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Effect of Grain Size and Doping Level of SiC on the Superconductivity and Critical Current Density in MgB_2 Superconductor

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***Abstract*—SiC doped MgB_2 polycrystalline samples were fabricated by in-situ reaction using different grain sizes (20 nm, 100 nm, and 37 μm) of SiC and different doping levels (0, 8, 10, 12, 15 wt%). Phases, microstructures, superconductivity, critical current density and flux pinning have been systematically investigated using XRD, SEM, TEM, and magnetic measurements. Results show that grain sizes of the starting precursors of SiC have a strong effect on the critical current density and its field dependence. The smaller the SiC grains are, the better the J_c field performance is. Significant enhancement of J_c and the irreversibility field H_{irr} were revealed for all the SiC doped MgB_2 with additions up to 15 wt%. A J_c as high as 20,000 A/cm^2 in 8 Tesla at 5 K was achieved for the sample doped with 10 wt% SiC with a grain size of 20 nm. Results indicate that the nano-inclusions and substitution inside MgB_2 are responsible for the enhancement of flux pinning.**

***Index Terms*—Critical current density, doping, magnesium diboride, silicon carbide.**

I. Introduction

MANY groups have attempted to improve the critical current density in the newly discovered MgB_2 superconductor [1] as it has a lower H_{c2} and H_{irr} than the commercial low temperature superconductors Nb_3Sn and NbTi. High critical current density values of 10^5 to 10^6 A/cm^2 have been achieved in MgB_2 in both pellets and in tapes and wires [2]–[6]. Despite the strong link grain boundary effects on critical current density [7], the J_c drops rapidly with increasing magnetic field due to poor flux pinning. Therefore, extensive research has been done on introducing pinning centers into this superconductor. Effective pinning centers can be induced by high energy ion irradiation [8]. Producing pinning centers via chemical doping is another effective method and more practical compared to physical techniques. It has been found that inclusions of oxygen or precipitates of nano-MgO can act as effective pinning centers in MgB_2 thin films [9]. Nano-sized chemical inclusions such as Y_2O_3 were reported to enhance flux pinning [10]. However, each of the improvements in J_c reported so far either has a better value only in low fields or a high H_{irr} only at low temperatures [11], [12]. Very recently, Dou *et al.* reported a significant improvement of H_{irr} at both high and low temperatures in nano-SiC doped MgB_2 bulk samples with only a slight reduction of T_c up to a doping level as high as 40% of boron [13]–[15]. It has been shown that both nano-inclusions and possible co-substitution of Si and C in the crystal lattice lead to this significant improvement. The objective of this paper is to study the grain size effect of the precursor SiC on the superconductivity and flux pinning and to further investigate the origin of the enhanced pinning. It was found that the particle size of SiC plays a critical role in controlling the reaction between $Mg+2B$ and SiC resulting in both substitution and nano-inclusions.

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II. Experimental

It has been reported that the MgB_2 can be formed by in-situ reaction between magnesium and amorphous boron in a very short time, as little as a few minutes at temperatures just above the melting point of magnesium [16], [17]. Furthermore, the samples sintered at temperatures above 750°C for only a few minutes are as good as those sintered for a long time. Therefore, MgB_2 pellet samples used in the present study were prepared by an in-situ reaction method, which has been described in detail previously [16]. Magnesium (99%) and amorphous boron (99%) were well mixed with commercial SiC (0, 8, 10, 12, 15 wt%). Powders having three different grain sizes were used; a very fine powder with particle sizes smaller than 20 nm (powder 1), powder 2 which has particle sizes ranging up to 300 nm and powder 3, a coarse crystalline SiC with particle sizes around 35 μm. These particle sizes were determined by TEM and SEM and will be explained in Section III. Pellets 10 mm in diameter and 2 mm in thickness were made under uniaxial pressure sealed in an Fe tube and then heated at temperatures ranging between 700–900°C for 1 hour in flowing high purity Ar. This was followed by furnace cooling to room temperature. The particles and crystallinity of the SiC powders, phases and microstructures in the samples were determined and investigated by SEM, TEM and XRD. The magnetization of samples was measured over a temperature range of 5 to 30 K using a Physical Property Measurement System (PPMS) in a time-varying magnetic field of sweep rate 50 Oe/s and amplitude 8.5 T. Samples in the form of bars were cut from the as-sintered pellets. All the samples have the same size ($0.56 \times 2.17 \times 3.73$ mm^3). A magnetic J_c was derived from the height of the magnetization loop $(M–H)$ using a Bean Model $J_c = 20\Delta M/[a/(1-(a/3b))]$ with $a < b$.

