Superconductivity of the bulk 
MgB$_2$ + nano(n)-SiC composite system: 
a high field magnetization study

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Abstract
We study the effect of nano(n)-SiC addition on the crystal structure, critical temperature ($T_c$), critical current density ($J_c$) and flux pinning in MgB$_2$ superconductors. X-ray diffraction patterns show that all the samples have MgB$_2$ as the main phase with a very small amount of MgO; further, with n-SiC addition the presence of Mg$_2$Si is also noted and confirmed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The $T_c$ value for pure MgB$_2$ is 18.9 K under 8 T applied field, while it is 20.8 K for the 10 wt% n-SiC doped sample under the same field. This points towards the increment in the upper critical field value with n-SiC addition. The irreversibility field ($H_{irr}$) for the 5% n-SiC added sample reached 11.3, 10 and 5.8 T, compared to 7.5, 6.5, and 4.2 T for the pure MgB$_2$ at 5, 10 and 20 K, respectively. The critical current density ($J_c$) for the 5 wt% n-SiC added sample is increased by a factor of 35 at 10 K and 6.5 T field and by a factor 20 at 20 K and 4.2 T field. These results are understood on the basis of superconducting condensate (sigma band) disorder and ensuing intrinsic pinning due to B-site C substitution clubbed with further external pinning due to available n-SiC/Mg$_2$Si pins in the composite system.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

MgB$_2$ superconductor has been regarded as a promising material for practical applications at around 20 K because of its high critical temperature ($T_c$), large coherence length ($\xi$), simple crystal structure, low material cost, high critical current density ($J_c$) and weak-link-free grain coupling [1, 2]. Extensive research has been done on the fabrication of this superconductor in various sample forms, such as polycrystalline bulk, single crystals, metal clad tapes and wires, and thin and thick films [3–5]. For most of the practical applications, high critical current density ($J_c$) in the presence of a magnetic field along with high upper critical field ($H_{c2}$) and high irreversibility field ($H_{irr}$) are required. The $J_c$ of undoped MgB$_2$ is high enough at low magnetic fields for practical application; however, $J_c$ drops rapidly with increasing magnetic field due to the low $H_{c2}$ and the lack of the effective pinning sites in MgB$_2$. Therefore the improvement of $J_c$ under magnetic field is indispensable for the development of MgB$_2$ material for magnet applications. An effective way to improve the flux pinning is to introduce flux pinning centers into MgB$_2$ through a dopant having size comparable to the coherence length (of the order of a few nm) of MgB$_2$.

It has already been established that moderate impurity doping in MgB$_2$ is effective in increasing $J_c$ through the introduction of flux pinning centers and/or enhancement of $H_{c2}$ [6–14]. Of the various elements and compounds being doped in MgB$_2$, carbon-containing compounds such as SiC, C and B$_4$C have been found to be most effective. Here, we are reporting the effect of nano-SiC addition on the superconducting properties of MgB$_2$ in high magnetic fields. We found that the addition of n-SiC into MgB$_2$ helped in significantly enhancing the $J_c$ and $H_{c2}$ in high fields with

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only slight reduction of $T_c$. This is due to the co-substitution of broken n-SiC for B in the MgB$_2$ lattice inducing intra-grain defects clubbed with high density of nano-inclusions as effective pinning centers. Nano-SiC doping is known to enhance both $H_c$ and flux pinning through a multiple scattering channel [15]. In the current paper, we revisit the MgB$_2$ + nano(n)-SiC composite system, and compare our results with those in the existing literature. Recently, in [16], we reported the low-field ($< 7$ T) magnetization of some of the presently studied MgB$_2$ + nano(n)-SiC samples at 10 and 20 K only, and inter-compared the same with MgB$_{2-x}$C$_x$. This was to highlight the role of C in the performance of MgB$_2$ superconductor. In the present paper we are reporting the detailed spectacular high-field (up to 14 T) superconducting performance of the same system but at various temperatures of 5, 10 and 20 K and for a complete series of samples. Further, the important superconducting parameter $H_{irr}$ (irreversibility field), which could not be seen in the earlier [16] study due to limitation of the applied field, is obtained in the present study. Further, it is observed that the high-field (up to 14 T) performance of n-SiC added MgB$_2$ is more spectacular than that found in the low-field studies. Our results clearly substantiate the view that the nano-SiC addition profoundly improves the high-field superconducting performance of MgB$_2$ superconductor.

