

Inorganic Compounds

Background prior art

5 Magnesium diboride is a metallic chemical compound which has the at present highest transition temperature among metallic superconductors, namely 39 K. The cooling necessary for superconduction can also be generated by means of refrigeration machines; cooling by means of liquid helium can be dispensed with at this relatively high transition temperature.

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Various processes for preparing magnesium diboride are known from the prior art:

Hanada et al. J. Mater. Chem. 18 (2008), 2611-2614, disclose a process for
15 preparing magnesium diboride by thermal decomposition of magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) under a helium atmosphere or various hydrogen pressures. This study has the objective of examining magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) as material for the reversible storage of hydrogen for the purposes of hydrogen storage technology. It was established that magnesium
20 borohydride ($\text{Mg}(\text{BH}_4)_2$) decomposes mainly in the range from 250 to 410°C and with increasing temperature forms magnesium hydride (MgH_2). After a further temperature increase from 410 to 580°C, the magnesium hydride (MgH_2) likewise gives off hydrogen and crystalline magnesium diboride (MgB_2) can be detected in the X-ray diffraction analysis.

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Chlopek et al. J. Mater. Chem. 17 (2007), 3496-3503, describe a process for preparing magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) and its thermodynamic properties with the intention of using this compound as medium for the reversible storage of hydrogen gas. As processes for the preparation of magnesium borohydride
30 ($\text{Mg}(\text{BH}_4)_2$), mention is made of the metathesis reaction of magnesium chloride with lithium borohydride or sodium borohydride. Furthermore, a direct synthesis of $\text{Mg}(\text{BH}_4)_2$ from magnesium hydride and triethylamine-borane adduct is mentioned. In the decomposition reaction of $\text{Mg}(\text{BH}_4)_2$ at temperatures of 450°C and above, MgB_2 together with Mg and further unknown products were detected
35 by X-ray diffraction analysis.

US 2007/0286 787 A1 describes a process for preparing crystalline magnesium

borohydride from magnesium alkyls or magnesium alkoxides and a base-stabilized borane in a hydrocarbon solvent.

EP 1 842 838 A2 discloses a process for preparing superconducting materials, in which powders containing magnesium, boron and magnesium diboride and having a core-shell structure are processed by means of the "powder-in-tube technology" to produce superconducting wires. The reaction to form magnesium diboride is carried out under an argon atmosphere in the range from 400 to 900°C.

WO 2006/040199 discloses a process for preparing magnesium diboride, in which powders composed of elemental magnesium and boron are mixed with one another and pressed and a current pulse is subsequently passed through the compact so as to lead to a plasma discharge in the voids between the particles and make the preparation of dense MgB_2 materials possible.

DE 10 2004 014 315 A1 discloses a process for preparing boron-rich single-crystal metal borides by means of a reaction melt having a particular boron : metal ratio.

Magnesium diboride is also prepared in the prior art by the following process: a mixture of elemental magnesium and elemental boron is prepared and subsequently subjected to a furnace process at temperatures of from 800°C to 1200°C under argon as protective gas. This reaction is strongly exothermic. The process has the disadvantage that it does not give pure magnesium diboride, i.e. oxygen-free magnesium diboride, but owing to the high affinity of the metals magnesium and boron for oxygen always gives magnesium diboride containing oxidic impurities which reduce the suitability as superconducting material. When this process is carried out industrially, contamination of the magnesium diboride with oxidic impurities is therefore virtually impossible to avoid. The oxidic impurities cannot be removed by reduction with hydrogen since boron hydrides would be formed from the elemental boron.

A further disadvantage of this process is that the magnesium diboride obtained has a coarse (> 250 μm) and multimodal particle size distribution – a situation which makes further use as powder filling material for MgB_2 superconductor wires difficult. Owing to the highly exothermic nature of the reaction and the

resulting heating of the mixture, the magnesium diboride powder obtained is not sufficiently sinter active. The reaction proceeds with melting of the magnesium.

