

# High pressure and hot-pressing manufactured magnesium diboride. Inclusions of higher borides as possible pinning centers in the material

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Properties of materials synthesized from Mg and B and sintered from MgB<sub>2</sub> using high-pressure (2 GPa) and hot-pressing (30 MPa) at 700- 1100 °C are discussed. The influence of Ta, Ti and Zr additions on the material structure and properties was studied. The average grain size of 15-37 nm was observed for materials produced under a pressure of 2 GPa. For high-pressure synthesized MgB<sub>2</sub>, the highest critical current densities known from literature have been obtained. Dispersed inclusions of higher borides with the stoichiometry close to MgB<sub>12</sub> and MgB<sub>7</sub> can act as pinning centers in the magnesium diboride material manufactured using high pressure and hot pressing.

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## 1. Introduction

Despite a comparatively low superconducting transition (about 39 K) and working temperatures (20-27 K) the interest in the MgB<sub>2</sub>-based materials can be explained on the one hand, by the simpler and cheaper preparation technique than in the case of MT-YBCO and on the other by the intensive development of technologies that use liquid hydrogen as an alternative fuel for motor, water and air transports and for transmission of electrical energy for long distances. Using high-pressure and hot-pressing techniques, we can surpass the evaporation of magnesium during the manufacturing process and obtain a dense material structure with high critical currents and mechanical characteristics.

The higher coherent length of MgB<sub>2</sub> (1.6-12 nm) as compared to MT-YBCO gives a possibility to attain high critical current densities in a polycrystalline material, because the sizes of grain boundaries are smaller than the coherence length and are no obstacles to superconductive current flow. According to the latest conceptions, the pinning centers in MgB<sub>2</sub> can be nanosized inclusions of TiB<sub>2</sub>, ZrB<sub>2</sub> (formed when Ti or Zr is added), C, SiC [1-3], etc. as well as MgB<sub>2-x</sub>O<sub>x</sub> precipitates in MgB<sub>2</sub> matrix with diameters larger than ~ 10 nm [4]. So, it should be possible to increase the critical current density of the material by chemical alloying. The presence of oxygen in small amount in MgB<sub>2</sub> is not harmful for SC

characteristics. We have been the first to investigate the effect of doping by Ta, Ti, Zr and SiC on the synthesis of MgB<sub>2</sub> under high pressure (2 GPa) – high temperature (800-1000 °C) conditions [5-7] and found that the mechanism of Ta, Ti and Zr effect is different from that was proposed in [2, 3].

Studying large amount of samples synthesized from Mg and B and sintered from MgB<sub>2</sub> of different types, the presence of oxygen in MgB<sub>2</sub> “matrix” and comparatively homogeneously distributed inclusions with stoichiometry that is close to MgB<sub>12</sub> or MgB<sub>7</sub> (in the MgB<sub>2</sub>-based materials obtained using high pressure (2GPa) or hot pressing (30 MPa), respectively) have been revealed. The correlations between the increase in the amount of these inclusions and the increase in the critical current density and the field of irreversibility have been revealed. Besides, it has been found that additions of Ta, Ti and Zr to the initial mixture provoke an increase of the amount of such inclusions in the synthesized materials. Our observations allow us to conclude that B-enriched (as compared to the MgB<sub>2</sub> stoichiometry) inclusions can be pinning centers in MgB<sub>2</sub>.

## 2. Experimental

Magnesium diboride samples were high-pressure (2 GPa) and high-temperature (700 – 1100 °C) synthesized from Mg and B and/or sintered from MgB<sub>2</sub> in recessed-

anvil high-pressure apparatuses. The samples were in contact with a compacted hexagonal BN powder that allowed creating a more homogeneous pressure distribution in the high-pressure cell and protecting material from contact with the graphite heater. The hot-pressing synthesis under 30 MPa has been performed in the graphite dies covered with a special layer of hexagonal boron nitride mixed with glue.

