

Boron – from eye drops to rocket propellants

The element boron was already known in ancient times in the form of borax. It was used for glazes in China and for embalming in Egypt. The name is derived from the Middle Persian word “burak” for borax.

Although in an impure form, elementary boron was discovered in 1808, simultaneously and independently, by Joseph Gay-Lussac and Louis Thénard through reduction of boron trioxide with potassium, and by Sir Humphry Davy through electrolysis of boric acid. However, the recovery of pure crystalline boron did not succeed until the 1950s.

Elementary boron can be obtained from boron compounds either as a black product (amorphous boron) or in two crystalline forms. When these forms are heated to 1,200° C in the absence of air, the so called red alpha-rhombohedral boron transforms into the more stable, dark, shiny beta-rhombohedral boron. With the exception of diamond carbon, this is the hardest of all elements. Natural boron consists of an isotopic mixture of 19.78 percent boron-10 and 80.22 percent boron-11. Because of its ability to absorb neutrons, the lighter isotope is important as an alloying component of boron steels used in nuclear reactors.

Fine boron powder ignites when heated to about 700° C in air. It burns with a red flame to boron trioxide. At high temperatures boron also bonds with nitrogen, chlorine, bromine and sulfur. Whereas concentrated sulfuric acid first interacts with boron at Temperatures of around 250° C, the element reacts relatively easily with concentrated nitric acid, which oxidizes it to boric acid. Sodium borate is obtained by fusion with caustic soda.

In nature boron is found only in its oxygen compounds, especially as boric acid, colemanite (calcium borate), ulexite (boronat-rocalcite) and borax (sodium borate). In recent times the Californian deposits of borax-like kernite or rasorite have played a large role in the recovery of boron and its compounds. Elementary boron apparently has no toxic effect. Physiologically, however, it plays an important role as a trace element in plant life. Some plants need a constant supply of boron for cell division and thus, for growth.

Signs of acute boron shortage are visible, for example, in the case of heart or dry rot infestation of sugar beets. On the other hand, boron does not seem to be essential for animals and microorganisms.

The antibiotic boromycin is a natural substance containing boron. Diluted solutions of boric acid have an antiinflammatory effect and are often used as an eye tonic. A facility for the production of boric acid was constructed in the chemical plant of Gebr. Borchers in the old city of Goslar as early as 1882. Borax production was added a year later.

Both units were moved to the newly constructed plant near the train station in the town of Oker near Goslar in 1901. By 1906 some 1,878,569 kilograms of borax and 205,038 kilograms of boric acid were manufactured in Oker. At that time elementary boron was not yet being produced.

The renaissance of an old business

The renaissance of the old boron business, although with completely different products, emerged after World War II. Elementary boron and not borax was at the top of the list of the highly ambitious industry. On the one hand, there were the operators of nuclear power plants that required boron to absorb the neutrons in the reactors. On the other was the entire pyrotechnical industry, which used elementary boron in powder form as an additive in solid rocket propellants to achieve a higher thrust force.

Back in 1950, there were only very few companies in the West capable of producing boron, and none of them was located in Europe. In other words, the company that would be capable for supplying this element as early as possible would probably encounter a rapidly growing market.

H.C. Starck began the second phase of its boron chemistry in 1951, when Dr. Heinz Haag from the chemical institute of the University of Freiburg joined the research department in Goslar. He had been an assistant to Professor Georg Brauer, an expert in the field of preparative inorganic chemistry and the author of a standard reference book on chemistry that is still used today in an updated form. With his expertise in boride production, Haag was a real asset to the company.

Learning from tantalum chemistry

At that time metal tantalum was produced in Goslar by reacting potassium fluorotantalate with sodium vapors. A boat filled with fluoride and sodium was placed in an iron tube that extended into a Heraeus furnace (see the description in chapter on tantalum). Hence, it was an obvious conclusion to use this reduction technology for the production of elementary boron.

The reaction principle based on the conversion of the easily accessible potassium fluoroborate with sodium was already described in a U.S. patent. However, tests performed in Goslar led to a highly impure product with a maximum boron content of 85 percent. The researchers in Goslar were not satisfied with these results.