- A further known process (WO 02/072 501) for preparing magnesium diboride
- 5 comprises preparing a mixture of crystalline magnesium and amorphous boron as in the above-described process followed by mechanical alloying of the starting materials under argon. This enables the reaction temperature to be reduced considerably.
- 10 The advantage of the magnesium diboride prepared by the latter process is that it is more suitable as powder filling material for MgB_2 superconductor wires than the MgB_2 prepared by synthesis from the elements according to the above processes.
- 15 The disadvantage of this process is that the mechanical alloying is very time-consuming and also increases contamination of the material, for example by abraded material. After the furnace process, the powder nevertheless has to be milled since although it is obtained in finer form than in the first, conventional process it still contains a considerable proportion of oversize particles. This
- 20 second product milling increases the proportion of impurities in the powder further, takes time and limits the throughput. To keep the oxidic contamination as low as possible, magnesium hydride is added during milling of the product. Likewise, doping constituents can be added to the powder before milling.
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Object of the Invention

- It is an object of the present invention to provide a particular quality of magnesium diboride (MgB_2) which can be used as superconducting material in powder-filled wires or as magnesium diboride sintered bodies. The achievable
- 30 current carrying capacity of the components or wires comprising magnesium diboride should also be as great as possible at high applied magnetic fields. Furthermore, the achievable sinter activity of the magnesium diboride obtained should be as great as possible even at low temperature. Finally, dopants should be able to be introduced in a simple manner into the magnesium diboride. In the
- 35 case of doping by means of Si and C compounds, the dopants should be present in very finely dispersed form in the MgB_2 , so that a "solid solution" is effectively present.

Description of the Invention

The MgB_2 qualities available in the prior art do not meet these requirements.

- 5 One problem in the production of superconducting magnesium diboride wires is the oxygen content of the magnesium diboride. Magnesium diboride is sensitive to oxygen and moisture. The disadvantageous materials property of magnesium diboride, which is, however, inherent in the chemical nature of this compound, is not disadvantageous in the finished filled wire itself since the filling material of
- 10 the wire is sealed from air. Even if the greatest care is taken in the preparation of magnesium diboride from the elements magnesium and boron and contact with air and moisture is avoided, the affinity of magnesium and boron for oxygen is retained in the material, i.e. the amounts of oxygen initially present in the elements are found in the finished product. Oxygen-free elemental magnesium
- 15 is difficult or impossible to prepare and store; this applies even more to the element boron.

- Furthermore, the preparation of MgB_2 should where possible be carried out under reducing conditions in order to rule out contamination by oxidic by-
- 20 products.

Finally, the magnesium diboride obtained should have a very fine particle size and be amorphous to partially crystalline.

- 25 The object of the invention is achieved by a two-stage process in which the intermediate magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) is firstly prepared from magnesium hydride (MgH_2) or magnesium alkyls (MgR_2) or magnesium alkoxides ($\text{Mg}(\text{OR})_2$) and borane (B_2H_6), with the oxidic impurities being separated off, and the magnesium borohydride is subsequently thermally
- 30 decomposed to give magnesium diboride (MgB_2). There are two alternative processes for the first step, the preparation of pure magnesium borohydride, in which either a nonpolar solvent or a polar solvent is used.

- In a **first alternative process (a1)**, a magnesium alkyl of the general formula
- 35 MgR_2 or a magnesium alkoxide of the general formula $\text{Mg}(\text{OR})_2$ is dissolved in a nonpolar solvent. Examples of radicals R are all alkyl radicals having from 1 to 5 carbon atoms, in particular: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-

butyl, tert-butyl, pentyl, isopentyl and neopentyl. Preference is given to using di(n-butyl)magnesium. In the case of the alkoxide radicals in Mg(OR)_2 , the above definition of the radical R applies analogously: the alkoxides -OR can be derived from the corresponding alcohols. Preference is given to using

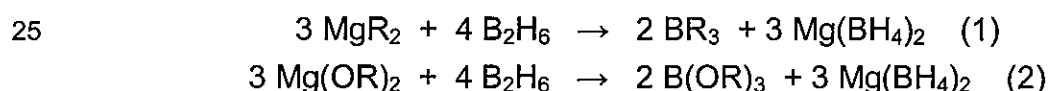
5 magnesium di-n-propoxide ($\text{Mg(O-n-C}_3\text{H}_7)_2$). Examples of nonpolar solvents are: hydrocarbons, e.g. pentane, hexane, heptane, octane, petroleum ether, benzene, toluene and xylene. Preference is given to using heptane.

