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Influence of Heat Treatment on Superconductivity of MgB₂ Bulk Sintered in Flowing Welding Grade Ar Atmosphere

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In this paper, MgB₂ samples were sintered in flowing welding grade Ar. The effect of the sintering time varying from 10 minutes to 3 hours on superconductivity of MgB₂ has been investigated. It has been found that both H_{c2} and H_{irr} increase with the sintering time and they have linear relationships with microstrain. The sample sintered for 30 min exhibits the highest J_c at high fields. The reason can be attributed to the improved connectivity and the increased H_{c2}.

Index Terms—MgB₂, microstrain, sintering time, superconductivity.

I. INTRODUCTION

THE critical current density J_c of MgB₂ is the most crucial quantity for use in commercial applications. J_c behavior of MgB₂ will be affected by not only processing conditions such as the precursor powders [1]–[6], the heating and cooling rate [7], and the processing temperature and duration [8], as well as the atmosphere [9] but also chemical doping [10]–[13]. Enormous efforts have been made to improve the critical current density, J_c, in MgB₂ through chemical doping. Among these doping elements, oxygen represents a special case, as nearly all types of MgB₂ materials have been treated in a protected atmosphere such as Ar. Oxygen alloying into MgB₂ reduced the critical temperature, T_c, but improved flux pinning in thin films [14]–[16] and bulks [17]. Recently, Senkowicz *et al.* have reported the effect of different amounts of exposure time to air during the ball-milling process for pre-reacted MgB₂ powder, which was used to prepare MgB₂ bulk or wires by the *ex situ* method [18]. In this case, the effect of atmosphere is limited to the commercially available pre-reacted MgB₂. Currently, our group studies demonstrated that the processing atmosphere would have a more significant effect on the superconducting properties in the *in situ* processed samples, as reactive components in the atmosphere can easily participate in the MgB₂ formation process from a mixture of Mg and B powders. The J_c, H_{irr} and H_{c2} for the welding grade Ar processed sample are improved in comparison with the samples treated in ultra-high and high purity argon [19]. In addition, Oxygen is incorporated in bulk MgB₂ in various forms such as nanometer-sized MgB_{2-x}O_x precipitates in the grains and MgO particles in the interior of the grains due to different annealing time and cooling rate [17], [20], [21]. In order to result in an optimal doping effect, we report here the effect of annealing time on the critical temperature T_c, resistivity, connectivity, the upper critical field H_{c2} and the critical current density J_c of MgB₂ bulk when sintered in flowing welding grade Ar atmosphere.

II. EXPERIMENTAL DETAILS

MgB₂ pellet samples were prepared by *in situ* reaction method which has been previously described in detail [10]. Powders of magnesium (99%) and amorphous boron (99%) with the stoichiometry of MgB₂ were well mixed. The mixed powder was pressed under a pressure of 5 tons in a hydraulic press, packed into a Fe tube without sealing, heated to 700°C, and then held for 10 minutes, 30 minutes, and 3 hours in flowing welding grade Ar (99.995%). The samples sintered for 10 min, 30 min and 3 h are termed as samples A, B, and C, respectively, in the following context. The reason for the use of the processing parameters of 700°C is because these are optimal conditions to achieve the best J_c(H) performance, based on our previous study [8]. Although heat treatment at 900°C or higher can achieve optimal T_c [8], [22]–[24], this does not provide optimal conditions for J_c(H) performance [8]. The Fe tubes were only used as sample holders. They had a diameter of 12 mm and a length of 20 mm, with the two ends open so that Ar could freely flow through the samples. The sintering was followed by furnace cooling to room temperature. Phase analysis was carried out by X-ray diffraction (XRD) in a Philips PW1730 Model diffractometer using Cu Kα radiation. Magnetic measurements of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS) after they had been polished into a cuboid shape for measurements. Their dimensions were accurately measured with a digital micrometer. The DC magnetic response was obtained in an applied low field of 1 Oe using the conventional zero-field-cooled (ZFC) and field-cooled (FC) procedures. The resistivity as a function of temperature and magnetic field was measured using a four-probe measurement technique.

