

# Borates in metallurgical applications

## Introduction

Metallurgy is a fairly substantial end use for borates. The applications include:

- Production and refining of steel
- Production and refining of non-ferrous metals
- Manufacture of alloys
- Precious metal recovery
- Brazing/welding/soldering fluxes
- Jewelry making
- Amorphous metals
- Rare-earth magnets
- Tube and wire drawing
- Plating
- Mining

## Production and refining of steel

**Fluxing agent:** Borates are a possible replacement for fluorspar in the steel manufacturing process for the following reasons:

1. Metallurgical grade fluorspar is becoming scarce
2. Fluorine pollution laws are becoming more stringent

Borates are being used for these purposes by several European and Japanese companies in the basic oxygen process for making steel.

**Deoxidizer:** In steel production, borates are normally used as a cover flux to prevent air oxidation at the surface of the molten steel and ingots formed during the time of cooling and solidifications. Molten steel is poured into molds to form ingots. As the molten steel cools, the ingot contracts usually leaving a concave cavity in the center of the ingot. This cavity would oxidize, and rust would form if the cavity were left exposed to the atmosphere.

The rust, in turn, would form imperfections in the sheet steel during the rolling operation. *Dehybor*® anhydrous borax can be added to the molten steel and it will melt and rise to the surface. Thus, as the steel cools, the anhydrous borax protects the surface from oxidation.

**Steel refining:** Furthermore, borates act as fluxes during melting, combining with metallic oxides at relatively low temperatures to bring them to the surface of the melt as a slag which can be decanted or skimmed off. The removal of metallic oxide contaminants is essential to the quality of steel produced.

**Improving steel properties:** Boron can be regarded as a unique and highly versatile alloying element in steels, resulting in very significant improvements in properties and processing behavior at concentrations of about 0.003 wt%. Boron can not be added to the steel in the form of a borate since it would rise to the surface as a flux. Alloys such as ferroboration (10–25% B), manganese-boron (15–20% B), and nickel-boron (15–18% B) are made through the reduction of boric oxide or boric acid in the presence of the alloying metal.

The advantages of boron in relation to properties of steel are formability, hardenability, creep ductility in strip and engineering grades, corrosion resistance, hot workability, and neutron absorption.

**Nitrogen embrittlement:** At the stoichiometric ratio B/N (wt%) of 0.8, boron is added to strip steels to remove nitrogen from solid solution and reduce the problems associated with high temperature coiling operations. The addition of boron also reduces the susceptibility to cold work embrittlement in strip steels. The effect is related to the segregation of boron atoms to the grain boundaries, thereby blocking the effects of embrittling phosphorus atoms.

**Hardenability:** Boron has a significant influence on the hardenability of low-alloy engineering steels, 0.003% soluble boron producing an increase of hardenability equivalent to about 0.5% of elements such as manganese, chromium, and molybdenum. However, the use of boron as a hardenability agent is generally confined to steels containing less than 0.4% C.

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**Creep ductility:** Additions of about 0.005% B produce a large increase of the creep ductility of 1 Mo-0.75V turbine bolting steels. The effect is associated with the stabilizing action of boron in  $V_4C_3$  precipitates close to the grain boundary regions, making the carbides more resistant to dissolution and retarding the formation of denuded zones.

**Hot workability:** Boron additions are beneficial to both the hot workability and the rupture ductility of austenitic stainless steels. The effect has been theorized to occur by trapping of vacancies by boron atoms which modifies the flow of vacancies to the grain boundaries.

**Neutron absorption:** In the nuclear power and fuel reprocessing industries stainless steels containing up to 1% B are now finding application as neutron absorption materials for storage and transportation vessels. At this level, most of the boron is present as a  $(FeCr)_2B$  eutectic phase, which causes embrittlement, but the steel can be rolled into plates satisfactorily and has adequate weldability.

### Refining of non-ferrous metals

#### Dissolving metal oxide impurities

This deals with the recovery of metals—such as brass, bronze, copper, lead, zinc—from scrap or from slag left over from a primary smelting operation. In order to produce a product as pure as primary metal it is necessary to remove all oxides and extraneous impurities. Borates act as fluxes during melting, combining with metallic oxides at relatively low temperatures to bring them to the surface of the melt as a slag which can be decanted or skimmed off. These other metallic oxides are thus considered contaminants.

