BORON NITRIDE RELEASE COATINGS

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Abstract

Boron nitride is an advanced ceramic material with outstanding chemical and thermal properties. It is often called "white graphite" because it has a graphite-like structure, but in contrast to graphite, it is white. It is an excellent high-temperature solid lubricant, is stable at high temperature and - most important for casting and foundry applications - is not wetted by many metallic melts like aluminium, magnesium and zinc.

In order to be able to use the advantages of boron nitride in casthouse and foundry applications, we developed coatings on the basis of boron nitride particularly for the application within casting shops. These coatings are applied like ordinary house paints by brushing or using a spray gun. They are perfect release agents used in aluminium foundries for the protection of ladles, dies ingot mould, permanent moulds thermocouples and ceramic structures. These coatings provide an excellent non- sticking and lubricating surface to which neither aluminium nor magnesium will adhere.

Boron nitride coatings are also proven release agents for coating thimbles, transition plates and refractory linings of distribution troughs of DC casting machines. During casting breaks, these coatings ensure the perfect and easy release of remaining aluminium without damaging the refractory substrate.

Boron nitride release coatings are available as water-based paints as concentrates as well as ready-to-use formulations. For an easier application in suitable environments, these coatings are available in aerosol cans too.

In contrast to graphite coatings and other (red mud) readily-used coatings boron nitride release coatings are stable in air (up to 1000°C), show excellent non-wetting behaviour (the best in the field of ceramics) and very good lubrication properties even at high temperatures. These very advanced characteristics make boron nitride release coatings a product of the first choice to foundrymen.

7th Australian Asian Pacific Conference
Aluminium Cast House Technology
Edited by P.R. Whiteley
TMS (The Minerals, Metals & Materials Society), 2001

Introduction

Release coatings are used in DC casting, ingot casting, sand casting and with different die casting processes. Beyond that they are used as a surface protection for ladles, troughs, launders and various other equipment which come into contact with metallic melts. They have the function

- to prevent a reaction of the melt with the mould material,
- to influence the heat transfer locally between melt and shaping surface,
- to enable a separation between casting and the mould when discharging the mould.

Beyond that coatings may react neither with the melt nor with the mould material. The coating should be able to be applied with an even layer thickness on the shaping surfaces, should not adhere at the surface of the cast parts partially and, if they are applied on as wear-coating, they should not build up.

Beyond that release coatings should be environmentally friendly. The characteristics like chemical and thermal stability, thermal conductivity and separation efficiency, necessary for the fulfilment of these functions, depend primarily on the refractory fillers used in the respective coatings.

Beside the classical refractory fillers such as graphite, zircon or talc also the use of advanced ceramic materials is considered. Here above all boron nitride is to be mentioned, which indicates a number of interesting characteristics, which make the use as a refractory filler in release coatings to appear meaningful (1, 2).

Physical and chemical characteristics of boron nitride and comparison with graphite

Boron nitride occurs in two modifications. The cubic high pressure modification however is ignored in the following paper and only the hexagonal modification is regarded. In the literature the hexagonal boron nitride is often called "white graphite", since it shows a structure very similar to that of graphite. Therefore it appears meaningful to compare the physical characteristics of boron nitride with those of graphite. Some important physical characteristics are shown in Table I.

Table I Physical and chemical characteristics of boron nitride and graphite

	Boron nitride	Graphite
Lattice constants		
a [pm]	250,4	245,6
c [pm]	666,1	669,6
Structure	hexagonal	hexagonal
Density [g/cm³]	2,27	2,267
Colour	white	black
Mohs hardness	<1	<1
thermal expansion [K-1] 20-1000°C*)	$0{,}8$ to $7{,}5 \cdot 10^{-6}$	2 to $20 \cdot 10^{-6}$
thermal conductivity [W·m-1·K-1]*)	15 to 30	2 to 10
specific resistance [W·cm]*)	$1{,}7$ to $2 \cdot 10^{13}$	$0{,}25$ to $4 \cdot 10^{-5}$

*) The different values are due to the anisotropy of the examined materials.

