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Abstract

Bulk MgB₂, with self-generated MgB₄ pinning centers, have experienced two-step sintering process, initially at 750°C and then 900-1000°C. On the contrary to the widely accepted point that MgB₄ deteriorates superconductivity, it was found that MgB₄ played a significant role in enhancing critical current density. The precipitation pattern of MgB₄ was studied from the lattice scale images. It was observed that the initial coherent relation between the MgB₄ and the matrix was destroyed to become semi-coherent and even incoherent as the second-step sintering temperature increased. Owing to the lattice distortion caused by the elastic accommodation of the coherent interface, the small-sized MgB₄ particles controlled by the sintering temperature, and the fine grain connectivity affected by the porosity, the critical current density was improved over the entire magnetic field. Finally, the dominating pinning mechanism within the crystal was confirmed to be $\Delta\kappa$ pinning in the two-step sintered MgB₂ sample, where the κ is the Ginzburg-Landau parameter, while the mechanism of one-step sintered sample is surface pinning. 2013 AIP Publishing LLC.

Keywords

mgb₄, bulk, mgb₂, density, current, containing, critical, impurity, enhancement, mechanism, pinning, variation, self, generated, coherent

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Cai, Q., Liu, Y., Ma, Z., Li, H. & Yu, L. (2013). Variation of pinning mechanism and enhancement of critical current density in MgB₂ bulk containing self-generated coherent MgB₄ impurity. *Applied Physics Letters*, 103 (13), 132601-1-132601-4.

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Citation: [Applied Physics Letters](#) **103**, 132601 (2013); doi: 10.1063/1.4822099

View online: <http://dx.doi.org/10.1063/1.4822099>

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Variation of pinning mechanism and enhancement of critical current density in MgB_2 bulk containing self-generated coherent MgB_4 impurity

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(Received 10 July 2013; accepted 8 September 2013; published online 23 September 2013)

Bulk MgB_2 , with self-generated MgB_4 pinning centers, have experienced two-step sintering process, initially at 750 °C and then 900–1000 °C. On the contrary to the widely accepted point that MgB_4 deteriorates superconductivity, it was found that MgB_4 played a significant role in enhancing critical current density. The precipitation pattern of MgB_4 was studied from the lattice scale images. It was observed that the initial coherent relation between the MgB_4 and the matrix was destroyed to become semi-coherent and even incoherent as the second-step sintering temperature increased. Owing to the lattice distortion caused by the elastic accommodation of the coherent interface, the small-sized MgB_4 particles controlled by the sintering temperature, and the fine grain connectivity affected by the porosity, the critical current density was improved over the entire magnetic field. Finally, the dominating pinning mechanism within the crystal was confirmed to be $\Delta\kappa$ pinning in the two-step sintered MgB_2 sample, where the κ is the Ginzburg-Landau parameter, while the mechanism of one-step sintered sample is surface pinning. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822099>]

The intermetallic compound MgB_2 with the superconducting transition temperature of 39 K has been the focus of worldwide attention for the past ten years due primarily to its potential for practical magnetic and electrical applications.¹ Although considerable progress have been made during this period, the application of pure MgB_2 remains limited by the sensitivity of critical current density (J_c) to increasing applied magnetic field as a result of the relatively weak flux pinning.²

A series of exciting achievements in improving the J_c performance have been made by chemical doping method, which has been considered as the most convenient and effective way, owing to the dopant's talents in introducing extra electrons or second-phase particles.^{3,4} For example, carbon-containing compound addition, originating from C substitution for B sites in the lattice, would induce the lattice distortion and the deviation of one more electron, and thus enhance the J_c . Elements Cu and Y addition would improve the J_c performance of MgB_2 by forming nano-sized MgCu_2 and YB_4 second phases with Mg and B, respectively.^{5–7} However, the dimension and the content of the second phase, even the sintering temperature and the original powder size, have to be seriously controlled, since only a small quantity of nano-scale particles embedded in the matrix were expected to function as effective pinning centers. As far as the investigation of pure MgB_2 , researchers have turned to mechanical milling to refine grains and irradiation to induce defects, both of which are likewise aimed at improving the pinning effects within the crystal.^{8,9} In view of that the operation of the applied techniques are generally complicated, it is meaningful to use a relatively easy way to introduce pinning centers into the MgB_2 bulks.

