Superconductivity in porous MgB$_2$

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Abstract. Porous magnesium diboride samples have been prepared by heat treatment of a pressed mixture of Mg and MgB$_2$ powders. It was found that linked superconducting structure is formed down to the minimum normalized density $\gamma = d/d_o \cong 0.16$ (percolation threshold), where $d$ is the density of MgB$_2$ averaged over the sample, $d_o = 2.62$ g/cm$^3$ is the X-ray density. The critical temperature of the porous samples decreases with increasing porosity (decreasing $\gamma$) and $T_c \cong 32$K is minimal at $\gamma \cong 0.16$.

1. Introduction

The weak grain-boundary links limit substantially the critical current in ceramic HTS [1]. In the magnesium diboride, the inter-grain resistance was also observed after machining as consequence of the high hardness of MgB$_2$. This decreases the critical currents of wires and the tapes made using PIT method [2] in comparison with the bulk samples synthesized by hot isostatic pressing [3,4]. On the other hand scanning tunnel microscopy [5] of samples with a high $J_c$ has revealed the presence of a normal inter-grain layer in a form of an amorphous region extending from 5 to 20 nm.

In this work, porous MgB$_2$ samples down to minimal average density were prepared and there superconductivity properties were investigated.

2. Samples and methods

Porous samples were prepared by heat treatment of MgB$_2$ and Mg mixed powders. As starting materials, we used single-phase (in terms of X-ray diffraction) MgB$_2$ (99.6 % purity) with a crystal size of less than 10 μm and Mg (99.9 % purity) with a particle size of less than 100 μm. The initial weight proportion MgB$_2$ : Mg was varied from pure magnesium diboride up to ratio 1:7. Powders were mixed carefully and pressed to pellets 5.1 mm in diameter and about 1.5 mm in height using the 3-T press. Pellets were placed in a stainless steel tube closed by a steel stopper and annealed at temperature of 900°C for 1 – 5 hours in a He atmosphere at a pressure of 1.5-1.7 bar. During heat treatment the boron does not evaporate practically, and its quantity in the sample does not change. Content of magnesium diboride in sample is characterized by the average density $d = M/\Omega$, where $M$ is the MgB$_2$ mass in the pellet and $\Omega$ is the volume of the sample. In case of absent MgB$_4$ phase we use the normalized average density of the magnesium diboride $\gamma = d/d_o$ , where $d_o = 2.62$ g/cm$^3$ is the X-ray MgB$_2$ density. The $\gamma$ determination error was less than 10%. Since the tube wasn’t closed hermetically, added magnesium could evaporate. We had to control quantity of remained magnesium in samples by choosing time of anneal and by changing volume of stainless steel tube. Annealed pellets had average
density $\gamma$ in the range from 0.7 to 0.16. The sample was set on the cold copper holder of the cryocooler having minimal temperature about 12 °C. The temperature was measured by special thermometer that was set together with the sample. Magnetic measurements were made using a Hall sensor having area 0.5x0.5mm$^2$. Magnetic field was applied along a perpendicular to the flat faces of the pellet. As a first step magnetic field $-$H (without sample) was measured. Then the local magnetic induction $-$ B (near the pellet) was measured. The gap between pellet and sensor was about 0.7 mm. Susceptibility was calculated as $\langle \chi \rangle = (B(\gamma) - H)/4\pi$. A dense pellet ($\gamma$=0.94) was used to calibrate the $\langle \chi \rangle$. In such samples local induction is zero ($B=0$) at low temperature and fields, but observed value $4\pi \langle \chi(\gamma) \rangle \approx 0.75$ was less than 1. This is explained by geometry of experiment (demagnetization factor and gap between pellet and Hall sensor). The error of the $\langle \chi \rangle$ definition did not exceed 10%.

Fig.1. The SEM photograph of the porous sample with $\gamma \approx 0.24$.

Fig.2. Susceptibility $-4 \langle \chi(T) \rangle$ (ZFC, H=3 Oe) vs. temperature for porous MgB$_2$ with the different $\gamma$.

