

METHOD FOR PURIFYING ELEMENTAL BORON

As a result of certain properties such as the high enthalpy of oxide formation, low molecular weight and good chemical stability, boron is used in many areas of technology. Large amounts of amorphous boron are used as additive in pyrotechnic mixtures. In chemical synthesis, boron is used as starting material for producing borides and also as fluxes during soldering.

Since January 2001, a discovery by Prof. Akimitsu (Nature, Vol. 410, No. 6824 (2001), 63-64) has been on everyone's lips: it was found that the well known chemical compound magnesium diboride (MgB_2) has superconductive properties at temperatures below 40 Kelvin. In contrast to so-called cuprate-based superconductors, magnesium diboride exhibits advantageous properties for use as superconductor in wires and other applications (e.g. sintered bodies). Magnesium diboride is usually produced by the reaction of finely divided boron and magnesium powders with one another.

As a result of the method of wire manufacture (inclusion of the magnesium diboride or of a mixture of elemental boron and magnesium into a metal sheath and subsequent drawing and, if appropriate, subsequent heat treatment to achieve a chemical reaction between boron and magnesium to give magnesium diboride in the case of a mixture of magnesium and boron being used (*in situ process*) in order to obtain a metal wire with a magnesium diboride core), various requirements are placed on the magnesium diboride which have hitherto not been achieved. Besides a high fraction of amorphous boron, a high purity, in particular a low content of oxygen, nitrogen, anionic impurities such as chloride or fluoride, but also customary metallic impurities such as alkali metal ions and alkaline earth metal ions and also other metal ions, are required. A relatively

small particle size is likewise demanded, as is the absence of oversized individual particles since these individual particles can lead to the tearing of the wire upon drawing, and impurities can result in a lower current bearing capacity. In addition, oversized individual particles ("oversize") prevent the complete chemical reaction of the boron with magnesium to give magnesium diboride during the processes that form the basis of the wire manufacture. Furthermore, the chemical reactivity of the boron is reduced by coating the surface with boron oxide and borates, which is reflected in a longer reaction time and the required higher reaction temperatures. This is a disadvantage particularly in the case of the in situ process for superconductive wire manufacture.

Conventional, commercially available boron is usually obtained by reducing boron trioxide with magnesium, meaning that there is a need for a further purification of standard commercial boron in order to allow further cost-effective production.

Surprisingly, it has been found that a simple option for purifying pulverulent boron with a low particle size can be achieved through acidic esterification of the impurities with subsequent heat treatment. It has also surprisingly been found that boron purified in this way is very suitable for producing magnesium diboride for the manufacture of superconductive wires even if the fraction of crystalline boron in the overall boron used for producing magnesium diboride is up to 30%.

The invention therefore relates to a method for purifying elemental boron, comprising the following steps:

- provision of elemental boron;
- grinding of the elemental boron in the presence of an alcohol in order to obtain a first suspension;
- admixing the first suspension with a strong

acid that is soluble in the alcohol in order to obtain a second suspension;

- heating the second suspension to boiling with reflux cooling in order to obtain a third suspension;
- separating off the solid present in the suspension;
- heat-treating the solid under reduced pressure.

The advantageous embodiments can be found in the patent claims.

In the method, the grinding is advantageously carried out in an attritor or a stirred ball mill since in these devices grinding in a grinding fluid is possible and a small particle size and effective comminution of the oversize particles and also a narrow, monomodal particle size distribution can be achieved. The alcohol used is preferably a lower alcohol having 1 to 5 carbon atoms, in particular methanol. The strong acid and/or the alcohol are particularly preferably anhydrous. Suitable strong acids are in particular all anhydrous acids, such as gaseous hydrogen chloride or toluene-sulfonic acid.

