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Nanoparticle structure of MgB\textsubscript{2} with ultrathin TiB\textsubscript{2} grain boundaries

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The microstructure of the Ti-doped MgB\textsubscript{2} which shows a significantly improved critical current density, \(J_c\) \cite{1}, is investigated. It is found that Ti does not occupy the atomic site in the MgB\textsubscript{2} crystal structure, but forms a thin TiB\textsubscript{2} layer (with a thickness about one unit cell of TiB\textsubscript{2}) in the grain boundaries of MgB\textsubscript{2}. Besides, MgB\textsubscript{2} grains are greatly refined by Ti doping, forming a strongly coupled nanoparticle structure. It is argued that the unique microstructure of the MgB\textsubscript{2} nanoparticles with TiB\textsubscript{2} nanograin boundaries may take responsibility for the improved superconducting properties of the material.

A series of Ti-doped MgB\textsubscript{2} samples with an atomic ratio of \(\text{Mg}:\text{Ti}:\text{B}=1-x:x:2\) and \(0 \leq x \leq 1.0\) were prepared by solid state reaction at ambient pressure. Details of the preparation conditions were reported previously\cite{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 \(0.41 \times 0.57 \times 0.83\) mm\textsuperscript{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\textsuperscript{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 \((x=0, 0.1, 0.2, \text{and} 0.4)\). For the undoped sample, only MgB\textsubscript{2} with a small amount of MgO

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can be seen. With increasing doping level, TiB₂ 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 TiB₂, other impurity phases such as pure Ti, TiB₄, etc., appear in the samples. The lattice constants of the MgB₂, 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 MgB₂ sample with $x = 0.1$, in which a dotted network is drawn for convenience to see the nanoparticle structure. The size of MgB₂ 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 ($\sim 1$ nm), as illustrated in Fig. 2(b). This is in great contrast with other MgB₂ 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.

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 MgB₂ 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 MgB₂ 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 MgB₂ grains.

The formation of a TiB₂ thin layer around the MgB₂ particles may be the cause of the formation of the MgB₂ nanoparticles since this layer may decrease the growth rate of the MgB₂ grains. In addition, no MgB₄ was observed at grain boundaries in the Ti-doped MgB₂. MgB₄ usually stays in the grain boundaries of MgB₂ (Refs. 3 and 4) and causes a loose connection between grains due to its large mismatch in the crystal structure and the lattice constants ($a = 0.3086$ nm and $c = 0.3524$ nm, whereas MgB₄ is of an orthorhombic structure with $a = 0.5464$ nm, $b = 0.7472$ nm, and $c = 0.4428$ nm). In contrast to MgB₄, the TiB₂ has a much better bonding with MgB₂ 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 MgB₂ can be obtained and shown in Fig. 3(b), in which the MgB₂ nanoparticles are separated by the thin TiB₂ grain boundary...
further increasing the Ti content with particles. This idea has been supported by the observation that the average thickness of the TiB₂ grain boundaries by the ratio of the amount of TiB₂ to MgB₂, which may be attributed to the surface energy of the MgB₂ nanoparticle assembly. Denoting the average size of the MgB₂ particles by \( D \), 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, \( \Delta \), is estimated to be about 0.33 nm, very close to the lattice constant of TiB₂. This estimation is consistent with the observation that the thickness of the grain boundary is about the size of the TiB₂ unit cell [see Fig. 2(b)]. Usually, TiB₂ forms at a rather high temperature (>1000 °C). In the present sample made between 600 and 900 °C, the formation of TiB₂ nanograin boundaries in MgB₂ nanoparticle assembly may be attributed to the surface energy of the MgB₂ 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 TiB₂ but forms other impurity phases since the surface area in MgB₂ 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 MgB₂ may be the main reason for its superior superconducting properties to other MgB₂ bulk samples. Because of the tight bonding between MgB₂ nanoparticles and the ultrathin TiB₂ grain boundaries, no weak-link effect exists as confirmed by its high \( J_c \) at high field, for example, \( 5 \times 10^4 \) A/cm² in 5 T at 5 K. 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 MgB₂ bulk sample, and is close to the pinning force of the established technological superconductors Nb₄₇wt %Ti₈ and Nb₃Sn, 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 Nb₃Sn, for which \( F_p \) is inversely proportional to the grain size.

In summary, we have investigated the crystal structure and microstructure of Ti-doped MgB₂ bulk material. We found that Ti does not occupy the atomic site in the MgB₂ crystal structure, but forms a thin TiB₂ layer in the grain boundaries of MgB₂. Besides, MgB₂ 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 MgB₂ nanoparticle structure may take responsibility for the enhancement of \( J_c \) in Ti-doped MgB₂ bulk superconductor.

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