



Nano-sized boron synthesis process towards the large scale production



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HIGHLIGHTS

- An innovative process to synthesize boron powder has been reported.
- The described process has demonstrated its suitability for the large scale application.
- Using the new process, the MgB₂ powder can be improved through a homogenous dispersion of dopants.

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ABSTRACT

In the present paper a new process for large scale production of nano-sized boron is reported. The process can be summarized in several steps: boron oxide solubilization in hot water, cryogenic freezing of liquid phase, freezing–drying process, magnesiothermic reduction of boron oxide, boron purification. Each step is described in order to show the innovations and then the purified boron has been employed to synthesize the superconducting MgB₂ powder. It is worth to note that for the first time the same MgB₂ precursors were used to prepare the superconducting phase following four different techniques and the results directly compared. So several MgB₂ conductors were prepared applying different techniques, ex-situ, in-situ, via MgB₄ and RLI, and then their superconducting properties investigated. Furthermore morphology, grain size and purity of B and MgB₂ powder were analyzed by SEM analysis and X-ray diffraction technique.

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1. Introduction

Boron is a relatively rare element in the Earth's crust, representing only 0.001% of the crust mass and it does not appear on earth in elemental form but is found combined with others elements in borax, boric acid, colemanite, kernite, ulexite and borates. Despite the rapid growth of boron applications, limited progresses have been made in the synthesis of nanometric boron powder, especially for doped powder. The most important method to produce elemental boron involved reduction of boron oxide (B₂O₃) with metals, such as Mg or Al, reaching a purity grade between 90% and 98%. Pure boron can be prepared by reducing volatile boron halides with hydrogen at high temperatures. Ultrapure boron for use in the semiconductor industry is produced by the decomposition of diborane at high temperatures and then further purified with the zone melting. Nearly all synthetic methods for boron

powder are based on the technologies that involve the usage of gas phase decomposition of highly toxic and flammable precursory gases (B₂H₆, H₂, BCl₃) under severe reaction conditions, and then they are inevitably expensive and dangerous processes. In order to provide a broader view about the techniques of B powder synthesis, the main synthesis reactions of B have been listed in the following:

Reduction of boron compounds by:

- metallothermic reaction: i.e. $B_2O_{3(l)} + 3 Mg_{(l)} \rightarrow 3MgO_{(s)} + 2B_{(s)}$ at 1000 °C;
- electrolysis from a melt: $B_2O_3-K_2O-KF$ or $B_2O_3-KBF_4-KF$ at 800–900 °C;
- hydrogen: i.e. $BCl_{3(g)} + 3/2 H_{2(g)} \rightarrow 3HCl_{(g)} + B_{(s)}$ on hot W (or Ta) filament at 1300 °C;

Thermal decomposition of boron compounds:

- boron hydrides: $B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)}$ on Ta filament at 950 °C;

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– boron halides: $BX_{3(g)} \rightarrow B_{(s)} + 3/2 X_{2(g)}$ on W (or Ta) filament at 1400 °C.

In the present paper we propose a new inexpensive technology for carbon-doping (C-doping) and nano-sizing of boron based on freezing-dry process step before the Moissan's magnesiothermic reduction of boron oxide. We can speculate that freeze drying (lyophilization) is a technique widely employed by pharmaceutical and food industries to remove water by sublimation from frozen phase, so it results a relatively inexpensive process compared to the plasma synthesis process [1].

The innovative preliminary step considers the preparation of a B_2O_3 or boric acid (H_3BO_3) solution in water. At this step, the introduction of a soluble organic molecule (carbohydrate), or an insoluble inorganic compound (SiC) or element (C) can be done. In this way it is possible to have a homogeneous solution or dispersion of the C-source in the H_3BO_3 medium at the end of the freeze-drying process. The C-doping is particularly useful for high magnetic field applications of the MgB_2 conductor [2–5]. In order to have the most possible fine precursor powder, the freezing process of the liquid solution has to be leaded in a cryogenic liquid (liquid N_2). Following the new boron synthesis process is possible to obtain a suitable precursor for MgB_2 -based conductor manufacturing with the same performance of conductors prepared using MgB_2 powders synthesized from commercial B precursor. In particular in previous articles we shown that the laboratory made B has the same critical current density (J_c) performance of milled MgB_2 powders [6–8].

The grain size of MgB_2 , as well as the doping of MgB_2 , plays a fundamental role in critical current performances. In fact, it is well known that MgB_2 follows a grain boundary pinning mechanism, and then finer the powder higher the pinning force and better in-field J_c behavior will be shown by the conductor. For the above considerations the grain size of B can play an important role, furthermore also the reactivity versus the magnesium will be improved using nano-sized B and the MgB_2 synthesis temperature and reaction time can be lowered.