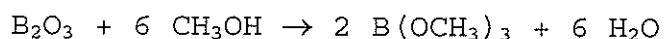
In general, boiling can be carried out for a period from about 1 to 24 hours under reflux. The optimum time depends on the individual case and can be ascertained by simple exploratory experiments. During this, the oxygen present, which is present in the form of boric acid, boron trioxide and the like on the surface of the boron particles, is esterified with the alcohol. Since this is an equilibrium reaction, the equilibrium should be shifted in the direction of the ester, which can be achieved through various measures. Firstly, the alcohol is used in excess. For this, it is possible to determine how high the oxygen content usually is with it having been established here that the boron comprises at most 2% oxygen. This means 1 kg of boron comprises ca. 20 g of oxygen, corresponding to

1.25 mol.

For an oxygen content of 2%, this corresponds to 0.4165 mol equivalents of B_2O_3 , corresponding to 0.833 mol of oxidically present boron, assuming that
5 the total oxygen is present in the form of boron trioxide.

The esterification reaction then corresponds, by way of example, to the example equation:

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Per mole of boron (in the boron oxide), 3 mol of alcohol are thus consumed.

15 2.499 mol of methanol are thus consumed, corresponding to 80.07 g; this corresponds for a density of 0.79 g/ml for methanol to 101.36 ml of methanol. If 1 kg of boron is suspended in approximately 2 liters of methanol, this then corresponds to 0.051% of the amount of
20 alcohol used, meaning that alcohol is clearly used in excess, based on the oxidic impurities in the boron.

The equilibrium can also (as is evident from the reaction equation) be shifted in the direction of the
25 ester by working with dry, as far as possible anhydrous, alcohol and as anhydrous as possible an acid.

Moreover, the water which is formed is advantageously removed from the condensate, just like the ester which
30 is formed.

This can be effected by, during the boiling with reflux cooling, passing the condensate, i.e. the reflux prior to returning it to the reaction mixture, over at least one alkali metal oxide or alkaline earth metal oxide
35 and at least one alkali metal hydroxide or alkaline earth metal hydroxide. The mixture of calcium hydroxide and calcium oxide are advantageously suitable here.

This is achieved in two ways: firstly, the water which

is formed in the reaction is bound by the alkali metal oxide or alkaline earth metal oxide, and secondly the volatile boric acid ester which is formed is saponified especially by the alkali metal hydroxide or alkaline earth metal hydroxide and remains as insoluble oxygen compound on the alkali/alkaline earth metal oxides and hydroxides used. The removal of water from the suspension is also supported by adding a suitable entrainer which forms azeotropes with water. For example, ethanol, tert-butanol, 1,2-dichloroethane, diethyl ether, ethyl formate, hexane or ethyl butyl ether are suitable; when using methanol, preference is given to using hexane or ethyl formate.

Preferably, this reaction, boiling under reflux, is carried out until boron can no longer be detected in the liquid phase of the reaction mixture. For this purpose, a sample is taken from the reactor, the solid is separated off and the alcohol is combusted. As soon as the color no longer exhibits a characteristic green coloration, the reaction is complete.

The solid is then separated off by filtration, centrifugation or distilling off of the liquid. If the liquid is distilled off, however, no removal of chloride-, fluoride- or iron-containing impurities takes place since the respective impurities are not volatile enough.

Since oxygen is also always present on the surface of the boron particles in chemisorbed form, ester groups are also bonded to the surface. These are driven off by the subsequent heat treatment under reduced pressure, during which an excessively high temperature or an excessively high pressure leads to the volatile oxygen impurities which are still present in the form of the ester being converted to nonvolatile oxygen impurities, which is undesired.

The process is therefore advantageously carried out in vacuo, in particular at a pressure of at most 10^{-3} mbar, preferably not more than 10^{-4} mbar.

Heating is carried out slowly in vacuo, at a heating rate of at most about 1°C/minute up to 1000°C, advantageously 400°C, the heating rate being reduced in the event of the pressure increasing too much as a
5 result of vaporizing oxygen impurities.