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 grain sizes from 0.8 to 10  $\mu\text{m}$  (in any particular case the detailed information about initial boron or magnesium diboride will be given). In experiments on synthesis of  $\text{MgB}_2$ -based materials, metal magnesium chips (Technical Specifications of Ukraine 48-10-93-88) and amorphous boron were taken in the stoichiometric ratio of  $\text{MgB}_2$ . To study the influence of Zr, Ti, Ta, the Zr (of size 2-5  $\mu\text{m}$ , MaTecK, 94-98% purity), Ti (of size 1-3  $\mu\text{m}$ , MaTecK, 99% purity) or Ta (technical specifications 95-318-75, an average particle size of 1-3  $\mu\text{m}$ ) powders were added to the stoichiometric  $\text{MgB}_2$  mixture of Mg and B in amounts of 2 - 10 wt%. The components were mixed and milled 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,  $\text{MgB}_2$  and B has shown that the materials contained no impurity phases with hydrogen (the method accuracy being about 3-5%).

The structure of materials was studied using SEM and X-ray diffraction analyses. The critical current density ( $j_c$ ) was estimated using Bean's model from magnetization hysteresis loops obtained on an Oxford Instruments 3001 vibrating sample magnetometer (VSM). Hardness was measured employing a Matsuzawa Mod. MXT-70 microhardness tester,  $H_v$  (using a Vickers indenter) and Nano-Indenter II,  $H_B$  (using a Berkovich indenter).

### 3. Results and discussion

We have not found the definite correlations between the oxygen content of the initial boron and magnesium diboride, oxygen content of sintered and synthesized materials and critical current density (Fig. 1). The synthesized materials exhibited higher critical currents than the sintered ones. The optimal temperature regime at high pressure (from the point of view of the highest critical currents and the fields of irreversibility) is between 800 and 1050  $^{\circ}\text{C}$ . For each type of the initial boron or  $\text{MgB}_2$  the optimal temperatures are different. The highest  $j_c$  in  $\text{MgB}_2$  synthesized at 2GPa without additions were observed for  $\text{MgB}_2$  prepared from amorphous boron at 2 GPa, 1050  $^{\circ}\text{C}$  for 1 h (boron -1.66 % O and <5  $\mu\text{m}$  grains) (Fig. 2e). The best SC characteristics for the high pressure-sintered material (2 GPa, 1050  $^{\circ}\text{C}$ ) were observed when the  $\text{MgB}_2$  powder of average grain size 9.6  $\mu\text{m}$  with 0.8% O was used. Studies of  $\text{MgB}_2$  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 patterns). The samples synthesized at 30 MPa (hot-pressed) had some lower critical currents, but can be manufactured as big blocks (up to 130 mm in diameter). The critical current density in the materials correlates with the amount, distribution and size of "black" D-inclusions (Fig. 3), the stoichiometry of which in high-pressure (2 GPa) synthesized and sintered  $\text{MgB}_2$  is close to  $\text{MgB}_{12}$  and in materials obtained by hot-pressing (30 MPa) is close to  $\text{MgB}_7$ . By X-ray diffraction analysis it is impossible to define the presence of phases with the stoichiometry of  $\text{MgB}_{12}$  or  $\text{MgB}_7$  in X-ray patterns, while they can be observed by SEM in composition image (Fig. 2 a, b).