Crystal structure

Both boron nitride and graphite crystallize in a hexagonal layer lattice with a very similar layer distance (see Figure 1) (3, 4). While for boron nitride a layer distance of 666.1pm was measured, graphite shows a value of 669,6pm. Additionally both materials show similar densities and Mohs hardness. Rubbed between fingers both substances appear similar to talc. This is due to the plate-like formation of both materials. The layers of the lattice may be shifted easily, therefore both graphite as well as boron nitride are suitable as solid lubricants. A scanning electron micrograph (Figure 2) shows the plate-like particles of boron nitride powder used as a starting material for boron nitride coatings

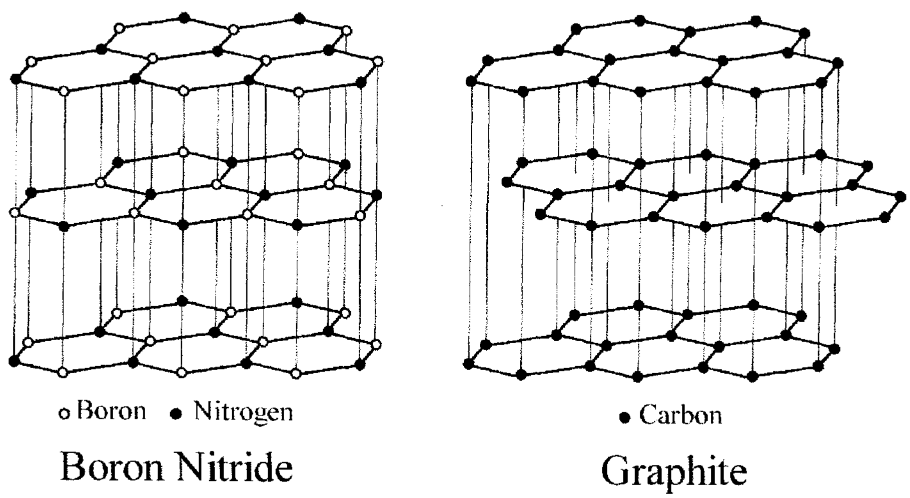

Figure 1: Structure of hexagonal boron nitride (left) and graphite (right).

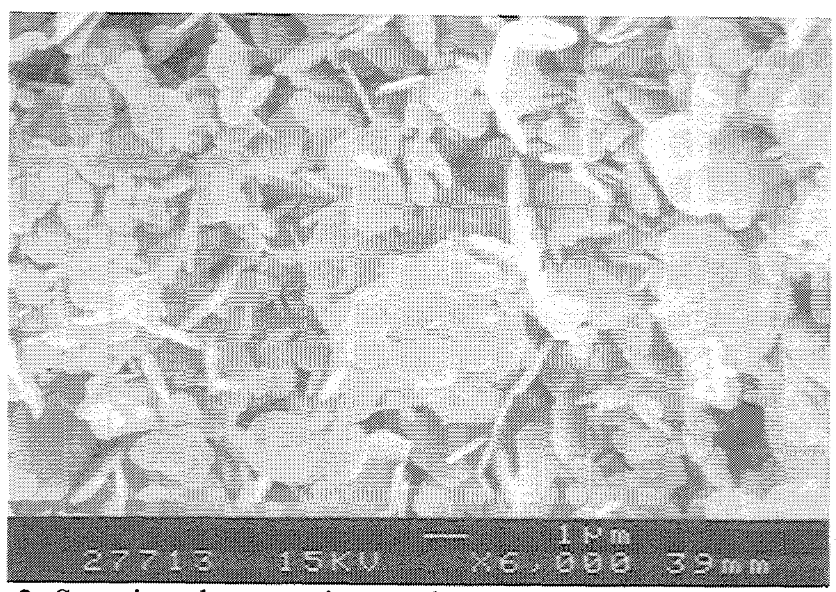

Figure 2: Scanning electron micrograph (secondary electron image) of boron nitride powder (magnification 6000-times).

