Improved Chemical Stability to Water in Ti-doped MgB2

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Improved chemical stability of Ti-doped MgB$_2$ in water

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We investigated the degradation of critical current density (J_c) and irreversibility field (H_{irr}) of pure and Ti-doped MgB$_2$ bulks by exposing the samples to water for a total of 10, 48, 100, and 124 h. We found that both J_c and H_{irr} of the samples were degraded by exposure to water, in various degrees depending on the doping level. In the same exposure duration, the Ti-doped samples exhibited a less sensitivity to water, which was confirmed by the less degradation of J_c and H_{irr}. Our results demonstrate that Ti doping is not only effective in improving the superconducting properties of MgB$_2$ but also in enhancing its chemical stability against water. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1465521]

The discovery of superconductivity at 39 K in MgB$_2$[1] provides the possibility of various engineering applications in a temperature range around 30 K, where the conventional superconductors, such as Nb$_3$Sn and Nb–Ti alloy, cannot play any roles because of low T_c. MgB$_2$ has also many other superior properties in superconducting and normal states, such as low density (2.55 g/cm^3), low resistivity near T_c (0.4–16 $\mu\Omega$ cm at 40 K), high upper critical field (14–39 T with $H//ab$) and high intrinsic J_c($>10^7$ A/cm^2).[2] Moreover, unlike the high temperature superconductors (HTS), MgB$_2$ has a simple chemical composition and crystal structure, and no weak-link problem at grain boundaries (GBs),[3,4] providing a high feasibility to scale-up the material to form bulk shapes like wires and tapes. So far, high-performance MgB$_2$ superconducting bulks, wires/tapes and thin films have been developed.[5–7]

Besides the physical properties, chemical stability is an issue of great concern for various superconducting device applications. As reported previously,[8,9] HTS are highly sensitive to water and moist air. Recently, Zhai *et al.*[10] found that the superconducting properties, such as the transition width and zero-resistance transition temperature, of MgB$_2$ films were also sensitive to water. It is thus very important to investigate the influence of this degradation on the application-related superconducting properties, such as critical current density (J_c) and irreversibility field (H_{irr}), to evaluate the possible consequence on applications for MgB$_2$. In addition, how to improve the chemical stability by means of the material processing, such as chemical doping or addition, is a more important task to fulfill the large-scale applications of MgB$_2$. In this letter, we report that the chemical stability of MgB$_2$ bulks exposed to water has been improved by Ti doping. In the same duration in water, the degradation of J_c and H_{irr} for Ti-doped MgB$_2$ is found to be much smaller than that for the undoped one. Our experiment offers

a route to sustain the high performance of MgB$_2$ when exposed to water or moist air.

A series of Ti-doped MgB$_2$ samples with an atomic ratio of Mg:Ti:B$=1-x$:x:2 ($x=$0%, 10%, 20%, and 40%) were prepared by solid state reaction at ambient pressure. Mg (99%), Ti (99.9%), and B (99%) fine powders were mixed and ground in air for 1 h. 5% extra Mg powder was added in the starting materials to compensate the loss of Mg due to its evaporation at high temperature. The mixed powders were pressed into cylinders with a diameter of 10 mm under a pressure of 600 kg/cm^2, then placed on a MgO plate, sintered in flowing Ar at 800 °C for 3 h, and finally cooled to room-temperature in furnace.

The as-prepared samples were cut into a regular shape with dimensions of 0.4×0.6×0.8 mm^3. After measuring the magnetization with a rf superconducting quantum interference device magnetometer (Quantum Design MPMSR2), the samples were successively submerged in filtered, de-ionized water at 25 °C for 10, 38, 52, and 24 h. At the end of each measurement, the total reaction time, t_R, for the samples submerged in water is 10, 48, 100, and 124 h. Following each water exposure, the samples were immediately dried and measured. There were no detectable changes in the dimensions of the samples after the water exposure. J_c values were deduced from the hysteresis loops using the Bean model.[11] H_{irr} values were determined from the closure of hysteresis loops with a criterion of 10^2 A/cm^2.

