

# Borates in ceramics



## 1. Introduction

Traditional ceramic products include floor and wall tiles, sanitary ware, domestic tableware/cookware/ washing appliances, pottery, brick, refractories, and abrasives. Important developments in traditional ceramics continue to occur, particularly in tile manufacturing. Higher aesthetic characteristics and technical performance have been achieved with less energy consumption and environmental impact at a lower operating cost. In recent years, companies have invested in automated and energy-efficient equipment to remain competitive.

In the manufacturing of traditional ceramics products, the key functions of borate are initiating glass formation in the early stage of melting; and increasing the mechanical strength of the product. In the production of advanced ceramic products, borates are an integral part of the molecular structure such as borides and carbides. In addition, glass ceramics containing borates are finding more numerous applications in glass ceramics.

There have been many changes in the advanced ceramics industry during recent years. The advanced ceramics can be classified into four specific areas: electronic ceramics, structural ceramics, ceramic-matrix composites, and ceramic coatings. Advanced ceramic products continue to grow as more and more applications are being developed.

## 2. Benefits of borate-based glazes

Unglazed ceramic objects, formed by a high temperature process, may be unsuitable for use for a variety of reasons including high solubility, porosity, insufficient resistance to surface damage or poor aesthetic appearance. Therefore, in order to fully utilize the ceramic it is often necessary to cover its surface with a thin glassy coating called glaze. Ceramic glazes are normally combinations of complex silicates and borates compounded to produce a covering which may be required to

fulfill any number of the following conditions:

- Very low solubility in water and the normal acids and alkalis likely to be encountered in use
- Resistance to scratching and mechanical damage
- Compatibility with the main ceramic body to limit faults such as crazing and peeling
- Suitable for the production of the desired decorative effects
- Fusible within the required temperature range to suit the body

Borates are included in glaze formulations to:

- Initiate glass formation in the early stages of melting
- Reduce the glass viscosity and surface tension, helping the glaze to mature rapidly and form a smooth surface
- Reduce the thermal expansion coefficient of the coating. This is very important where a good “thermal fit” between the glass and ceramic body is required.
- Increase the refractive index (luster) and improve the glaze appearance
- Improve the durability and resistance to aqueous or chemical attack.
- Increase the mechanical strength and scratch resistance
- Act as a base for dissolving coloring agents, again enhancing the appearance and reducing melting times

Generally borates are used due to a combination of above reasons with the final glazes benefiting from their influence on both the melting and final physical properties of the glass.

Because borates are either soluble in water, or undergo violent reactions during heating, the borates are “fritted” before being incorporated in glazes. Fritting consists of melting the borate (along with other raw materials) in a furnace, then quenching the molten glass in water. This “frit” is then mixed with the other constituents to make the correct final glaze composition, then milled (ground) in water to produce a slurry. The slurry is then applied onto the surface of the ceramic or metal substrate. Usually, glazes are applied as a wet

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slurry by several methods including dipping, wet spraying, or electric spraying of charged particles onto the ceramic body. With a metal substrate, they can also be applied dry by electrostatic spraying.

There is no such thing as a “typical” glaze formula. There are hundreds, even thousands of compositions, each formulated for a particular need depending entirely on the final application and the properties required.

### 3. Traditional ceramic products

Glazes are used on many different ceramic wares, including wall and floor tiles, tableware, earthenware, bone china, porcelain, and bricks and roof tiles.

#### 3.1 Glazes for wall and floor tiles

The high degree of both aesthetic as well as technical diversification of the glazed surface of wall and floor tiles has been progressively achieved. In recent years different firing techniques have been implemented to reduce energy and labor costs. This, together with the need to adapt each glaze to the manufacturing variables and composition of each body, are the causes justifying the great number of compositions which have been formulated. The firing techniques include traditional double-firing, fast double-firing, and fast single-firing. Nearly all new installations use fast single-firing due to its lower overall cost.

