Development of 4 T Class MgB_2 Bulk Magnets Doped by Ti

Takafumi Yoshida, Tomoyuki Naito, and Hiroyuki Fujishiro

***Abstract*—We have studied the trapped field properties of Ti-doped MgB_2 bulks that were fabricated by a hot isostatic pressing method. The trapped field values of Ti5% doped bulk with 38 mm in diameter and 7 mm in thickness were about 3.6 T at 13.2 K and 2.8 T at 20 K, which were 1.3 times larger than those of the pristine bulk at each temperature. The critical current density was also enhanced by the Ti-doping from 1.7×10^2 A/cm^2 for the pristine bulk to 3.0×10^3 A/cm^2 for the Ti5% doped bulk at 20 K under 4 T. The improvement of the flux pinning properties originated from the TiB_2 thin layer at the periphery of the Ti precipitates, which was acted as a strong pinning center.**

***Index Terms*—Critical current density, MgB_2 superconductors, microstructure, superconducting bulk magnet, trapped field properties.**

I. Introduction

MgB_2 has the highest superconducting transition temperature $T_c = 39$ K among intermetallic compounds. Since its coherence length is long in comparison with RE-Ba-Cu-O (RE: rare earth elements) system [1], we can discard the weak-links at grain boundaries, and can realize a superconducting bulk magnet using a polycrystal. Several groups have reported that a MgB_2 bulk trapped the tesla-order magnetic field [2]–[6]. We reported the trapped magnetic field, B_T, of 1.77 T at 15.5 K for an in-situ MgB_2 bulk with 38 mm in diameter and 9 mm in thickness fabricated under an ambient pressure by the capsule method [2]. This bulk had a low filling factor of about 50%, which was intrinsically caused by the *in-situ* reacting process. Therefore, the high-pressure sintering was expected to enhance the filling density and the critical current density, J_c, i.e., B_T. We have succeeded a 3 T class MgB_2 bulk magnet using the highly dense MgB_2 bulk fabricated by a hot isostatic pressing (HIP) method under a pressure of 98 MPa [3]. The similar result was reported by Viznichenko *et al.*, who achieved the B_T value of about 2.3 T at 6 K for the MgB_2 bulk with 28 mm in diameter and 11 mm in thickness which was sintered under a much higher pressure of 2 GPa [4]. Recently, Durrel *et al.* reported the B_T value over 3 T at 17.5 K in stacked MgB_2 bulks (diameter 25 mm and thickness 5.4 mm) which were fabricated by uniaxial hot pressing method under a pressure of 25 MPa [5], and Fuchs *et al.* obtained quite high B_T of 5.4 T at 12 K for the hot pressed MgB_2 bulk (diameter 20 mm and thickness 8 mm) [6]. Therefore, the densification is an essential way to develop the strong MgB_2 bulk magnet.

Chemical doping is usually performed to improve the flux pinning properties; C and Ti are known to be effective dopants for MgB_2 [7]–[9]. Dou *et al.* demonstrated that J_c and the irreversibility field, B_{irr}, of MgB_2 wire prepared by a powder-in-tube method were significantly enhanced by SiC-doping, in which J_c was 2.4×10^5 A/cm^2 at 20 K under 2 T for the 10wt% SiC doped sample [7]. On the other hand, Zhao *et al.* reported that Ti-doping also brought about high J_c for the Ti10%-doped MgB_2 sample, in which J_c was 1.3×10^6 A/cm^2 in the self-field and 9.4×10^4 A/cm^2 under 2 T at 20 K [8]. Doped Ti did not occupy the atomic site in the MgB_2 crystal, but formed a thin TiB_2 layer between the grain boundaries. Besides, MgB_2 grains were greatly refined by Ti-doping, resulting in a strongly coupled nanoparticle structure [9]. They concluded that the enhancement in J_c originated from both the existence of TiB_2 layer as the novel flux pinning center and the densification.

In this paper, for the purpose of the improvement of the trapped field properties of MgB_2, we fabricated Ti-doped MgB_2 bulks by HIP method and studied the effect of Ti-doping on their flux pinning properties and microstructure.

