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Nanoparticle structure of MgB_2 with ultrathin TiB_2 grain boundaries

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The microstructure of the Ti-doped MgB_2 which shows a significantly improved critical current density, J_c [Appl. Phys. Lett. **79**, 1154 (2001)], is investigated. It is found that Ti does not occupy the atomic site in the MgB_2 crystal structure, but forms a thin TiB_2 layer (with a thickness about one unit cell of TiB_2) in the grain boundaries of MgB_2. Besides, MgB_2 grains are greatly refined by Ti doping, forming a strongly coupled nanoparticle structure. It is argued that the unique microstructure of the MgB_2 nanoparticles with TiB_2 nanograin boundaries may take responsibility for the enhancement of J_c in the Ti-doped MgB_2 bulk superconductor. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1456969]

The discovery of superconductivity at 39 K in MgB_2 (Ref. 1) offers the possibility of wide engineering applications in a temperature range of 20–30 K, where the conventional superconductors, such as Nb_3Sn and Nb–Ti alloy, cannot play any roles because of low T_c. Besides a high T_c, MgB_2 also has many superior properties in superconducting and normal states, including 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), high intrinsic J_c ($>10^7$ A/cm^2), etc. (see review article by Buzea and Yamashita[2]). However, the applications of MgB_2 have been hampered so far by its poor mechanical properties (brittleness) and the degradation of J_c in high magnetic fields. For sintered MgB_2 bulk materials including those prepared under a high pressure of several GPa, the grain size of MgB_2 is usually very large, ranging from 0.1 to 10 μm,[3,4] making it difficult to form tight packing. Thick grain boundaries of several nanometers or more are formed in the bulk material, resulting in a poor grain connection of MgB_2 bulk material. Therefore, a fine and well-bonded particle structure of superconducting phase with introduced fine second-phase particles is pursued in preparing MgB_2 superconducting material for practical applications, as achieved in the MgB_2 thin films.[5] Recently, by doping 10% Ti in MgB_2, the superconducting properties of MgB_2 bulk superconductor have been significantly improved and a J_c of 1 MA/cm^2 at 20 K in zero applied field has been achieved.[6]

In order to understand the underlying mechanism for Ti-doping effect on J_c, detailed analyses on the crystal structure and microstructure for Ti-doped MgB_2 are necessary. In this letter, we present results which reveal that a strongly coupled MgB_2 nanoparticle structure with TiB_2 thin layer (about 0.3 nm) staying in the grain boundaries has been achieved in Ti-doped MgB_2 bulk material. This unique microstructure may take responsibility for the improved superconducting properties of the material.

A series of Ti-doped MgB_2 samples with an atomic ratio of Mg:Ti:B$=1-x:x:2$ and $0\leqslant x\leqslant 1.0$ were prepared by solid state reaction at ambient pressure. Details of the preparation conditions were reported previously.[6] The crystal structure was investigated by powder x-ray diffraction (XRD) using a MXP18 diffractometer with a Cu$K\alpha$ radiation. The microstructural and compositional analyses were performed by a field emission high-resolution transmission electron microscope equipped with energy-dispersive x-ray spectroscopy (EDX) system. The dc magnetization was measured using a rf superconducting quantum interference device magnetometer (Quantum Design MPMSR2). The typical dimensions of the samples used for magnetization measurement are $0.41\times0.57\times0.83$ mm^3. The field was applied in the direction along the shortest dimension of the sample. J_c values were deduced from the hysteresis loops using the Bean model.[7]

The crystal structure for all Ti-doped samples was examined with XRD analysis. Figure 1(a) shows the XRD patterns for the typical samples ($x=0$, 0.1, 0.2, and 0.4). For the undoped sample, only MgB_2 with a small amount of MgO

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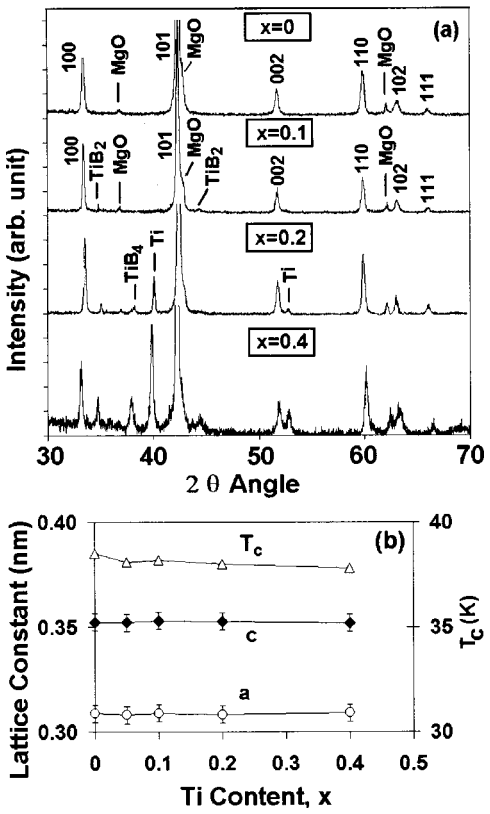

FIG. 1. (a) XRD patterns for Ti-doped MgB_2 samples with doping level of $x=0$, 0.1, 0.2, 0.4. (b) Doping level dependence of the lattice constants and T_c for Ti-doped MgB_2.

