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Superconductivity in multi-phase Mg-B-O compounds

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Abstract

Structures of MgB_2-based materials manufactured under pressure (up to 2 GPa) by different methods having high superconducting performance and connectivity are multiphase and contain different Mg-B-O compounds. Some oxygen can be incorporated into MgB_2 and boron into MgO structures, MgBx (X=4-20) inclusions contain practically no oxygen. Regulating manufacturing temperature, pressure, introducing additions one can influence oxygen and boron distribution in the materials and thus, affect the formation, amount and sizes of Mg-B-O and MgBx inclusions and changing type of pinning, pinning force and so affect critical current density j_c. The boron concentration increase in initial Mg and B mixture allows obtaining sample containing 88.5 wt% of MgB_{12} with T_C of 37.4 K (estimated magnetically).

Keywords: magnesium diboride; higher magnesium borides; nanostructure; critical current density, pinning force.

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1. Introduction

Despite the comparatively simple structure of the MgB_2 elementary unit cell, the nanostructure of MgB_2-based materials is very complicated. A rather high amount of oxygen (4–15 wt.%) are usually present in the MgB_2 matrix as well, as inclusions of higher magnesium borides [1-3]. The atomic resolution study of oxygen incorporation into bulk MgB_2 [4] shows that 20–100 nm sized precipitates of Mg(B,O) are formed by ordered substitution of oxygen atoms for boron lattice sites, while the basic bulk MgB_2 crystal structure and orientation are preserved. The presence of these precipitates correlates well with an improved critical current density and superconducting transition behavior, implying that they act as pinning centers [4].

Pressure is of great importance in the manufacture of superconducting MgB_2-based bulk materials because it allows suppressing a volatility of Mg, impeding its oxidation, and promoting the formation of a mechanically stable denser structure. A denser material usually exhibits higher superconducting properties; it is more stable against degradation during exploitation, less reacts with a moisture, etc. [1]. The advantage of high-pressure (HP)-manufactured (2 GPa, 800-1050 ^oC, 1 h) MgB_2 bulk is the possibility to get almost theoretically dense (1-2% porosity) material with very high critical current densities reaching at 20 K, in 0–1 T j_c=1.3–1.0·10^6 A/cm^2 (with 10% SiC) and j_c= 9.2–7.3· 10^5 A/cm^2 (without doping) [1, 5], the highest irreversibility fields (B_{irr}(18.4 K) =15 T and B_{irr} (0 K) = 32.5 T) and upper critical fields (B_{C2} (22 K) =15 T and B_{c2}(0 K) ~ 42.1 T (in materials synthesized at 2 GPa, 600 ^oC, 1h). The spark plasma synthesized (SPS) material (50 MPa, 600-1050 ^oC 1.3 h, without additions and 3–10 % porosity), demonstrated at 20 K, in 0–1 T j_c= 4.5–4·10^5 A/cm^2. Hot pressed materials (at 30 MPa, 800–1000 ^oC, 2 h, with 10 % of Ti additions and 8–15 % porosity) exhibited j_c= 3.4–2.3·10^5 A/cm^2. Usually the j_c of in-situ prepared materials (from MgB_2 powder) is higher than of ex-situ prepared ones (from Mg and B powders) [1, 5].

The paper presents results of SEM, Auger and X-ray structure study of the typical structures of materials formed under 2 GPa pressure and high temperature from Mg and B mixtures taken in MgB_2, MgB_7 and MgB_{12} stoichiometry in connection with their superconducting and mechanical properties. The established correlations and regularities of the formation of superconducting Mg-B-O (or MgB_2-based) materials will be discussed based on the estimation of the type of pinning (using method proposed in [6]) in materials manufactured at different pressures and comprehensively studied earlier [1–3, 5].