When the sintering temperature is high and the B phase is locally excessive, MgB_4 will generate as the impurity phase from Mg and B or MgB_2 and B.¹⁰ Little attention has been paid to the effects of MgB_4 on the J_c performance of MgB_2 in the past study. It was argued that the generation of MgB_4 is the dominating reason that leads to the decrease of the critical current density.¹¹ As we considered above, however, could the MgB_4 serve as effective pinning centers if the particles were restricted to a small dimension and the content was controlled to be appropriate?

In this study, we returned to the investigation of pure MgB_2 . Two-step sintering method was employed, and a relatively high sintering temperature was set, with the purpose of self-generating MgB_4 pinning centers. By restricting the content and the dimension, we expect to obtain MgB_2 bulks with enhanced J_c performance. In addition, we focused on the inherent mechanism of the enhancement of J_c , especially on the relationship between the precipitation pattern and the pinning mechanism.

Amorphous B powders (95% purity, 100 nm in size) and Mg powders (99.5% purity, 100 μm in size) were mixed in an atomic ratio of MgB_2 . After ground thoroughly in an agate mortar, the mixture was pressed into cylindrical pellets ($\Phi 5 \times 1.5 \text{ mm}$) under a pressure of 5 MPa. The obtained pellets were then sintered in the differential thermal analysis apparatus (Netzsch DSC 404C) at 750 °C for 0.5 h with a heating rate of $10 \text{ K} \times \text{min}^{-1}$, followed by heating up with the same rate to 900, 950, and 1000 °C, respectively. Without temperature holding, the samples were then cooled down to room temperature in the apparatus with a cooling rate of $40 \text{ K} \times \text{min}^{-1}$. The whole process was accomplished under flowing high-purity Ar gas to prevent the samples from oxidation. The corresponding samples were designated as S750-900, S750-950, and S750-1000, respectively. Furthermore, the sample only sintered at 750 °C for 30 min

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was employed as a reference, and was denoted as S750. After that, the phase composition and microstructure were detected by means of X-ray diffraction (XRD, Rigaku D/max 2500 CuK α), scanning electron microscopy (SEM, Hitachi S-4800), and transmission electron microscopy (TEM, JEM-2100), respectively. The superconducting properties were measured by the magnetic property measuring system (SQUID-VSM, Quantum Design) after the samples were cut into a slab of size about $4 \times 2 \times 1 \text{ mm}^3$. The corresponding J_c values were calculated from the width of magnetization hysteresis loops based on the extended Bean model: $J_c = 20\Delta M/[a/(1 - a/3b)]$,¹² where M is the volume magnetization, and a and b are the sample dimensions, orthogonal to H (applied magnetic field).

Figure 1 shows the XRD patterns of the samples S750, S750-900, S750-950, and S750-1000. The sample only sintered at 750°C was composed of MgB_2 as the main phase and MgO as the only inevitable impurity. In comparison, no additional characteristic peaks corresponding to new phase were distinguishable in the XRD pattern of sample S750-900. When the sample was further heated to 950°C after holding at 750°C , peaks of MgB_4 phase, whose volume fraction was estimated to be 1.7% from the peak area in the XRD results, have been appeared. Furthermore, an increasing number of peaks indicating MgB_4 phase was observed in the sample heated to 1000°C , and the volume fraction of MgB_4 was estimated to be 26%, which is relatively excessive.

The lattice-scale HRTEM images of the samples S750-900, S750-950, and S750-1000 are shown in Fig. 2, from which the second phase MgB_4 was found to embed in the matrix. The precipitation form of MgB_4 , especially the phase relation with the matrix, was explicit in the figure. Although no diffraction peaks of MgB_4 exhibited in the XRD patterns, we found the MgB_4 particles in the matrix of the sample S750-900 by matching the interplanar spacing with the Powder Diffraction File (PDF) card. More interestingly, a coherent interface was recognized between the MgB_4 second-phase particle and the matrix, and a misfit accompanied by the lattice distortions, due to the elastic accommodation, also occurs both in the second-phase particles and the matrix. The inexistence of MgB_4 peaks is

FIG. 1. X-ray diffraction patterns for one-step sintered MgB_2 sample S750 and two-step sintered samples S750-900, S750-950, and S750-1000.