#### Cover flux to prevent air oxidation

During melting, borates will protect metal from the oxidizing atmosphere of the furnace. Borates near the bottom of the furnace will melt last and float up to the surface of the molten metal dissolving oxides, silica (sand) and other non-metallic impurities. If the metal is to be refined at this stage any special additives or alloying fluxes should be introduced under the borate cover. The borate slag can usually be skimmed from the metal easily

before pouring. If the slag is too thin, it may be thickened by addition of a small quantity of sand.

The great advantages of the borates as cover fluxes are:

- Ease and safety of handling
- Non-combustibility with minimum fuming tendency
- High solvent action on metal oxides and siliceous material present
- Formation of highly fluid slags with only mild attack on refractories
- Ease with which slag can be thickened if necessary, and skimmed

Purification is performed by adding borates to the furnace, placing the scrap or dross on top and turning on the heat. Usually the surface is also covered with borates to provide a molten cover to prevent oxidation during heating. The borate at the bottom melts and rises through the molten and/or partially molten metal dissolving the oxides and extraneous impurities and brings them to the surface forming a slag. This operation applies to cupola type furnaces while in reverberatory furnaces the borate is charged into the furnace directly with the scrap.

#### Smelting operation

In smelting non-ferrous scrap, *Dehybor* is recommended. Anhydrous forms are preferred to avoid puffing and intumescence (with possible steam explosions) as occurs when hydrated borates are heated vigorously. Anhydrous borates form an excellent liquid flux for most bronzes, brasses, and similar alloys, and also serve as scavengers to dissolve and carry out oxides, dirt, and sand which so often contaminate non-ferrous scrap.

While quantities will naturally vary somewhat with types of furnace and quality of the metal to be melted, from 0.006% to 0.01 wt% will generally purify the metal and serve as a cover. Sufficient *Dehybor* should be used to form a cover about 0.25" thick.

About half of the borate should be distributed over the bottom of the furnace before the metal is charged. The remainder should be added evenly over the metal.

**Nickel:** Nickel ores usually contain large amounts of iron, copper sulfide, nickel sulfide, and sodium sulfide and

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varying amounts of precious metals. The ore is smelted and then blown in a basic converter to remove the iron. The remaining matter is then remelted and the major portion of the copper sulfide and sodium sulfide form an upper layer while the nickel sulfide still contaminated with some iron, precious metals, and copper sulfide remains in the lower level. The two layers are separated and the contaminated nickel sulfide layer is formed into impure anodes. These anodes are then placed in an electrolytic cell containing a nearly neutral solution of nickel sulfate. When an electric current is passed through the electrolyte, the impure anode slowly dissolves and the pure nickel deposits on the cathode. The cells are specially constructed to keep the cathodes away from any contaminants and the contaminants are recovered from the impure electrolyte.

The neutral condition noted above is maintained by the addition of a borate and other chemicals to control pH. Borates used to control pH include *Optibor*® boric acid, boric oxide (anhydrous boric acid), and *Dehybor*.

**Aluminum:** Borates can be used in the actual process of preparing bauxite ore into aluminum. Low-grade fluoboric acid ( $\text{HBF}_4$ ), produced from hydrofluoric acid and boric acid or boric oxide, is used in the manufacture of cryolite ( $\text{Na}_3\text{AlF}_6$ ) for the electrolytic production of aluminum. The Alcoa® Alzak process of electropolishing of aluminum also requires fluoboric acid. Ammonium fluoborates can also be used as fluxes for aluminum reduction. Boron is a grain refiner and hardening agent for aluminum.

It can be added to the crucible melt in the form of aluminum-boron master alloy prepared from  $\text{KBF}_4$  or directly as boric oxide to the electric furnaces where alumina and  $\text{B}_2\text{O}_3$  are reduced to aluminum and elemental boron. The presence of boron in aluminum can improve appearance and reduce tearing on rolling into thin sheets. A small amount of borate is used in the preparation of activated alumina catalysts.

Cyanide forms as a result of a reaction between carbon, sodium and nitrogen in the lining of Hall-Héroult cells during the aluminum production. This has led to the

classification of spent potliner as hazardous waste. Attempts to suppress cyanide formation by sealing cells to avoid the penetration of air have brought at best partial success. On the other hand, adding suitable reactants to the potlining shows considerable promise. In laboratory tests, boric oxide was found to suppress cyanide formation almost completely, at conditions generally favoring the reaction of sodium, carbon, and nitrogen to form sodium cyanide. The resulting cyanide levels in the potlining were reduced to as low as a few ppm.

### Precious metal recovery

The gold and silver refining industry and assaying laboratories use *Dehybor* as part of their flux formulations. The other ingredients in the flux formulation will vary depending on whether the gangue associated with the ore is acidic, basic, or reducing in character. The major reason for using a form of borate is that it readily associates with the metallic oxide contaminants at a sufficiently low temperature to minimize the loss of precious metal and to give longevity to the melting equipment.