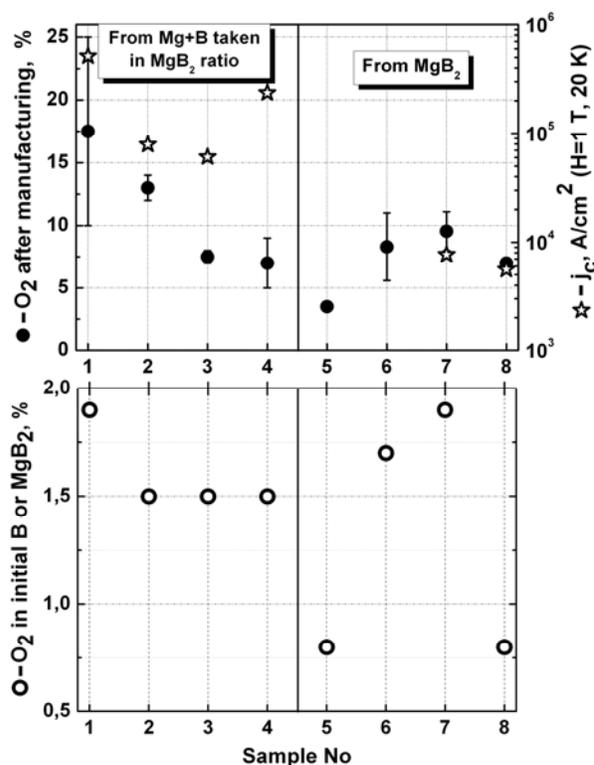


Fig. 1. The amount of oxygen in the initial boron or  $\text{MgB}_2$  powder ( $\circ$ ) and in the manufactured ( $\bullet$ ) materials (synthesized from Mg and B taken in  $\text{MgB}_2$  ratio or sintered from  $\text{MgB}_2$ ) and critical current density ( $\star$ ) in 1 T field at 20 K estimated using VSM in different samples manufactured at 1 GPa for 1h at 800 (Nos 1, 2, 5), 900 (Nos 3, 6, 7) and 1000  $^{\circ}\text{C}$  (No 8). The shape of hysteresis loops of samples 5 and 8 witnessed about the absence of connectivity between the superconductive grains in the materials, so as a whole materials were not superconductive. The sample 1 prepared from boron with average grain size 1.4  $\mu\text{m}$ , samples 2, 3, 4 from 4  $\mu\text{m}$  boron, samples 5 and 8 from 10  $\mu\text{m}$ , 6 from 9  $\mu\text{m}$ , 7 from 1.4  $\mu\text{m}$   $\text{MgB}_2$ .