#### 3.2 Glazes for tableware, sanitaryware and studio ceramics

Many other household items are also glazed with frit-containing glazes, and all of these frits contain borates. Examples are tableware — bone china, earthenware, hotel porcelain—and studio ceramics or craft pottery. The pottery houses make their own glazes using boric acid, anhydrous borax, and some Gerstley borates. Glazes on decorative

items such as vases, statues, etc. are usually made by the individual potter and contain Gerstley borate.

Some traditional ceramics such as sanitaryware and hard paste porcelain are fired at such a high temperature that frits in the glaze are not needed, and only insoluble raw materials are used. These glazes typically do not contain borates.

#### 3.3 Enamels for metals

Enamel is a glaze on a metal (or sometimes glass) substrate. In a molten state it can be applied to a workpiece in one or more layers, sometimes with additional materials included. It is commonly used as glassy coatings on metal objects such as domestic cookers and washing machines, pots and pans, jewelry, signage, and architectural enamel sheeting. The desirable attributes of enamel are as follows:

- To protect base metal against corrosion and deterioration
- To improve the appearance such as color and brilliance
- To give a surface resistance from attack by household acids and chemicals
- To give a sanitary finish—germ-free, smooth, and easy to clean

Conventional enameling is applied in two coats. As the first coat, the base enamel (ground coat) contains the cobalt oxide and the nickel oxide required for the bonding action onto the metal substrate. As a second application the cover coat is applied to the work piece giving the finished surface the appropriate characteristics of color and physical/chemical properties.

In the last few decades, “direct on” white enameling has become increasingly important. The bonding reaction during this process depends on the degree of the nickel treatment of the steel sheets, but similar chemical reactions are involved. Economic factors encouraged this development; another consideration was the need to reduce the thickness of the enamel coating in order to minimize the tendency to chip on impact or deformation. The degree to which the glass surface

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can distort is highly dependent on the coat thickness. The thinner the glass or enamel coating the more resistant it will be to impact and flex damage.

### 3.4 Refractories

Refractories are materials used for constructing various types of industrial furnaces, kilns, and other apparatus operated at high temperatures. Industries that use refractories include: iron and steel, non-ferrous metals, glass, gas/steam/nuclear power, ceramics, cement and lime manufacture, incinerators, paper mills, and enameling. As so many industries use refractories, there is a very wide range of products available.

Borates and boron are not widely used in refractories. Boric acid is used in chemically bonded firebricks and castables requiring high temperature resistance, corrosion and abrasion resistance. Castables possess a uniform structure with low porosity and offer high-temperature strength throughout the low and intermediate temperature range. They include unfired refractories which are installed in the furnace or other structure where they are applied by ramming, casting or gunning and are then fired by heating the structure. The cold setting bond is usually formed by a hydrated substance or organic binder. However, with many compositions there is an intermediate temperature (800-1200°C) where the structure is relatively weak because the cold setting bond has decomposed but the ceramic bond has not yet formed. Boric acid and Borax act as a secondary binder to give the refractory mixture sufficient strength to retain its shape and configuration until the ceramic bond forms.

Borates are used in the manufacture of magnesia bricks of furnace linings. Magnesia and magnesite-chrome are the main refractory bricks used in steel furnaces. Traditionally, the bonding of magnesia for shaping of the bricks was achieved using boric acid as a binder but modern practice uses fusion casting for bricks which do not require a binder. Increasing requirements in steel production processes are imposing greater demands on steel furnace refractories which

are met by carbon-bonded bricks such as magnesia-carbon and alumina-carbon bricks. As a thermally stable material, carbon increases the thermal shock resistance of refractory compositions and prevents wetting by metal and slag, but it is highly susceptible to oxidation. When antioxidants are used to protect the carbon in bonded refractories against steel melts, excellent results are provided by boron compounds. In addition, they also enhance the mechanical properties of carbon-bonded refractory materials. Boron compounds such as  $B_4C$ ,  $CaB_6$ ,  $TiB_2$ , and  $ZrB_2$  are distinguished by a high melting point and a high sensitivity to oxidation. These properties are the principal reasons for their use as antioxidants in refractories (usually in the amount of just 1 wt. % will greatly reduce oxidation of the carbon). Recent literature suggests that these boron-containing antioxidants can be produced during the manufacture of carbon-bonded bricks with the addition of boric acid or anhydrous boric acid. This will significantly reduce the cost of these antioxidants.