Thermal stability

However large differences can be observed to thermal stability and oxidation resistance of boron nitride and graphite. Both materials show a very high point of sublimation which is clearly situated above that of other ceramic materials. In Figure 3 the melting points or points of sublimation of different ceramic materials are shown. Thus graphite has a point of sublimation of 3650°C. Boron nitride with a sublimation point of almost 3000°C is in second place. This is clearly above other ceramic materials such as Si_3N_4, SiC or Al_2O_3 or even ZrO_2. However, the application temperature of all ceramic materials is well below these melting/sublimation points.

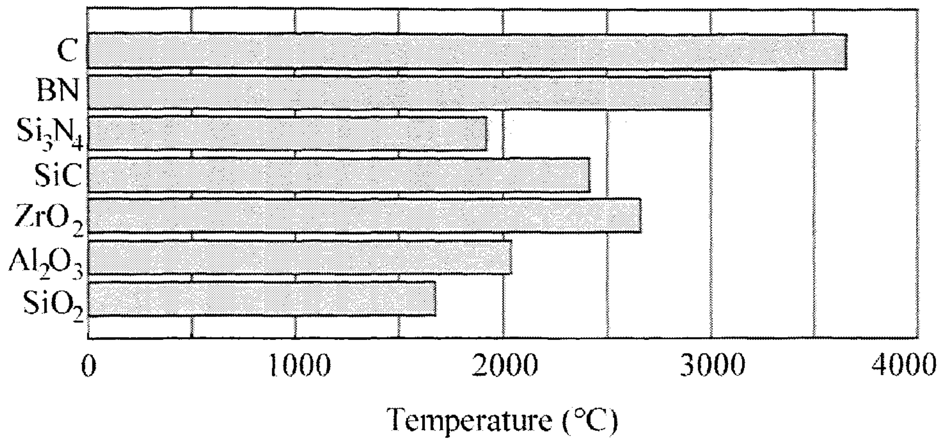

Figure 3: Melting/sublimation points of various ceramic materials compared to that of boron nitride (C graphite, BN boron nitride, Si_3N_4 silicon nitride, SiC silicon carbide, ZrO_2 Zirconium dioxide, Al_2O_3 alumina, SiO_2 silicon dioxide).

The max. application temperature of graphite and boron nitride are shown in Figure 4. At the same time the application conditions, i. e. oxidizing or reducing atmosphere are considered. Under reducing conditions boron nitride can be used to about 1650°C, graphite in contrast to about 2500°C. With oxidizing conditions the situation is inverted. Here, graphite is stable in air to about 400°C, at higher temperatures it oxidizes to CO_2. Boron nitride is stable in air up to 900°. With good crystallinity use to 1000°C is possible. With a thermal stability to 900 ... 1000°C boron nitride is clearly superior to graphite. Thus boron nitride is thermally stable in the temperature range light metal alloys are poured.

