Low Temperature Physics/Fizika Nizkikh Temperatur, 2014, v. 40, No. 8, pp. 964–967

Effect of temperature and pressure to pinning centers in bulk MgB_2 under high pressure

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Received December 18, 2013, published online June 23, 2014

The MgB_2-based samples were synthesized at 2 GPa at 800 and 1050 °C for 1 hour with and without Ti and SiC. X-ray, SEM and Auger structural studies showed that with increasing of manufacturing temperature grain boundary pinning transforms into point pinning, which is well correlated with the transformation of discontinuous oxygen enriched layers into separately located Mg–B–O inclusions in MgB_2. Ti and SiC additions can influence the oxygen and boron distribution, but cannot change the type of pinning at relatively low temperatures.

PACS: 74.70.Ad Metals; alloys and binary compounds (including A15, MgB_2, etc.);
74.62.Dh Effects of crystal defects, doping and substitution;
74.62.Fj Effects of pressure.

Keywords: superconductivity, magnesium diboride, titanium, silicon carbide, critical current density.

Introduction

The great interest in MgB_2-based superconductors is determined by their coherence length ($\xi_{ab}(0)$ = (3.7–12) nm, $\xi_c(0)$ = (1.6–3.6) nm). This value is comparatively large and allows high critical current flow in polycrystalline MgB_2 through the grain boundaries [1]. It is widely believed that in MgB_2, any inclusions of secondary phases comparable with the coherence length and grain boundaries themselves [2] can pin nonsuperconducting vortices leading to a critical current density increase. Up to now only grain boundary pinning, i.e., pinning of many nonsuperconductive vortices along the boundary of grains, has been observed for MgB_2. On the other hand, so-called point pinning, where only one vortex can be pinned by a structural defect, was never observed. The upper critical field B_{c2} of MgB_2 can be successfully increased by introducing some disorder into the MgB_2 crystal lattice (by adding carbon, for example), which reduces its anisotropy and opens up the possibility to attain higher currents at high magnetic fields [3].

The improved material performance needs clean grain boundaries between the MgB_2 grains and a good connectivity between them; the latter can be successfully achieved by manufacturing (synthesis or sintering) under enhanced or high pressure. A denser material not only exhibits better superconducting and mechanical properties, which is of great importance because of the necessity to work in strong magnetic fields under thermocycling conditions, but also higher stability against degradation because it reacts less with moisture and gases.

Several previous investigations have shown that MgB_2-based materials usually contain a high amount of admixed oxygen in their structure, which does not prevent their excellent superconducting performance [4–6]. This oxygen enters in $Mg(B,O)_2$ inclusions, which can be pinning centers in MgB_2 [7].

Our previous study [8] showed that MgB_2-based bulk materials prepared under high pressure had higher critical current densities in high magnetic fields, when preparation temperatures were 600–800 °C, and in lower magnetic fields — when preparation temperatures were 1050 °C. It has been shown by the authors of paper [8] that increasing the pressure during manufacturing enhances the volume pinning force and moves the position of the maximum to higher magnetic fields. A similar shift was observed, when Ti or SiC was added. It has been established that temperature syntheses materials is correlate with volume of pinning and with formation of Mg–B–O oxygen-enriched regions.

Experiment

The MgB_2-based samples were prepared by heating pre-compacted Mg and B powder mixtures with and without additions of Ti and SiC up to 800–1050 °C under a high quasi-hydrostatic pressure of 2 GPa in a recessed-anvil-type high-pressure apparatus. Boron powder with grain size < 5 μm was used as starting materials. The boron powders and metal magnesium turnings Mg 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, 99% purity) or SiC (200–800 nm) were added to the Mg and B powder mixture.

The structure of the materials was examined by x-ray diffraction (with Rietveld refinement) and by SEM with microprobe x-ray and Auger (JAMP−9500F) options. The critical current density was obtained from magnetization measurements in an Oxford Instruments 3001 vibrating sample magnetometer (VSM) using the Bean model. The pinning mechanism was estimated using a method proposed in [9]: $k = B_{\text{peak}}/B_n$, where B_{peak} is the field, where the volume pinning force is maximal ($F_{p(\max)}$) and B_n is the field, at which $F_{p(\max)}$ drops to half on the high field side; k is expected to be at 0.34 and 0.47 for grain boundary (GBP) and point pinning (PP), respectively. Connectivity, B_{c2} and B_{irr} were estimated based on resistivity measurements by the four-probe method (direct current flow through the materials) in magnetic fields of up to 15 T. The typical dependence of the critical current densities for the HP-synthesized materials is shown in Fig. 1.