The next logical step was to modify the American process by varying the reaction parameters. H.C. Starck's chemists extensive practice with experimentation was a great advantage in this endeavor. They finally were successful in obtaining a yield of 95 percent boron with an average purity of 98.6 percent. This was done by using an excess of 5 to 10 percent sodium and conducting the reaction under lower pressure (0.1 torr) with subsequent chemical and mechanical concentration of the reaction cake, re-roasting of the crude boron and a renewed high-frequency treatment. A German patent was granted for this improvement in the process.

Shortly thereafter, the chemists in Goslar discovered that the purity of the boron could be increased to 99 percent with the help of a heat treatment at 1,350-2,000° C and a vacuum of more than 0.001 torr. This secondary treatment was protected by an additional patent for H.C. Starck.

Until July 1953 tests involving the repurification of the boron were conducted only on a pilot plant scale. Subsequent work performed in high-vacuum furnaces at Degussa and Balzers in 1953 and 1954 corroborated the laboratory tests in terms of the volatility of the impurities. Using this method, crude boron, which had a boron content of only about 90 percent due to the longer storage time, could be enriched to 98.5 percent boron through purification roasting at 1,400° C and 0.00007-0.00008 torr.

Several paths lead to boron

Despite these experimental successes, the production process for boron via potassium fluoroborate and repurification was not a solution because it was too expensive. There were three other methods used to produce boron in the 1950s:

- 1) reducing boron trichloride with hydrogen
- 2) thermal conversion of diboran
- 3) reducing boron trioxide with magnesium.

At the beginning of the 1950s, scientists in the United States had already started to recover amorphous boron with a 90-92 percent boron content directly, by treating boron oxide with magnesium and following this with an acid treatment.

By the early 1960s adding amorphous boron (90-92 percent boron) to solid propellant rocket motors in order to improve propulsion performance had gained wide acceptance. Thus a specification covering the composition of the boron and also the analytical methods to be used were introduced in August 1962: the MIL-B-51092. The "boron 90/92" that was produced in the United States by the company Trona largely fulfilled the requirements. The production process consisted of magnesium reduction of boron oxide, acid leaching of the reaction cake, washing with water, drying and deagglomeration of the dried cake.

Another producer in those days was Kawecki Berylco, which reduced the boron oxide in the facilities of the Penn-Rare Metals Division in Revere, Massachusetts. Around 1965/1966 H.C. Starck and Kawecki agreed to cooperate on the production of boron.

Optimizing the production process Goslar's attempts to reduce boron oxide by magnesiothermal methods at first turned out to be unexpectedly difficult. Initial experiments to replace boron oxide with cheaper raw materials like boric acid or rasorite ended in some extremely strong reactions, including some explosions. Subsequent experiments with boron oxide and magnesium mixtures, filled in iron boats and reacted in iron tubes at 600°-700° C, were such a total failure that the production of 100 kilograms of crude boron resulted in the wearing out of 20 iron tubes and 200 iron boats. Cooled crucibles made from Thermax sheet metal offered some help. The reaction cake was processed as before. The resulting product was a fine "boron 90/92." The only drawback in those days was that for military reasons, the United States preferred to use domestic boron for its rocket engines, almost without exception. This meant that the boron 90/92 produced by H.C. Starck could not be sold to the U.S. government. So it was decided in 1964 to concentrate production in Goslar on the quality grade "boron 95/97."

By 1966, after optimizing the process, H.C. Starck was capable of manufacturing some 2,866 kg of the product in its cellar pilot plant. A major part of this output, 2,495 kg, was sold to Kawecki. The know-how on the optimized process was also passed on to Kawecki so that a plant was set up in Boyertown, Pennsylvania, in the United States in 1969.

During a subsequent visit to the plant, H.C. Starck's boron experts discovered that the Americans had made modifications to the details provided by Goslar. Apparently, the aim was to reduce personnel in production. For example, they tried to automatize the washing process by using a thickener, which did not work in the end. Soon thereafter the facility was shut down for good because the sales volume was too low.