Figure 1 shows the typical temperature dependence of magnetization, $M(T)$, measured in zero-field-cooling (ZFC) process in 2 mT for samples submerged in water for various durations. For the samples exposed to water for only 10 h, almost no detectable changes can be found from the $M(T)$ curves. With increasing t_R, the transition widths become larger and the values of magnetization become smaller, although the onset T_c (=37.6 K) are almost the same before and after the water exposure. This phenomenon is consistent with the observation in the resistive measurement for MgB$_2$ films,[10] which shows the degradation of superconducting

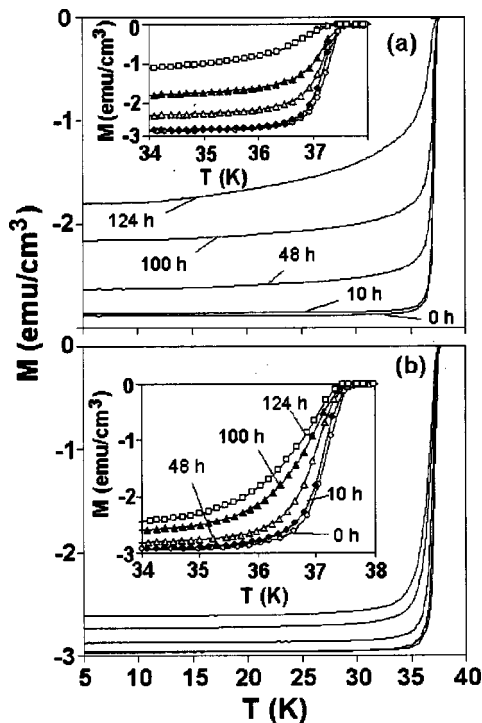[a)]Electronic mail: zhao@istec.or.jp

FIG. 1. Temperature dependence of ZFC magnetization for (a) pure and (b) Ti-doped MgB_2 samples exposed to water for various durations. The insets show the enlarged views near the superconducting transitions.

properties of MgB_2 in water. However, comparing the behavior in the reaction-time dependence of $M(T)$ curve between the pure and the Ti-doped MgB_2, the pure one is much more sensitive to water than the Ti-doped ones. For example, as a measure of the sensitivity, we compared their changes in magnetization at 5 K in 2 mT for a given duration in water. The relative change of the magnetization for the samples exposed to water for $t_R=0$ and 124 h, defined as $[M(0)-M(124h)]/M(0)$, is 48% for $x=0\%$, 12% for $x=10\%$, 16% for $x=20\%$ and 13% for $x=40\%$ [the $M(T)$ curves for $x=20\%$ and 40% are not shown here].