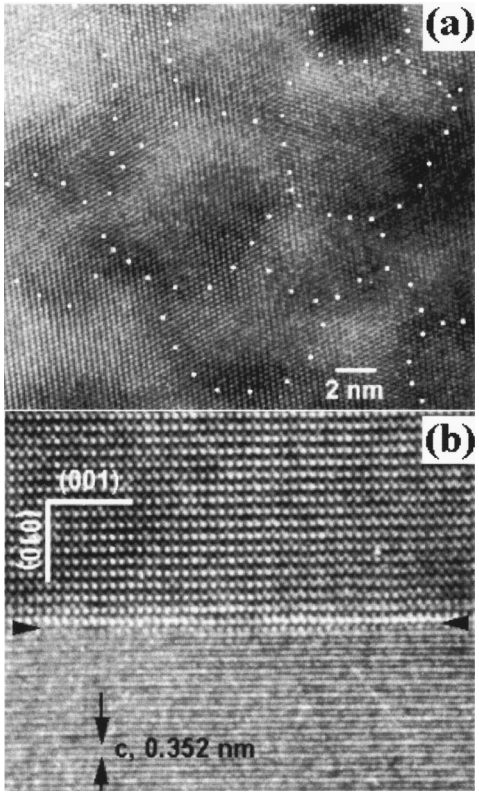

FIG. 2. (a) HRTEM photograph for Ti-doped MgB_2 ($x=0.1$). A dotted network is drawn for convenience to enable one to see the nanoparticle structure. (b) A typical grain boundary (indicated by closed triangles) which shows a very small grain boundary thickness.

can be seen. With increasing doping level, TiB_2 appears and its amount increases slightly for $0<x<0.1$. It is interesting to note that when the doping level reaches or exceeds $x=0.2$, instead of forming more TiB_2, other impurity phases such as pure Ti, TiB_4, etc., appear in the samples. The lattice constants of the MgB_2, which is the main phase in all of the samples with $x<0.5$, do not change with the doping level, as shown in Fig. 1(b). This is consistent with an almost invariant T_c for the samples of various doping levels [see also Fig. 1(b)].

Figure 2(a) shows the typical microstructure for the Ti-doped MgB_2 sample with $x=0.1$, in which a dotted network is drawn for convenience to see the nanoparticle structure. The size of MgB_2 grains is found to be about 8 nm on average. Between two neighboring grains, a small orientation difference exists. The connection between the nanoparticles is very tight since the thickness of the grain boundaries is small (<1 nm), as illustrated in Fig. 2(b). This is in great contrast with other MgB_2 bulk materials prepared under ambient pressure, for which a loose packing of the coarse particles and an amorphous boundary with a thickness of 10 nm or more are often observed.[3,4]

Figure 3(a) shows the EDX mapping for the two-dimensional global distribution of the Ti in the same sample as in Fig. 2. The experiment was done using a relatively large spot size (3 nm) in a relatively short time (20 min) in order to avoid the possible shift of both the sample and the electron beam. A network formed by the Ti-rich area can be clearly seen which is very similar to the network formed by the MgB_2 nanograin boundaries, as schematically drawn in Fig. 2(a). Because the used spot size (3 nm) is much larger than the size of the Ti-rich boundary area (usually<1 nm), the detected Ti signal in the EDX mapping may have been broadened by a 3 nm disk window function. To obtain more precise and local distribution of the Ti in the sample, the point EDX analysis was done with a spot size of 1 nm in both the grain boundaries and grains. As shown in the inset of Fig. 3(b), Ti element was found only in the grain boundaries but could not be detected inside the MgB_2 grains. This is also consistent with the results of XRD and the doping level dependencies of the lattice constants and T_c mentioned previously. All these reveal that Ti does not occupy the atomic sites in the lattice, but merely forms impurity phases staying outside the MgB_2 grains.

