Peculiarities of high-pressure and hot-pressing manufacture of MgB$_2$-based blocks with high critical currents for electrical machines

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Abstract. Structure and properties of MgB$_2$-based materials in the form of cylinders, rings, quadratic and rectangular blocks manufactured using high-pressure (2 GPa), hot-pressing (30 MPa), hot isostatic pressing (0.1 GPa), and atmospheric pressure (with predensification by broaching) from different types of B and MgB$_2$ are considered. The blocks have been synthesized from Mg and B or sintered from MgB$_2$ at 800 - 1100°C (with and without additions of Ti or Ta). The inclusions of higher borides (with stoichiometry near MgB$_{12}$ in the high pressure-manufactured magnesium diboride or near MgB$_7$ in the hot-pressing-synthesized material) can effect critical current density: higher amount and finer dispersion of the above inclusions are observed in the materials with higher critical currents. Samples synthesized (at 4 GPa) from the MgB$_{12}$ stoichiometric mixture of Mg and B that, according to the SEM microprobe analysis, contained MgB$_{12}$ (more than 50 %) and MgO phases and, according to X-ray analysis, along with the above phases some amount of MgB$_2$ demonstrated superconducting behavior. From high-pressure synthesized MgB$_2$ blocks the first reluctance-type superconductive electromotor (1,3 kW) has been constructed and successfully tested.

1. Introduction

Bulk nanostructural MgB$_2$-based materials are promising for application in superconducting electrical machines and pumps for liquid gases working at the liquid hydrogen and neon temperatures (20-27 K)
because of their high critical currents at these temperatures and high mechanical characteristics. MgB$_2$-based materials can be much easier and quicker produced than melt-textured YBCO or other 123-based structural type superconductors and are much cheaper. In our previous investigations of high-pressure (2 - 3.5 GPa) synthesis and sintering of MgB$_2$ the following peculiarities have been established. As the SEM study using compositional image and microprobe analysis has shown, the structure of all materials prepared under high pressure from magnesium diboride powder (high-pressure sintering) or boron and magnesium mixture taken in the MgB$_2$ ratio (high-pressure synthesis) without or with additions of Ti, Ta or Zr, consists of Mg-B-O matrix (in which Mg and B are in near-MgB$_2$ stoichiometry and oxygen in the amounts of 7 – 12 wt%) and dispersed Mg-B inclusions with near MgB$_{12}$ stoichiometry practically without oxygen (0 - 2 wt %), and in the cases of additions, rather big inclusions with near TiH$_2$, TaH$_2$ or ZrH$_2$ stoichiometry have been observed [1-4]. The highest critical currents were obtained in the cases of high-pressure-high temperature synthesis at 800 and 900 °C. The higher amount of Mg-B inclusions with near MgB$_{12}$ stoichiometry (the sizes of which can be 200 nm or even smaller, but sometimes can be as big as 10 µm) were usually observed in the materials with higher critical current density, especially in high magnetic fields at 10-35 K. The additions of Ti, Ta or Zr facilitate an increase of critical current density; the mechanism of their influence is different than that proposed in [5], but not quite understandable: they absorb impurity hydrogen (that can come from the materials of high-pressure cell that surround the manufactured sample), thus preventing the formation of MgH$_2$, harmful for superconductive characteristics, in materials, and what is more, promote the increase of the amount of Mg-B (MgB$_{12}$) inclusions. In studies of high-pressure synthesis of magnesium diboride from Mg and B in the 700-1000 °C temperature range without additions, we observed the following: as the synthesis temperature increases, the amounts of MgH$_2$ phase and Mg-B (MgB$_{12}$) inclusions decrease, but to attain the higher critical currents, it is better to conduct the process at a lower synthesis temperature (800 °C), when the amount of Mg-B (MgB$_{12}$) inclusions is higher, and add Ti, Ta or Zr to prevent the MgH$_2$ formation. Usually some amount of magnesium is present in the structure of materials synthesized at low temperatures. The amount of MgO in the materials is normally rather small and practically independent of synthesis or sintering temperature. X-ray patterns did not exhibit the MgB$_{12}$ phase, possibly due to a small amount and high dispersion of its inclusions, besides the MgB$_{12}$ etalon is absent in the X-ray database and the X-ray diffraction patterns of this phase found in the literature are rather contradictious. But the SEM study using the compositional image reveals the Mg-B (MgB$_{12}$) inclusions even in the structure of synthesized and sintered materials that according to X-ray diffraction patterns are practically single-phased MgB$_2$ with a very small amount of MgO.