2. Experimental details

Our polycrystalline MgB$_2$-n-SiC$_x$ ($x = 0\%, 3\%, 5\%, 7\%$ and $10\%$) samples were synthesized by the solid-state reaction route. The Mg powder used is from Reidel-de-Haen and the amorphous B powder is from Fluka (of assay 95–97%). The n-SiC powder is from Aldrich, having average particle size (APS) of 5–12 nm. For synthesis of the samples, stoichiometric amounts of ingredients were ground thoroughly, pelletized using a hydraulic press and put in a tubular furnace at 850 °C under a flow of argon gas at ambient pressure. This temperature was held for 2.5 h, and the samples were subsequently cooled to room temperature under the same atmosphere of argon. The x-ray diffraction patterns of the compounds were recorded by using Cu K$_\alpha$ radiation. The scanning electron microscopy (SEM) studies were carried out on these samples using a Leo 440 (Oxford Microscopy, UK) instrument. The magnetoresistivity, $\rho(T)$, was measured with $H$ applied perpendicular to the current direction, using the four-probe technique. The magnetization measurements were carried out on Quantum Design PPMS, equipped with a VSM attachment.

3. Results and discussions

The x-ray diffraction (XRD) patterns of MgB$_2$-n-SiC$_x$ ($x = 0\%, 3\%, 5\%, 7\%$ and $10\%$) are shown in figure 1. In the case of pure MgB$_2$, all characteristic peaks are obtained and their respective indexing is shown in the figure itself. The structure of MgB$_2$ belongs to space group $P6/mmm$. It can be seen that all doped samples along with the undoped one exhibit well-developed MgB$_2$ phase, with only a small amount of MgO present, marked by the symbol ‘o’ in figure 1. The presence of a small quantity of MgO with the MgB$_2$ main phase is consistent with earlier reports on similar samples [17–19]. No other impurity phases such as Mg$_2$C$_3$ and MgB$_2$C$_2$ are detected.

As we increase the added n-SiC content in MgB$_2$-n-SiC$_x$, the presence of Mg$_2$Si ($\ast$) and unreacted SiC ($\ast$) is noticed. At lower doping level ($x < 7$ wt%) the sample consists of a major phase of MgB$_2$ with minority phase of Mg$_2$Si, and as we increase ($x \geq 7$ wt%) the doping level of n-SiC, the amount of this non-superconducting phase is increased. In particular, for MgB$_2$-n-SiC$_x$ ($x = 7\%$ and $10\%$), the \{hkl\} reflections [111], [220] and [400] of Mg$_2$Si are noticed clearly in figure 1. The presence of Mg$_2$Si has been reported in a recent paper [20]. As far as the majority MgB$_2$ phase is concerned, the peak situated between $2\theta = 33^\circ$ and $34^\circ$ shifts towards the higher $2\theta$ values with increasing $x$, indicating the contraction of the $a$-axis in the crystal lattice. The lattice parameters, $a$ and $c$, of the hexagonal AlB$_2$-type structure of MgB$_2$ have been calculated using these peak shifts, and their variation is tabulated in [16]. The decrease in $c$ parameter with increasing $x$ (content of n-SiC) is relatively small as compared to that of the $a$ parameter. The variation in $a$ parameter indicated the partial substitution of B by C [21, 22].

The grain morphology of pure and 10 wt% n-SiC added MgB$_2$ is shown in figure 2. The pristine MgB$_2$ grains are of average size less than a micron; also seen are some porous/MgO insulating white regions; see figure 2(a). The presence of Mg$_2$Si can be noticed in 10 wt% n-SiC added MgB$_2$ as large spherical white regions in the MgB$_2$ matrix along with smaller insulating MgO. The elemental analysis of these micrographs showed the presence of Si in the sample shown in (b) but not in that shown in (a). This is consistent with the fact that unreacted free Si is present in n-SiC doped...
samples to form the desired Mg$_2$Si phase, being seen in the XRD results in figure 1. Though, all the elements being present in MgB$_2$ or n-SiC doped samples such as Mg, B, and O in former and in addition Si, and C in later are seen in the EDS results, the actual percentage ratio is not determined because of very light elements boron and carbon in comparison to others. The sensitivity of SEM is known to be relatively poor for lighter elements such as B, C and O.