3. Results and discussion

Fracture of annealed samples was investigated by SEM. The photograph of the porous sample with $\gamma \approx 0.24$ is shown in fig. 1. It is seen large cavities in sample. They were formed after the magnesium evaporation. The granules have size from units up to tens microns. The X-ray analysis in this sample has shown the presence of about 5% Mg and less than 2% of MgO.

The temperature dependences $-4 \langle \chi(T) \rangle$ before and after heat treatment are shown in Fig. 2. They were obtained in the field H= 3 Oe (after ZFC). Initial tablets ($\gamma \equiv 0.28$ extruded in Fig. 2) have small susceptibility that goes to zero at the temperature equal to the critical temperature $T_c$, corresponding to a bulk sample [4, 6]. The weak diamagnetism in extruded sample is explained by the fact that MgB$_2$ particles in a magnesium matrix have no superconducting interface. After annealing porous samples acquire a large susceptibility at low temperatures, which value coincides with susceptibility of the dense sample with $\gamma \approx 0.94$ (labeled by asterisks). Large value of diamagnetic susceptibility suggests that the external magnetic field is screened completely by inter-grain surface currents. The value and behavior of $\langle \chi(T) \rangle$ depends on anneal time. However, after 2-h annealing at $T = 900^\circ$C for the samples with initial density $\gamma \geq 0.16$, the susceptibility was found virtually to be unchanged and looks like it is shown in Fig. 2. Moreover, the composition of samples can be changed from 20% Mg excess up to 15% content of non-superconducting MgB$_4$ phase after a 4-h anneal. However, $\langle \chi(T) \rangle$ dependence is identical within the accuracy of measurements. As seen in Fig.2 the dense samples (with $\gamma \geq 0.7$) exhibit a single superconducting transition. With increasing porosity ($\gamma$ decreases), two superconducting transitions are observed. The first (at $T_{\gamma_1}$) is attributed to initial MgB$_2$ phase, and the second characterizes the disappearance of the macroscopic currents. We believe that the second superconducting transition (at $T_{\gamma_2}$) appears due to the new phase of MgB$_2$, arisen after annealing.

Comparison of the initial and annealed tablet (curve 3 and extruded $\gamma \equiv 0.28$ on fig. 2) in a range of $T_{\gamma_1} < T < T_{\gamma_2}$ allows us to see that, with the appearance of diamagnetism in the porous medium, the susceptibility of the initial MgB$_2$ phase decreases, whereas their critical temperature $T_{\gamma_2}$ remains
unchanged. The reduction of susceptibility magnitude is caused by the reduction of the volume of the initial crystallites phase, and released MgB$_2$ escapes on a new phase formation.

**Fig.3.** Susceptibility (in left) and normalized resistance (in right) for different fields vs. temperature. Sample has $\gamma \cong 0.24$. Approximating lines determine $T_{c2}$ in which superconducting currents disappear ($H=3$Oe) and $T_{c2}(0)$ for zero resistance ($H=0$).

Left curve in fig.2 shows the $-4 < (T)>$ dependence for the sample with initial density $\gamma \equiv 0.11$. After heat treatment density has increased up to $\gamma \equiv 0.16$. Critical temperature $T_{c2}$ of this sample coincides with $T_{c}$ of the sample having the same initial density $\gamma \equiv 0.16$ (curve 4). It is seen, that the magnitude of the susceptibility of this pellet is noticeably less (curve 5). This is due to the reduction of tablet size after treatment, and also because the density of the sample is near to percolation threshold $\gamma$. Linked superconducting structure doesn’t exist below $\gamma$. Annealing of tablets with the initial density of $\gamma < 0.16$ led to the reduction of tablets both in height and in diameter and $\gamma$ increases accordingly. In such samples the superconducting linked structure arises only when density reaches the critical value. The critical density $\gamma \equiv 0.16$ is explained in terms of a percolation theory [7]. In case of MgB$_2$ the superconducting linked structure in whole volume of the sample is observed at $\gamma < \gamma$. Supposing the grains in sample are distributed randomly and independently of each other, $\gamma$ is the probability that the site in the porous media is occupied by a superconducting grain and $(1-\gamma)$ is probability that the site is empty. In this case the theoretically predicted lower limit for percolation threshold in 3-D space is $\gamma = 0.16$ [7]. This value coincides with minimum density of porous MgB$_2$.