The present paper compares the structure and properties of MgB$_2$-based materials manufactured by high-pressure (2 GPa), hot pressing (30 MPa), hot isostatic pressing (0.1 GPa), and atmospheric pressure (with predensification by broaching) from Mg and B or from MgB$_2$ at 800 - 1100 °C using different types of B and MgB$_2$, which can be used in superconducting electrical machines and pumps

2. Experimental

The initial powders of magnesium diboride contained from 0.8 to 3.5 % oxygen and of amorphous boron from 0.66 to 3.5% oxygen with different grain sizes from 1.4 to 10 µm (in any particular case the detailed information about initial boron or magnesium diboride will be given). In experiments on synthesis of MgB$_2$-based materials, metal magnesium chips (technical specifications of Ukraine 48-10-93-88) and amorphous boron were taken in the stoichiometric ratio of MgB$_2$. Components were mixed and milled in a high-speed activator with steel balls for 1-3 min. The Zr (of size 2-5 µm, MaTecK, 94-98% purity), Ti (of size 1-3 µm, MaTecK, 99% purity) or Ta (technical specifications 95-318-75, an average particle size of 1-3 µm) powders were added to the stoichiometric MgB$_2$ mixture of Mg and B in amount of 10 wt%. When we tried to synthesize the MgB$_{12}$ phase, Mg and B were taken in the MgB$_{12}$ stoichiometry and powders were also milled and mixed in a high-speed activator with steel balls for 1-3 min. The resulting powder has been compacted into tablets. The X-ray
study of the initial Mg, Ti, Ta, Zr, B and MgB₂ has shown that the materials contained no impurity phases with hydrogen (the method accuracy being about 3-5%).

In the case of high pressure (2 GPa) and temperature (700 - 1000 °C) sintering and synthesis the recessed-anvil high-pressure apparatuses were used [1]. The samples were in contact with a compacted hexagonal BN powder that prevents the material from contacting the graphite heater. The hot-pressing synthesis at 30 MPa has been performed in graphite dies covered with a special layer of hexagonal boron nitride mixed with glue. The rings at first were formed from the initial mixture of Mg, B and Ti in the gap between two steel concentric rings by gradual broaching and then synthesized under argon atmospheric pressure at 900 °C or pressed under high isostatic pressure (HIP) of 0.1 GPa at 900 °C.

The material structures were studied using SEM and X-ray diffraction analysis. The average crystallite sizes were estimated from line broadening in the diffraction patterns. The Jc was estimated from magnetization hysteresis loops obtained on an Oxford Instruments 3001 vibrating sample magnetometer (VSM) using Bean’s model. Hardness was measured employing a Matsuzawa Mod. MXT-70 microhardness tester, HV (using a Vickers indenter) and Nano-Indenter II, HB (using a Berkovich indenter).