Magnesium alkyls and magnesium alkoxides are sensitive to oxygen and

10 moisture. Magnesium alkyls and magnesium alkoxides therefore always contain magnesium oxide (MgO) or magnesium hydroxide (Mg(OH)_2). When the relatively nonpolar magnesium alkyls or magnesium alkoxides are dissolved in the abovementioned solvents, the magnesium alkyls or magnesium alkoxides go into solution while the oxidic impurities, for example magnesium oxide (MgO)

15 and magnesium hydroxide (Mg(OH)_2), do not go into solution because of their polar character. The undissolved constituents are separated from the solution of the magnesium alkyls or magnesium alkoxides by a known solid/liquid separation method, for example by filtration or centrifugation. This gives a solution of the magnesium alkyls or alkoxides which is free of oxidic impurities

20 and into which gaseous diborane (B_2H_6) is passed. The reaction of the magnesium alkyls or magnesium alkoxides can be described by the following reaction equations (1) and (2), which essentially represent a metathesis of the alkyl or alkoxide groups.



The diborane B_2H_6 used is naturally free of oxygen and moisture since it reacts with oxygen and moisture to form boron oxide and boric acids, respectively. The

30 reaction with diborane forms magnesium borohydride ($\text{Mg(BH}_4)_2$) which precipitates as polar salt in these solvents. The boron organyles BR_3 or boric esters B(OR)_3 which are at the same time formed in small amounts as by-products are soluble in the nonpolar solvent because of their nonpolar nature. This also applies to unreacted magnesium alkyls or magnesium alkoxides which

35 likewise remain in solution. Renewed phase separation, for example by filtration, gives the pure magnesium borohydride ($\text{Mg(BH}_4)_2$) which is free of oxidic impurities in the solid state. This can be used in the second step of

thermolysis. During the entire process, strict exclusion of oxygen and moisture has to be ensured.

In a **second alternative process (a2)**, the complex hydride magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) is prepared from magnesium hydride (MgH_2) and boron hydride (diborane; B_2H_6) in a polar aprotic solvent. This reaction can be described by the following reaction equation:



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This reaction preferably takes place in a polar aprotic solvent which has one or more oxygen and/or nitrogen atoms as donor function. These donor atoms have the function of coordinating to the magnesium atom and thus ensuring a preferred solution of the magnesium borohydride formed. Suitable solvents are dipolar aprotic solvents in general, which can comprise the following functional groups: ethers, tertiary amines and amides. Specific examples include diethyl ether, tert-butyl methyl ether, dioxane, tetrahydrofuran, N-methylmorpholine, dimethylformamide and the like. Preference is given to using tert-butyl methyl ether.

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Magnesium hydride is sensitive to oxygen and moisture. Commercial magnesium hydride therefore always contains magnesium oxide (MgO) and/or magnesium hydroxide ($\text{Mg}(\text{OH})_2$). Nevertheless, magnesium hydride is used together with the oxidic impurities in this step of the process of the invention.

Magnesium hydride is insoluble in the solvent mentioned and is slurried therein for the purposes of the reaction. Gaseous diborane is subsequently passed through the slurry of the magnesium hydride, forming magnesium borohydride which dissolves in the donor solvent used.

A critical aspect is the fact that magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) dissolves in the solvents mentioned while the oxidic impurities such as MgO and $\text{Mg}(\text{OH})_2$ and also boron oxide and boric acid are insoluble therein. This solubility difference between the soluble magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) and the insoluble oxidic impurities thus allows the oxidic by-products to be separated off from the intermediate magnesium borohydride. In this variant (a2) too, solid/liquid phase separation gives a solution of magnesium borohydride which is free of oxidic impurities. The solvent is removed by evaporation to give a solid

magnesium borohydride in which the donor solvents are coordinated to the magnesium. In all process steps, strict exclusion of oxygen and moisture has to be ensured.