III. RESULTS AND DISCUSSION

The XRD patterns for MgB₂ samples processed under different annealing times are shown in Fig. 1. As can be seen, all samples show high-purity MgB₂ phase with MgO as a minor impurity phase. There is a small amount of MgB₄ in sample A. The Rietveld refinement method was performed to analyse the XRD measurements. The refined parameters include the weight

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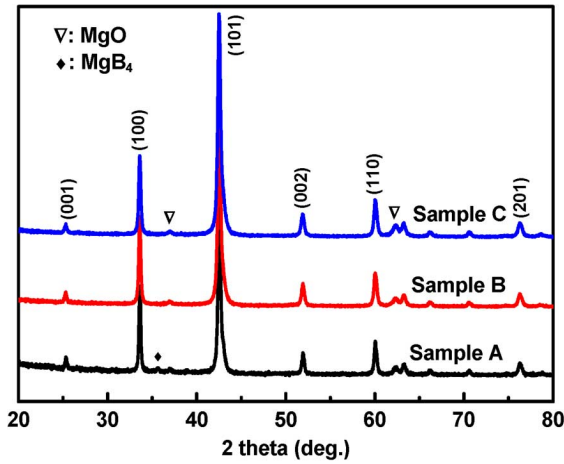
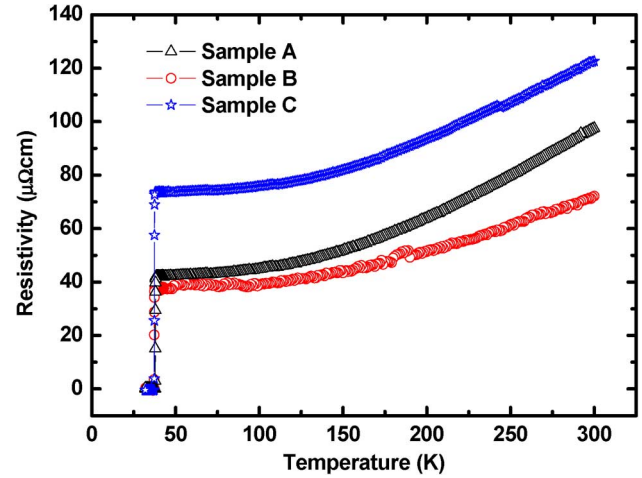

 Fig. 1. Powder XRD patterns of MgB₂ samples.


Fig. 2. Resistivity versus temperature.

 TABLE I
 PARAMETERS FOR THE THREE SAMPLES

Samples	Sintering time	MgO (%)	MgB ₄ (%)	Lattice parameters	
				a (Å)	a (Å)
A	10 min	4.75	5.82	3.083	3.524
B	30 min	6.44		3.082	3.522
C	3 h	8.5		3.085	3.526
Samples	Microstrains (%)	T _c (K)	ρ _{300K} (μΩcm)	ρ _{40K} (μΩcm)	A _F
A	0.348	37.48	97.55	41.99	0.13
B	0.426	37.09	72.16	37.45	0.21
C	0.456	37.24	122.67	73.59	0.15

fraction of each phase, the lattice parameters of MgB₂ and the microstrain. They are shown in Table I.

From Table I it can be seen that as the sintering time increases from 10 min to 30 min, lattice parameters a and c decreases. Lattice parameter a of sample B has been reduced below the ideal value ($a = 3.083 \text{ \AA}$). This indicates that oxygen atoms have diffused into the MgB₂ lattice. They may squeeze into the lattice as the interstitial atoms or replace the boron atoms to form MgB_{2-x}O_x precipitates [21], leading to the reduced lattice parameters. Since the diffusion density of the oxygen atom increases with the sintering time, the lattice parameters decreases from sample A to sample B. However, when the sintering time is further increased, the diffused oxygen atoms saturate and part of them react with Mg atoms to form MgO for long sintering time (3 hours in sample C). Table I has shown that the fraction of MgO increases when the sintering time increases from 30 min to 3 hours. The reaction of the diffused oxygen atoms and Mg atoms reduces the interstitial oxygen atoms and induce the Mg deficiency, both of which result in the increased lattice parameters in sample C as shown in Table I.