FIG. 2. Lattice scale HRTEM images for two-step sintered samples (a) S750-900, (b) S750-950, and (c) S750-1000, and (d) HRTEM image for sample S750-1000.

attributed to the coherency of diffraction caused by the coherent relation between the second phase and the matrix.¹³ When the sample was heated to a higher temperature, 950°C , the coherent interface was partly destroyed, and misfit dislocations could be observed in Fig. 2(b). The relation between the second phase and the matrix became semi-coherent, and edge dislocations with the extra half-planes oriented perpendicular to the interfacial plane. As a result, the lattice around the dislocations would become distorted. For sample S750-1000, the large amount of MgB_4 (26 vol. %) leads to its growth and aggregation, and the coherent relation was completely destroyed. The incoherent interface could be observed in Fig. 2(c).

On the other hand, the particle size of the second phase MgB_4 in samples S750, S750-950, and S750-1000 was measured to be about 5, 10, and larger than 20 nm, respectively. High temperature will lead to an increasing particle size of MgB_4 , even larger than the coherent length of MgB_2 , as in sample S750-1000 (see Fig. 2(d)). To sum up, small-sized MgB_4 second phase generated at relatively low temperature ($<950^\circ\text{C}$) might serve as effective pinning centers, and the induced lattice distortion and dislocations due to the coherent or semi-coherent relation might pin the applied field as well. However, relatively high temperature ($>1000^\circ\text{C}$) would result in a large quantity of large particles (see Fig. 2(d)), which might be harmful to the critical current density.

The SEM images for samples S750, S750-900, S750-950, and S750-1000 were shown in Fig. 3, from which the grain size and the porosities can be identified. Although the thermal process was changed, no apparent variation in grain size was observed in these samples. Considered the grains present cuboid, the average size (length of the cuboid) was measured to be about 800 nm in all the samples. Apart from this, it is noted that the difference between the samples lies in the porosity. The samples S750-950 and S750-1000

FIG. 3. SEM images for two-step sintered samples (a) S750, (b) S750-900, (c) S750-950, and (d) S750-1000.

contained more porous regions than the samples S750 and S750-900. Porosity is a key factor determining the critical current density by affecting the grain connectivity. The connectivity can be defined by a parameter K , $K = \Delta\rho_g/\Delta\rho$, where ρ represents the resistivity, $\Delta\rho_g = 6.32 \mu\Omega \times \text{cm}$, and $\Delta\rho = \rho(300 \text{ K}) - \rho(40 \text{ K})$.¹⁴ The temperature dependence of resistivity for the samples was shown in Fig. 4(a), and using the resistivity values at 300 K and 40 K, the K values for the samples S750, S750-900, S750-950, and S750-1000 were calculated to be 0.215, 0.408, 0.251, and 0.217, respectively. The results indicated that the samples S750-900 and S750-950 showed better grain connectivity than the sample S750, and accordingly, the J_c performance is likely to be improved. However, the K value for sample S750-1000 becomes decreased to almost the same level as sample S750, implying that the J_c values of sample S750-1000 may not be significantly affected by the variation of grain connectivity compared with sample S750, but by the large-sized second-phase particles.

The measured J_c - H characteristics of all the samples were illustrated in Fig. 4(b). As expected, the samples S750-900 and S750-950 exhibited excellent J_c performances. The highest J_c values were obtained in sample S750-900, which showed higher J_c values over the entire field in contrast with sample only sintered at 750 °C. However, sample S750-1000 showed uncompetitive current carrying capability. In order to obtain a deeper insight into the pinning properties, an extended analysis of $F_p = \mu_0 J_c H$ is examined,

FIG. 5. Variation of b (H/H_{max}) dependence of flux pinning force f ($F_p/F_{p,\text{max}}$) and the fit curves for one-step sintered MgB₂ sample S750, and two-step sintered samples S750-900, S750-950, and S750-1000.