Figure 3 shows the resistance versus temperature curves under magnetic field $R(T)H$ up to 8 T for the undoped, 5% n-SiC and 10% n-SiC doped samples. The transition temperature ($T_c$) for the pure sample is 38.1 K in zero applied field. For the 10 wt% n-SiC added sample $T_c$ decreased to 34.5 K in zero applied field. Further, it is noted that the $R(T)$ curves for the doped samples shifted with increasing magnetic field much more slowly than those for the pure sample. The $T_c$ value for the pure MgB$_2$ is 18.9 K for 8 T applied field while it is 20.8 K for the 10 wt% n-SiC doped sample under the same field.

A further important point is that the nominal resistance of these samples is very different, $R(40$ K) being 290 $\mu\Omega$ for the undoped sample, 490 $\mu\Omega$ for the 5 wt% n-SiC doped sample and 800 $\mu\Omega$ for the 10 wt% n-SiC doped sample. This is shown in figure 4. It shows that the scattering increases with increasing n-SiC content. In the inset of figure 4, the temperature dependence of normalized resistance $R(T)/R(275$ K) is shown for the pure and 10% SiC doped samples. The residual resistivity ratio (RRR = $R_{275$ K}/$R_{\text{onset}}$) values for the pure and 10% SiC doped samples are 3.15 and 1.74, respectively. Both C doping (revealed by contraction in the $a$ parameter and reduction in $T_c$) and the inclusion of Mg$_2$Si (revealed by XRD) can enhance the electron scattering, and hence the decreased RRR values. Further, the higher values of room temperature resistivity for doped samples indicate that the impurity scattering is stronger due to the carbon substitution at boron sites. This is in agreement with previous studies on MgB$_2$$_{2-x}$C$_x$ systems [21, 23].

The variation of upper critical field with respect to reduced temperature is shown in figure 5, with the help of the resistive transitions shown in figure 3. All the doped samples show...
higher values of critical field in comparison to the pure sample at all temperatures. The n-SiC reacts with the Mg and releases highly reactive free C on the atomic scale at the same temperature at which the formation of MgB$_2$ takes place. Because of the availability of reactive C atoms at that time, the C can be easily incorporated into the lattice of MgB$_2$ and substitute into B sites [24]. The C substitution into B sites in lattice is responsible for creating the disorder on the lattice site of B, which leads to the enhancement in value of upper critical field. Further, it is worth mentioning that the magnetic field which is required to destroy the bulk superconductivity is smaller than the magnetic field needed to destroy the surface superconductivity; the latter is 1.6946 ($\eta$) times higher than the former [25, 26]. Although this ratio ($\eta$) varies with temperature for two-band superconductors, in [25] Denis discussed that at a temperature near the transition temperature ($T_c$), $\eta$ takes its highest value, which is near about 1.7; overall, $\eta$ takes values from $\approx 1.7$ to $\approx 1.64$ for temperature variation from $T_c$ down towards 0 K. Therefore, in figure 5 we show the variation of upper critical field $H_c$, where $H_c = 1.7 \times H$ at $R \rightarrow 0$ ($T \rightarrow T_c$), against the reduced temperature.

The magnetic hysteresis loop for all the doped samples MgB$_2$ + n-SiC$_x$ ($x = 0\%, 3\%, 5\%, 7\%$ and 10\%) are shown in figure 6 at $T = 5, 10, 20$ K and under up to 13 T applied field. This figure clearly demonstrates that at $T = 5$ K the closing of the $M(H)$ loop for the pure sample is at 7.5 T, while the loop is closed at 11.3 T for the 5\% n-SiC doped sample. This indicates that there is quite an improvement in irreversibility field values by the addition of n-SiC to the parent compound. The irreversibility fields ($H_{irr}$) are derived from the fields at which the magnetic hysteresis loop gets nearly closed, with the criterion of $J_c = 100$ A cm$^{-2}$. To know the effect of doping level of n-SiC on $H_{irr}$ values a plot is drawn in $H_{irr}$ versus $x$ (concentration of n-SiC), and it is shown in figure 7 at 5, 10 and 20 K. Doping with n-SiC has significantly improved the $H_{irr}$. At all temperatures the 5\% n-SiC doped sample gives the best value of $H_{irr}$. The values of $H_{irr}$ for the 5\% n-SiC added sample reached 11.3, 10 and 5.8 T, compared to 7.5, 6.5, 4.2 T for the pure one at 5, 10 and 20 K respectively. Worth mentioning is the fact that in an earlier preliminary study [16] by some of us, the closing of $M(H)$ loops for n-SiC added samples could not be achieved due to the non-availability of higher applied fields. The spectacular enhancement in $H_{irr}$ values, seen in figure 7, is definitely due to the improvement in flux pinning in MgB$_2$ by the n-SiC doping.
Figure 7. Variation of irreversibility field $H_{irr}$ with respect to n-SiC concentration at 5, 10 and 20 K.