3. Results and discussions.

Studies of MgB₂ high-pressure synthesis and sintering from different initial materials allow us to obtain nanostructural materials with 15-37 nm average grain sizes (as estimated from X-ray pattern). We have not found the definite correlation between the oxygen content of the initial boron and magnesium diboride, oxygen content of sintered and synthesized materials and critical current density. In sintered materials amount of oxygen varied from 3.5 to 9 wt% and in synthesized ones from 7 to 17 wt%, but in general the synthesized materials exhibited higher critical currents than the sintered ones. The optimal regime (from the point of view of the highest critical currents and the fields of irreversibility) is between 800 and 1050 °C and is different for each type of initial B and MgB₂. The critical current density correlates with the amount, distribution and size of “black” D-inclusions (Figures 1,2), the stoichiometry of which in high-pressure (2 GPa) synthesized and sintered MgB₂ is near MgB₁₂ and in materials obtained by hot-pressing (30 MPa) is near MgB₇. The X-ray phase analysis (Figure 2) is rather rough and gives no possibility to observe the presence of phases with the stoichiometry of MgB₁₂ or MgB₇ in X-ray patterns, while they can be observed by SEM in composition image (Figure 2). Materials contained some free Mg demonstrated the higher fields of irreversibility at 35-10 K (Figure 1). The higher amount of D-inclusions correlates with higher critical currents and the fields of irreversibility; finer and more homogeneous distribution of D-inclusions (e.g., MgB₁₂ in the materials manufactured under high pressure) correlates with higher critical current densities in low magnetic fields at 20-10 K. The finer D-inclusions were observed in the material prepared from finer initial boron (1.4 µm).

The specially high pressure-synthesized material from the mixture of Mg and B taken in the MgB₁₂ stoichiometry (Figure 3) demonstrated SC behavior, but we did not exclude that it was due to the presence of some MgB₂ in the material. The absence of a reliable etalon X-ray diagram does not allow us to determine the amount of this phase in the material by X-ray phase analysis, but according to SEM study, the amount of this phase is above 50 % (along with a high amount of MgO). The MgO phase agglomerated into big regions under the applied synthesis conditions. The careful investigations of the properties of obtained MgB₁₂-based materials are in progress. Mechanical characteristics of the MgB₁₂ phase is higher than that of MgB₂ and sapphire Al₂O₃ (nanohardness at 50 mN were 32.4 GPa of MgB₁₂, 27.3 GPa of Al₂O₃ and 17.4 GPa of MgB₂; Young moduluses were 385±14 of MgB₁₂ and 416 ± 22 of Al₂O₃; microhardness at 4.9 N were 32 GPa of MgB₁₂, 25.1 GPa of Al₂O₃ and 16.9 GPa of MgB₂).

The general view of blocks and rings synthesized from Mg and B (with additions of Ti and Ta) and the dependences of their critical current densities on magnetic field at various temperatures are shown in Figure 4. The lowest porosity (98%) and critical currents demonstrated materials sintered and synthesized at 2 GPa. The critical currents of MgB₂ synthesized by hot-pressing (30 MPa) technique is
Figure 1. Dependences of critical current density, $j_c$, on magnetic fields, $\mu_0H$ and X-ray patterns of the samples synthesized from Mg and B taken in the MgB$_2$ stoichiometry: (a) at 2 GPa, 800 $^\circ$C for 1 h (B of type I -1.9 % O and 1.4 $\mu$m grains); (b) at 2 GPa, 800 $^\circ$C for 1 h (B of type II -1.5 % O and 4 $\mu$m grains); (c) at 2 GPa, 1000 $^\circ$C for 1 h (B of type II -1.5 % O and 4 $\mu$m grains); (d) at 2 GPa, 1050 $^\circ$C for 1 h (B of type III -1.66 % O and < 5 $\mu$m grains).