The heat treatment is continued in vacuo at the respective end temperature, which is generally 1000°C, advantageously 400°C, over a period from 1 to 3 hours. After the heat treatment, cooling is carried out under
10 an inert gas atmosphere, which must be different from nitrogen, preferably argon or helium.

The invention further provides purified boron obtainable by the method according to the invention. After this last heat-treatment step, a completely
15 purified and very reactive surface is present which reacts especially well with magnesium metal.

The invention therefore also relates to elemental boron which has a boron content of at least 96.8% by weight, an oxygen content of at most 1.6% by weight, a nitrogen
20 content of at most 0.2% by weight, a crystallinity of 30% by weight or less and a particle size distribution with a d100 value of 9 µm or less, preferably 6 µm or less.

The content of anionic impurities is at most 0.4% by weight, where chloride or fluoride are present in
25 amounts of at most in each case 0.2% by weight. The boron according to the invention comprises at most 1.0% by weight, preferably 0.8% by weight, of metallic impurities, which are in most cases alkali metal or
30 alkaline earth metal or a metal of the fourth period of the Periodic Table of the Elements. These can be present as impurities in elemental form or in ionic form. The content of alkali metal is at most 0.4% by weight, advantageously at most 0.3% by weight. In most
35 cases, this is potassium and/or magnesium, where potassium may be present in amounts of less than 0.3% by weight and magnesium may be present in amounts up to 0.4% by weight.

The metal of the fourth period of the Periodic Table of the Elements is present in amounts of at most 0.2% by weight, advantageously at most 0.1% by weight; in general, it is iron.

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Examples

The starting material used in each case were ca. 1 kg of standard commercial boron, grade I from H.C. Starck. The boron was ground in two different ways in a methanolic suspension (in each case 1 kg of boron per ca. 2 l of methanol), "boron a" in an attritor and "boron b" in a stirred ball mill.

Afterwards, both suspensions were further processed in the same way. Firstly, 100 ml of hexane are added to 2 l of suspension. The suspension is saturated with HCl by introducing HCl gas with stirring. The suspension is then boiled under reflux for ca. 10 h and the condensate of the reflux is passed over a contact mass consisting of one part calcium oxide and one part calcium hydroxide. After passing the contact mass, the condensate flows back again into the boiling suspension. When the reaction is complete, the mixture is left to cool to room temperature and a solid-liquid separation of the suspension is carried out using a standard commercial centrifuge. The solid which is formed is washed again with fresh methanol freed from water by means of known methods, and dried by means of known methods such that a flowable powder is left behind. This powder is then passed to the vacuum treatment. For this, it is taken to a vacuum furnace and heated to 400°C at 1°C per minute. If the pressure in the furnace exceeds about 10^{-4} mbar, the heating rate is reduced until the pressure in the furnace has dropped to below 10^{-4} mbar again. When 400°C is reached, it is left for a further three hours at this temperature, then the furnace is filled with argon and left to cool. The boron which is formed in the process is only further handled under protective gas (here

argon).

After the purification, it was found that the magnesium content could be reduced from 0.58% by weight to 0.46%
5 by weight and the oxygen content could be reduced from 1.8% by weight to 1.6% by weight.

The particle size distributions were determined by Fraunhofer diffraction using a Mastersizer S
10 instrument. Figure 1 shows the particle size distributions of pure boron according to the invention which have been ground as described above in the attritor and in a stirred ball mill.

15 The boron according to the invention was used to produce magnesium diboride, which was used to manufacture superconductive wires. Compared with the standard commercial boron grade I, the current bearing capacity in a low field was greater by a factor of 1.1,
20 and in a high field (greater than 3 Tesla) was more than ten times greater.

