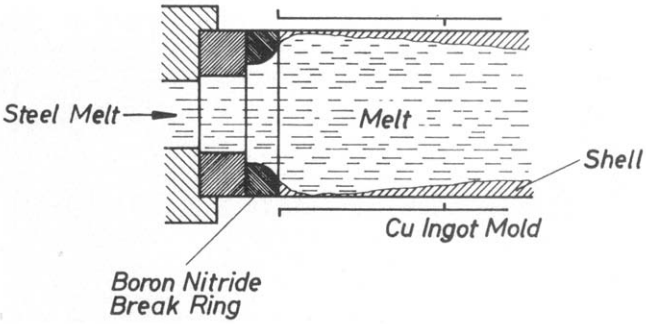

**Fig. 6.** Cross-section of a mold for horizontal continuous casting.

Until now the least wear of all BN composites (Table 2) has been shown by the SC–BN material; today 100–200 tonnes of steel per break ring in low alloy steel and 40–100 tonnes in high alloy steel can be cast using this new SC–BN material.[21]

Other BN metallurgical processing applications include crucibles for molten sodium carbonate at 900–1150°C and crucibles for production of single crystals in high vacuum (Al–Li and Cu–Ti alloys). Figure 8 gives examples of some crucibles, boats and nozzles.

### 5.4 Pyrolytic boron nitride crucibles

A low-volume but high-value use for pyrolytic BN is for crucibles for growing GaAs single crystals by the liquid encapsulation technique.

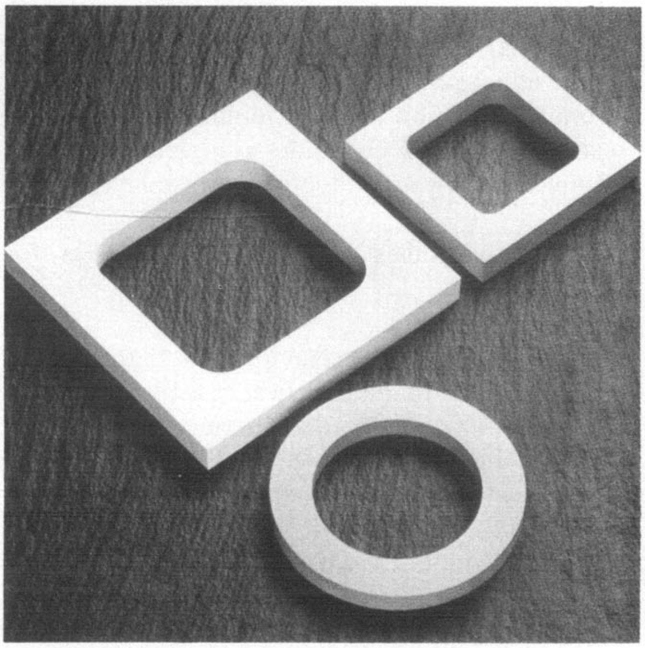

**Fig. 7.** $\alpha$-BN break rings.

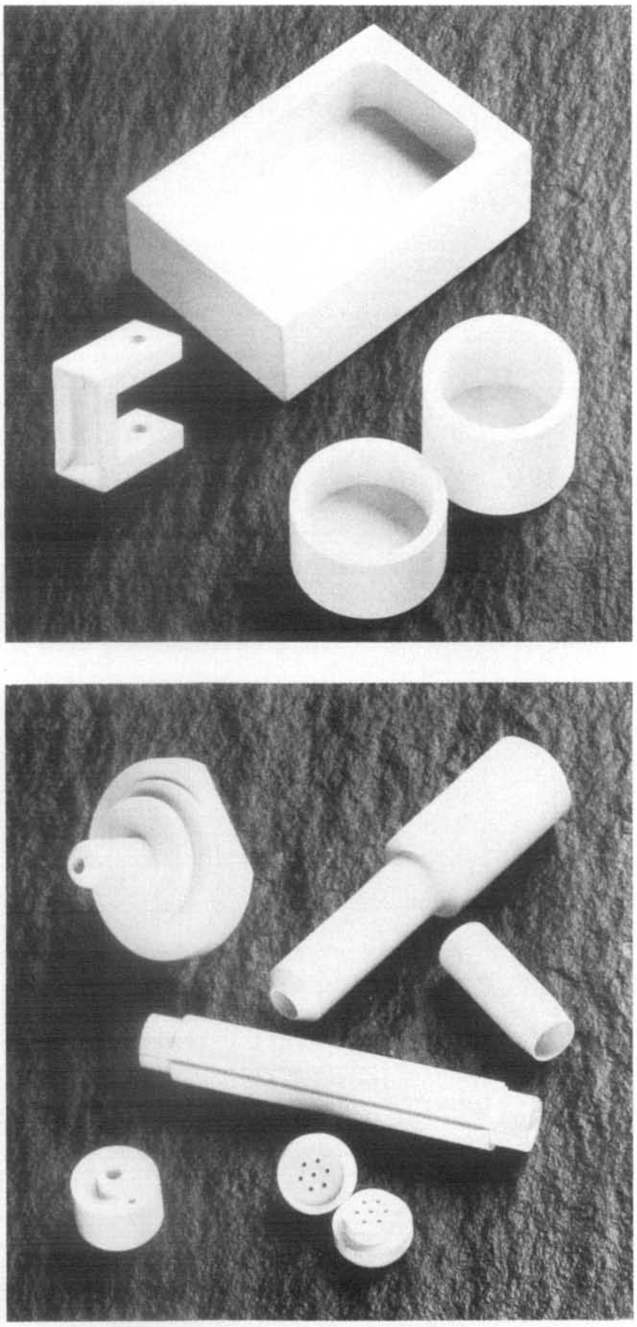

**Fig. 8.** α-BN crucibles, boats and nozzles for molten metals.

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