T_cs are listed in Table I. Sample B has a smallest value. T_c varies within a small range of 0.5 K. This indicates that the sintering time does not significantly affect T_c. Fig. 2 shows the resistivity-temperature curves for the three samples. The resistivity (ρ) for sample C is the largest among samples. The values of $\rho_{40 \text{ K}}$ and $\rho_{300 \text{ K}}$ are collected from Fig. 2 and listed in Table I. Sample B exhibits the smallest $\rho_{40 \text{ K}}$ and $\rho_{300 \text{ K}}$,

whereas sample C has the largest value. The values for $\rho_{40 \text{ K}}$ listed in Table I are higher than the single crystal ($5.3 \mu\Omega\text{cm}$, [25]) and the dense filament made by chemical vapor deposition (CVD) ($7.3 \mu\Omega\text{cm}$, [26]). The reason can be attributed to poor connectivity in the studied samples. The XRD patterns in Fig. 1 show the existence of MgO in the samples. MgO is mainly present in the grain boundary as an insulating phase, which reduces the effective cross-sectional area of the samples and then increases the resistivity. The effective cross-sectional area (A_F) can be estimated by the equation, $A_F = \Delta\rho_{\text{ideal}}/(\rho_{300 \text{ K}} - \rho_{40 \text{ K}})$, which was proposed by Rowell [22]. $\Delta\rho_{\text{ideal}}$ is the ideal change in resistivity from 300 K to 40 K for a fully connected sample. It is set to be $7.3 \mu\Omega\text{cm}$ according to [27]. The calculated A_F is displayed in Table I. It can be found that all samples have low A_F s, indicating poor connection in the samples.

Sample B has larger A_F than sample A. This may be due to the improved crystallinity and disappearance of MgB₄ with increased sintering time. However, A_F in sample C is smaller than sample B. The reason can be attributed to larger amount of MgO in sample C, which obstructs the flow of the current and increases the resistivity.

From the resistivity curves under different magnetic fields, the irreversibility field (H_{irr}) and the upper critical field (H_{c2}), can be derived, using the 10% and 90% of the normal state resistivity. The results are shown in Fig. 3. It can be seen that H_{c2} has the concave temperature-dependence curves. It is evident that H_{c2} and H_{irr} in the limited field regime measured increase with the sintering time. H_{c2} s and H_{irr} s at $T/T_c = 0.7$ for the three samples have been collected from Fig. 3 and plotted against microstrain in the inset of Fig. 3. It is clear that both H_{c2} and H_{irr} linearly increase with microstrain. The low microstrain indicates less lattice distortion inside the MgB₂ grains and then larger mean free path (l) of the superconducting electrons. This will increase the coherence length (ξ) due to the relation: $1/\xi = 1/\xi_0 + 1/l$, where ξ_0 is the value of ξ for the pure superconductor. According to $H_{c2} = \Phi_0/(2\pi\mu_0\xi^2)$, where Φ_0 is the superconducting flux quantum and μ_0 is the magnetic permeability, H_{c2} will decrease as ξ increases.

Fig. 4 shows the $J_c(H)$ curves for the three samples at 5 K and 20 K. It can be seen that the J_c performance in sample B shows a

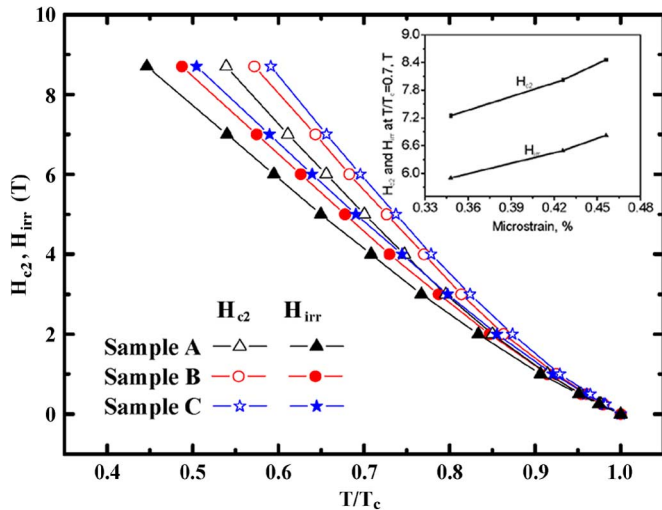


Fig. 3. Temperature dependence of H_{c2} and H_{irr} .