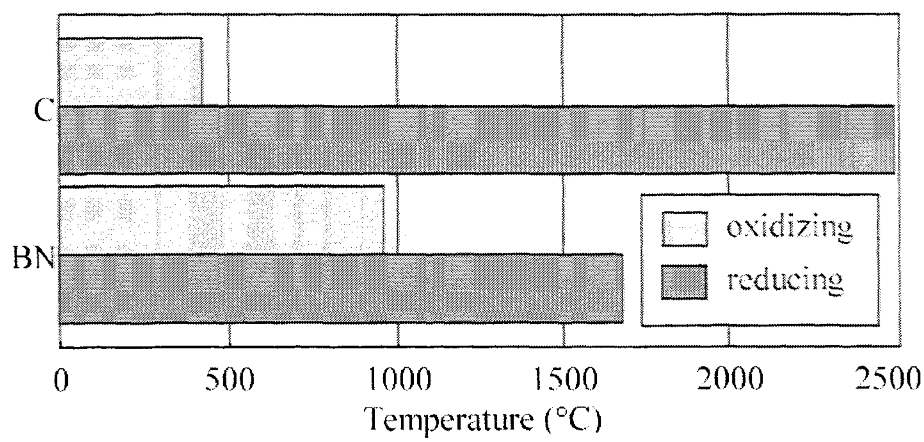

Figure 4: Max application temperature of boron nitride (BN) and graphite (C) under oxidizing and reducing conditions.

Lubrication properties

Due to the layer structure mentioned before both boron nitride and graphite can be used as high temperature solid lubricants. However, the lubrication property strongly depends upon the temperature range of intended application. Figure 5 shows the coefficient of friction for boron nitride compared with that of graphite in the temperature range from 20 ... 1000°C (5). At temperatures up to 600°C graphite shows a lower coefficient of friction than boron nitride. The strong increase of values between 600 and 800°C is caused by the oxidation of graphite. Here, boron nitride shows advantageous values of the coefficient of friction. The climb in the curve of boron nitride between 800 ... 1000°C is caused by its oxidation and subsequently forming of B_2O_3.

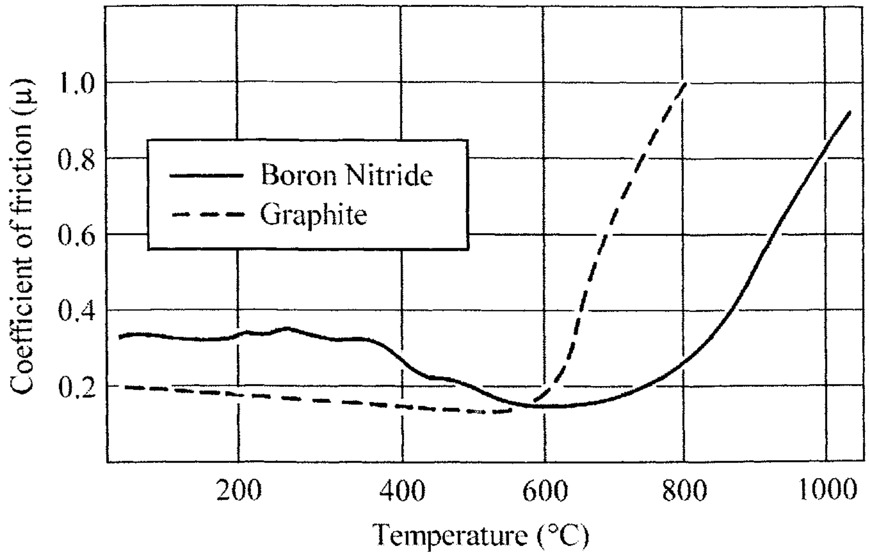

Figure 5: Comparison of friction data for boron nitride and graphite in air in dependence on the temperature.

Wetting behaviour

One of the most well-known properties of boron nitride is its poor wettability against many metal melts. These include among others melts of aluminium and magnesium. The wetting of ceramic material by a melt is usually described by the wetting angle Θ which is determined by using a heating microscope according to the method of the sessile drop. Here, the contact angle Θ of a melt drop is measured on the substrate (see Figure 6). Large angles (>90°) mean a poor wettability according to the drawn example, small angles (<90°C) in contrasts represent a good wettability.

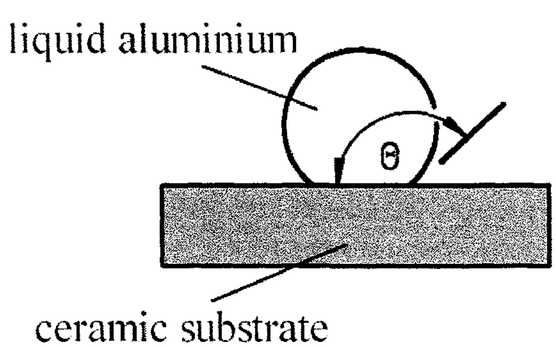

Figure 6: Definition of the contact angle Θ of melts on ceramic substrates in order to describe their wetting behaviour.