II. Experimental Details

A. Sample Preparation

MgB_2 bulks were fabricated by the HIP method [3]. Raw powders of Mg (99.5% in purity, $\leqq$ 180 μm in grain size, Kojundo Chemical Laboratory Co., Ltd), amorphous B (99% in purity, 300 mesh in grain size, Furuuchi Chemical Corp.) and Ti (99% in purity, $\leqq$ 45 μm in grain size, Kojundo Chemical Laboratory Co., Ltd) were weighted with Mg : B : Ti $= (1-x)$: 2 : x ($x = 0$, 0.05, 0.1, and 0.2) in molar ratio and ground. The mixture was pressed into pellet 40 mm in diameter and 20 mm in thickness under an uniaxial pressure of about 12 MPa, and the pellet was further densified by a cold isostatic pressing method under a pressure of 196 MPa. The precursor pellet was sealed in the stainless steel container by electron beam welding in vacuum, and subsequently was sintered at temperature of 900 °C for 3 h under a pressure of 98 MPa in the HIP furnace. Typical size of the shaped bulk is 38 mm in diameter and 7 mm in thickness. The filling factor, F, which was the ratio of the measured mass density to the theoretical mass density of the MgB_2-Ti composite, was larger than 90%. This means that the filling factor of the MgB_2 part in the Ti-doped bulk was above

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TABLE I
SPECIFICATION OF THE PRISTINE AND Ti-DOPED MgB_2 BULKS

Sample name	T_c(K)	F(%)	V_f(%)	Max of B_T	B_T at 16 K
Pristine	38.1	94	94	2.5 T at 16.0 K	2.5 T
Ti5%	38.3	91	87	3.6 T at 13.2 K	3.3 T
Ti10%	38.3	92	84	3.5 T at 14.4 K	3.3 T
Ti20%	38.4	96	78	3.4 T at 15.3 K	3.3 T

90%. We also estimated the volume fraction, V_f, of the MgB_2 phase in the Ti-doped bulks as follows, 87% for Ti5%-doped, 84% for Ti10%-doped, and 72% for Ti20%-doped bulks, which are also found in Table I. Specifications of the bulks are listed in Table I.

B. Measurements

The MgB_2 bulk was magnetized by field cooling (FC) in a magnetic field of 5 T parallel to the thickness direction using a 10-T cryogen-free superconducting magnet (JMTD-10T100, Japan Superconductor Technology (JASTEC) Inc.), and then the applied field was decreased to 0 T at a rate of 0.022–0.222 T/min. The trapped field value, B_T, at the center of the bulk surface was measured by a cryogenic Hall sensor (BHT-921, F.W. BELL Inc.). After the FC experiment, we evaluated the critical temperature, T_c, and the critical current density, J_c, by measuring the magnetization of a small piece cut from the bulk using a commercial SQUID magnetometer (MPMS-XL, Quantum Design Inc.). J_c was estimated from the hysteresis loop using the extended Bean model. Crystal structure and phase evaluation were investigated by the powder X-ray diffraction (XRD) with a Cu Kα radiation using the X-ray diffractometer (Multi Flex, Rigaku Corp.). Microstructure and composition analysis of the Ti-doped MgB_2 bulks were investigated by electron probe micro analyser (EPMA) (JXA-8100, JEOL Ltd.).

III. RESULT AND DISCUSSION

Fig. 1 presents the temperature dependence of the trapped field, $B_T(T)$, of the pristine and Ti-doped MgB_2 bulks. The maximum B_T values of the pristine bulk, Ti5%-, Ti10%-, and Ti20%-doped bulks, respectively, are 2.5 T at 16.0 K, 3.6 T at 13.2 K, 3.5 T at 14.4 K, and 3.4 T at 15.3 K. For comparison, the B_T values at 16 K are estimated by interpolation for all the bulks, as described in Table I. Those of Ti-doped bulks are about 1.3 times larger than that of the pristine bulk. Although we succeed in the improvement of the trapped magnetic field by Ti doping, the $B_T(T)$ curves of Ti-doped bulks hardly depend on the Ti-doping levels, which cannot be explained by the fact that the volume fraction decreases with increasing Ti-contents.