Results

Figures 2–5 present the microstructure of materials synthesized under high pressure 2 GPa. As can be seen from the photos, their structure contains dark inclusions of higher magnesium borides MgB_x ($x > 2$). For the HP samples, the stoichiometry of higher borides was usually $x > 8$–12. However for the SPS (spark plasma sintering, 50 MPa) samples, the stoichiometry of higher borides was not higher than $x = 4$–7. Materials synthesized at low temperatures (800 °C) generally contain a higher amount of higher borides and the inclusions are coarser. Another type of inclusions observed in the material structures as bright areas. The composition of these inclusions is close to Mg:B:O in a ratio 1:0.8:0.9. Probably that they have MgO structure with embedded B, because the x-ray phase analysis (with Rietveld refinement) usually shows two phases: MgB_2 and MgO (up to 5–30 wt%).

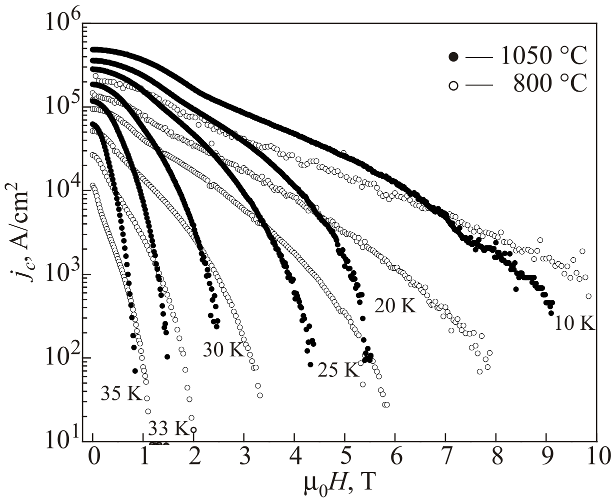

Fig. 1. Typical dependence of the critical current density at different temperatures on magnetic field for materials synthesized at 2 GPa at 800 °C and 1050 °C for 1 h.

Higher magnesium borides with $x > 4$ are not seen in the x-ray diffraction patterns [5], possibly because their inclusions are dispersed in the structure and have complicated unit cells with many reflection planes (which makes the x-ray reflections of higher borides rather weak, looking like noise on the MgB_2 background). SEM and Auger studies showed some other results that x-ray analysis with Rietveld refinement. For example MgB_2 with high critical current density synthesized under 2 GPa at temperature 1050 °C (Fig. 3) showed 75 wt% of MgB_2 and 25 wt% of MgO by x-ray, but careful SEM and Auger studies showed the presence Mg–B–O inclusions with stoichiometry 1 : 0.5–0.8 : 0.8–0.9 and 1 : 11–13 : 0.2–0.5 (close to MgB_{12}). These inclusions are visible in the image of the microstructure as small white and black areas. The gray matrix phase that fills the space between them, has the stoichiometry 1 : 1.7–2.2 : 0.3–0.6 (close to MgB_2). Thus, some oxygen is present in any point of the sample, but nevertheless its distribution is not uniform. With increasing temperature (from 800 to 1050 °C), the number of white inclusions increases and the boundaries between areas are becoming sharper.

Figures 2, 3 show the evolution of the oxygen and boron distribution in the structure of materials prepared at 2 GPa with the manufacturing temperature from 800 to 1050 °C. With increasing manufacturing temperature the segregation of admixed oxygen and the formation of separate oxygen enriched Mg–B–O inclusions are more pronounced. In the materials prepared at 800 °C the formation of oxygen-enriched Mg–B–O layers (15–30 nm) were observed. In the materials prepared at 1050 °C local Mg–B–O inclusions are forming.

The addition of SiC at low processing temperature (800 °C) also changed the oxygen distribution. So-called “layered” Mg–B–O structure (Fig. 2) was transformed into a structure with separate Mg–B–O inclusions (Fig. 4) due to the addition of SiC. However, this redistribution at 800 °C does not affect the type of pinning.