- 5 Furthermore, a step of recrystallization from organic solvents can be carried out to achieve further purification of magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), regardless of whether the magnesium borohydride has been prepared according to variant (a1) or (a2). The solvents for the recrystallization are the same as those for variant (a2).

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In both cases (a1 and a2), a pure starting material $\text{Mg}(\text{BH}_4)_2$ which is free of oxidic impurities and is suitable for the preparation of magnesium diboride is obtained. This intermediate $\text{Mg}(\text{BH}_4)_2$ can be used in a second step (b) to prepare a magnesium diboride MgB_2 which is also free of oxidic by-products.

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Magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) has been found to be a particularly advantageous intermediate since it can be recrystallized from organic solvents.

- A further advantage of the intermediate magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) is that it is obtained with a soft consistency and a small particle size in the preparation. Magnesium borohydride forms a turbid suspension in heptane which settles only slowly. A fine particle size distribution of the magnesium borohydride can be concluded from this. It is difficult to determine a particle size distribution with exclusion of oxygen and moisture. A further after-treatment, for instance a milling step for further reducing the particle size, is not necessary.

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In a **second step (b)**, the magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) obtained is subjected to thermal decomposition to form magnesium diboride (MgB_2). The thermolysis proceeds according to the following reaction equation:

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- The thermolysis of the magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) is carried out at temperatures in the range from 250°C to 1600°C, preferably at a temperature in the range from 500°C to 1000°C. The thermolysis is particularly preferably carried out at a temperature of from about 500°C to 600°C. An amorphous to partially crystalline magnesium diboride is obtained. The reactivity toward

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dopants is significantly higher in the case of the magnesium diboride according to the invention than that of the crystalline magnesium diboride according to the prior art. Likewise, the magnesium diboride prepared according to the invention has a higher sinter activity than that prepared by the conventional process.

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The pressure in the thermolysis reaction is preferably atmospheric pressure; preference is given to using a protective gas at atmospheric pressure. A possible protective gas is, in particular, argon. As an alternative, a superatmospheric pressure of hydrogen can also be used. On the other hand, if
10 the thermolysis of the magnesium borohydride is carried out in a high vacuum, reversal of the formation reaction for this compound (see reaction equation (3)) occurs. As a consequence, magnesium hydride and diborane would be obtained again. A preferred reactor for the thermolysis of magnesium borohydride at atmospheric pressure is a reactor having a moving bed.
15 Examples include a rotary tube furnace and a fluidized-bed reactor. As an alternative it is also possible to use a reactor having a static bed.

The thermolysis reaction of the magnesium borohydride has the following advantages:

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The donor solvents coordinated to the magnesium atom are given off at temperatures as low as from 50 to 250°C in a stream of argon. However, the magnesium borohydride is stable to decomposition at these temperatures. The
adduct of magnesium borohydride and donor solvent therefore has no
25 disadvantage in terms of having an adverse effect in the decomposition of magnesium borohydride which commences only above 250°C.

Only hydrogen is formed as sole by-product during the thermolysis reaction. Thus, no oxygen which could lead to contamination as a result of the formation
30 of oxidic impurities is formed during the thermolysis or participates in the thermolysis reaction.

The hydrogen formed can, as gas, easily be separated off from the solid magnesium diboride. Furthermore, no solvents or auxiliaries which coat the
35 surface of the magnesium diboride being formed and may thus outgas and impair the superconductivity of the magnesium diboride are used in this step. Coating of the surface is avoided from the beginning in the process of the

invention, so that no reaction products or by-products can be formed. The formation of hydrogen is therefore also ideal from this point of view.

Magnesium borohydride can be thermolyzed easily and completely. The
5 thermolysis commences at temperatures of about 250°C. The heat of reaction for the formation of magnesium diboride MgB_2 by thermolysis of magnesium borohydride is relatively low compared to the formation from the elements. This situation is an advantage in the preparation of magnesium diboride for use in superconduction. The lower the temperature or the heat of reaction for
10 formation of magnesium diboride, the lower the particle size and crystal growth of the magnesium diboride obtained and the poorer the crystallinity of the magnesium diboride. According to the Tammann rule, crystal growth is particularly great when the temperature of a mixture is close to the theoretical melting point. A high heat of reaction thus promotes crystal growth. However, a
15 very small particle size is preferred for the present use in superconduction.