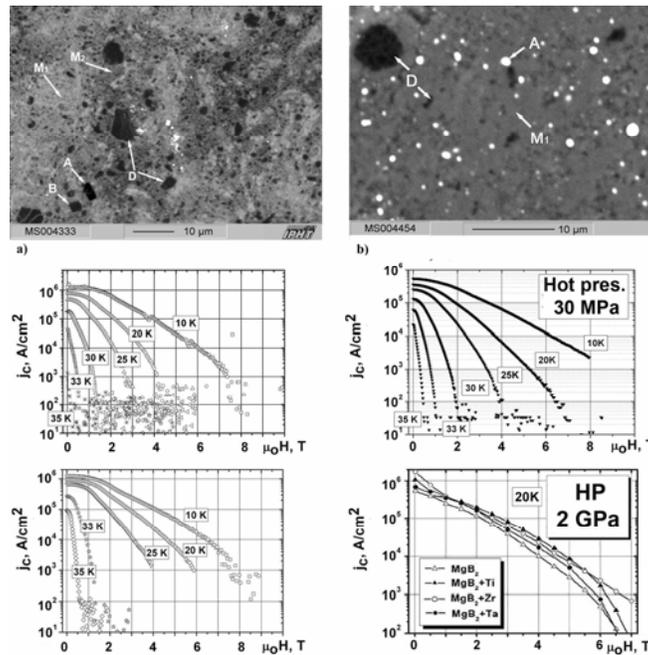


Fig. 2. Structure of the samples obtained by SEM in COMPOSitional contrast: (a) synthesized from Mg and B (type II: 4  $\mu\text{m}$ , 1.5% O) at 2 GPa, 1000  $^{\circ}\text{C}$ , 1 h D- inclusions (dark gray): 82 wt% B, 14.3 wt% Mg and 4.0 wt% O ( $\text{MgB}_{12}$ ?); or 85 wt% B, 14.0 wt% Mg and 1.3 wt% O; or 81 wt% B, 13.5 wt% Mg and 3.5 wt% O;  $M_1$  – light matrix: 45 wt% B, 45 wt% Mg and 9 wt% O;  $M_2$  – grey matrix: 60 wt% B, 32 wt% Mg and 5 wt% O; (b) synthesized from Mg+B (4  $\mu\text{m}$ , 1.5% O) + 10% Ta, in BN, 30 MPa, 900  $^{\circ}\text{C}$ , 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 ( $\text{MgB}_7$ ?). Dependences of critical current density,  $j_c$ , on magnetic fields,  $\mu_0 H$  of the samples synthesized from Mg and B: (c) at 2 GPa, 800  $^{\circ}\text{C}$  for 1 h (boron -1.9 % O and 1.4  $\mu\text{m}$  grains); (d) at 30 MPa, 900  $^{\circ}\text{C}$ , 2h, with 10% Ta (boron - 1.5% O, 4  $\mu\text{m}$  grains); (e) at 2 GPa, 1050  $^{\circ}\text{C}$  for 1 h (boron -1.66 % O and <5  $\mu\text{m}$  grains); (f) the generalized dependences of critical current density  $j_c$  on magnetic field  $\mu_0 H$  for high-pressure synthesized  $\text{MgB}_2$  (at 2 GPa 750-900  $^{\circ}\text{C}$  for 1 h) without and with additions of Ta, Ti, Zr (2 and 10 wt %)

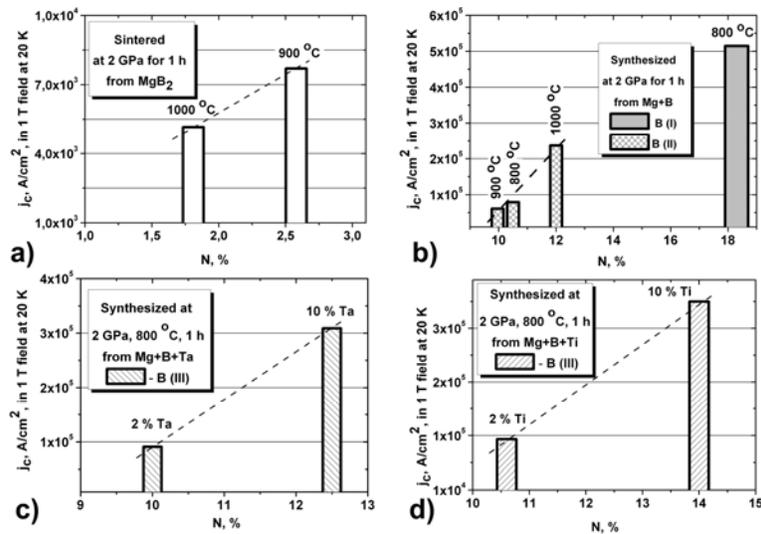


Fig. 3. Dependences of critical current density,  $j_c$ , estimated in 1T field at 20 K on the relative amount of “black” Mg-B ( $\text{MgB}_{12}$ ) inclusions, N, for high pressure-high temperature manufactured  $\text{MgB}_2$  samples without additions: (a) - sintered from  $\text{MgB}_2$  (0.8 % oxygen and 10- $\mu\text{m}$  grains), (b)- synthesized from B of type I, II (1.5 % oxygen and 4- $\mu\text{m}$  grains) and (c, d) - synthesized from boron of type III (amorphous, 1  $\mu\text{m}$ , MaTecK, 95-97% purity) with additions of Ta and Ti, respectively. The amount of the “black” inclusions, N, was calculated as a ratio of the area occupied by the “black” inclusions at the COMPO image obtained at 1600x magnification to the total area of this image and does not correspond to the weight percent of the phase in the material.

