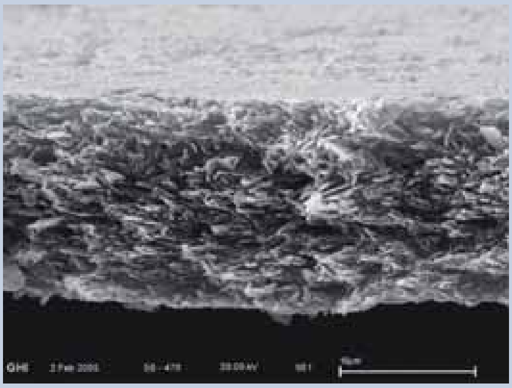
New generation of boron nitride

Figure 1



SEM picture of a cross section of EKamold Cast-C Coating (Photo: ESK)

Figure 2

Casting table for aluminium billet production coated with EKamold Cast-C prior to use (Photo: AGN)

With its new generation of boron nitride, ESK Ceramics GmbH & Co. KG in Kempten/Germany supplies the casting industry tailored materials for launders, ladles, dies and crucibles that offer unrivalled protection against aggressive molten aluminium. A critical factor in this advance in casting technology is a novel nanoscale binder that allows boron nitride coatings to be produced that adhere strongly to different materials.

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Molten aluminium is the basis for all aluminium products worldwide. It is crucial that molten aluminium be free from contamination when transferred from the furnaces to further production units. A typical example is the transport of molten aluminium in foundries, which is usually performed in launders with a refractory lining. Of course, such launders have poor thermal conductivity, which prevents the melt from cooling down rapidly. However, a thin oxide skin is formed on the surface of the hot aluminium. A release agent must be added to prevent this skin from sticking to the surface. Traditionally, bone ash is added, which does indeed have the required release properties, but must be repeatedly replenished because of poor adhesion, since it is “entrained” by the flowing molten aluminium.

Boron nitride versus bone ash

Ceramic coatings offer an alternative to bone ash. These foundry coatings, which are applied as liquids and dry to form a solid film, should have a high thermal and chemical stability and a thermal expansion similar to the coated surface in order to prevent the coating from flaking off.

A material that ideally meets all these requirements is boron nitride (BN). The graphite-like chemical structure of BN (see “Box” and Figure 1) makes it an ideal release agent and lubricant. However, unlike graphite, which oxidizes at > 500 °C in air, boron nitride is characterized by a high thermal stability that allows it to be processed up to over 900 °C. That makes boron nitride completely thermally stable in the temperature range used for light-metal casting.

A property that is particularly attractive for casting is the poor wettability of its surface by liquid aluminium and other molten metals. They do not stick to the smooth surface, but roll off like water droplets from a lotus leaf. The wetting of ceramics by melts is usually described by means of the wetting angle. The contact angle of a melt droplet on the substrate is measured by forming a tangent. Large angles of over 90 ° mean poor wetting, while small angles of less than 90 ° indicate good wetting properties. At a temperature of 900 °C, boron nitride has a wetting angle of 160 °, which corresponds to poor wetting.

However, this generally excellent property also has its drawback, since the

Figure 3

Casting table for aluminium billet production coated with EKamold Cast-C after use (Photo: AGN)

poor wetting of the BN platelets also impairs their adhesion to the substrates to be coated, such as ceramic launders, ladles, crucibles, dies or metal moulds. Therefore, to improve adhesion, a refractory binder must be used. In the coatings, these binders bond the BN particles together as well as to the substrate. In the past, phyllosilicates, monoaluminium phosphate and magnesium silicate have been the chief refractory binders.

Why boron nitride has similar properties to graphite

Boron nitride, a synthetic substance with the chemical formula BN, is a sort of “inorganic carbon”. That means the chemical and physical properties of BN are very similar to those of graphite, since both compounds crystallize with the same layer lattice and almost identical dimensions. Two adjacent carbon atoms of the graphite lattice can therefore be substituted with a nitrogen and a boron atom, since two carbon atoms together have exactly the same number of electrons as a boron-nitrogen pair. Accordingly, graphite and BN are isosteric, which, as with other “isosteric pairs”, such as nitrogen and carbon monoxide or nitrous oxide and carbon dioxide, is manifested as a striking physical and chemical similarity. For example, at temperatures of around 1600 °C and pressures of 50.000 bar, graphite-like α-BN can, in a similar way to carbon, be transformed into two diamond-like cubic high-pressure allotropes with similar hardness to diamond.

