Fabrication of Bulk Targets of MgB_2 with Stoichiometric and Nonstoichiometric Contents

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Abstract: Powder of magnesium diboride was obtained by solid phase reaction of mixture of magnesium (> 99% pure) and amorphous boron (> 99% pure) powders at 650-900 °C temperatures in inert atmosphere. During synthesis process main attention was paid to removing oxide layer of surfaces of powder particles by organic solvents in Glovebox, where concentration of oxygen and water steam is less than 5 ppm. Homogenization and activation of powders were conducted in a planetary nano-mill by WC balls in an inert area. Pressing of the obtained powders was conducted in an argon atmosphere. MgB_2 nonstoichiometric powders contained excess boron and magnesium. Magnesium hydride was used as source of excess boron, which is fragile compound and easy to grind in nano-mill. It decomposes with metallic magnesium and hydrogen up to 280 °C temperature. Commercial magnesium diboride powder (Aldrich, > 99%) was used for fabrication of MgB_2 bulk targets. Powders systems of MgB_2 -Mg, MgB_2 - MgH_2 , MgB_2 -B homogenized by nano-mill in Glove box was used for fabrication of composites with nonstoichiometric contents. The targets were cylinders with diameters of 27-52 mm and height of 5-15 mm. Consolidation of pressed powdery composites was conducted in argon atmosphere. Synthesis of MgB_2 from mixture of magnesium and amorphous boron powders and simultaneous consolidation were conducted by hot pressing (HP) method. Phase content of the obtained targets were established by XRD method after dry polishing. Superconducting characteristic of the obtained samples were measured by vibrational magnetometer. The superconducting transition with an onset at 39 K was observed in a good agreement with the results of the other groups obtained on samples prepared by conventional techniques. The phase exists near the nominal composition without a significant homogeneity range.

Key words: Superconductors, chemical synthesis, magnesium diboride, hot pressing, microstructure.

1. Introduction

After discovery of MgB_2 superconductivity [1] of the many experiments has been conducted to improve the superconductive characteristics of these materials. The most efficient sintering method for obtaining high density bulk materials is hot pressing of MgB_2 powders or mixture of the Magnesium and Boron elemental precursors.

Pressure allows to suppress a volatility of Mg, Impeding its oxidation and promoting the formation of

a mechanically stable denser structure [2-4]. A denser material usually exhibits higher superconducting properties; it is more stable against degradation during exploitation, less reacts with a moisture, etc. [5-7].

Even in case of pressure less synthesis or sintering a preliminarily densification i.e., pressure treatment, plays a great role in attaining high superconducting and mechanical characteristics of the produced materials. Recently the efficiency of high-pressure densification has been shown for wire manufacturing process, in particular [8].

Despite the comparatively simple lattice structure of

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MgB_2 , to find correlations between the MgB_2 -based material structural features and its superconducting properties is a very complicated task. It can be explained by a considerable difficulty that arises from the electronic structure, by the necessity to detect the amount and distribution of light element boron to analyze the boron-containing compounds [9] in nanostructural materials, which are often porous and in addition can easily react with oxygen and hydrogen.

Magnesium diboride has potential for superconducting applications among other materials because of its low mass density. This would allow fabrication of desirable shapes specimens such as blocks, cylinders, rods and wires with good mechanical strength. For possible applications, the use of bulk boron based superconductors is constrained by poor mechanical properties caused by weak grain to grain contacts and inadequate porosity of the samples [10, 11].

Most of the known preparative methods for magnesium diboride are based on treatment of the elements at temperatures above the melting point of magnesium. Heating of the elements in an Ar/H_2 or Ar atmosphere in Mo or Ta containers at temperatures of 873 K to 1,223 K followed by hot pressing at 1,073 K (10 GPa) has been already applied [12, 13]. The direct reaction between the components (without pressure) in a Ta container was also performed [14].

In the present study, we report results of studying the structure and superconducting properties of the MgB_2 -based materials obtained by hot pressing.