### Brazing/welding/soldering fluxes

Almost all dry and paste welding and brazing fluxes contain borates. The function of a flux in welding or brazing is to dissolve any oxides at the point of joining and leave a clean surface for the joint. The borates used by the industry are *Optibor*, *Dehybor*, potassium borates, and—in some rare cases—potassium fluoborates. Several companies are also making welding rods where the flux is bound to the rod via a binder. These companies purchase anhydrous borax, borax glass, and boric acid.

The ideal flux for these uses performs several functions:

- It covers the surface of the metal thereby excluding air and preventing oxidation of the metal
- It acts as a solvent in dissolving the metal oxides surrounding the area to be jointed
- It acts as a detergent, cleaning and floating away dissolved oxides, grease, and other foreign matters

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There are numerous flux formulations such as:

- Brazing flux (for brass, copper, monel, stainless steel): Potassium fluoride (35%), borax (10%), boric acid (45%), and water (10%)
- Nickel-chrome alloy welding flux: Calcium fluoride (13%), calcium hydroxide (14%), boric acid (35%), and sodium silicate (38%)
- Hard soldering, brazing or welding: Boric acid (38%), borax (3.8%), potassium silicofluoride (50%), potassium acid fluoride (10%), and water (23.2%)

### Jewelry making

Borates are essential to jewelry making. It is difficult to join two gold or silver wires without borate-containing solder. Using a solder which is half borax decahydrate and half powdered silver, a seamless join can be made in seconds. Gold wire behaves in exactly the same way. Silver—like most metals—forms a thin coating of oxide on its surface when heated in air. This silver oxide coating acts as a barrier to the metal fusing which is the object of the soldering process. A metallurgical flux is needed to overcome this problem.

Borax decahydrate behaves as a flux by melting below the melting point of silver to a liquid molten salt phase, and bathing the surface of the silver with a thin film that has a low viscosity and low surface tension. This liquid sodium borate both helps to protect the silver surface from oxidation and, because molten borax is an excellent solvent for metal oxides, dissolves any silver oxide that does form. With the silver oxide barrier layer removed, the clean metal surfaces readily melt together to form a solder joint.

The soldering is a two-step process: first the whole object is dipped in a strong borax solution; then the area to be joined is sprinkled with the solder mixture (which includes traces of copper as well as the borax and silver). In the early stages, each element of the jewelry design is individually soldered, later, as the object acquires its own rigidity, several solders can be made at the same time.

### Other metallurgical applications (non-flux)

#### Amorphous metals

Transformers are employed in the electricity distribution system to convert high grid voltages to the lower voltages required by the consumer. During the conversion, considerable energy losses occur in transformers containing cores of conventional soft (non-permanent) magnets. The loss also represents a significant wastage of fuels used in the generation of electricity.

Substantial reduction (70 to 85%) in the extent of energy loss can be achieved through the use of soft magnetic cores made from amorphous metal alloys. These typically contain 13–16% boron. The alloys are produced by such rapid cooling of the melt, that the atoms have insufficient time to form a crystalline pattern, and the presence of boron ensures the required amorphous quality. The boron component is incorporated as a ferroboron.

The ultra rapid quenching of iron-boron-silicon alloys produces amorphous metals which have a glass-like structure and excellent soft-magnetic properties. They are used, in the form of foils, as transformer cores and give rise to increased efficiency by reducing power loss.

#### Rare-earth magnets

The rare earth-iron-boron alloy permanent magnet powder, comprising iron, boron, and a rare earth element has drawn general attention as a permanent magnet material which exhibits superior magnetic properties, and it has since been in the development stage as a magnet powder for bonded magnets.

A large amount of technological interest has been focused on rare earth-iron-boron alloys (eg, 26.7% Nd – 72.3% Fe – 1% B) as a result of their promising magnetic properties for permanent magnet applications attributable to the magnetically hard  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase. Commercial permanent magnets of these alloys having anisotropic, aligned structure exhibit high potential energy products. Such energy levels are much higher than those exhibited by Sm-Co alloys previously regarded as having optimum

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magnetic properties. The rare earth-iron-boron alloys are also advantageous over the Sm-Co alloys in that the rare earth and Fe are much more abundant and economical than Sm and Co. As a result, rare earth-iron-boron permanent magnets are used in a wide variety of applications including, but not limited to, audio loud speakers, electric motors, generators, meters, scientific instruments, and the like.