Figure 7 shows the contact angles of molten aluminium in contact with boron nitride, silicon nitride and alumina in dependence of the temperature (6). Up to 900°C boron nitride is only poorly wetted by aluminium and shows contact angles of 160°C. Between 900 ... 1000°C the contact angle value decreases, but is well above those of Al_2O_3 and Si_3N_4. However, in the temperature range which is interesting to aluminium casters, the wetting behaviour of boron nitride is far superior to oxide ceramics like alumina and even a little better than other nitrides like silicon nitride. Thus boron nitride is an ideal release agent for casting and shaping processes in light metal casthouses and foundries.

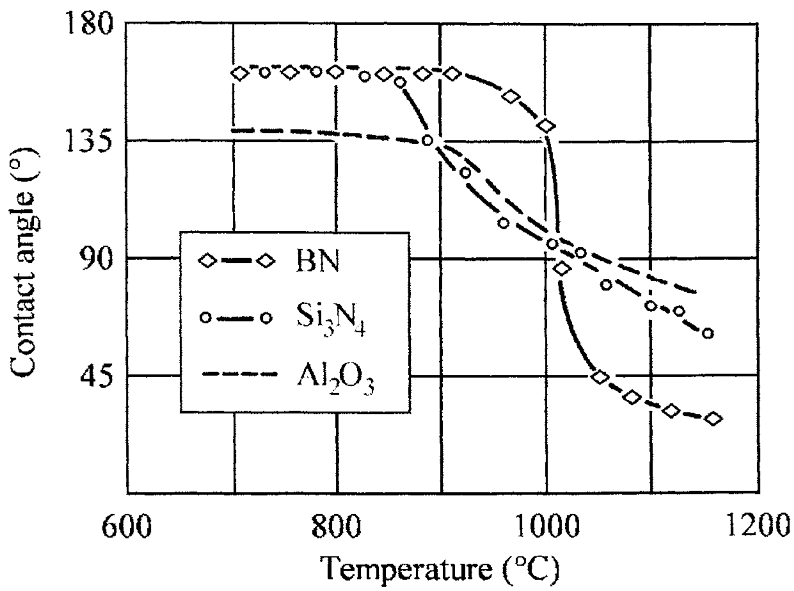

Figure 7: Contact angle data of aluminium on BN, Si_3N_4 and Al_2O_3 in dependence on the temperature (BN boron nitride, Si_3N_4 silicon nitride, Al_2O_3 alumina).

Composition of coatings based on boron nitride

Various types of boron nitride coatings are available on the market. They differ in types of boron nitride used for the production of such coatings, in carrier liquids preferred as well as in the solid content and refractory binder.

Boron nitride

Boron nitride are commercially available with BN concentrations between 95 and 98 mass-% for refractory and common casting applications. If higher BN concentrations are required, e. g. for laboratory and research applications, BN concentrations >98.5 mass-%. The balance will be mainly B_2O_3.

Carrier liquids

The choice of carrier liquids is mainly governed by technological aspects, but other points of view such as environmental and safety concerns must also taken into account. Water is an inexpensive, readily available and non-hazardous option. However, forced drying of applied coatings will be necessary in most cases. Alternatively organic solvents such as alcohols (ethanol, 2-propanol) may be used, but these formulations have to be labelled according to hazardous materials regulations.