2. Experiments

Magnesium diboride powder has been obtained by magnesium (> 99% pure) and amorphous boron powders (> 99% pure) mixture solid phase reaction 650-900 °C in an inert atmosphere. Main attention during sintering was paid to the removal of powder particles surface oxide layer by means of oxygen-free ultrapure organic solvents in Glovebox (Vigor Gas Purification Technologies Inc) where concentration of

oxygen and water steam is less than 5 ppm. Nonstoichiometric MgB_2 powders included 2%, 5% and 10% excess boron or magnesium. Magnesium hydride has been used as excess magnesium source being brittle compound and easily powdered in a nanomill (FRITSCH “Premium Line”). Homogenization and activation of powders were conducted in planetary nano-mill by WC balls in inert area. Pressing of obtained powders was conducted in argon atmosphere. MgB_2 nonstoichiometric powders contained excess boron and magnesium. Magnesium hydride was used as source of excess Magnesium, which is fragile compound and easy to grind in nano-mill. Up to 280 °C temperature it decomposes with metallic magnesium and hydrogen.

Commercial magnesium diboride powder (Aldrich, > 99%) was used for fabrication of MgB_2 bulk targets. Powders systems of MgB_2 - Mg , MgB_2 - MgH_2 , MgB_2 - B , homogenized by nano-mill in Glove box, was used for fabrication of composites with nonstoichiometric contents.

The obtained targets represent cylinders with a diameter 25-55 mm, and height 7-10 mm. Consolidation of powder compositions has been performed in an argon atmosphere. Powders have been sintered without preliminary pressing by hot pressing (HP) synthesis method under the following conditions: current 700-1,300 A, pressure 60-800 MPa, voltage 5-15 V, sintering duration: 6-10 min.

3. Results and Discussion

3.1 Consolidation

Rapid nontraditional consolidation methods give us possibilities to reduce duration of samples hitting temperature duration, which stipulates limitation of increasing grains sizes and high density of compacted samples.

Hot pressing synthesis method has been chosen from the known pressing methods.

During HP synthesis method, impulsive current, leaking in powder, preliminarily compacted at low

pressure generates high energy plasma discharge on particles interface. HP synthesis method has been characterized by: (1) accumulating influence of external parameters (pressure and electrical current) on powders compacting and phase generating; (2) rapid volume heating, that gives possibilities to reduce increasing kinetic of grain sizes. HP synthesis gives possibilities of implementing process by rapid heating and cooling.

Powder compacting process via HP synthesis method can be implemented by choosing different parameters of constant, alternating and impulsive current.

General view of HP synthesis device is given on Fig. 1a. The device is equipped with chamber, working in vacuum and inert atmosphere (Fig. 1b).

Working pressure in the device is formed by hydraulic system. Maximum loading is 25,000 kg. The main knot of heating system is lowering transformer, which is operated by electronic block. Heating system gives possibilities to leak (flow) alternating or constant current up to 4,000 A. In compacting knot KM54-15 graphite is used as a punch, which gives possibilities to vary working pressure up to 100 MPa. Registration of compacting parameters (pressure, current, resistivity, temperature, motion of punches) is conducted by using of the computing block.

MgB_2 synthesis has been carried out by current leaking (flowing) in mixture of Mg and amorphous B powders (500-2,000A), and also by heating of graphite die up to 500-900 °C in vacuum with constant current. For this purpose, graphite die were made (27 and 52 mm diameter).

In purpose of easily taking out consolidated MgB_2 from the die, SIGRAFLEX plate has been put in graphite die (thickness 0.5 mm), that is coated by BN layer.

BN layer is formed using Boron Nitride Aerosol Lubricoat (Manufactured for: ZYP coatings Inc.). Mixture of Mg and B powders or tablets, made from

this mixture, that is preliminarily pressed in the die under 2,000-4,000 kg/cm^2 pressure, were put in the die. Graphite die with Mg-B powders mixture or their tablets are put in HP synthesis device, those simplified schemes are given on Fig. 2.