The magnetic $J_c$ for all the samples was calculated from the $M(H)$ loops at 5, 10 and 20 K. Figures 8(a) and (b) show the magnetic $J_c$ versus $H$ for all the samples at 20 and 10 K respectively. At low fields all the samples attain about $10^6$ A cm$^{-2}$ $J_c$ at both temperatures. Of all the doped samples the 5% n-SiC doped sample gives the best performance. For the undoped sample, $J_c$ drops rapidly in the presence of magnetic field and is almost negligible above 4.2 T and at 6.5 T at 20 and 10 K respectively. On the other hand the 5% n-SiC doped sample exhibits a $J_c$ of the order of $10^3$ A cm$^{-2}$ at the corresponding fields at both temperatures. The $J_c$ is 35 times higher than that of the pure sample at 10 K in 6.5 T field in the case of the 5% n-SiC doped sample and 20 times higher at 20 K in 4.2 T for the same sample. Because of the dual reaction [24], the first reaction of n-SiC with Mg forming Mg$_2$Si and second of free C being incorporated into MgB$_2$ both help in the pinning of vortices and result in improved superconducting performance. Mg$_2$Si and excess carbon can be embedded within MgB$_2$ grains as nano-inclusions. Due to the substitution of C at the B site the formation of a nanodomain structure takes place due to the variation of Mg–B spacing. These nanodomain defects, having the size of 2–3 nm, can also behave as effective pinning centers. So, highly dispersed nano-inclusions within the grains and the presence of nanodomain defects act as pinning centers and thus result in the improved $J_c(H)$ behavior for the n-SiC doped samples.

To confirm the improved flux pinning behavior through SiC doping, the field dependence of the normalized flux pinning force ($F_p/F_{p,\text{max}}$) is shown in figures 9(a) and (b) at 20 and 10 K. The relationship between flux pinning force and critical current density could be described by [27, 28]

$$F_p = \mu_0 J_c(H) H$$  \hspace{1cm} (1)

where $\mu_0$ is the magnetic permeability in vacuum. These figures depict a significant improvement in pinning forces by n-SiC doping at both temperatures for fields greater than 2 T. Flux pinning curves for the doped samples are shifted to the right as compared to pure MgB$_2$. As described earlier, nano-inclusions and nanodomains having a size comparable to the coherence length of MgB$_2$ can work as point pinning centers, causing a shift in the $F_p/F_{p,\text{max}}$ versus $H$ curve towards higher field. It can be seen from figure 9 that for the 5 wt% n-SiC doped sample the peak is much broader than those of other samples, indicating that the highest pinning strength is for this sample; this is confirmation of the $J_c$ results. As far as the type of pinning, i.e., grain boundary, point defects or order parameter change, is concerned, in our case it is seemingly the combination of grain boundary and point defects. The former are due to the presence of grain boundary precipitates of Mg$_2$Si and the latter due to inclusions of n-SiC. This we presume because the $F_p/F_{p,\text{max}}$ versus $H$ peak does not only get broadened (grain boundary pinning) with n-SiC addition but there is a slight right direction shift in peak position to higher fields as well [29].

Worth mentioning is the fact that though all n-SiC added samples up to 10 wt% addition are superior to pristine MgB$_2$,
the 5 wt% n-SiC added one is the optimum. In our other recent paper [16] in which we discussed the role of carbon in the MgB$_2$ lattice to enhance the flux pinning performance comparatively at lower fields, we found that a 7 wt% n-SiC added sample from a different batch showed the highest improvement in the flux pinning. Therefore, we can say that due to n-SiC doping the superconducting performance enhances profoundly and the optimum is found between say 3 and 7 wt% addition. The fact is that 5 wt% or 7 wt% amount of n-SiC is not the optimum for achieving the best $J_c$, $H_{irr}$ and $H_{c2}$; it all depends on various other factors such as synthesis temperature, heating rate, annealing time, magnetic field and resultant sample quality, etc [7, 30].

4. Conclusions

In summary, the effect of nano-SiC doping on the critical temperature ($T_c$), critical current density ($J_c$) and flux pinning was investigated under a wide range of magnetic field. We found that a significant flux pinning enhancement in MgB$_2$ can be easily achieved using nano-SiC as an additive. The Si and C released from the decomposition of nano-SiC at the time of formation of MgB$_2$ formed Mg$_2$Si and substituted at B sites respectively. The C substitution for B resulted in a large number of intra-granular dislocations and dispersed nanosize impurities, which are both responsible for the significant enhancement in flux pinning.