Figure 2 shows the results of the $J_c(H)$ curves up to 7 T at various temperatures for the samples with $x=0\%$, 10%, and 40%, and exposed to water for $t_R=0$ and 124 h. The results for $t_R=10$, 48, and 100 h are not shown here, for simplicity. For the same reason, the results of the sample with $x=20\%$ are not presented. Before exposed to water, all the samples exhibit a high J_c, especially for the undoped sample which has a higher J_c than what we achieved previously[5] since an optimized processing condition for $x=0\%$ was employed in this study. After exposed to water for 124 h, J_c decreases in all the fields between 0 and 7 T. However, compared to the pure MgB_2, the degradation of $J_c(H)$ curves is significantly reduced in Ti-doping samples. This can be seen, for example, from the changes of J_c at 5 K in zero applied field (denoted as $J_c^{5\,K}$) for the samples exposed to water for $t_R=0$ and 124 h (see the inset of Fig. 3). Before exposure to water, the pure MgB_2 sample has a $J_c^{5\,K}$ lower than that for $x=10\%$, but higher than those for $x=20\%$ and 40%. After exposure to water for 124 h, all of the Ti-doped samples show a higher $J_c^{5\,K}$ than the pure one. By normalizing the $J_c^{5\,K}$ at $t_R=124$ h with the value at $t_R=0$ (see Fig. 3), we can see more clearly that the degradation of
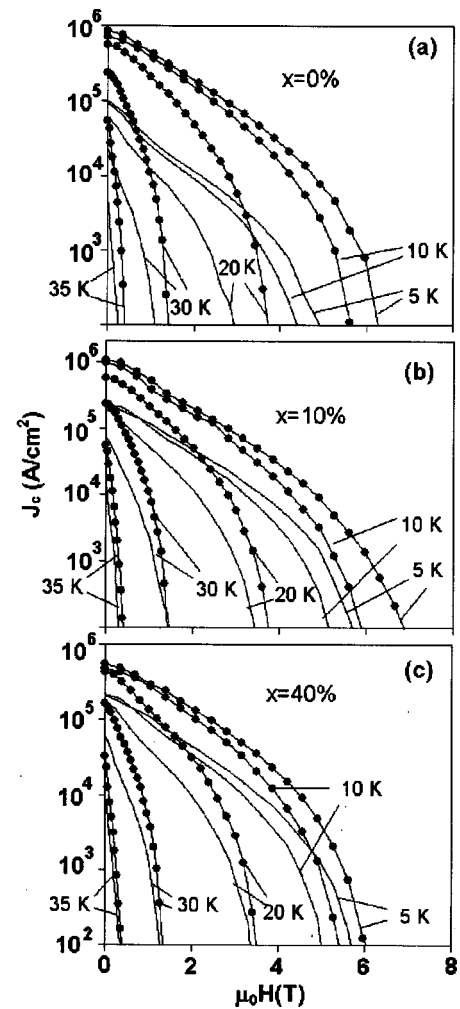

FIG. 2. Field dependence of J_c at various temperatures for Ti-doped MgB_2 samples with (a) $x=0\%$, (b) $x=10\%$, and (c) $x=40\%$. The lines with solid marks represent the results for the as-prepared samples and the solid lines represent the results for those submerged in water for 124 h.

$J_c^{5\,K}$ is greatly reduced through the Ti doping.

The influence of the Ti doping on the degradation of the superconducting properties of MgB_2 is also investigated by comparing the relative changes of H_{irr} at 5 K (denoted as $H_{irr}^{5\,K}$) for various durations in water, and at various doping levels. The results are plotted in Fig. 4, in which $H_{irr}^{5\,K}$ are normalized with their values at $t_R=0$. Once again, we can see clearly that the sensitivity of the MgB_2 sample to water has been significantly reduced by Ti doping. Typically, for the pure MgB_2, $H_{irr}^{5\,K}$ is decreased by about 25% when exposed to water for 124 h (i.e., $H_{irr}^{5\,K}$ is only 75% of its value at $t_R=0$). However, $H_{irr}^{5\,K}$ is decreased by only 5% for 40% Ti-doped sample submerged in water for the same duration. From the inset of Fig. 4, we can also see the absolute changes of $H_{irr}^{5\,K}$ for the samples of various doping levels and exposed to water for $t_R=0$ and 124 h, respectively. The as-prepared samples show a higher $H_{irr}^{5\,K}$ compared to those with $x=20\%$ and 40%. After exposure to water for 124 h, all of the Ti-doped samples show a higher $H_{irr}^{5\,K}$ than the undoped MgB_2. This behavior is consistent with the changes of $J_c^{5\,K}$ shown in the inset of Fig. 3, further confirming that the degradations of the application-related superconducting properties of MgB_2 have been suppressed by doping titanium.
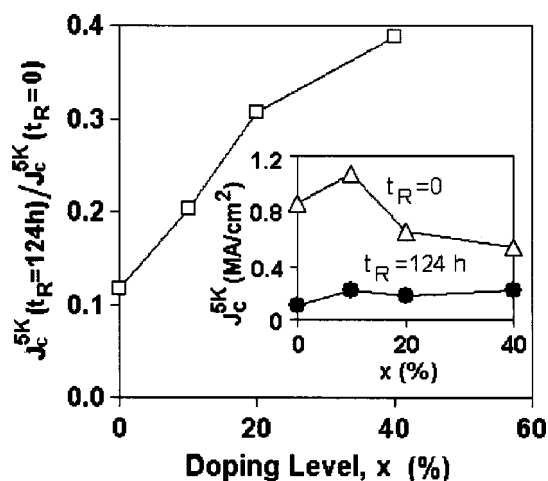
FIG. 3. Doping level dependence of normalized $J_c^{5\,K}$ for the samples exposed to water for 124 h. The inset shows the doping level dependence of the unnormalized $J_c^{5\,K}$ for the as-prepared samples and those exposed to water for 124 h.