The die with powders' mixture has been heated by conducting 500-2,000 A current in vacuum. The powders are pressed by using hydraulic system, temperature increases gradually up to 900 °C and they are kept at this temperature for ~5/7 min. After taking off pressure, they are cooled in vacuum until 150-200 °C. Cooling of the die is conducted in Ar atmosphere. Grinding and polishing obtained tablets have been conducted by using dry abrasive papers (SiC) in inert atmosphere, after this BN and SIGRAFLEX remains have moved away surfaces. Polished tablets are kept in vacuum polyethylene bag

Fig. 1 HP synthesis device. (a) general view, (b) chamber of compaction.

Fig. 2 Simplified scheme of hot pressing device and die with SIGRAFLEX.

1. graphite punches, 2. graphite die, 3. SIGRAFLEX plate. Its middle part (4) is covered with BN layer, 4. BN layer, 5. Amperemeter, 6. Source of constant current.

and are put in exsiccator in N_2 or Ar atmosphere. Isolation of powder with BN layer is stipulated by the fact, that ~50% of mixture of Mg and B powders is metallic magnesium powder, which is good conductor of current.

3.2 Microscopic Morphology and Superconductive Properties

The samples prepared by the HP route are obtained as pellets (diameter 27 mm, thickness 5-10 mm) without any cracks. The pellets were cut with a diamond saw and ground. The bulk samples were dry polished thin surface layer (< 0.5 mm). After polishing, the samples were analyzed by X-ray powder diffraction (Fig. 3). The XRD patterns of the samples showed reflections of magnesium diboride and traces of magnesium oxide originating from the oxygen impurity in the starting boron powder. Magnesium oxide can be detected at the diffraction angle of the strongest reflection of MgO only as a bump with intensity slightly higher than the background. Chemical analysis of the residual oxygen content show a mass fraction of $0.63 \pm 0.07\%$ (equals about 1.9 mol.% MgO). Carbon contamination from the graphite die has not been detected. The obtained material is an air and moisture sensitive.

In addition some the obtained samples have MgB_4 structure depending on the conduction of the obtaining process (sintering temperature, time of loading during HP). We also have investigated powders of the obtained samples, which corresponded to the MgB_2 stoichiometric phase.

X-ray phase analysis confirm, that obtained MgB_2 contains low concentration of MgO and MgB_4 phases. In case of using 98% boron, MgO containing increases in synthesized MgB_2 (Fig. 4.) caused by the fact that amorphous boron contains H_3BO_3 and B_2O_3 , those are reduced by metallic magnesium at high temperatures.

Fig. 3 X-ray pattern for sinthezed powders (a); consolidated samples (b).

Fig. 4 Microstructure of a typical MgB_2 sample obtained by HP synthesis

The microstructure of the samples exhibits a homogeneous distribution of small pores with diameters in the order of 1 to 5 μm . The diameter of the pores is less than 20 μm , the average grain size is less than 5 μm (Fig. 4).

3.3 Superconducting Characteristics

Measurements of temperature dependence of magnetization has been performed in order to analyze the superconducting characteristic of the obtained samples (Fig. 5). The vibrational magnetometer is produced by CRYOGENIC Ltd. and operates in temperature range 2–300 K and magnetic field up to 5 T has been used. The samples were cooled in zero magnetic field (ZFC) down to 2 K, then magnetic field $B = 20$ G was applied and magnetization was measured on sample heating (ZFC process). The same

Fig. 5 Temperature dependence of magnetization under an applied field of 20 G for MgB_2 powders (a); and for MgB_2 consolidated samples (b).

measurements were performed by cooling the samples from above T_c with the same applied magnetic field (FC). If the sample is superconductor, a negative magnetic moment (of diamagnetic origin) is induced due to screening effect, which disappears at superconducting transition temperature T_c . A strong Meissner effect, indicating the onset of superconductivity has been observed for the powder at 39 K and for consolidated samples at 38.5 K.

4. Conclusions

It is found that hot pressing method for fabrication MgB_2 have great potential. The hot pressing synthesis of magnesium diboride from MgH_2 and amorphous B powders results in a product and gives the possibility of a controlled reaction without loss of the volatile component to achieve high mass density values and the formation of the magnesium diboride compound in a short time at relatively low temperatures.

The superconducting properties have been investigated with magnetization versus temperature measurement. Onset of superconductivity has been revealed ~38.5–39 K with sharp transition.

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