The formation of a TiB_2 thin layer around the MgB_2 particles may be the cause of the formation of the MgB_2 nanoparticles since this layer may decrease the growth rate of the MgB_2 grains. In addition, no MgB_4 was observed at grain boundaries in the Ti-doped MgB_2. MgB_4 usually stays in the grain boundaries of MgB_2 (Refs. 3 and 4) and causes a loose connection between grains due to its large mismatch in the crystal structure and the lattice constants with MgB_2 (which is of a hexagonal structure with $a=0.3086$ nm and $c=0.3524$ nm, whereas MgB_4 is of an orthorhombic structure with $a=0.5464$ nm, $b=0.7472$ nm, and $c=0.4428$ nm). In contrast to MgB_4, the TiB_2 has a much better bonding with MgB_2 due to the same crystal structure and very close lattice constants ($a=0.3030$ nm and $c=0.3230$ nm). Therefore, a schematic of the microstructure of the Ti-doped MgB_2 can be obtained and shown in Fig. 3(b), in which the MgB_2 nanoparticles are separated by the thin TiB_2 grain bound-

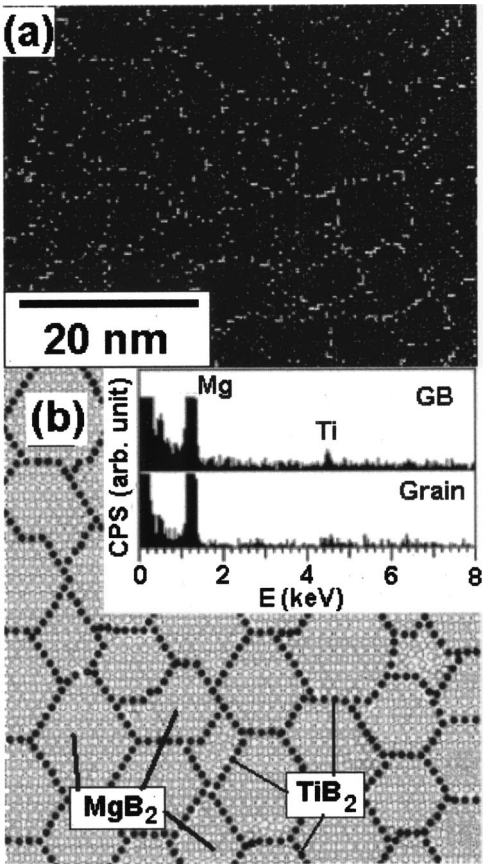

FIG. 3. (a) Two-dimensional EDX mapping for the distribution of the Ti element in which the white points represent the Ti-rich area. (b) Schematic illustration of the MgB_2 nanoparticle structure with TiB_2 nanograin boundaries. Inset: EDX spectra using a nanoprobe show that the Ti element exists only in the grain boundary (GB).

aries. Denoting the average size of the MgB_2 particles by D and the average thickness of the TiB_2 grain boundaries by Δ, the ratio of the amount of TiB_2 to MgB_2, β, will be $\beta = 3\Delta/D$, by assuming that the particles are spheres with the diameter D (or cubes with an edge length D). Taking $D = 10$ nm and $\beta = 10\%$, the thickness of the grain boundary, Δ, is estimated to be about 0.33 nm, very close to the lattice constant of TiB_2. This estimation is consistent with the observation that the thickness of the grain boundary is about the size of the TiB_2 unit cell [see Fig. 2(b)]. Usually, TiB_2 forms at a rather high temperature ($>1000\,°C$). In the present sample made between 600 and 900 °C, the formation of TiB_2 nanograin boundaries in MgB_2 nanoparticle assembly may be attributed to the surface energy of the MgB_2 nanoparticles. This idea has been supported by the observation that further increasing the Ti content with $x > 0.1$ does not increase the amount of TiB_2 but forms other impurity phases since the surface area in MgB_2 nanoparticle structure is limited. More detailed study is necessary to clarify the formation mechanism of such a unique microstructure in the present system.

The unique microstructure in Ti-doped MgB_2 may be the main reason for its superior superconducting properties to other MgB_2 bulk samples. Because of the tight bonding between MgB_2 nanoparticles and the ultrathin TiB_2 grain boundaries, no weak-link effect exists as confirmed by its high J_c at high field, for example, 5×10^4 A/cm^2 in 5 T at 5 K.[6] Besides, the bulk pinning force, $F_p(H) = \mu_0 H J_c(H)$, reaches 7 GN m^{-3} at 5 K, which is one order of magnitude higher than the best result for the pure MgB_2 bulk sample, and is close to the pinning force of the established technological superconductors Nb47wt %Ti[8] and Nb_3Sn,[9] which lie in the range 15–30 GN m^{-3}. The enhanced pinning force may be attributed to the increased area of the grain boundaries which provide strong grain boundary pinning like Nb_3Sn, for which F_p is inversely proportional to the grain size.[10]

In summary, we have investigated the crystal structure and microstructure of Ti-doped MgB_2 bulk material. We found that Ti does not occupy the atomic site in the MgB_2 crystal structure, but forms a thin TiB_2 layer in the grain boundaries of MgB_2. Besides, MgB_2 grains are greatly refined by Ti doping, forming a strongly coupled nanoparticle structure. The enhanced bonding between grains and increased area of grain boundaries by forming the MgB_2 nanoparticle structure may take responsibility for the enhancement of J_c in Ti-doped MgB_2 bulk superconductor.

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