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High critical current density of MgB_2 bulk superconductor doped with Ti and sintered at ambient pressure

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Ti-doped MgB_2 superconductors with different doping levels were prepared by solid-state reaction at ambient pressure. The density, diamagnetic signal, and J_c of the samples change significantly with the doping level, with the best result achieved at $x=0.1$. At 5 K, the J_c reaches 2×10^6 A/cm^2 in the self-field and 5×10^4 A/cm^2 in 5 T. At 20 K, the J_c is still as high as 1.3×10^6 A/cm^2 in the self-field and 9.4×10^4 A/cm^2 in 2 T. It is observed that partial melting occurs in the Ti-doped samples, resulting in an excellent grain connection and extremely high density. In addition, some fine particles (with sizes from 10 to 100 nm) of the second phases induced by Ti doping are distributed in the MgB_2 matrix, and this may play an important role in flux pinning enhancement. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1396629]

The recent discovery of superconductivity in MgB_2 by Akimitsu and co-workers[1] introduced a new and important member of the family of superconductors that have a relatively high critical temperature ($T_c=39$ K). MgB_2 could be promising in applications in a temperature range of 20–30 K, where conventional superconductors cannot play a role because of their low T_c. In addition, unlike high temperature superconductors (HTS), MgB_2 has a simple chemical composition and crystal structure, and supercurrent flow in MgB_2 bulk materials is not reduced by grain boundaries,[2,3] thus providing a high feasibility of scaling up the material to form bulk shapes like wires and tapes.

As reported so far by several groups,[3–5] however, the critical current density, J_c, of MgB_2 is relatively low compared to in conventional A15 compound superconductors. Usually MgB_2 bulk materials sintered at ambient pressure are not dense, and result in a small volume fraction of the superconducting phase and a poor connection between grains, and thus a low J_c. By high-pressure sintering, fully dense bulk materials are obtained and a much higher J_c is achieved.[6,7] On the other hand, the $J_c(H)$ behavior at high fields is poor in MgB_2, and it is caused by the movement of magnetic flux lines permeating the material. This cannot be solved by simply increasing the mass density of the materials. A strong pinning force must be applied to prevent flux movement by introducing structural defects of proper size and with sufficient density. As reported by Bugoslavsky *et al.*,[8] the J_c of MgB_2 has been significantly increased with modest levels of atomic disorder induced by proton irradiation. However, these techniques used to increase J_c are not practical in producing superconducting wires and tapes. How highly dense MgB_2 bulk materials are made at ambient pressure and how their performance can be improved to a practical useful level are two key points in making wires and tapes for large-scale applications.

Chemical doping has been widely used to investigate the effect of electronic and structural changes on the physical properties in the normal and superconducting states of HTS[9] and MgB_2.[10,11] So far, the results of chemical doping have been limited by the effect on T_c in MgB_2, and can be categorized into two types: one is the doping which leads to the decrease of T_c and the loss of superconductivity (such as doping of Al, Li),[10,11] the other one is doping which cannot dope the element in the lattice and has no effect on T_c, as was reported for Be-doped MgB_2.[12] In the second type of doping, since the dopant yields nonsuperconducting phases without decreasing the T_c of the superconductor matrix, they may work as pinning centers if a proper microstructure of the second phases can be formed in MgB_2.

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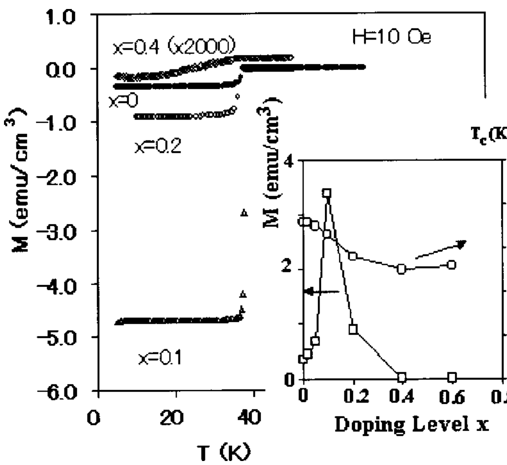

FIG. 1. Volume magnetization vs temperature curves for Ti-doped MgB_2 with doping levels of $x=0$, 0.1, 0.2, and 0.4, measured at 10 Oe in the ZFC process. The data for the sample with $x=0.4$ are multiplied by a factor of 2000. Inset: Variation of critical temperature T_c and the diamagnetic signal (represented by the volume magnetization at 5 K and 10 Oe) with doping level x for Ti-doped MgB_2 samples.