Dolomite refractories are used in open-hearth steel furnaces and the lining of basic oxygen furnaces. During the manufacture of dolomite bricks, dicalcium silicate dehydrates with a 10% volume increase. This inversion will cause even a strong brick to disintegrate into a powder. Boric acid is used as a stabilizer to prevent this inversion.

Graphite crucibles used in the foundry industry are quite porous and do not stand up well under constant heating and cooling cycles. To make these crucibles leak-proof and longer lasting they are dipped in a *Neobor*<sup>®</sup>—boric acid solution (vacuum impregnation) or coated with a ceramic mixture containing anhydrous borax and fired at high temperatures. Alumina-graphite materials used for continuous casting of steel, such as ladle shrouds and submerged entry nozzles, are also susceptible to oxidation in service, and are often protected with a borate-containing glaze coating.

In addition, gunning and patching compounds used to extend the life of basic refractories in steel furnaces contain some borate products such as borax and boric acid.

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### 3.5 Abrasives

Borates have been used as an additive for binding agents for use in the manufacture of grinding wheels. Due to their extreme hardness and abrasiveness, boron carbide and boron nitride, as well as metal borides are also used in the manufacture of specialty abrasive wheels and saw blades.

### 3.6 Bricks and roof tiles

Both scumming and efflorescence are due to the surface migration of soluble sulfates which are naturally present in the brick clay. Scumming results from migration of soluble salts during the drying process, and appears as an aesthetically undesirable stain on the surface of the fired article. Efflorescence occurs later when the pieces are exposed to natural weather conditions and appears as a white encrustation on the surface when in use. The addition of a small amount of borate can potentially:

- Reduce scumming and efflorescence
- Enhance color and durability
- Increase strength
- Reduce firing temperatures
- Provide protection of the bricks by forming glaze on the surface

As borates are typically soluble in water, they can migrate to the surface of the clay body while drying. This is controlled by adding a migration inhibitor in the form of a sugar.

## 4. Advanced ceramic products

### 4.1 High-tech ceramics

High tech boron ceramics include boron carbide, boron nitride, titanium diboride, zirconium diboride, as well as other borides that have found increasing applications commercially.

Boron carbide is the third hardest material known, relative to diamond and cubic boron nitride.  $B_4C$  powders can be formed by a variety of reactions. One reaction is the carbon reduction of several boron-oxygen compounds, including boric oxide, boric acid, borax and boracite. Another reaction is the direct combination of the elements. Use of boron carbide is based on its low specific gravity, extreme hardness and wear resistance, high mechanical strength at both low and high temperature, thermal and chemical resistance, nuclear properties and chemical reactivity.  $B_4C$  powders are used in polishing and abrasive cutting applications in a loose or slurry form. The extreme hardness and wear resistance properties are utilized in blast nozzles. In nuclear applications,  $B_4C$  is used in control rod pellets, shutdown balls, combustible poisons and shielding for such uses as high-density storage of spent nuclear fuel. It is the precursor used for producing most non-oxide boron chemicals due to its reactivity with halogens at high temperatures. It is also used in some reaction schemes to produce refractory metallic borides.

Boron nitride is commercially produced in two allotropic forms, hexagonal boron nitride and cubic boron nitride. Cubic boron nitride is an extremely hard material second only to diamond. Both forms have high electrical and corrosion resistance. Cubic boron nitride is used primarily in abrasive wheels for grinding and polishing ferrous materials such as nickel and cobalt-based super alloys but can also be used in powder form for precision grinding close-fitting parts such as turbine blades for jet aircraft engines. Hexagonal boron nitride powder is used as a mold-release agent, as a filler in high-quality coaxial cable, as a thermal insulator in electronic devices, as a high-temperature dry lubricant and as the raw material for hot-pressed solid shapes of boron nitride.