Fig. 2 shows the temperature dependence of the normalized magnetization, $M(T)$, in a magnetic field of 4 Oe after zero-field cooling. The critical temperature, T_c, defined at the midpoint of the transition is 38.1–38.4 K for all the bulks regardless of the Ti-doping levels. This indicates that Ti does not substitute for the Mg-site, because, in general, the site substitution suppresses the T_c value.

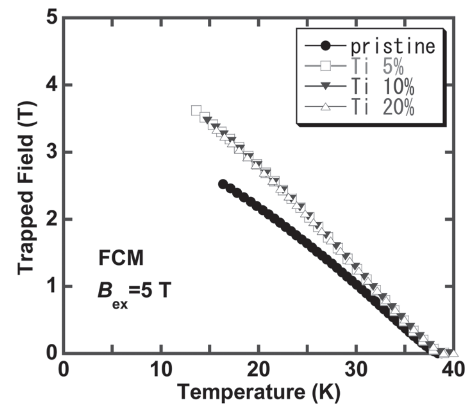

Fig. 1. Temperature dependence of trapped field, $B_T(T)$, of the pristine and Ti-doped MgB_2 bulks with various Ti-doping.

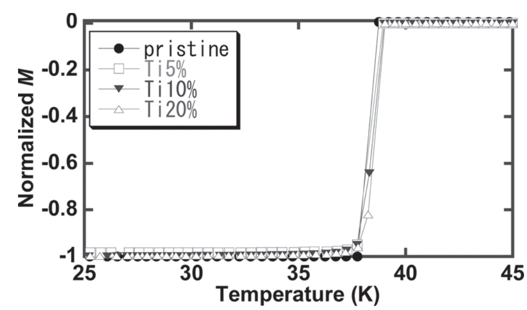

Fig. 2. Temperature dependence of normalized magnetization for the pristine and Ti-doped MgB_2 bulks, in 4 Oe after the ZFC process.

Fig. 3(a) shows the magnetic field dependence of the critical current density, $J_c(B)$, at $T = 10$–30 K for the pristine and Ti-doped MgB_2 bulks. The $J_c(B)$ values of the Ti-doped bulks are much higher than that of the pristine bulk for all the measured temperatures. Fig. 3(b) and (c) shows the Ti-doping amount dependence of J_c at $T = 10$ K and 20 K for various magnetic fields. The J_c value increases clearly by Ti-doping for each applied field, takes a slight maximum at the 10% doping and decreases at the 20% doping except for at 20 K under 3 T and 4 T at which the maxima are observed at the 5% doping. However, the doping dependence of J_c higher than 5% is very small, which is a clear contrast to the results reported previously [8] and can explain the Ti-content independent B_T curves in Fig. 1. Difference in J_c between the pristine and Ti-doped bulks tends to increase conspicuously with the increase in the magnetic field. The J_c values of the pristine and Ti10%-doped bulks are listed in Table II, in which the J_c values of pristine bulk are 8.3×10^3 A/cm^2 at $T = 10$ K and 1.7×10^2 A/cm^2 at $T = 20$ K under 4 T. On the other hand, the J_c values of Ti10%-doped bulks are 3.5×10^4 A/cm^2 at $T = 10$ K and 2.7×10^3 A/cm^2 at $T = 20$ K under 4 T. It is noteworthy that although the absolute value of J_c of the Ti10%-doped bulk at 10 K under 0 T is comparable to the reported value [8], that of the Ti10%-doped bulk at 20 K under 4 T is about two orders of magnitude larger than the reported value [8]. This indicates that the Ti-contained impurities act as the effective pinning center at higher magnetic fields in comparison with [8].

Fig. 4 shows the X-ray diffraction patterns of the pristine and Ti-doped bulks at room temperature. For the pristine bulk, only