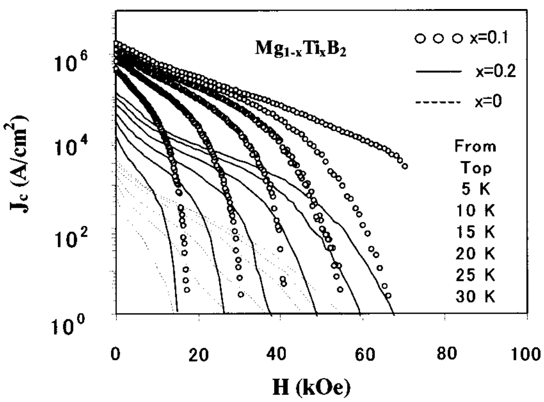

FIG. 2. Magnetic field dependence of the critical current density J_c at various temperatures for Ti-doped MgB_2 samples with doping levels of $x=0$, 0.1, and 0.2.

In this work, we have synthesized a series of Ti-doped MgB_2 compounds and investigated the doping effect of Ti on the microstructure and J_c of MgB_2. Excellent performance of J_c in magnetic fields of up to 7 T has been achieved in highly dense Ti-doped MgB_2 bulk materials sintered at ambient pressure.

Ti-doped MgB_2 samples with an atomic ratio of Mg:Ti:B$=1-x$:x:2 with $x=0$, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 were prepared by solid-state reaction at ambient pressure. Mg (99%), Ti (99%), and B (99%) powders were mixed and pressed into cylinders 7 mm in diameter and 6 mm in height. The cylinders were placed on a MgO plate, and sintered in flowing Ar in a tube furnace at 600 °C for 1 h, 800 °C for 1 h, 900 °C for 2h, and cooled down to room temperature inside the furnace. The crystal structure was investigated by powder x-ray diffraction (XRD) using an ac 10 000 diffractometer with Cu$K\alpha$ radiation. Microstructural and compositional analyses were performed by a high-resolution transmission electron microscope (HRTEM) equipped with an energy dispersive spectroscopy (EDS) spectrum. The magnetization was measured using a dc superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMSR2). The J_c of the Ti-doped MgB_2 samples was deduced from the hysteresis loops using the Bean model.[13] The irreversibility field was determined from the closest point of the hysteresis loops at a given temperature using a criterion of 10 A/cm^2. In order to compare the physical properties of samples of different compositions, the samples used in this study were all shaped to dimensions of $0.7\times0.8\times1.0$ mm^3.

Typical results of the temperature dependence of magnetization for the Ti-doped MgB_2 samples are shown in Fig. 1. The critical temperatures span a small range, 37.5–38.6 K, while varying the doping levels, decreasing slightly with increasing doping levels (see the circles in the inset of Fig. 1). However, the amplitude of the diamagnetic signal with zero-field cooling (ZFC) in 10 Oe varies significantly with the doping level, changing in a nonmonotonous way and reaching a maximum at $x=0.1$ (see the squares in the inset of Fig. 1). X-ray diffraction and HRTEM analyses reveal that only a very small amount of Ti atoms might be introduced into the lattice of MgB_2, whereas the majority of them form impurity phases whose amounts increase with the doping level. A slight variation of T_c with the doping level may be the effect of Ti partially replacing Mg in the MgB_2 lattice.

The nonmonotonous change of the amplitude of the diamagnetic signal with the dopant content may be attributed to changes of the microstructure and the amount of impurity phases, *given in* detail below. At a low doping level ($x \leqslant 0.05$), the sample is relatively pure in phase but is porous and of low density and, accordingly, the diamagnetic signal is small and the J_c is low (as shown in Fig. 2). Poor diamagnetic behavior and low J_c of the samples with low doping levels show that the processing used here is not optimized for synthesizing pure MgB_2. With increasing doping level, the samples become denser, and the diamagnetic signal increases. However, the improvement in the microstructure is not significant until the doping level reaches $x=0.1$. This may be one of the reasons why 5% Ti doping cannot improve the J_c, as reported most recently by Jin *et al.*[14] As the doping level increases to $x=0.1$, the density of the sample sharply increases and, at the same time, the diamagnetic signal is enhanced significantly. As the doping level further increases to $x=0.4$, the diamagnetic signal decreases rapidly although the samples are still quite dense. The decrease of the diamagnetic signal in the samples with $x=0.2$ and 0.4 can be attributed to a decrease of the amount of the MgB_2 phase, as revealed by XRD analysis. For samples with very high doping levels ($x \geqslant 0.6$), the superconductivity gradually disappears. XRD and TEM results reveal that these high-doping-level samples contain only a small amount of MgB_2 phase (with $x=1$, no MgB_2 phase exists at all), and their density is much lower than that of the sample with $x=0.1$. Since both the highest density and the largest diamagnetic signal are achieved in the sample with $x=0.1$, in the following we will focus on the behavior of $J_c(H)$ and the microstructure of samples with $x=0$, 0.1, and 0.2.