where the F_p is the flux pinning force, and the μ_0 is the magnetic permeability in vacuum.¹⁵ Normalized pinning force density $f = F_p/F_{p,\text{max}}$ is often scaled with $b = H/H_{\text{max}}$, instead of $b = H/H_{\text{irr}}$,¹⁶ and the normalized field b dependence of the normalized flux pinning force f was illustrated in Fig. 5. The scaling of f - b for high- T_c superconductors is often analyzed by using the following equations:^{16–18}

$$f(b) = 3b^2(1 - 2b/3), \quad (1)$$

$$f(b) = \frac{9}{4}b\left(1 - \frac{b}{3}\right)^2, \quad (2)$$

$$f(b) = \frac{25}{16}\sqrt{b}\left(1 - \frac{b}{5}\right)^2. \quad (3)$$

The normalized force values of the three samples at low field are all in agreement with the fit curves of Eq. (2), indicating that below H_{max} the dominating mechanism is surface pinning. However, the values at high field became separated and are in accordance with different equations. The properties for sample S750 were dominantly affected by the surface pinning, since the grain boundary might be the only pinning effects in MgB₂ sintered at 750 °C. For samples S750-900 and S750-950, the enhancement of the J_c performance should be attributed to the lattice distortion as well as the small content of MgB₄ pinning centers, and the dominating mechanism is $\Delta\kappa$ pinning, whose fitting degree is the optimal

FIG. 4. (a) Temperature dependences of resistivity and (b) measured J_c - H characteristics at 20 K for one-step sintered MgB₂ sample S750, and two-step sintered samples S750-900, S750-950, and S750-1000.

in Fig. 5. The small MgB_4 precipitates of 5–10 nm diameters contain B content slightly higher than that of the MgB_2 matrix. Such compositional fluctuation will cause spatial variation of the Ginzburg-Landau parameter (κ), which then provides additional flux pinning ($\Delta\kappa$ pinning).^{19–21} Unfortunately, the pinning effects in sample S750-1000 was weakened as a result of the large particle size, as shown in Fig. 5, that the $F_p/F_{p,\max}$ values stay away from all the fit curves at high field.

The coherent or incoherent interface was largely associated with the precipitation process of MgB_4 , which may start with the formation of the particles. Very small local enrichments of B atoms first generated as soon as the Mg phase volatilized at the temperature higher than the melting point 649 °C, above which the standard Gibbs free energy (ΔG^θ) of the reaction $\text{Mg(l)} + 4\text{B(s)} = \text{MgB}_4\text{(s)}$ ($-107.95 + 0.11T$, $\text{kJ} \times \text{mol}^{-1}$) is more negative than that of the reaction $\text{Mg(l)} + 2\text{B(s)} = \text{MgB}_2\text{(s)}$ ($-116.90 + 0.21T$, $\text{kJ} \times \text{mol}^{-1}$).²² This indicates that the latter could proceed spontaneously and more easily than the former. The original motivation of sintering up to 900–1000 °C followed by no holding process is to control the content of MgB_4 . MgB_4 first nucleates at the B-rich region with its (121) crystal face coherent with the (101) face of pre-generated MgB_2 . The MgB_4 will further wrapped by the MgB_2 that underwent a partial dissolution and re-precipitation after the Mg phase was melted. As the sintering temperature is relatively high, the MgB_4 particles became coarse, and the coherent relation with the MgB_2 matrix was destroyed, to semi-coherent relation, even incoherent relation.

In conclusion, the presence of the small-sized MgB_4 impurities in bulk MgB_2 prepared by two-step sintering has been observed to function as effective pinning centers and generate significant lattice distortion in the MgB_2 lattice to yield improved J_c performance over the entire applied field. The fine grain connectivity also contributes to the improvement of J_c in sample experiencing two-step sintering at 750 and 900 °C. The lattice distortion mainly derives from the coherent or semi-coherent relation between MgB_4 and the matrix, but the relation was destroyed to become incoherent when the second-step sintering temperature reaches 1000 °C, leading to a decrease in J_c . Owing to the MgB_4 , the dominating pinning mechanism in MgB_2 bulk varies from surface pinning to $\Delta\kappa$ pinning, which should be responsible for the enhancement in J_c . Similar to the disappearance of coherent

relation, however, the pinning effects become invalid eventually when the sintering temperature increased to 1000 °C, since the MgB_4 has grown into large particles.

The authors are grateful to the National Natural Science Foundation of China (Grant Nos. 51077099 and 51302186) and the Natural Science Foundation of Tianjin (Grant No. 13JCZDJC32300) for grant and financial support.

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