However, the striking difference between graphite and BN is that the latter is white and does not conduct electricity. That is because BN, unlike graphite, does not possess any mobile π-electrons, since, because the member atoms of the lattice are dissimilar, the “excess” electrons remain fixed to the nitrogen as “lone” electron pairs. However, regarding the application in the aluminium industry, an important characteristic is its resistance to oxidation up to 900°C compared to graphite which will already start to oxidise at 500°C.

In its most widespread form, as a graphite-like hexagonal boron nitride, the snow-white material shows an exceptional thermal and chemical resistance. At the same time, the highly thermally conductive material but electrically insulating boron nitride also has a good lubricity. This unique combination opens up a wide field of applications in which the material often provides the critical enhancement to high-end products. Some would not be possible at all without boron nitride. In this manner, the range of applications extends from electrical insulation in high-temperature furnaces to applications in the cosmetics industry.

High adhesion thanks to nanoparticles

According to Christiane Klöpfer of the technical marketing department at ESK Ceramics, the binders that have been commercially available so far are not ideal for the casting industry. A major disadvantage is the fact that they are only suitable for the application of thin coatings, because otherwise the rapid temperature cycles could cause them to flake off. In looking for improved high-temperature binders, ESK Ceramics hit on sol-gel systems reinforced with nanoscale particles.

The patented binder system, as a BN coating for the casting industry, is named EKamold Cast-C and is a real innovation for high-temperature applications (Figure 2). The system is effective in situ when heat treated during the first casting cycle, similar to two-pack adhesives, and forms a film that is resistant to both heat and abrasion. Compared to conventional boron-nitride-based coatings, this product innovation offers unrivalled durability together with ease of application and extremely low requirements on the substrate (Figure 3).

There are also processing advantages to using boron nitride (BN). For example, BN coatings can be applied by spraying, brushing, or dipping. Although BN coatings develop their protective effect at a few microns’ thickness, the new BN foundry coatings from ESK can be applied in a thickness of up to 1 mm. That means the coating can be readily applied by untrained staff. The new coating can be used wherever liquid aluminium is processed. The range of applications extends from compact aluminium ingots to aluminium car wheels and engine blocks.

Furthermore, the new BN coatings for the first time ever allow damaged coatings and cracks in the substrate to be repaired. In the traditional process, if the coatings were damaged, they had to be painstakingly removed and then reapplied. With the new systems, damaged areas of the coating can be repaired – for example with a brush. Moreover, the coatings can seal cracks and chipping in the substrate by infiltrating them.

No Sedimentation thanks to thixotropy

"Traditional" BN coatings generally had the problem of sedimentation of the BN solid particles, and had to be very carefully stirred to prevent settling out, which would change the properties. The new ESK coating offers a further advantage, since, although it becomes gel-like after standing for a long time, it can be easily liquefied again by stirring or shaking – a property known as "thixotropy." All these completely new possibilities offer major advantages to users. Casthouses and foundries are harsh environments, where users must be able to depend on the materials used operating flawlessly. The new coatings have already been subjected to practical tests in aluminium foundries.

The German billet manufacturer AGN Aluminium Nachrodt emphasises the high abrasion resistance of the new BN coatings. Traditional coatings used to be entrained by the flow of the molten aluminium. The new product has improved adhesion and no need for frequent reapplication. The coatings have a longer lifetime if the liquid aluminium has no chance to attack the substrate. This could greatly reduce downtimes. The bottom line for aluminium processors is a significant boost in efficiency as a result of time savings and higher productivity. The improvement is documented by the results of quality control. With the BN coatings that were tested before, in contrast to traditional materials such as bone ash, the castings did not contain any residues.

Besides their high mechanical stability, the new BN coatings are also characterized by high flexibility. To reconcile apparently contradictory material properties, a third component was incorporated into BN coatings besides the binder. This innovation, which has also been patented, is an additive that imparts hitherto unachievable elasticity to the coatings. The coatings have a levelling effect since, within certain limits, they adapt to their environment and can expand and shrink without suffering damage.

The flexibility also applies to the adhesion of the binder to the substrate to be coated, which may be smooth or porous. ESK was even able to make boron nitride adhere to graphite. This additional property is important for graphite parts that are used in aluminium casthouses and foundries. They include rotors for melt degassing or boron-nitride-coated graphite thermocouple tubes.

Other additives are under development. Boron nitride has high thermal conductivity, which is counterproductive for aluminium production. For example, liquid aluminium cools by about 1 °C per second on average when transported in ladles. This heat loss has to be compensated by auxiliary heating. ESK is currently working on BN coatings precisely tailored to the needs of the aluminium-processing industry. The aim of this work is to find another additive that will make a boron nitride with reduced thermal conductivity.