In the present paper we report the scaling-up of the laboratory process, producing 0.1 kg both of pure and Si-doped B. It is worth to note that: 0.5 kg of Mg and 2.3 kg of H_3BO_3 are needed in order to produce 0.1 kg of B. The resulting raw B must be processed with acid leaching to remove 2.7 kg of secondary products, MgO , B_2O_3 , and MgB_2 . A big amount of mass is involved in the process here described. Anyway, it is not a problem to process a bigger amount of reactants for a chemical factory, which could obtain 10 kg (or more) per batch. 10 kg of B powder give 20 kg of MgB_2 useful for 20 km of cable.

It is interesting to note that the reduction with elemental Mg is carried out with excess of B_2O_3 respect to the Mg, in order to limit the side reaction, so instead to use the stoichiometric ratio 1:3 ($B_2O_3:Mg$) we adopt 1:1.1 ($B_2O_3:Mg$). In this way the side reaction due to direct reaction between Mg and B (just formed) is attenuated. However, the reaction has a low yield with respect to the starting amount of reactants. In order to have 1 kg of B will be necessary to react 13 kg of B_2O_3 with 5 kg of Mg. The theoretical product yield of the stoichiometric ratio using 5 kg of Mg is 1.4827 kg of B; instead the yield of the process using the B_2O_3 excess is only 1 kg. The 67% of yield is principally due to the contemporary formation of magnesium borate ($x B_2O_3 \cdot y MgO$) and magnesium boride (MgB_2) of the respective side reactions.

2. Experimental details

The process to prepare boron can be summarized in the following steps:

- (1) Solubilization of H_3BO_3 (as well as of the doping source),
- (2) Cryogenic freezing,
- (3) Freeze-drying,
- (4) Reduction to raw elemental boron,
- (5) Acid leaching and heat treatment at high temperature of B.

The last step is the conversion of B (using Mg) into MgB_2 phase, which is used for the MgB_2 conductor manufacturing by ex-situ powder in tube (P.I.T.) process, or other techniques.

Steps (1), (2) and (3) represent the innovation introduced into the Moissan's process [9].

The process is summarized in Fig. 1.

2.1. B_2O_3 precursor preparation

The H_3BO_3 (2.3 kg) was dissolved in boiling deionized water (10 l) to maximize g/l ratio, i.e. 276 g/l at 100 °C against 46.5 g/l at room temperature. At this step some doping agents can be added, for this work was chosen 10% w/w SiO_2 . So the process was used to prepare two different nano-sized B powders: pure B and 10% w/w Si-doped B. Independently, each solution was cryogenically frozen in liquefied nitrogen (LN_2) to obtain a solid phase useful for freezing–drying process. A sloping plan has been used to keep a polypropylene LN_2 container in front of bain-marie containing the boiling solution. Then the boiling solution is sprayed directly into the LN_2 using compressed air (2 bars). Cryogenic freezing has the double purpose to maintain the chemical homogeneity during the solid phase formation and to lead the biggest surface area of solid phase useful for the sublimation process. The solid phase is then placed in the Coolsafe™ freeze-dryer (model 55–4) in order to remove water by sublimation, experimental conditions are summarized in Fig. 2.

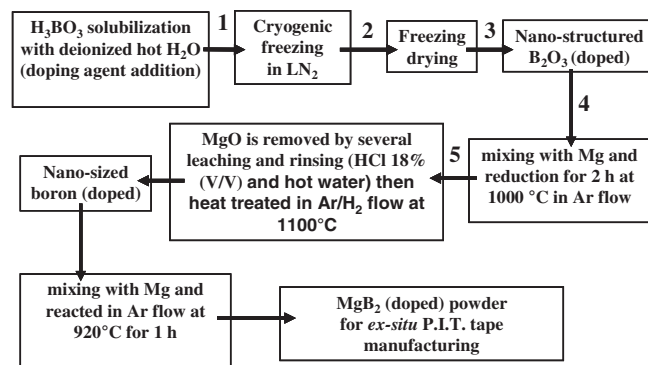


Fig. 1. Stages of the B powder synthesis and MgB_2 preparation.

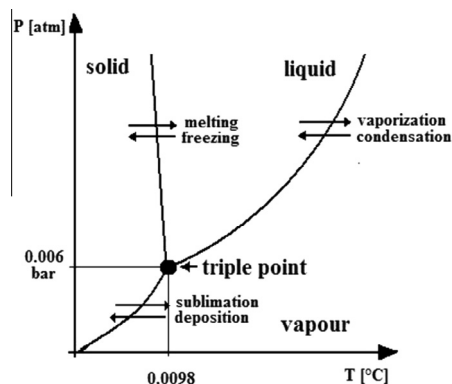


Fig. 2. Pressure–temperature diagram of water.

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