The highest  $j_c$  in zero field were 1300 kA/cm<sup>2</sup> at 10 K, 780 kA/cm<sup>2</sup> at 20 K and 83 kA/cm<sup>2</sup> at 35 K and in 1 T field 1200 kA/cm<sup>2</sup>, 515 kA/cm<sup>2</sup> and 0.1 kA/cm<sup>2</sup>, respectively for high pressure-synthesized magnesium diboride; the field of irreversibility at 20 K was above 8 T. The material with 10 % Zr added demonstrated  $j_c$  of 1800 kA/cm<sup>2</sup> at 20 K in zero field and 1 kA/cm<sup>2</sup> in the 7 T field. The high pressure-synthesized MgB<sub>2</sub> with additions of Ti showed  $j_c$  above 100 kA/cm<sup>2</sup> at 10 K up to 4.5 T field and at 20 K up to 3 T. The samples measuring  $\varnothing 32 \times h 10$  mm,  $17 \times 17 \times 5$  mm and  $25.5 \times 17 \times 5$  mm can be high pressure-high temperature manufactured. The hot-pressed square-shaped blocks measuring  $58 \times 58 \times 10$  mm<sup>3</sup> synthesized from Mg and B with 10% of Ta added showed in zero field  $j_c$  of 740 kA/cm<sup>2</sup> at 10 K, 360 kA/cm<sup>2</sup> at 20 K and 22 kA/cm<sup>2</sup> at 35 K; in 1 T field  $j_c$  was 442 kA/cm<sup>2</sup> at 10 K and 245 kA/cm<sup>2</sup> at 20 K.

As the amount of these inclusions increases, the critical current density increases, so the inclusions or their grain boundary can be pinning centers in MgB<sub>2</sub>. SEM and TEM studies show that after the high-pressure synthesis the additions of Ti, Ta and Zr transform into hydrides absorbing impurity hydrogen that may come from the materials, which are around the samples and in contact with them during the manufacturing process. Besides, the additions of Ti, Ta and Zr promote an increase of the amount of Mg-B (MgB<sub>12</sub>) inclusions in the material structure. According to the microprobe analysis, the matrix of materials contained about 3.5-14 % of oxygen, the black inclusions with stoichiometry close to MgB<sub>12</sub> contained practically no oxygen (0-1.5%), but 5.9% of O was registered in the inclusions with close to MgB<sub>7</sub> stoichiometry (in hot-pressed samples).

The hardness of the high pressure-high temperature manufactured material estimated using a Vickers indenter under a load of 4,9 N was:  $12.65 \pm 1.39$  GPa (without additions),  $13.08 \pm 1.07$  GPa with 10% Ta added and  $12.1 \pm 0.08$  GPa with 2% Ti added. Because of the absence of cracks under a load of 4.9 N, we estimated the fracture toughness at a load of 148.8 N:  $K_{IC} = 4.4 \pm 0.04$  MPa·m<sup>0.5</sup> for the material without additions and  $K_{IC} = 7.6 \pm 2.0$  MPa·m<sup>0.5</sup> for the samples with addition of 10% Ta.

#### 4. Conclusions

The high-pressure and hot pressing methods allow one to produce parts of superconductive electromotors and pumps with high superconductive and mechanical characteristics. The pinning centers in the MgB<sub>2</sub> can be the inclusions of higher borides but due to their small amount and high dispersion in the material structure they can be detected only by SEM.

#### References

- [1] S. X. Dou, S. Soltanian, J. Horvat, et al., Applied Physics Letters. **81**(18), 3419-3421 (2002).
- [2] Y. Zhao, Y. Feng, C. H. Cheng et al., Applied Physics Letters. **79**(8), 1154-1156 (2001).
- [3] D. Goto, T. Machi, Y. Zhao et al., Physica C **392-396**, 272-275 (2003).
- [4] R. F. Klie, J. C. Idrobo, N. D. Browning, Appl. Phys. Lett. **80**(21), 3970-3972 (2002).
- [5] T. A. Prikhna, W. Gawalek, A. B. Surzhenko et al., Physica C **372-376**, 1543-1545 (2002).
- [6] T. A. Prikhna, W. Gawalek, Ya. M. Savchuk et al. Physica C **402**, 223-233 (2004).
- [7] T. Prikhna, W. Gawalek, N. Novikov et al., Journal of Materials Processing Technology **181**, 71-75 (2007).

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