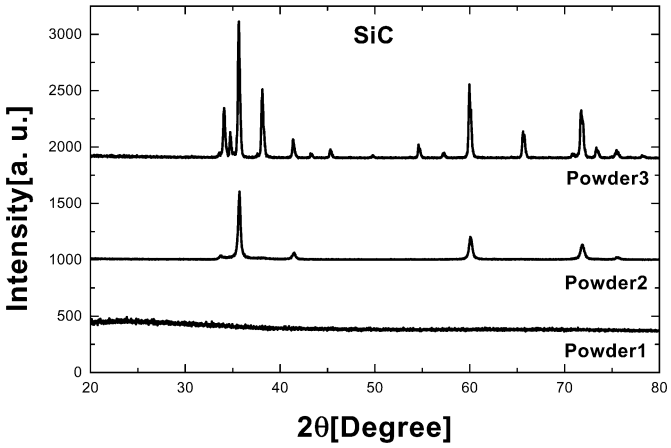

Fig. 1. The XRD pattern of the starting SiC powders with different grain sizes.

III. Results and Discussions

A. Effect of Grain Sizes of SiC

Fig. 1 shows the XRD patterns for the three different SiC powders used in this work. It can be seen that there are no diffraction peaks for powder 1, indicating that this powder is amorphous. Powders 2 and 3 show diffraction peaks, indicative of their crystalline natures. Powder 3 gives a strong diffraction intensity as well as sharp peaks in agreement with its bigger particle size. On the other hand powder 2 shows a few peaks, which are wider than the equivalent peaks in the powder 3, especially the $2\theta = 33.7°$ and 38° peaks that are very wide with low intensity. This XRD pattern indicates that powder 2 contains a wide range of particle sizes.

Fig. 2 shows TEM images of powders 1 and 2 (Fig. 2(a) and (b)) as well as a SEM image of powder 3 (Fig. 2(c)). We can see that the grains of SiC in powder 1 are very fine with almost the same grain size of about 10 nm to 20 nm, (Fig. 2(a)). On the other hand it can be clearly seen that powder 2 contains grains with a wide range of grain sizes from about 10 nm to about 300 nm (Fig. 2(b)), consistent with its XRD pattern. The SiC particles in powder 3 are almost uniform crystalline grains with an average size of about 37 μm (Fig. 2(c)). The XRD patterns of the samples after reaction as well as the reference MgB_2 sample are shown in Fig. 3. All three samples were doped with 10 wt% SiC. Mg_2Si is the main impurity phase for the sample that was made using powder 1 (sample a), in agreement with previous results [13]–[15]. However, we can still see some un-reacted SiC in the samples that were made using powders 2 and 3, samples b and c, respectively. In addition, no Mg_2Si was found in sample c. This means that only part of the SiC takes part in the reaction with Mg and B and becomes doped into MgB_2. Fig. 4 shows an SEM image of sample c which was made using crystalline SiC powder (Powder 3). The big grains of Un-reacted SiC can be easily seen in the MgB_2 matrix, which is in agreement with its XRD pattern. This means that the coarse SiC powder is very stable and did not react with Mg + B. Therefore; little or no substitution for B by Si and C can be expected. However, for very fine powder substitutions take place as Mg_2Si was formed. This is the big difference in the phases of samples made by coarse and fine powder. This difference is responsible for the significant difference in J_c field dependence as shown below. However, this pattern does not show that all the SiC powder was consumed in sample a. AC susceptibility measurement results for all samples are presented in Fig. 5. T_c values of about 37.65 K, 37.5 K, 37 K and 36.25 K were found for the reference sample, sample c, sample b and sample a respectively. The small change in the T_c for such a large amount (10 wt%) of added material confirms the recent results that Si and C co-doping counterbalanced the negative effect of single element doping [13]–[15]. Also we can see that the smaller grain size leads to lower T_c, which is understandable, as smaller grains can react more readily than larger ones.