As revealed recently,[5,12] Ti doping at a certain level can significantly improve the J_c and H_{irr} of MgB_2 bulk material, due to the formation of MgB_2 nanoparticle structure with ultrathin TiB_2 layer at GBs. The improved chemical stability
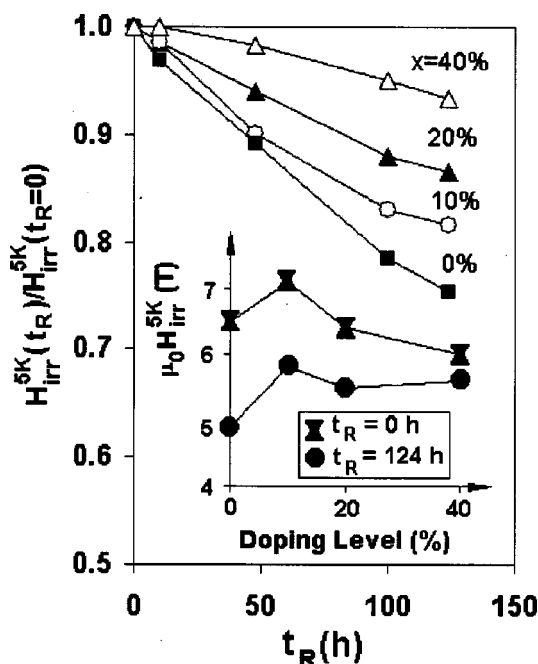

FIG. 4. Variation of the normalized irreversibility filed at 5 K with t_R for samples with various Ti-doping levels. The inset shows the doping level dependence of unnormalized irreversibility field for the as-prepared samples and those exposed to water for 124 h.

observed in the present experiment may also be attributed to this unique microstructure which features largely in the enhanced grain coupling. Usually, GBs are weak points in chemical stability due to the existence of the so-called "grain-boundary energy" as well as the Coulomb interaction between the GB and the impurity atoms. By forming a strongly coupled MgB_2 nanoparticle assembly, on one hand, Ti doping has greatly reduced the GBs thickness and improved the density of the material.[12] On the other hand, as an impurity phase in the GBs of MgB_2 TiB_2 may decrease the GB energy, and thus enhance the chemical stability of GBs. So far, the real mechanism beneath the phenomena observed here is not clear. Detailed studies on both the surface chemistry and the microstructure modification in water for Ti-doped MgB_2 are necessary to clarify the mechanism.

In summary, we have investigated the degradation of critical current density and irreversibility field of the pure and the Ti-doped MgB_2 bulks by exposing the samples to water for a total of 10, 48, 100, and 124 h. Both J_c and H_{irr} were degraded by exposure to water, in various degrees depending on the Ti-doping level. In the same exposure duration, the degradations of J_c, H_{irr}, and other superconducting properties for the Ti-doped MgB_2 are much less drastic than those for the pure MgB_2, indicating a significant improvement of the chemical stability against water.

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