By comparison, the facility in Goslar ran perfectly. The demand in the West for boron 95/97 could be met easily. Some 53,068 kg of the product were sold from 1966 to the end of 1982, and another 19,145 kg were processed further internally to crystalline boron and borides.

Ultrafine grains for rocket engines

In the mid 1970s there was an interesting development in West Germany in the field of rocket engines. In collaboration with its subsidiary, Bayern Chemie, MBB in Ottobrunn was working on the principle of the "solid-propellant ducted rocket" (SDR). The central feature of this development was a new propellant system, which was referred to as the ram jet engine. A control valve was placed between the gas generator and the combustion chamber to regulate propulsion.

Since the gas generator of the system was under high pressure, the opening of the regulating valve had to be appropriately narrow. As a result, reliable methods for characterizing the grain size distribution of the solid boron 95/97 additive had to be calculated because it was feared that coarse boron grains would interfere with the ability to regulate the engine. As a result, customers demanded an amorphous boron with a two-percent maximum of grains larger than 2 μm and no grains larger than 5 μm .

Subsequent experiments at H.C. Starck to obtain a major change in the grain size distribution by modifying the composition of the reaction mixture or its lot size did not improve the results. The attempt to separate coarser particles with the help of sedimentation also turned out to be ineffective. Even air classifying tests with available classifiers by which a granular batch is separated into groups of uniform final rates of fall with the help of a gas current brought no major changes in the grain size distribution.

By comparison, tests conducted with the so called Donaldson classifier were more successful. After promising preliminary test results, H.C. Starck received one of these devices from MBB to continue its operational experiments.

Despite positive results and a grain size distribution that met customer specifications, this route could not be taken because the yield was only 60 percent. Including screening, the price for the product would have had to be doubled, which of course no customer would have accepted. Consequently an agreement was reached on the basis of a specification dating from 1980.

Production quantities hit their peak with 11,137 kg in 1984 and 13,800 kg in 1985. The development of the solid propellant ducted rocket ended at about this time, and it never went into mass production.

Igniter in the airbag

A new area of application for amorphous boron emerged at the end of the 1980s. Spurred by the aim of airbag producers to equip the gas generators of these lifesaving automobile safety systems with ignition mixtures that were both absolutely reliable and also nontoxic, the demand for boron 90/92 in the United States and boron 95/97 in Germany skyrocketed.

A densified powder mixture of sodium nitrate and amorphous boron is triggered by an electric impulse in such airbag igniters, which are supplied by Bayern-Chemie in Ottobrunn, as well as other companies. With the energy created by this primary ignition, sodium azide, which is distributed around the igniter in the form of pellets, decomposes in the gas generator in a fraction of a second to nitrogen and sodium. While the sodium is removed with the help of silicates, the released nitrogen inflates the airbag.

As this entire process occurs in just a few milliseconds, the highest demands are made on the ignition mixture. Boron has proved highly successful as a lifesaving component in this system.

Crystalline and pure isotopes

Not only amorphous, but also crystalline boron was able to develop into an interesting business for H.C. Starck. Orders from the French national nuclear energy authority, CEA, were the deciding factor for these developments. Besides designating the purity, the customer also had prescribed the exact grain size distribution, which resulted in the return of crystalline boron with grain sizes of less than 20 μm . After initial difficulties, substantial improvements in the product quality, not only with regard to the prescribed grain sizes, were made in subsequent years.

A particular challenge was the request of a customer to process pure isotope boron oxide to crystalline boron. Because of the extremely high prices of the starting material – boron-10 is the rarer of the two natural isotopes, and its enrichment is difficult because of the very similar chemical and physical properties of the two isotopes – the processing conditions with regard to yield, purity, B-10 content, grain size distribution and documentation were prescribed with painstaking exactness.

A special problem was the fact that the production staff had been involved for years in the production of boron with its natural isotope distribution. The pure isotope product – which is more expensive than gold – does not vary in color or behavior from the boron processed up to then. To process the molded parts made from the production of crystalline boron, a separate room was made available for crushing and screening, which reduced dust losses nearly to zero.

After providing a test sample of 2.7 kg, which held up to the scrutiny of the customer, H.C. Starck received the order. By May 1992 the company had completed the work on time and in compliance with all conditions.

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