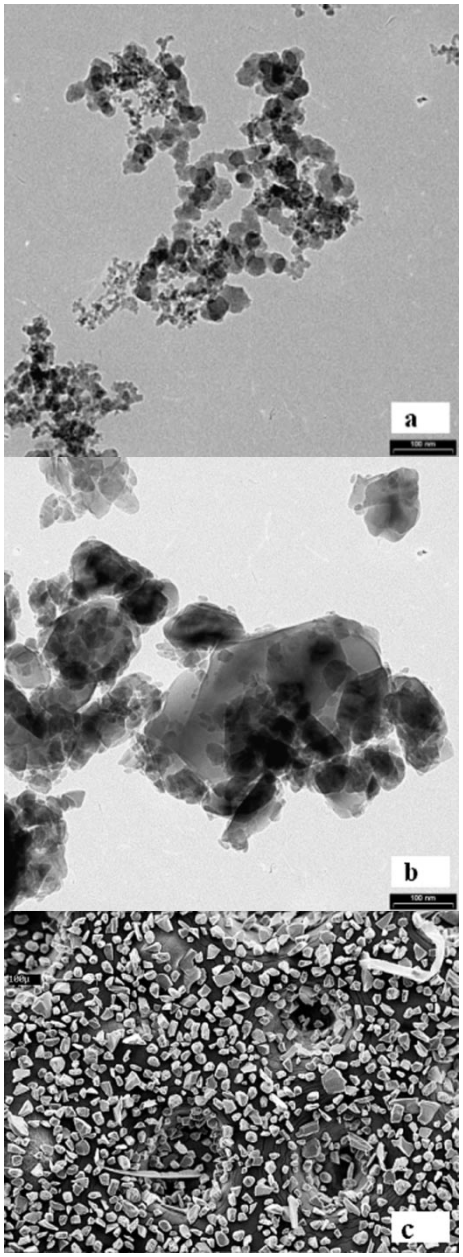

Fig. 2. a. TEM image of starting powder 1. Powder contains almost uniform particles with an average grain size of 10 nm to 20 nm. b. TEM image of starting powder 2. Powder contains different particles with a wide range of grain sizes from 10 to 300 nm. c. SEM image of starting powder 3. Powder contains almost uniform particles with an average grain size of 35 μm.

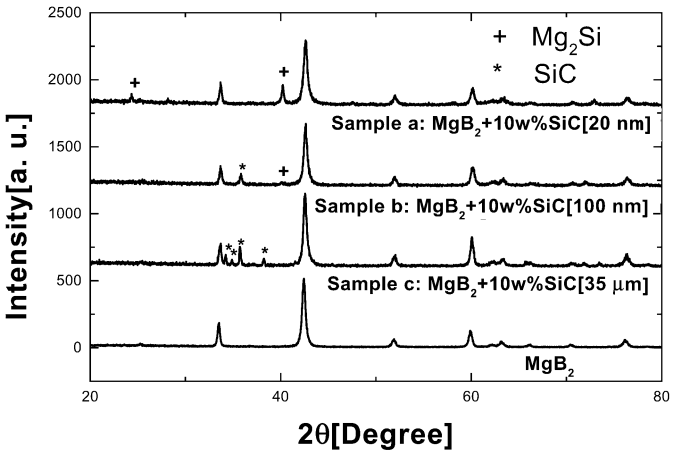

Fig. 3. XRD patterns of MgB_2 samples doped by 10 wt% of different SiC powders as well as the reference sample.

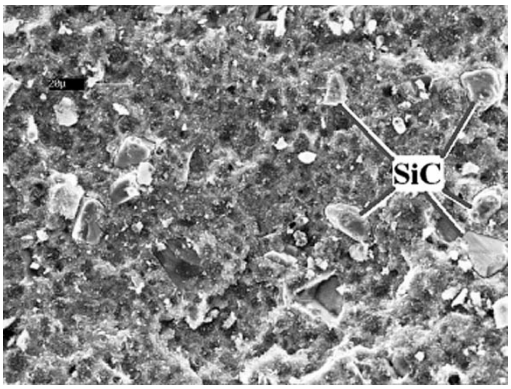

Fig. 4. SEM image of sample c after reaction. The large grains of un-reacted SiC can be easily seen in the MgB_2 superconductor.

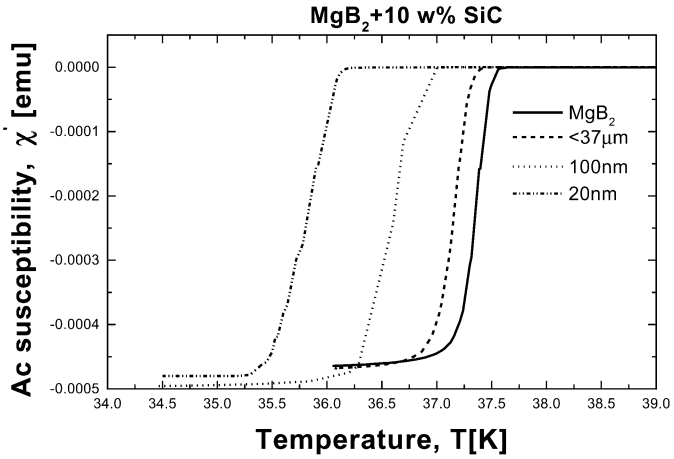

Fig. 5. The Ac susceptibility of MgB_2 samples doped by 10 wt% of different SiC powders as well as the reference sample at different temperatures.