The increase in the synthesis temperature up to 1050 °C caused a total change in value of pinning and its type [10]. In the synthesis of the samples under a pressure of 2 GPa at 1050 °C, the pinning force was $7.6 \cdot 10^9$ N/m^3 for

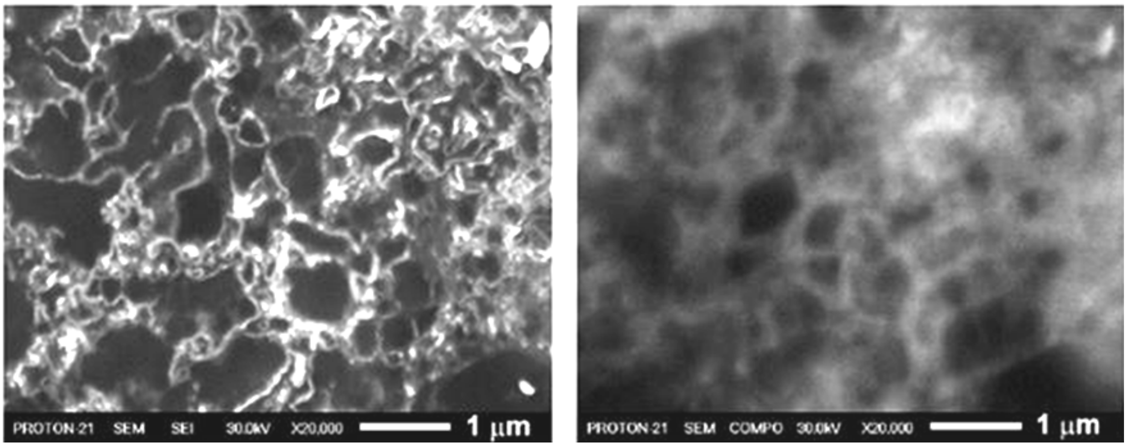

Fig. 2. The microstructure (SEI and COMPO) of MgB_2 materials prepared from Mg:2B mixtures without additions at 2 GPa, 800 °C for 1 h.

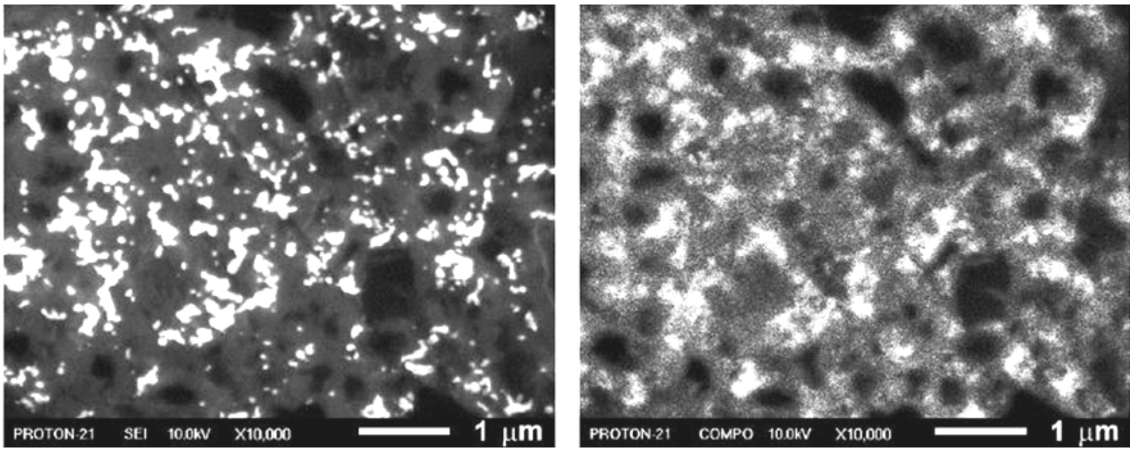

Fig. 3. The microstructure (SEI and COMPO) of MgB_2 materials prepared from Mg:2B mixtures without additions at 2 GPa, 1050 °C for 1 h.

pure MgB_2, $10.9 \cdot 10^9$ N/m^3 for MgB_2 with addition of SiC and $4.8 \cdot 10^9$ N/m^3 for MgB_2 with addition of Ti. If the synthesis temperature was 800 °C, the pinning force was $1.6 \cdot 10^9$ N/m^3 for pure MgB_2 and $1.9 \cdot 10^9$ N/m^3 for MgB_2 with addition of SiC and Ti. In the first case there is a point pinning; in the second — grain boundary pinning. In sample with additions of titanium and temperature of synthesis 1050 °C is observed a so-called mixed pinning (something intermediate between the point and the grain-boundary pinning).So pinning force, as studies have shown, is highly dependent on the synthesis temperature.