Refractory binder

Boron nitride coatings can be produced without any refractory binder; the adherence of the particles can be achieved with their surface energy alone. Specific surface areas of at least $25m^2/g$ are necessary for this. Most applications, however, require a coating with reasonable adherence which makes the use of refractory binders necessary. For coating ceramic substrates with low thermal expansion, phosphate-containing binders have proven to be well suited. These binders harden when heated to 800 ... 900°C and result in a strong yet brittle bond. They cannot be used for high-thermal-expansion substrates like metals. Here binders on the basis of Al_2O_3 for higher temperatures (>1000°C) or $Al_2O_3 \cdot SiO_2$ for temperatures below 1000°C can be used. If the coating is meant to remain soft throughout the whole temperature range, clay minerals may be the binder of choice.

Application of coatings based on boron nitride

In order to use boron nitride in casthouses and foundries it is necessary to apply in the form of coatings. In most cases these coatings are water-based suspensions like house paint. These boron-nitride-coatings are applied like ordinary house paints by brushing or dipping. If it is required to coat small objects, dipping can be an application method of choice as well. Spraying is also possible and is recommended for coating larger surfaces and for hot objects which are difficult to paint. For spraying, a blow cup or a spray gun operated by pressurized air can be used. Nozzle sizes of 1.5mm will give best results.

Application to DC casting systems

The most commonly used application of Boron-Nitride-Coating in the DC casting process is the coating of mould transition plates. A coat of boron-nitride-coating ensures the non-wetting of the melt during casting and the release of remains of aluminium during the casting breaks. boron-nitride-coating is applied to the ceramic transition plate by brushing or spraying. However, with the application it is important not to coat the porous graphite ring, because this would interrupt the gas flow through the mould.

Another similar application of boron-nitride-coating is the coating of the thimbles, usually made of fused silica. boron-nitride-coating is applied by brushing or spraying on the inner surface. This enables the operator to easily remove the remaining metal during the casting breaks. The coating is applied before the casting table is put into service for the first time and between casting breaks when the remaining metal is removed.

The third application to DC machines is the coating of the refractory lining of the distribution trough. In contrast to the application to transition plates and thimbles discussed before, this application is done by spraying. However, the first coat can be done by brushing. The spraying is done during each casting break, when the trough is tilted and the casting pit emptied. The boron nitride ensures an easy and quick removal of the remaining aluminium. The boron-nitride-coating makes cleaning of the trough easier and is well accepted by the working force. The recoat is done after each casting. However, in contrast to terracote red mud coatings and bone ash coatings, extremely thin layers for this coating are needed only for a successful application.

Casting of ingots

Boron-nitride-coatings find its application in the area of the secondary metal producers and recycling firms, too. With this application the ingot moulds are coated in order to ensure for the perfect release and high quality surfaces of their ingots. The boron-nitride-coatings can be used for casting aluminium and magnesium as well as for zinc and lead. When casting magnesium with boron-nitride-coatings it will be noticed that the formation of oxides of the surface of the ingots is suppressed. This makes recycling of magnesium easier because the oxides cannot be removed from the melt because of their density being in the same order of magnitude of the molten metal.

Die casting / gravity die casting

It is generally known to use boron-nitride-coatings for the coating of dies in gravity die casting and low pressure die casting processes. The very good high temperature lubricating and release properties ensure the perfect release of the casting from the mould. The boron-nitride-coating dramatically reduces the sticking of the casting to the mould. The boron-nitride-coating also suppresses or reduces the distortion of the casting, especially during the unloading of low pressure die moulds.

Summary

Boron-nitride-coatings have an excellent thermal and chemical stability in the temperature range that is of interest to aluminium casters. It does not react with the metal melt or the refractory nor does it disintegrate. Boron nitride shows a very good non-wetting behaviour, one of the best known in the fields of ceramics. Boron nitride is an excellent high-temperature lubricant; therefore it is an excellent lubrication and parting agent when unloading castings from the moulds or removing remains of aluminium from the casting machines. Boron nitride is of white colour. Therefore, in contrast to graphite, it is a good way to keep the casthouse / foundry cleaner.

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