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References

[1] Buzea C and Yamashita T 2001 Supercond. Sci. Technol. 14 R115
[2] Iwasa Y, Labalestier D C, Okada M, Penco R, Sumption M D and Xi X 2006 Trans. Appl. Supercond. 16 1457
[3] Canfield P C, Bud’ko S L and Finnemore D K 2003 Physica C 385 1
[4] Flukiger R, Suo H L, Musolino N, Beneduce C, Toulemonde P and Lezza P 2003 Physica C 385 286
[5] Lee S 2003 Physica C 385 31
[6] Dou S X, Soltanian S, Horvat J, Wang X L, Zhou S H, Ionescu M, Liu H K, Munroe P and Tomsic M 2002 Appl. Phys. Lett. 81 3419
[7] Yeoh W K, Kim J H, Horvat J, Xu X, Qin M J, Dou S X, Jiang C H, Nakane T, Kumakura H and Munroe P 2006 Supercond. Sci. Technol. 19 596
[8] Yamada H, Hirakawa M, Kumakura H and Kitaguchi H 2006 Supercond. Sci. Technol. 19 175
[9] Cheng C H, Zhang H, Zhao Y, Feng Y, Rui X F, Munroe P, Zeng H M, Koshizuka N and Murakami M 2003 Supercond. Sci. Technol. 16 1182
[10] Senkowicz B J, Giencke J E, Patnaik S, Eom C B, Hellstrom E E and Labalestier D C 2005 Appl. Phys. Lett. 86 202502
[11] Wilke R H T, Bud’ko S L, Canfield P C and Finnemore D K 2004 Phys. Rev. Lett. 92 217003
[12] Xiang J Y, Zheng D N, Li J Q, Li S L, Wen H H and Zhao Z X 2003 Physica C 386 611
[13] Yeoh W K and Dou S X 2007 Physica C 456 170
[14] Matsumoto A, Kumakura H, Kitaguchi H and Hatakeyama H 2003 Supercond. Sci. Technol. 16 926
[15] Dou S X, Baccini V, Soltanian S, Klie R, Zhu Y, Wang X L and Labalestier D C 2004 J. Appl. Phys. 96 7549
[16] Awana V P S, Vajpayee A, Mudgel M, Rawat R, Achraya S, Kishan H, Takayama Muromachi E, Narlikar A V and Felner I 2007 Physica C 467 67
[17] Yan S C, Yan G, Lu Y F and Zhou L 2007 *Supercond. Sci. Technol.* **20** 549
[18] Dou S X, Pan A V, Zhou S, Ionescu M, Wang X L, Horvat J, Liu H K and Munroe P R 2003 *J. Appl. Phys.* **94** 1850
[19] Dou S X, Pan A V, Zhou S, Ionescu M, Liu H K and Munroe P R 2002 *Supercond. Sci. Technol.* **15** 1587
[20] Dou S X et al 2006 *Adv. Mater.* **18** 758
[21] Bharthi A, Balaselvi S J, Kalavathi S, Reddy G L N, Sastry V S, Hariharan Y and Radhakrishnan T S 2002 *Physica C* **370** 211
[22] Avdeev M, Jorgensen J D, Ribeiro R A, Budko S L and Canfield P C 2003 *Physica C* **387** 301
[23] Balaselvi S J, Gayathri N, Bharthi A, Sastry V S and Hariharan Y 2004 *Supercond. Sci. Technol.* **17** 1401
[24] Dou S X et al 2007 *Phys. Rev. Lett.* **98** 097002
[25] Gorokhov Denis A 2005 *Phys. Rev. Lett.* **94** 077004
[26] Lyard L et al 2002 *Phys. Rev. B* **66** 180502(R)
[27] Martinez E, Mikheenko P, Martinez-lopez M, Millan A, Bevan A and Abell J S 2007 *Phys. Rev. B* **75** 134515
[28] Shen T M, Li G, Cheng C H and Zhao Y 2006 *Supercond. Sci. Technol.* **19** 1219
[29] Tarantini C et al 2007 *Physica C* **463–465** 211
[30] Chen S K, Tan K S, Glowacki B A, Yeoh W K, Soltanian S, Horvat J and Dou S X 2005 *Appl. Phys. Lett.* **87** 182504