The pure magnesium diboride MgB_2 formed has the advantage that it is obtained in finely particulate form and does not have to be subsequently milled because it does not sinter during the thermolysis reaction and that it can be
20 used directly as material for filled wires. A milling step would also mean contamination as a result of abrasion. The magnesium diboride MgB_2 obtained has a monomodal particle size distribution with $D_{100} \leq 15 \mu\text{m}$, preferably $D_{100} \leq 10 \mu\text{m}$.

25 The magnesium diboride prepared according to the invention is amorphous or partially crystalline. The amorphous or partially crystalline magnesium diboride of the invention therefore has a proportion of crystalline material of not more than 25% by weight, preferably not more than 15% by weight and particularly preferably not more than 10% by weight. In contrast, the crystalline magnesium
30 diboride of the prior art (from H.C. Starck) has no significant proportion of amorphous magnesium diboride.

Compared to the virtually exclusively crystalline magnesium diboride of the prior art, the magnesium diboride prepared according to the invention has the
35 advantage of higher ductility. This materials property is important when powder-filled wires filled with magnesium diboride are processed by drawing and rolling. In addition, the magnesium diboride prepared according to the invention has a

higher current carrying capacity than that of the prior art.

The magnesium diboride prepared by the process of the invention is free of
oxidic impurities and has an oxygen content of not more than 2000 ppm,
5 preferably not more than 500 ppm, particularly preferably not more than
100 ppm.

In addition, the magnesium diboride prepared by the process of the invention
can readily be doped. In the prior art, doping is usually carried out by milling
10 magnesium diboride or its starting materials with the dopant, so that abrasion
during milling represents a source of contamination. Doping of the magnesium
diboride intended for superconducting applications with various materials
promotes high current carrying capacities or current densities. Doping with
carbon or silicon carbide or doping with a mixture of the two is particularly
15 sought after by wire manufacturers.

According to the invention, doping is carried out using gases which are added to
the protective gas in the step of thermolysis of the magnesium borohydride.
This enables a particularly fine dispersion of the dopant, namely the desired
20 "solid solution", to be achieved. Doping with carbon (C doping) can be achieved
in the thermolysis process by enriching the protective gas with gases which give
carbon on decomposition. Suitable gases are, for example, acetylene, ethylene,
propane and butane. Preference is given to using acetylene.

25 Various methylsilanes which on thermolysis give silicon carbide, possibly with
an excess of one element, are possible for doping with silicon carbide.
Examples of methylsilanes are tetramethylsilane ($\text{Si}(\text{CH}_3)_4$) and tetramethyl-
disilylene ($(\text{CH}_3)_2\text{Si}=\text{Si}(\text{CH}_3)_2$). Preference is given to using tetramethylsilane
($\text{Si}(\text{CH}_3)_4$). Furthermore, it is possible to use further compounds, in particular
30 gases, which can be decomposed to form the desired dopants during the
thermolysis process.

The magnesium diboride of the invention can, due to its high purity and its fine,
homogeneous particle size distribution, advantageously be employed in
35 superconduction. Here, a metal wire containing a core of magnesium diboride is
used.

The conventional methods of wire manufacture place various demands on the

magnesium diboride which have hitherto not been able to be met. Such a wire can be obtained in a conventional way by enclosing a mixture of elemental boron and magnesium in a metal sheath, subsequently drawing a wire and then carrying out a heat treatment to bring about a chemical reaction of boron and
5 magnesium to form magnesium diboride and obtain a metal wire having a magnesium diboride core.

Apart from a high proportion of amorphous boron, a high purity, in particular a low content of oxygen, nitrogen, anionic impurities such as chloride or fluoride and also usual metallic impurities such as alkali metal and alkaline earth metal
10 ions and also other metal ions, is required. Likewise, a low particle size and the absence of oversize individual particles is demanded, since these individual particles lead to rupture of the wire during drawing and impurities can result in a lower current carrying capacity.