Two different approaches are currently in use to produce isotropic permanent magnets from rare earth-iron-boron alloys. One approach involves rapidly solidifying the Nd-Fe-B alloy by spinning the melt to produce a near-amorphous, fine grained ribbon material, mechanically comminuting the ribbon to form flake particulates, and then vacuum hot pressing the flakes in a die cavity to consolidate the material. The second approach involves mechanical comminution of a chill cast ingot and “powder metallurgy” consolidation of the resulting fine comminuted alloy powder wherein the fine comminuted powder is pressed and sintered using liquid phase sintering and long time anneals to consolidate the powder. High-performance permanent magnets based on alloys of iron and neodymium need boron to prevent the two main constituents from separating.

### Tube/wire drawing

The manufacture of steel or stainless steel tubes is accomplished by taking a solid billet of the metal and heating it to a high temperature. The hot billet is then pierced in the center with a rod to form a hole through the center of the billet. *Dehybor* or a mixture of 3 parts anhydrous borax and 1 part coal slack are then thrown into the end of the opening and the billet is passed over an expander (welding ball or plug). Due to the relatively low melting point of the anhydrous borax, it readily melts as it rides along in front of the expander forming a then slick lubricating film. Additional quantities of the anhydrous borax or the mixture are added on repeated passes over the expander. The quantity varies depending on the length and diameter of the tubing being fabricated.

Wire is made by pulling steel rod through a series of dies with smaller and smaller openings until the diameter desired is attained. In order to protect the dies and the surface of the wire, a lubricant, usually a soap, is applied to the surface of the rod prior to the entry into the die. The lubricants have a tendency not to stick to the surface of the steel rod and it is therefore necessary to apply a lubricant carrier to the rod prior to its extrusion.

Borax decahydrate acts as such a lubricant carrier and will protect the rod from rusting in storage prior to extrusion. The usual method for applying the lubricant carrier is:

1. Clean the rod of all rust by dipping in a tank of either hydrochloric or nitric acid
2. Remove excess acid by a water rinse
3. Remove grease and dirt by dipping in a hot water detergent tank
4. Rinse with water
5. Dip in a borax solution made from borax 5 mol
6. Allow rod to dry and either place it in storage or send it directly to the extruder

### Plating

In the electroplating of nickel using a Watts bath, a current is passed through an electrolyte composed of nickel sulfate, nickel chloride and boric acid. The nickel salts breakdown to nickel, and the corresponding acidic component and the nickel is deposited in the cathode which is the material to be plated. A typical electrolyte for nickel plating is:

1. Nickel sulfate: 300 grams/liter
2. Nickel chloride: 60 grams/liter
3. Boric acid: 38 grams/liter

The nickel sulfate provides the major portion of the nickel to be deposited. The chloride improves anode behavior, allows higher rates of deposition and helps form smooth fine grade deposits. *Optibor* is used to control pH, acts as a buffer during electrolysis, and prevents the nickel deposits from being hard, cracked, and pitted.



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Other buffers could be used, but boric acid is preferred as it is stable and easily obtained in relatively pure and economical form.

Other bath types being used are the chloride bath and the nickel fluoborate bath. The nickel salts used to make up the electrolyte are different, but in each case boric acid is used as the preferred buffer.

The major applications for fluoboric acid are plating solutions (including electroplating of printed circuits) and as an intermediate in the manufacture of fluoborate salts. The largest end use for antimony, cadmium, cobalt, copper, indium, iron, lead, nickel, silver, tin, and zinc fluoborates in

plating solutions, including electroplating of printed circuit boards. Small amounts are also consumed as catalysts. Zinc fluoborate is also used by the textile industry as a curing agent in applying resins for crease-resistant finishes.

### Mining

Ammonium nitrate-fuel oil (AN-FO) explosives are unstable in certain mineral sulfide regions in copper mines. Natural oxidation causes what is called “hot spots,” which in turn causes the AN-FO explosives to be unstable and react. The “hot spots” can be controlled by spraying the blasting holes with ammonium pentaborate solutions.

### 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 650 customers with more than 1,800 delivery locations globally. We supply around 30% of the world’s need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles.

### About 20 Mule Team products

U.S. Borax produces the *20 Mule Team*® borates family of products from naturally occurring minerals and have an excellent reputation for purity and safety when used as directed. Borates are key ingredients in a number of industrial applications including fiberglass, glass, ceramics, batteries and capacitors, wood preservatives, and flame retardants.

High quality, high reliability, high performance borate products. It’s what we’re known for.



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