2. Experimental, results, discussions and conclusions

Samples were prepared by heating of pre-compacted Mg (I or II) and B (I-III) mixtures or MgB_2 (98% purity) powder with and without additions of Ti, SiC, or C (up to 600–1150 ^oC: (1) under a high quasi-hydrostatic pressure of 2 GPa in a recessed-anvil-type high-pressure apparatus [3] (HP), (2) under a uniaxial pressure of 16–50 MPa by spark plasma sintering (SPS) [9], (3) under 30 MPa by uniaxial hot pressing (HotP), and (4) pressureless synthesis at 0.1 MPa of Ar (PL). Several types of amorphous boron (type I - grain size <5 μm, 0.66 wt% O, 0.31 wt% C, 0.48 wt.% N, 0.32 wt.% H; type II - grain size 4 μm, 1.5 wt% O, 0.47 wt% C, 0.40 wt% N, 0.37 wt% H and type III - grain size <1 μm, 3.5 wt% C was specially added during boron manufacturing, 1.02 wt.% N, 0.87 wt% H;) were used as starting materials. The boron powders and metal magnesium turnings Mg(I) (Technical Specifications of Ukraine 48-10-93-88) or a fine powder of magnesium Mg (II) <1 μm (-325 mesh) produced by the HyperTech (USA) were mixed and milled in a high-speed planetary activator with steel balls for 1-3 min. To investigate the effect of additions, 10 wt% Ti (grain size 1-3 μm, MaTecK, 99% purity), or SiC (200–800 nm) were added to the Mg and B mixture.

The dominant pinning mechanism has been determined from the volume pinning force j_cB, according to a scaling procedure proposed in [4]. The field B_{peak}, where the maximum of the volume pinning force takes place, is normalized by the field B_n, at which the volume pinning force drops to half its maximum (on the high field side). The position of the peak, $k=B_{peak}/B_n$, is expected to be at 0.34 and 0.47 for grain boundary (GBP) and point pinning (PP), respectively. The microstructure of the materials was characterized by X-ray structure (with Rietveld refinement) and SEM with microprobe X-ray and Auger (JAMP−9500F) analyses. The critical current density, j_c, was estimated from magnetization measurements in an Oxford Instruments 3001 vibrating sample magnetometer (VSM) by using the Bean model; transition temperature was estimated using a SQUID magnetometer.

Table 1 gives materials characteristics vs. preparation conditions: *in-situ* (from Mg and B mixture with and without 10 wt.% of SiC, Ti, or 3.5 wt.% of C) or *ex-situ* (from MgB_2). An increase in pressure (up to 2 GPa) usually leads to a reduction in porosity (from 47 % to 1%) and enhancement in critical current density. In addition, high pressure synthesis or sintering increases the maximal pinning force, $F_{p(max)}$, in materials prepared at high temperatures [5]. $F_{p(max)}$ also increases by the addition of Ti or SiC both in low- and high-temperature-synthesized materials. It is larger in *in-situ* than in *ex-situ* prepared samples. The position of $F_{p(max)}$ shifts to higher magnetic fields with (1) manufacturing pressure, (2) the addition of Ti or SiC and (3) in-situ preparation (compared to ex-situ) [5]. Data of Table 1 show that GBP dominates in materials prepared at low temperatures (600–800 ^oC), while high-temperature preparation results mainly in PP or mixed pinning (MP) behavior. Exceptions were found in materials produced by SPS (k values were too high for the PP mechanism), which needs an additional study. These materials have high variety of higher borides MgBx (X=4-20) in their structures [1, 5].

Fig.1 shows typical structure of materials prepared from Mg(I) and B(II) taken in Mg:2B and Mg:12B ratio and their SC characteristics together with some other synthesized materials. The Auger study (zone of excitation being 10 nm in diameter and two lattice parameters in depth) showed that a structure in Fig. 1a had composition: $MgB_{0.5-0.8}O_{0.8-0.9}$ white inclusions, $MgB_{11-13}O_{0.2-0.5}$ black inclusions and $MgB_{2.2-1.7}O_{0.3-0.6}$ gray matrix. Comparing these results with that of X-ray structure analysis we can conclude that boron is incorporated in the MgO structure. Repeated etching in Ar (in the JAMP−9500F chamber during study) and quantitative Auger analysis showed practically the same oxygen concentration in gray matrix of the structure in Fig.1a after 30 cycles, which points to the oxygen incorporation into the MgB_2 lattice. The material connectivity estimated by DC measurements turned out to be 80%, shielding (or SC) fraction estimated magnetically was 98%. The Auger analysis of the structure in Fig.1b showed $Mg_{1.1-1.3}OB_{0.8-1.2}$ stoichiometry for white areas and $MgB_{6-12}O_{0.6-1.2}$ stoichiometry for black areas. Line profile showed no near MgB_2 stoichiometry. Despite the fact that amounts of shielding fraction in samples 4 and 5 (Fig.1c) are rather small 7–10% and 1–1.5%, respectively, they exhibited T_c =37.5 K and j_c =2-5·10^2 A/cm^2 at 20 K (estimated magnetically) (Fig.1c, d), but they did not conduct the DC current.