Furthermore, oversize individual particles ("oversize") prevent complete
15 chemical reaction of the boron with magnesium to form magnesium diboride. Conventional, commercially available boron is usually obtained by reduction of boron trioxide with magnesium, so that there is a need for further purification of the commercial boron in order to make further inexpensive production possible. As an alternative, such a superconducting wire can be obtained by enclosing
20 the magnesium diboride in a metal sheath and subsequently drawing a wire. The magnesium diboride of the invention or the magnesium diboride obtained by the process of the invention is particularly suitable for this manufacturing method since, owing to its high purity, uniform particle size distribution and the

small particle size, it overcomes many disadvantages of the prior art.

25 The present invention therefore also provides a process for producing superconducting wires having a metal sheath and a core of magnesium diboride, wherein magnesium diboride according to the invention is provided, enclosed in a metal sheath and subsequently converted into a wire having a metal sheath and a core of magnesium diboride by wire drawing.

Claims

1. Amorphous or partially crystalline magnesium diboride, characterized in that it has a proportion of crystalline material of not more than 25% by weight determined by X-ray powder diffraction.
2. Magnesium diboride according to Claim 1, characterized in that it has an oxygen content of not more than 2000 ppm.
3. Magnesium diboride according to Claim 1 or 2, characterized in that it has a monomodal particle size distribution with a D_{100} of less than or equal to 15 μm .
4. Process for preparing magnesium diboride according to any of Claims 1 to 3, wherein
 - a1) magnesium alkyls (MgR_2) or magnesium alkoxides (Mg(OR)_2) and diborane (B_2H_6) are reacted in a nonpolar solvent to form magnesium borohydride ($\text{Mg(BH}_4)_2$) and the oxidic impurities and also the by-products are separated off, where the radical R is an alkyl radical having from 1 to 5 carbon atoms, or alternatively
 - a2) magnesium hydride (MgH_2) and diborane (B_2H_6) are reacted in a dipolar aprotic solvent to form magnesium borohydride ($\text{Mg(BH}_4)_2$) and the oxidic impurities are separated off, and
 - b) magnesium borohydride is decomposed at atmospheric pressure and temperatures of from 250°C to 1600°C under a protective gas atmosphere to give magnesium diboride.
5. Process according to Claim 4, wherein the magnesium borohydride obtained in step (a1) or (a2) is recrystallized from a dipolar aprotic solvent.
6. Process according to Claim 4 or 5, wherein the protective gas is admixed in step (b) with a gas which during thermolysis results in doping of the magnesium diboride with carbon or silicon in the form of a solid solution.

7. Use of the magnesium diboride according to any of Claims 1 to 3 for superconduction.
8. Process for producing superconducting wires having a metal sheath and a core of magnesium diboride, wherein magnesium diboride according to one or more of Claims 1 to 6 is provided, enclosed in a metal sheath and subsequently converted into a wire having a metal sheath and a core of magnesium diboride by wire drawing.
9. Process according to Claim 8, wherein
- a1) Magnesium alkyls (MgR_2) or magnesium alkoxides (Mg(OR)_2) and diborane (B_2H_6) are reacted in a nonpolar solvent to form magnesium borohydride ($\text{Mg(BH}_4)_2$) and the oxidic impurities and also the by-products are separated off, where the radical R is an alkyl radical having from 1 to 5 carbon atoms, or alternatively
- a2) magnesium hydride (MgH_2) and diborane (B_2H_6) are reacted in a dipolar aprotic solvent to form magnesium borohydride ($\text{Mg(BH}_4)_2$) and the oxidic impurities are separated off, and
- b) the magnesium borohydride obtained is decomposed at atmospheric pressure and temperatures of from 250°C to 1600°C under a protective gas atmosphere to give magnesium diboride,
- c) the magnesium diboride obtained is enclosed in a metal sheath and
- d) a wire having a metal sheath and a core of magnesium diboride is obtained by wire drawing.