J_c versus field at 30, 20 and 5 K are plotted as shown in Fig. 6. The performance of the J_c field dependence was improved by decreasing the grain sizes of the SiC precursor powder. The finer the SiC powders, the better the J_c field dependence is. For the coarse powders $(-400$ mesh$)$, the J_c field dependence is slightly better than for the MgB_2 reference sample due to limited reaction between the particles, which can react with $Mg + B$. The resultant impurities or remaining SiC can embed in the MgB_2 grains acting as pinning centers. For this sample the J_c

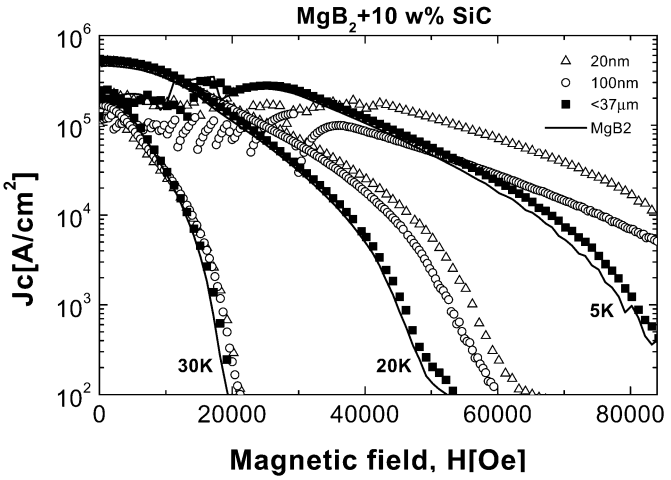

Fig. 6. The J_c field dependence of MgB_2 samples doped by 10 wt% of different SiC powders as well as the reference sample at different temperatures of 5, 20 and 30 K.

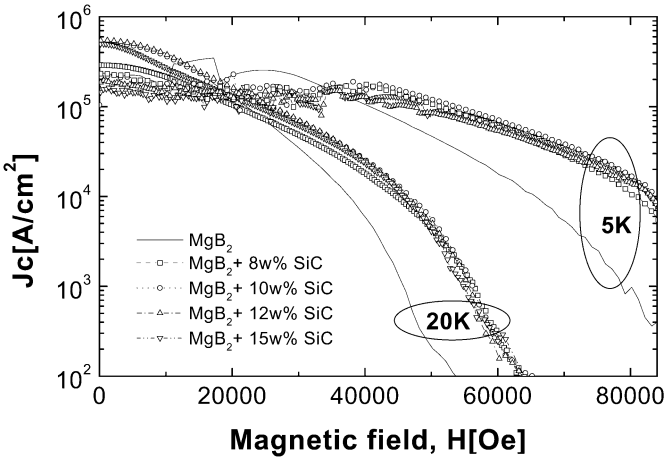

Fig. 7. The J_c field dependence of MgB_2 samples doped with SiC weight% of 0, 8, 10, 12, 15 at the 5 K and 20 K.

value of about 20 000 A/cm^2 was achieved at 5 K and 8 T, which is more than one order of magnitude higher than that of the MgB_2 reference sample at the same field and temperature. TEM results show that there are large numbers of nano-inclusions embedded inside the MgB_2 grains. This is because the SiC is very fine, so that it can be readily form as inclusions inside the MgB_2 grains and substitute in the lattice during the formation of MgB_2 as determined by EDS in TEM examination [13]. However, the crystalline SiC powders may distribute around grain boundaries acting as a weak links due to their poor chemical activity.

B. Effect of SiC Doping Levels

As the very fine powders of SiC (20 nm) produce the best results, we can use this fine powder to study the effect of the amount of SiC on the flux pinning in the SiC-doped MgB_2 samples in order to optimize the addition of SiC. Samples with SiC weight% of 0, 8, 10, 12, and 15 were studied in this work. The XRD patterns show that there is almost no difference in phase purity with only an increase of Mg_2Si when SiC increases. T_c also changed only slightly in all the samples. The J_c field dependence at different temperatures is shown in Fig. 7. It can be seen that all the SiC doped samples have almost the same J_c

values as a function of field and temperature at all the doping levels studied. However, it seems the sample doped by 10 wt% SiC has slightly better performance, compared to the MgB_2 reference sample. This means that the MgB_2 is very tolerant to the amount of SiC. Further studies with more precisely defined procedures are in progress.

IV. Conclusion

SiC doped MgB_2 polycrystalline samples were fabricated by in-situ reaction using different grain sizes (20 nm, 100 nm, and 37 microns) of SiC and different doping levels (0, 8, 10, 12, 15 wt%). Grain sizes of the precursor SiC have a strong effect on the critical current density and its field dependence. The smaller the SiC grains are, the better the J_c field performance and H_{irr} is. It is found that very fine SiC powder plays an important role in the reaction between Mg + B and SiC. Significant enhancement of J_c and H_{irr} were revealed for all the SiC-doped MgB_2 with added levels up to 15 wt%. A J_c value as high as 20 000 A/cm^2 in 8 Tesla and 5 K was achieved for the sample doped with 10 wt% SiC having grain sizes of about 20 nm. The high performance of the nano-SiC doped MgB_2 superconductor will have great potential for practical applications.

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