As shown in Fig. 2, the J_c of the sample with $x=0.1$ is much higher than that of the samples with $x=0$ and 0.2 prepared under the same process. At $T=5$ K, the J_c reaches 2×10^6 A/cm^2 in the self-field, 3×10^5 A/cm^2 in 2 T, and 5×10^4 A/cm^2 in 5 T. At $T=20$ K, the J_c is as high as 1.3×10^6 A/cm^2 in the self-field, 3.1×10^5 A/cm^2 in 1 T,

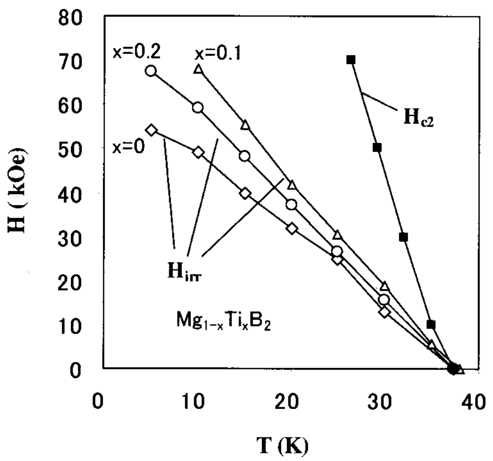

FIG. 3. Temperature dependence of the irreversibility field and upper critical field H_{c2} for Ti-doped MgB_2 samples with doping levels of $x=0$, 0.1, and 0.2. The H_{c2} data are determined from the reversible $M(H)$ curves at different temperatures for the sample with $x=0.1$. The H_{c2} data determined from samples with $x=0$, 0.05, and 0.2 have almost the same values.

9.4×10^4 A/cm^2 in 2 T, and 1.7×10^4 A/cm^2 in 3 T. Even at $T=35$ K, the J_c is still as high as 1.2×10^5 A/cm^2 in the self-field (the result is not shown in Fig. 3 for $T=35$ K). All these J_c data are much higher than the best results reported so far for MgB_2 bulk materials including those prepared under high pressure (the typical value of J_c is 2×10^4 A/cm^2 at 20 K and 1 T),[6] proton-irradiated MgB_2 fragments (the typical value of J_c is 2×10^5 A/cm^2 at 20 K and 1 T),[8] and dense wires (the typical value of J_c is 3×10^4 A/cm^2 at 20 K and 1 T).[5,14]

Besides the great enhancement of J_c in the whole range of the magnetic field up to 7 T, the irreversibility field H_{irr} of MgB_2 is also significantly improved by Ti doping (see Fig. 3). The typical results of H_{irr} for the sample with $x=0.1$ are 67 kOe at 10 K, 40 kOe at 20 K, 19 kOe at 30 K, and 6 kOe at 35 K. These data for H_{irr} are comparable to the best result achieved in fully dense MgB_2 prepared by high pressure sintering.[6,7]

The high performance of J_c in the whole range of magnetic field up to 7 T and the improved irreversibility behavior in the Ti-doped MgB_2 samples may be attributed to a good connection between grains and strong pinning in the samples. As revealed by microstructural analyses, partial melting occurs in the Ti-doped sample, resulting in an excellent grain connection and extremely high density. This means that the Ti doping plays an important role in enhancing the sintering process of MgB_2. Besides, some fine particles (10–100 nm in size) of the second phases induced by Ti doping are inserted into the MgB_2 matrix with a thin and clear interface boundary (see Fig. 4). These particles may play an important role in flux pinning, similar to the role of Y_2BaCuO_5 in $YBa_2Cu_3O_7$.[15] Our most recent results (which are not given here, but will be published separately) of microstructure studies of these samples strongly support second phase particle pinning in Ti-doped MgB_2.

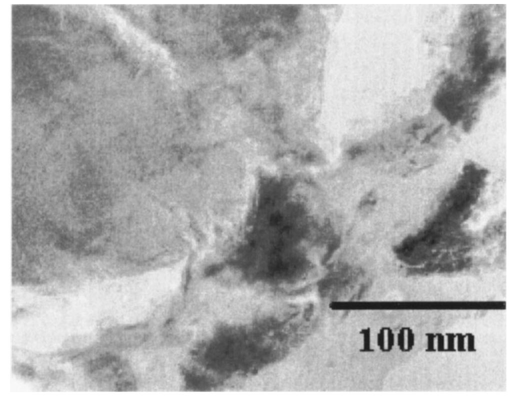

FIG. 4. TEM image showing the second phase particles in the MgB_2 matrix.

In conclusion, Ti-doped MgB_2 samples with different doping levels were prepared by solid-state reaction at ambient pressure. Highly dense, good performing bulk material has achieved, at $x=0.1$, a J_c that reaches 2×10^6 A/cm^2 in the self-field and 5×10^4 A/cm^2 in 5 T at 5 K, and 1.3×10^6 A/cm^2 in the self-field and 9.4×10^4 A/cm^2 in 2 T at 20 K. Microstructural analyses reveal that Ti may act as a sintering assistant which enhances the sintering process, leading to an excellent grain connection and extremely high density. Fine particles of 10–100 nm of Ti-rich phases may be responsible for flux pinning.

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