rather high and large-sized blocks (porosity 22%) can be produced by this method. Using broaching for precompaction of raw materials followed by synthesis at atmospheric argon pressure or HIP (0.1 GPa), one can produce big rings with critical currents shown in Figure 4. Both synthesized at atmospheric pressure and HIP-produced materials are rather porous (porosity 40 % and 38 %, respectively). The superconducting properties of the rings are somewhat lower than that of manufactured at high pressure and hot pressing, but using preliminarily broaching with a subsequent atmospheric or HIP synthesis big parts can be produced with superconducting and mechanical properties suitable for practical applications.
Figure 2. Structure of the samples obtained by SEM in COMPOsitional contrast:
(a) synthesized from Mg and B (type I: 1.4 µm, 1.9 % O) at 2 GPa, 800 °C, 1 h: D1- 60 wt% B and 40 wt% Mg; D2- 51 wt% B and 49 wt% Mg; M1 – light matrix: 25 wt% B, 50 wt% Mg and 25 wt% O; M2 – grey matrix: 40 wt% B, 50 wt% Mg and 10 wt% O;
(b) synthesized from Mg and B (type II: 4 µm, 1.5% O) at 2 GPa, 1000 °C, 1 h: D-: 82 wt% B, 14.3 wt% Mg and 4.0 wt% O (MgB12?); or 85 wt% B, 14.0 wt% Mg and 1.3 wt% O; or 81 wt% B, 13.5 wt% Mg and 3.5 wt% O; M1 – 45 wt% B, 45 wt% Mg and 9 wt% O; M2 – 60 wt% B, 32 wt% Mg and 5 wt% O; (c) synthesized from Mg and B (type II -1.5 % O and 4 µm grains) at 2 GPa, 800 °C for 1 h; D –82 wt% B and 15.8 wt% Mg, 2% O (MgB12?) or 85 wt% B and 13.5 wt% Mg 1.5% O (MgB12?); M –36 wt% B, 50 wt% Mg and 14 wt% O or 33 wt% B, 55 wt% Mg and 12 wt% O; (d) synthesized from Mg and B (type II: 4 µm, 1.5% O) and 10% Ta, in BN, 30 MPa, 900°C, 2h; M –47.6 wt % B, 48.4 wt % Mg, 3.9 wt % O; D - 71.4 wt% B, 5.9 wt% O and 22.7 wt% Mg (MgB7?), A – TaH2.

Figure 3. Structure (a), dependences of \( j_c \) on \( \mu_0H \) (b) and X-ray patterns (c, d) of sample synthesized from Mg and B (type II - 1.5 % O and 4 µm grains) taken in MgB12 stoichiometry at 4 GPa, 1000 °C for 1 h; in figure (a): A- bright region containing mainly MgO, D1- 85% B, 13 % Mg, 1.5% O, D2 - 86% B, 13 % Mg, 1.5% O.
Figure 4. General view of blocks and rings synthesized from Mg and B taken in the stoichiometric mixture MgB$_2$ with 10% adding of Ti and Ta: 1-4 high-pressure synthesized at 800 °C, 2GPa, 1h (with additions of Ti); 5- hot pressed at 900 °C, 30 MPa, 1 h (with additions of Ta); 6 - broached and HIPed at 0.1 GPa, 900 °C, 1 h (with additions of Ti); 7 - rotor of reluctance motor with high-pressure (2 GPa) synthesized MgB$_2$ plates with 10% Ti adding (a); the generalized dependences of critical current density $j_c$ on magnetic field $\mu_0H$ for high-pressure synthesized MgB$_2$ (at 2 GPa 750-900 °C for 1 h) without and with additions of Ta, Ti, Zr (2 and 10 wt %) at 20 K (b); dependences of $j_c$ on $\mu_0H$ obtained by VSM for the items: hot-pressed block (c); rings synthesized under ambient argon pressure (e) and HIPed (f), respectively; characteristics of MgB$_2$-based SC rotor at 15-20 K (d).

The world first MgB$_2$ reluctance-type motor (working temperature 20 K) from high-pressure synthesized MgB$_2$ was produced in 2005 (Figures 4a, d). The comparison study showed that the efficiency of a rotor manufactured from MgB$_2$ and tested at the same temperatures (15–20K) as MT-YBCO did not differ essentially in performance. Highly dense MgB$_2$-based materials are rather hard and brittle and cannot be machined with water because of the decomposition to form poison boranes. To minimize the mechanical treatment, a special process aimed at obtaining samples in the form of quadratic and rectangular blocks to be used in reluctance-type motors has been developed.

Conclusions

MgB$_2$ synthesized and sintered at high-pressure and medium hot pressing are dense materials, demonstrate high superconductive characteristics and can be produced in the form of rectangular and square blocks as well as in large rings suitable for practical applications. The positive effect of boron-enriched (as compared to MgB$_2$ composition) inclusions on MgB$_2$ SC properties in the materials obtained by high-pressure and hot pressing has been verified. A material containing large amount of phase with near MgB$_{13}$ stoichiometry was high-pressure synthesized. It demonstrated SC behavior and higher mechanical characteristics than that of MgB$_2$.

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