Titanium diboride is produced by reacting titanium dioxide with carbon and boron carbide or boric oxide. It is a ceramic material that can be machined, which is unusual. Because of its refractories, hardness and electrical properties, it may be fabricated into very hard, dense objects by hot pressing or its may be used in powder form as a component of cements.  $TiB_2$  has become available in commercial quantities fairly recently although there is not widespread use of this material.

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However, there is an increasing amount of research being conducted on  $TiB_2$  with applications in special refractories; wear resistant items such as cathodes in Hull cell production of aluminum; ceramic armor; anvils, gauges and guides; bearings or bearing liners; cutting tools; jet nozzles or venturiers; crucibles arc or electrolytic electrodes; resistance elements; high temperature conductors of electricity; contact points; hard facing welding rod coatings; and metallurgical addition agents.

Zirconium diboride is produced by reacting zirconium oxide with carbon and boron carbide or boric oxide. Many of its properties are similar to those of titanium diboride. The very high melting point, combined with hardness and resistance to corrosion by many molten metals and slags, make  $ZrB_2$  a candidate for such applications as rocket nozzles, combustion chamber liners and other high-temperature structural uses where impact loading is not encountered. Its resistance to molten metals and slags make it potentially useful in pouring spouts and die-casting machine components.

## 4.2 Glass ceramics

Glass ceramics have a variety of established uses dependent on their uniform reproducible fine-grain microstructures, absence of porosity and wide-ranging properties which can be tailored by changes in composition and heat treatment. Because the glass ceramic process begins with a glass, all the well established glass-forming techniques including blowing, casting, pressing, and rolling can be employed to manufacture components with a variety of complex shapes. Subsequently the glass component is readily converted into a fine-grained polycrystalline ceramic by a controlled nucleation and crystal

growth heat treatment. The established compositions and uses of glass ceramics are extensive including cookware, cooker range tops, heat-resistant windows and telescope mirror blanks. A good example of a borate glass/ceramic is Macor (Corning), containing 8.5%  $B_2O_3$ , which has applications as precision electrical insulators, windows for microwave tubes and gamma ray telescope frames.

In recent years, new compositions, processing methods and applications have begun to emerge. Among the recent developments considered are new phosphate-based compositions, the use of sol-gel processing, glass ceramic matrix composites, glass ceramics in microelectronics packaging, glass ceramics bonded to metals and joining media, high-strength and high-toughness materials and machineable compositions in the calcium-phosphate-based glass ceramic system.

New optical glass ceramics have recently been developed. These include integrated lens arrays, luminescent materials, and zero-expansion passive optical materials, the latter recently used in the ring-laser gyroscope. An interesting new range of glass ceramics with very low thermal expansion has been recently reported in the calcium, strontium and barium aluminoborate systems. These glass ceramics were produced from powdered glass compacts, sintered and crystallized below  $1000^\circ\text{C}$ . They have high strength, high fracture toughness and excellent electrical properties. Potential applications in substrates for microelectronics packaging, sealing frits for low-expansion materials, coatings for metals and thermal shock resistant ceramics.

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### About U.S. Borax

U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 500 customers with more than 1,700 delivery locations globally. We supply 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles. We pioneer the elements of modern living, including:

- **Minerals that make a difference:** Consistent product quality secured by ISO 9001:2015 registration of its integrated quality management systems
- **People who make a difference:** Experts in borate chemistry, technical support, and customer service
- **Solutions that make a difference:** Strategic inventory placement and long-term contracts with shippers to ensure supply reliability

### About 20 Mule Team® products

20 Mule Team® borates are produced from naturally occurring minerals and have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.