Together with susceptibility, resistance transitions to the superconducting state were studied. The highly porous MgB$_2$ samples are very brittle. For resistance measurements mechanically strong samples are needed. In this case we used samples having extra magnesium of about 20% (by weight). The resistance was measured using a four-probe technique on a rectangular bar $5 \times 2 \times 1.5$ mm$^3$ in size that was cut from a pellet. The current and voltage leads were attached to one or another surface of sample. Temperature dependences of the normalized resistance $\rho(T)/\rho(39K)$ at superconducting transitions were the same for primary and cut off surface and resistance went to zero below $T_{c2}(0)$. Therefore we believe that the linked superconducting structure exists in the whole volume of porous samples. In fig. 3 the $\rho(T)$ measured in different fields for the sample with $\gamma \equiv 0.24$ are shown. For comparison, $-4 < (T)>$ dependence is presented. The $\rho(T)$ as well as $< (T)>$ has double step shape and characterizes two phases, i.e. initial granules and a new phase. It is obvious that, after disappearance of the inter-granular superconducting currents (at $T > T_{c2}$), the resistance should be appear. It is seen from fig. 3, that in a field 3Oe extracted from magnetic measurements $T_{c2}$ is noticeably smaller, than $T_{c2}(0)\equiv 34$K obtained from resistance data ($H=0$). In order to determine $T_{c2}$ in zero field, susceptibility was measured in magnetic field range 0.3 – 200Oe and results were extrapolated using square approximation $H \propto (1-T_{c2}/T_{c2}(0))^2$. The instance of this dependence is shown in inset in fig. 4. The
$T_c(0)$ obtained from such extrapolation coincides with $T_c(0)$ at which resistance become zero. Dependence of the relative critical temperature $T_c(0)/T_{co}$ of the new phase versus $\gamma$ is shown in fig. 4. For dense samples ($\gamma > 0.7$) critical temperature increases with density very slowly. With decreasing density $T_c$ decreases and it is minimal at $\gamma \approx 0.16$. It is known that $T_c$ decreases with lattice parameters reduction. It takes place with pressure [8] and atomic substitution [9]. In porous samples $T_c$ can decrease as a result of defects that exist in the new phase. X-ray analysis has shown that lattice parameters $a$ and $c$ are reduced with decreasing density. At $\gamma > 0.7$ they are the same as at initial powder. In the sample with $\gamma \approx 0.16$ the $a$ is low by 0.33 % and $c$ by 0.14 % in comparison with initial MgB$_2$. Most probably, the boron vacancies induce strain in crystal structure and reduce the lattice parameters.

A double step transition in weakly connected structures is interpreted often as arising from intra- and inter-granular transition [10]. In this case grains have critical fields and currents on the order of magnitude larger then inter-granular weak links have. In [11] resistive transition in HTS had been investigated. Authors had shown that superconducting transition has two distinct sections, a steep part associated with the onset of superconductivity in the individual grains and a transition tail due to the weak links coupling the grains. With applied field the steep section remained unchanged while the tails moved considerably to lower temperatures. Magnetic measurements [12] had established also that magnetic flux penetrates into inter-granular weak links in the fields significantly lower then into grain. But in our case resistance measurements of porous samples has shown that magnetic field shifts onset of superconductivity and tails to lower temperatures approximately in the same way (see fig.3). Additionally from the magnetic measurements it was found that magnetic flux begins to penetrate into porous samples at external field of about 1000e at 15K. This field is comparable with the first critical field $H_c$ reported for pure dense bulk MgB$_2$ [13]. Therefore we believe that weak links have no visible effect on the superconducting properties of the porous sample. Thus, after the MgB$_2$ annealing in the Mg atmosphere the homogeneous superconducting phase is formed between granules. The allied MgB$_2$ structure exists up to the critical density $\gamma \approx 0.16$ and it about to percolation threshold. The critical temperature of porous phase decreases with decreasing average density of MgB$_2$. Grains boundaries of the porous samples don’t display nature of weak links.

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