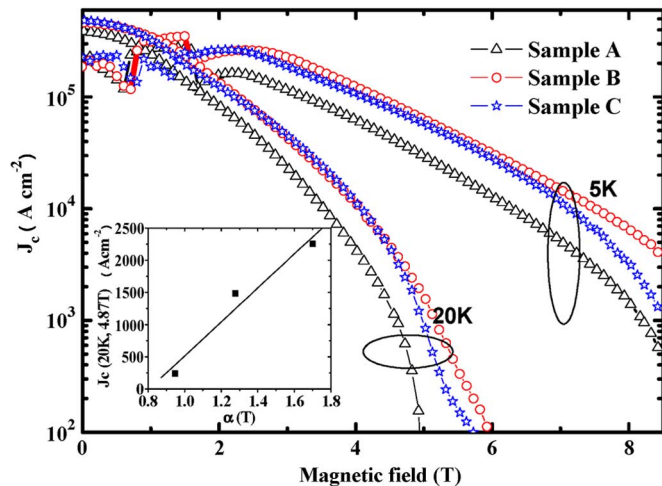


Fig. 4. $J_c(H)$ curves at 5 K and 20 K for MgB₂ samples. The inset shows J_c at 20 K and 4.87 T as a function of $\alpha = A_F \cdot H_{c2}$ for the three samples.

significant improvement under high fields at both 5 K and 20 K. Sample B exhibits the highest J_c of $\sim 6722 \text{ Acm}^{-2}$ at 5 K and 8 T, which is more than five times higher than that of sample A and almost 2 times higher than that of sample C. The J_c values at 20 K and 4.87 T follow the same trend, namely 360 Acm^{-2} , 2450 Acm^{-2} and 1840 Acm^{-2} for sample A, B and C, respectively. It has been known that the grain boundary pinning is the major pinning mechanism at high fields in MgB₂. The J_c caused by the surface pinning can be calculated by $\mu_0 S_V (H_{c2} - H)^2 / 4\kappa^2 H_{c2}^{1/2} H^{1/2}$ [28], where S_V is the grain boundary surface area per unit volume, H_{c2} is the upper critical field, κ is the Ginzburg-Landau parameter and H is the applied field. It can be concluded from this equation that J_c at high fields near H_{c2} is dominantly determined by H_{c2} and S_V [29]. In addition, the connectivity (A_F) also affects J_c . Fig. 5 shows field emission gun scanning electron microscope (FEG-SEM) images of samples A, B and C. It can be seen that the grain size has no significant change among samples. Therefore, the J_c difference is not caused by the change of S_V . We calculate a parameter $\alpha = A_F H_{c2}$, which combines two major factors (A_F and H_{c2}) influencing J_c and plot α against J_c s at 20 K and 4.87 T for

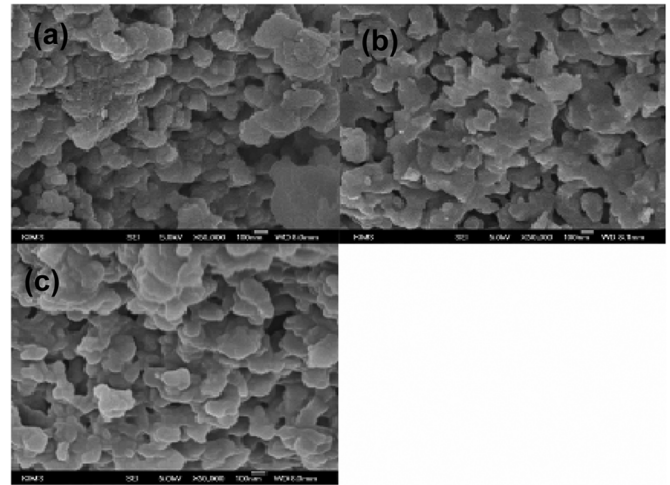


Fig. 5. FEG-SEM images for (a) sample A, (b) sample B and (c) sample C.

three samples in the inset of Fig. 4. Fig. 3 could not give the H_{c2} values at 20 K. H_{c2} at 22.5 K is roughly used to replace H_{c2} at 20 K. This figure produces a very good linear relationship between α and J_c . It clearly indicates that the improved J_c is mainly caused by the improved connectivity and the increased H_{c2} .

IV. CONCLUSION

MgB₂ samples were prepared by *in situ* reaction method and sintered in flowing welding grade Ar. The effect of the sintering time on superconductivity of MgB₂ has been investigated. The sintering time changes by 10 minutes, 30 minutes and 3 hours. It has been found that the amount of MgO increases with the sintering time and the sample with 30 minutes sintering time has the smallest lattice parameters. H_{c2} and H_{irr} increase with the sintering time and they have linear relationships with microstrain. The sample sintered for 30 min exhibits the highest J_c at high fields. The reason can be attributed to the improved connectivity and the increased H_{c2} .

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