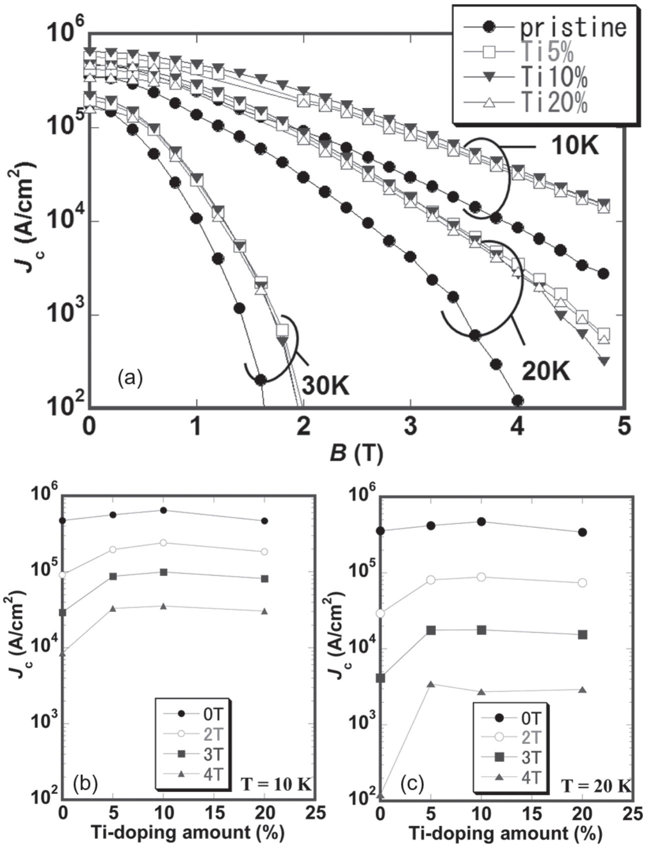

Fig. 3. (a) Magnetic field dependence of the critical current density J_c at 10–30 K for the pristine and Ti-doped MgB_2 bulks. Ti-doping amount dependence of the critical current density J_c at (b) $T = 10$ K and (c) 20 K in various magnetic fields.

TABLE II
J_c VALUES OF THE PRISTINE AND Ti10% DOPED MgB_2 BULKS

T (K)	J_c (A/cm^2)			
	Pristine bulk		Ti10% doped bulk	
	0 T	4 T	0 T	4 T
10	4.7×10^5	8.3×10^3	6.4×10^5	3.5×10^4
20	3.5×10^5	1.7×10^2	4.7×10^5	2.7×10^3
30	1.7×10^5	-	2.2×10^5	-

the peaks of MgB_2 are observed. For the Ti-doped bulks, in addition to the dominant MgB_2 phase, the peaks of Ti and TiB_2 are found as the impurity phases. The peak intensity of TiB_2 and Ti increases with increasing Ti-doping level.

Fig. 5 shows the composition images on the surface of the Ti-doped MgB_2 bulks, which was obtained by the backscattered electrons using EPMA. The dominant gray region is the MgB_2 matrix phase and the black parts are voids and cracks. The white portion of the images represents Ti-metal which is identified in Fig. 6 and increases with increasing Ti-doping. Fig. 6 shows the characteristic X-ray images of Mg, B, and Ti for the Ti5% doped bulk; white color represents the corresponding element. From Figs. 5(a) and 6(c), the white regions in the composition image are Ti and their size is typically several tens micrometers. In addition, it should be noted that B accumulates at the periphery of Ti particles as found in Fig. 6(b). This thin layer containing both Ti and B may be the TiB_2 phase observed in the

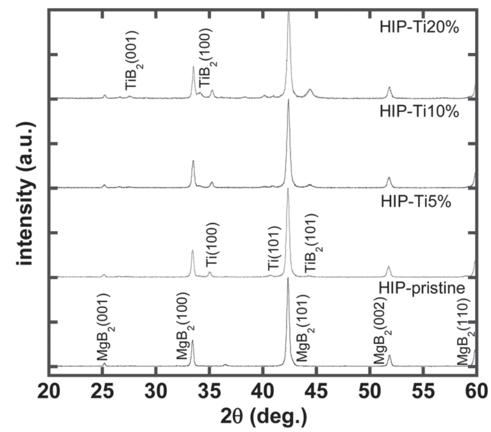

Fig. 4. X-ray diffraction patterns of the pristine and Ti-doped MgB_2 bulks.