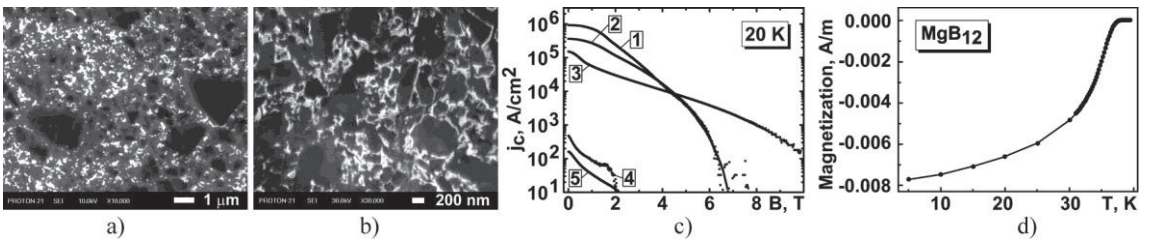

Fig. 1. (a, b) Structures obtained by SEM (SEI) of HP-synthesized at 2 GPa, 1200 ^oC, 1 h materials from Mg(I) and B(II) taken in Mg:2B and Mg:12B ratio, respectively, which according to X-ray structure analysis contained: 76 wt % MgB_2, 24 wt % MgO (a) and 88.5 wt % MgB_{12}, 2.5 wt % MgB_2, 9 wt % MgO (b); (c) j_c vs. magnetic field, $\mu_0 H$, of HP-synthesized at 2 GPa for 1h: 1 – from Mg(II):2B(I) at 1050 ^oC, 2 - from Mg(I):2B(II) at 1200 ^oC, 3 – from Mg(II):2B(III) at 600 ^oC, 4– from Mg(I):12B(II) at 1200 ^oC, 5– from Mg(I):7B(II) at 1400 ^oC (according to X-ray structure analysis, material contained 53 wt % MgB_{12}, 31 wt %MgB_{20}, 16 wt % MgO); (d) - Tc of sample 4.

Table 1. Characteristics of MgB_2-based materials prepared under pressure, P, at temperature, t, from Mg and B taken in MgB_2 stoichiometry without and with additions of SiC, Ti (10 wt%) or C (3.5 wt%) or from MgB_2 powder. PP, GBP, MP- point, grain boundary, mixed type of pinning, respectively.

Preparation, addition	Type of B	P, MPa	t, ^{o} C	$F_{p(max)}/10^9(N/m^3)$	k= B_{peak}/B_n	pinning
in-situ, SiC (HP)	I	2000	1050	10.9	0.51	PP
in-situ, SiC (HP)	I	2000	800	1.9	0.31	GBP
in-situ, (HP)	I	2000	1050	7.6	0.53	PP
in-situ, (HP)	I	2000	800	1.6	0.36	GBP
in-situ, Ti, (HP)	II	2000	1050	4.8	0.42	MP
in-situ, Ti, (HP)	II	2000	800	1.9	0.24	GBP
in-situ, (HP)	II	2000	1050	2.3	0.43	MP
in-situ, (HP)	II	2000	800	0.8	0.30	GBP
ex-situ (HP)	-	2000	1050	3.1	0.30	GBP
in-situ, (SPS)	II	50	1050	4.6	0.63	>PP*
ex-situ (SPS)	-	50	1050	3.3	0.58	>PP*
in-situ, (SPS)	II	50	800	2.7	0.56	>PP*
in-situ, C (HP)	III	2000	600	0.6	0.31	GBP
in-situ, Ti (HP)	II	30	1000	2.7	0.42	MP
ex-situ (SPS)	-	16	1150	1.5	0.45	PP
in-situ, (PL)	II	0.1	800	1.9	0.35	GBP

* Note: type of pinning is impossible to characterize because of high k ratio; ** all “in-situ” materials were prepared from Mg(I) and only C added from Mg(II).

In matrices of MgB_2-based materials synthesized at low temperatures the oxygen admixture is distributed more homogeneously than in those synthesized at higher temperatures and materials prepared under higher temperatures usually demonstrate higher j_c in low and medium magnetic fields, while prepared under lower temperature have higher j_c in high magnetic fields [1–5]. The amount and size of inclusions of higher borides decrease as the synthesis temperature increases. Additions of Ti, Ta, Zr, SiC and pressure can affect the distribution of oxygen and boron in the materials. In materials with Ti added a decrease of oxygen in the MgB_2 matrices has been fixed. So, temperature, pressure and additions are the factors, which can influence oxygen and boron distribution in MgB_2–based materials, thus affecting the pinning and critical current density.

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