Claims

1. Elemental boron which has a boron content of at least 96.8% by weight, an oxygen content of at most 1.6% by weight, a nitrogen content of at most 0.2% by weight, a crystallinity of 30% by weight or less and the particle size distribution has a d₁₀₀ value of 9 μ m or less, preferably 6 μ m or less.
2. Elemental boron as claimed in claim 1, which has a content of anionic impurities of at most 0.4% by weight.
3. Elemental boron as claimed in claim 2, where the anionic impurities are chloride or fluoride and are present in amounts of at most in each case 0.2% by weight.
4. Elemental boron as claimed in one or more of claims 1 to 3, comprising at most 1.0% by weight of metallic impurities.
5. Elemental boron as claimed in claim 4, where the metallic impurities is alkali metal or alkaline earth metal or a metal of the fourth period of the Periodic Table of the Elements.
6. Elemental boron as claimed in claim 4 or 5, where the alkali metal is present in amounts of at most 0.4% by weight, advantageously at most 0.3% by weight.
7. Elemental boron as claimed in one or more of claims 4 to 6, where potassium and/or magnesium is present as metallic impurity.
8. Elemental boron as claimed in one or more of

claims 4 to 7, where the metal of the fourth period of the Periodic Table of the Elements is present in amounts of at most 0.2% by weight, advantageously at most 0.1% by weight.

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9. Elemental boron as claimed in claim 8, where the metal of the fourth period of the Periodic Table of the Elements is iron.

10 10. A method for purifying elemental boron, comprising the following steps:

- provision of elemental boron;
- grinding of the elemental boron in the presence of an alcohol in order to obtain a first suspension;
- 15 - admixing the first suspension with a strong acid that is soluble in the alcohol in order to obtain a second suspension;
- heating the second suspension to boiling with reflux cooling in order to obtain a third suspension;
- 20 - separating off the solid present in the suspension;
- heat-treating the solid under reduced pressure.

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11. The method as claimed in claim 10, where the grinding is carried out in an attritor or a stirred ball mill.

30 12. The method as claimed in claim 10 or 11, where the alcohol is methanol.

13. The method as claimed in one or more of claims 10 to 12, where the strong acid and/or the alcohol are anhydrous.

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14. The method as claimed in one or more of claims 10 to 13, where the strong acid is gaseous hydrogen

chloride or toluenesulfonic acid.

15. The method as claimed in one or more of claims 10 to 14, where heating is carried out for a period
5 from 1 to 24 hours under reflux.
16. The method as claimed in one or more of claims 10 to 15, where the alcohol is used in excess, based
10 on the boron oxide equivalent that can be calculated from the oxygen content.
17. The method as claimed in one or more of claims 10 to 16, where, upon boiling with reflux cooling,
15 the reflux is passed over at least one alkali metal oxide or alkaline earth metal oxide and at least one alkali metal hydroxide or alkaline earth metal hydroxide.
18. The method as claimed in one or more of claims 10 to 17, where the solid is separated off by
20 filtration, centrifugation or distilling off of the liquid.
19. The method as claimed in one or more of claims 10 to 18, where the heat treatment is carried out in
25 vacuo, in particular at a pressure of at most 10^{-3} mbar, preferably not more than 10^{-4} mbar.
20. The method as claimed in one or more of claims 10 to 19, where the heat treatment is carried out in
30 vacuo at a maximum temperature of 1000°C , advantageously 400°C .
21. The method as claimed in one or more of claims 10 to 20, where the heat treatment in vacuo involves
35 a heat treatment at a temperature of 400°C over a period from 1 to 3 hours.

22. The method as claimed in one or more of claims 10 to 21, where, after the heat treatment, cooling is carried out under an inert gas atmosphere, preferably argon or helium.
- 5 23. Elemental boron obtainable by a method as claimed in one or more of claims 10 to 22.
- 10 24. The use of boron as claimed in one of claims 1 to 9 or 23 for producing magnesium diboride, which is used for producing superconductive shaped bodies such as superconductive sintered bodies or wires.
- 15 25. A method for producing boron which comprises a purification method as claimed in one or more of claims 10 to 22.