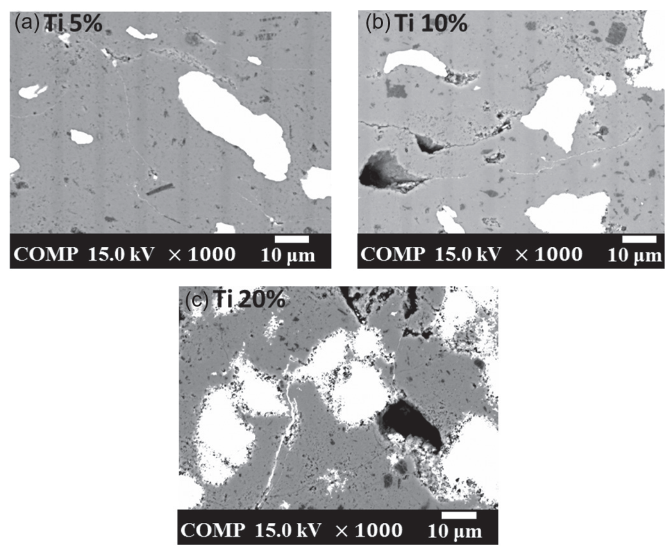

Fig. 5. Composition images of the Ti-doped MgB_2 bulks.

XRD patterns. We consider that the TiB_2 layers act as the strong flux pinning center and enhance both J_c and B_T values, because the size of Ti particles is too large to pin the flux effectively. The size of TiB_2 is quite different from that observed in the literature [9], which possibly gives higher J_c in higher magnetic fields. On the other hand, the trapped field is generally degraded with decreasing the volume fraction V_f of MgB_2 phase in the bulk. Therefore, the trapped field independent of the Ti-contents as shown in Fig. 1 may originate from the competition between the increase of the number of the vortex pinning centers and the decrease of the volume fraction of MgB_2 phase.

IV. CONCLUSION

We have investigated the trapped field, B_T, the critical current density, J_c, microstructure and composition of the Ti-doped MgB_2 bulks which were fabricated by the HIP method. The TiB_2 thin layer found at the periphery of the Ti precipitate acted as the effective vortex pinning center at higher magnetic fields, and, as a result, highly improved both B_T and J_c.

The important obtained results are described in the following.

1) The highest B_T of 3.6 T was realized at 13.2 K for the Ti5% doped bulk, which was 1.3 times larger than that

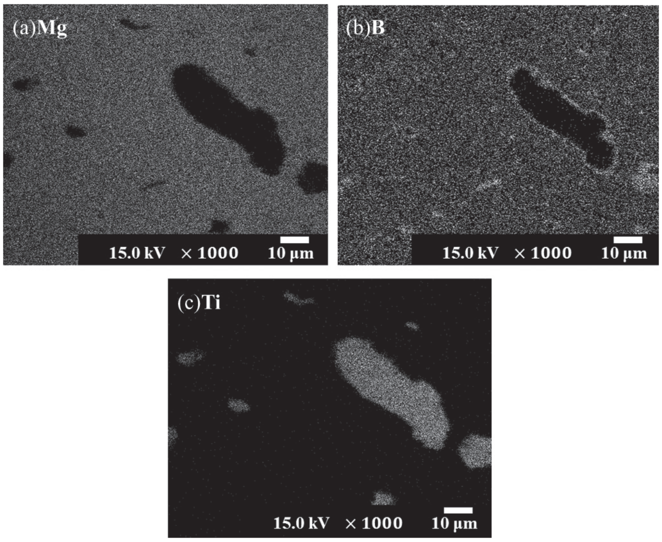

Fig. 6. Characteristic X-ray images of (a) Mg, (b) B, and (c) Ti for the Ti5% doped MgB_2 bulk.

of the pristine bulk. However, further doping did not enhance $B_T(T)$; the $B_T(T)$ curves of both Ti10% and Ti20% doped bulks were almost the same as that of Ti5% bulk. Extra Ti was precipitated as Ti particles.

2) The critical temperature, T_c, was about 38.1–38.4 K for all the bulks regardless of the Ti-doping levels, which indicated that doped Ti did not substitute for the Mg-site.
3) The J_c values of the Ti-doped bulk were about one order of magnitude higher than that of the pristine bulk in the magnetic fields. The J_c value increased clearly by Ti-doping for each applied fields, took a slight maximum at the 10% doping and decreased at the 20% doping.
4) TiB_2 was found as the thin layer at the periphery of the Ti particles, which acted as the strong pinning center and enhanced both B_T and J_c.

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