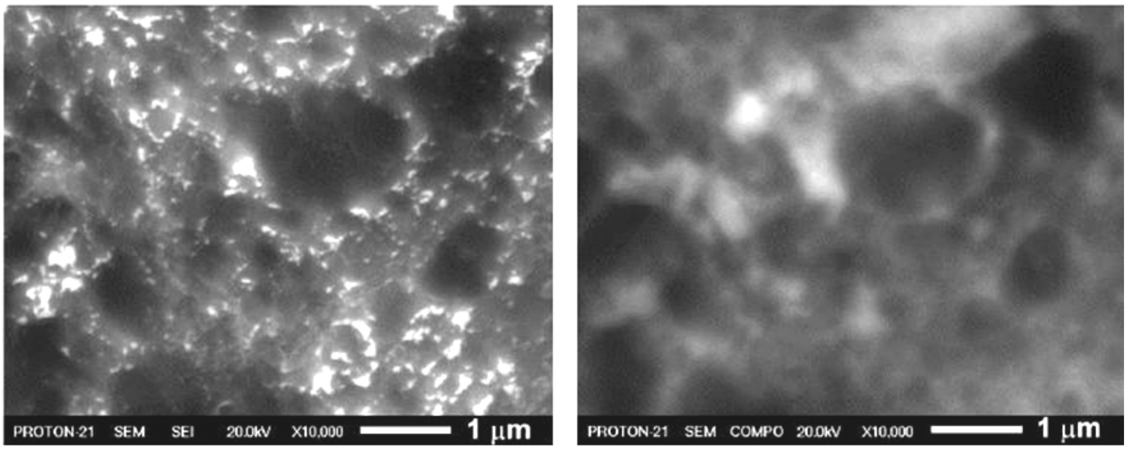

Fig. 4. The microstructure (SEI and COMPO) of MgB_2 materials prepared from Mg:2B mixtures with addition of SiC (10%) at 2 GPa, 800 °C for 1 h.

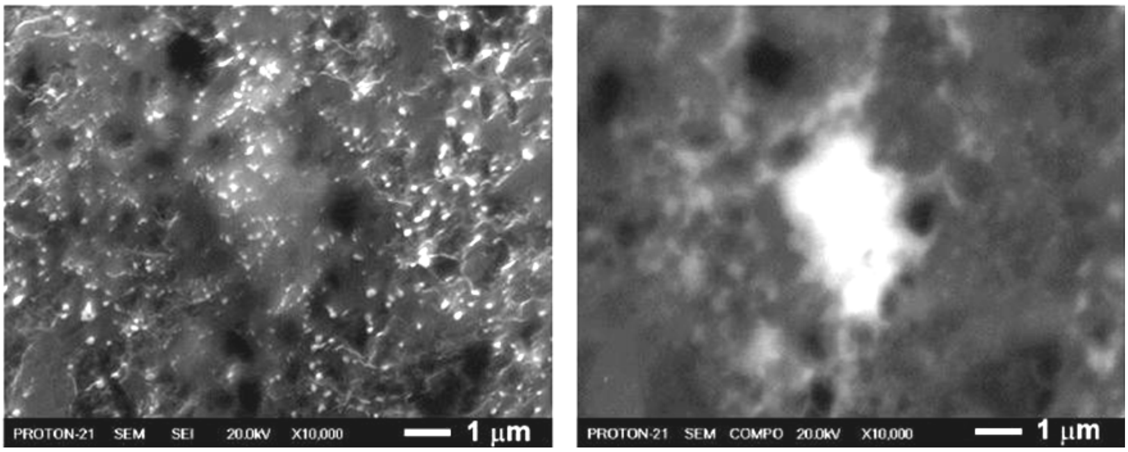

Fig. 5. The microstructure (SEI and COMPO) of MgB_2 materials prepared from Mg:2B mixtures with addition of SiC (10%) at 2 GPa, 1050 °C for 1 h.

All materials prepared at 1050 °C demonstrated high connectivity — 80–87%.

Summary

The effect of temperature on the structure of magnesium diboride synthesizing under 2 GPa is mainly a redistribution of boron and oxygen. With increasing temperature (from 800 to 1050 °C), the number of inclusions with high content of oxygen increase and the boundaries between areas are becoming sharper. Also segregation of admixed oxygen and the formation of separate oxygen enriched inclusions occurs. Adding silicon carbide and titanium is even more prominent, segregation of oxygen and with increasing temperature changes the type of pinning, from grain boundary to a point pinning.

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