Boron Nitride plus Binder – a Synonym for Higher Productivity

With its new generation of boron nitride, ESK Ceramics GmbH & Co. KG in Kempten, Germany is providing the casting industry with tailored materials for launders, ladles, dies and crucibles that offer unrivalled protection against aggressive molten aluminum. 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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In smelters and foundries aluminium is in liquid form at a temperature of around 700°C. Since this melt is very aggressive, the contacting surfaces must be protected. That is to counteract wear of the tools and vessels and, to prevent the aluminium from being contaminated with dissolved foreign matter, specifically the launders in casthouse applications as well as crucibles, ladles and dies used in foundries. The surfaces that come into contact with the molten aluminium must be coated to prevent corrosion. The quality of these surfaces not only determines the lifetime of the equipment and tools used, but also has a critical effect on the quality and mechanical and physical properties of the resulting castings.

A typical example is the transport of molten aluminum in casthouses that is usually performed in launders with a refractory lining. Such launders have poor thermal conductivity that prevents rapid cooling of the melt and a thin oxide skin rapidly forms on the surface of the molten aluminum. A release agent must be added to prevent this skin sticking to the surface. Traditionally bone ash is added, which does indeed have the required release properties but because of its poor adhesion must be repeatedly replenished, since it is "entrained" by the flowing molten aluminum.

Boron Nitride versus Bone Ash

Ceramic coatings offer an alternative to adding bone ash. These foundry coatings, which are applied as liquids and dry to form a solid film, should have high thermal and chemical stability and a similar thermal expansion 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) makes it an ideal release agent and lubricant. However, unlike graphite, which oxidizes at above 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 within 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 aluminum 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 over 90° mean poor wetting, while small angles less than 90° indicate good wetting. At a temperature of 900°C, boron nitride has a wetting angle of 160°, which corresponds to poor wetting.

However, this welcome property also has a downside, since the 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 molds. To improve adhesion, therefore, 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, monoaluminum phosphate and magnesium silicate have been the chief refractory binders.

Casting table for aluminum billet production coated with EKamold® Cast-C prior to use

High Adhesion thanks to Nanoparticles

"The binders that have been commercially available so far are not ideal for the casting industry," says Christiane Klöpfer, of the technical marketing department at ESK Ceramics GmbH & Co. KG in Kempten, Germany. A major disadvantage is that they are only suitable for applying thin coatings, since otherwise the rapid temperature cycles could cause them to flake off. "In looking for improved high-temperature binders, we hit on sol-gel systems reinforced with nanoscale particles," explains Klöpfer.

The patented binder system, as a BN coating for the casting industry, is called EKamold® Cast-C, and is a real innovation for high-temperature applications. The system develops its effect 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.

Coatings Can Be Repaired

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 thicknesses up to 1 mm. That means the coating can be readily applied by untrained staff. The new coating can be used wherever liquid aluminum is processed. The range of applications extends from compact aluminum ingots to aluminum car wheels and engine blocks.

Furthermore, the new BN coatings developed by ESK, 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," enthuses Dr. Thomas Jüngling, Chief Technology Officer of the California-based Ceradyne Incorporation. Casthouses and foundries are harsh environments, where users must be able to depend on the materials used operating

Casting table for aluminum billet production coated with EKamold® Cast-C after use

flawlessly. "The casting industry is very interested in the new boron nitride coatings," observes Jüngling. The new coatings have already been subjected to practical tests in aluminum foundries.

Boron Nitride Coatings Last Longer ...

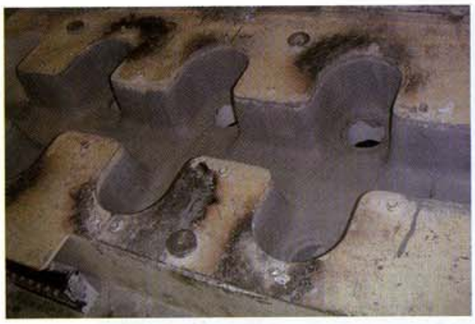
Guido Heuts of the Dutch company Ceranex, a supplier of heat-resistant and chemically resistant materials for manufacturing industry, emphasizes the high abrasion resistance of the new BN coatings. Heuts is responsible for the aluminum industry division in his company and understands the particular challenges faced by this sector. "Traditional coatings were always entrained by the flowing molten aluminum. But the new product adheres much better and does not have to be reapplied as often," he explains. The coatings have much longer lifetimes if the liquid aluminum does not have a chance to attack the substrate. This could greatly reduce downtimes. The bottom line for aluminum processors is significant boost in efficiency as a result of time savings and higher productivity. The improvement is documented by the results of the quality control. "With the BN coatings we tested before, in contrast to traditional materials such as bone ash, the castings did not contain any residues," Heuts assures.

... and They Are Flexible

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 leveling effect since, within certain limits, they adapt to their environment and can expand and shrink without suffering damage," explains Christiane Klöpfer.

The flexibility also applies to the adhesion of the binder to the substrate to be coated, which may be smooth or porous. "We were even able to make boron nitride adhere to graphite," Klöpfer says. This additional property is important for graphite parts that are used in aluminum 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. That is counterproductive for aluminum production," continues Klöpfer. For example, liquid aluminum cools by about 1°C per second on average when conveyed with ladles. This heat loss has to be compensated by auxiliary heating. ESK is currently working on BN coatings precisely



SEM picture of a cross section of EKamold® Cast-C Coating

tailored to the needs of the aluminum-processing industry. The aim of this work is to find a further additive that will allow us to market a boron nitride with reduced thermal conductivity.

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 BN's chemical and physical properties 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 □-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 *f*-electrons, since, because the member atoms of the lattice are dissimilar, the "excess" electrons remain fixed to the nitrogen as "lone" electron pairs. However, more important for the application in the aluminum industry is the resistance against oxidation up to 900°C compared to graphite which will start to oxidize already at 500°C.

In its most widespread form, as a graphite-like hexagonal boron nitride, the snow-white material possesses exceptional thermal and chemical resistance. At the same time, the highly thermally conductive material but electrically insulating boron nitride also has 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.

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