The effect of synthesis temperature on the superconducting properties of n-SiC added bulk MgB$_2$ superconductor

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Abstract
We study the effect of synthesis temperature on the phase formation in nano(n)-SiC added bulk MgB$_2$ superconductor. In particular we study: lattice parameters, amount of carbon (C) substitution, microstructure, critical temperature ($T_c$), irreversibility field ($H_{irr}$), critical current density ($J_c$), upper critical field ($H_{c2}$) and flux pinning. Samples of MgB$_2$ + (n-SiC)$_x$ with $x = 0.0, 0.05$ and $0.10$ were prepared at four different synthesis temperatures, i.e. 850, 800, 750 and 700 $^\circ$C with the same heating rate and holding time of 10 $^\circ$C min$^{-1}$ and 2.5 h, respectively.

We found 750 $^\circ$C to be the optimal synthesis temperature for n-SiC doping in bulk MgB$_2$ in order to get the best superconducting performance in terms of $J_c$, $H_{c2}$ and $H_{irr}$. Carbon substitution enhances the $H_{c2}$ while the low temperature synthesis is responsible for the improvement in $J_c$ due to the smaller grain size, defects and nano-inclusion induced by incorporation of C into the MgB$_2$ matrix, which is corroborated by HRTEM (high-resolution transmission electron microscopy) results.

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

1. Introduction
The discovery of superconductivity in MgB$_2$ with $T_c = 39$ K [1] attracted much attention from fundamental to applied research. Due to its relatively high critical temperature, low cost and transparency of the grain boundaries to the current flow [2], MgB$_2$ superconductor is one of the best candidates for engineering applications in the temperature range 20–30 K and can be competitive with traditional Nb based superconductors and with the so-called second generation HTS wires. However, its critical current density ($J_c$) is suppressed under magnetic fields due to low upper critical fields ($H_{c2}$) and poor flux pinning in the clean material. Therefore, improvement of $J_c$ in magnetic fields is needed for applications in a wide variety of fields. There have been several demonstrations of enhanced vortex pinning and critical current density, $J_c$, in the magnesium diboride by partial substitution of boron for carbon, through doping with SiC, B$_4$C, carbon nanotube (CNT) and nano-C doping [3–11]. Substitution of C in the B site also significantly increases the upper critical field, $H_{c2}$ [12–14]. However, the resulting pinning effects by doping were not quantitatively consistent among many research groups [15]. Since superconducting properties of MgB$_2$ are very sensitive to phase purity, the size of the starting boron powder and synthesis conditions, so the flux pinning properties of the samples varied accordingly in each paper [16].

Some of us previously found that a significant flux pinning enhancement in MgB$_2$ could be easily achieved using nano-SiC as an additive [3]. 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 nano-size impurities, which are both responsible for the significant enhancement in flux pinning.
However, other microstructural factors such as grain size or connectivity of MgB$_2$ grains, which determine the flux pinning properties of undoped MgB$_2$, have not been well clarified as functions of synthesis temperature. Based on this background, here we study the effect of synthesis temperature on phase formation, critical temperature ($T_c$), upper critical field ($H_{c2}$), critical density ($J_c$), irreversibility field ($H_{irr}$) and microstructures of doped MgB$_2$.

2. Experimental details

Our polycrystalline MgB$_2$ + n-SiC$_x$ ($x = 0, 5$ and $10$ wt$\%$) samples were synthesized by a solid-state reaction route. The Mg powder used is from Reidel-de-Haen, the amorphous B powder is from Fluka (of assay $95–97\%$) and the n-SiC powder is from Aldrich ($<100$ nm). For synthesis of the samples, stoichiometric amounts of ingredients were ground thoroughly, pelletized using a hydraulic press and put in a tubular furnace for $2.5$ h in an argon atmosphere at four different temperatures: $700$, $750$, $800$ and $850$ $^\circ$C. Finally, the furnace cooled in the same argon atmosphere to room temperature.

Constituent phases of the samples were analyzed by the Rigaku Miniflex II powder x-ray diffractometer using Cu Kα radiation. The grain morphology and microstructures were examined by high-resolution transmission electron microscopy (HRTEM) (model Tecnai G2 F30 STWIN field emission gun supported, operated at an electron accelerating voltage of $300$ KV). The magneto-resistivity was measured with $H$ applied perpendicular to the current direction, using a four-probe technique within an accuracy of $\pm 0.01$ K. The magnetization measurements were carried out on Quantum Design Physical Properties Measurement System (PPMS), which has a magnetic field accuracy of $\pm 1$ Oe. The critical current density ($J_c$) was determined from the magnetization loop using the extended Bean model.

3. Results and discussion

3.1. Phase formations and crystallographic interpretations by powder XRD

In order to clarify the influence of synthesis temperature ($T_s$) on the phase formation of MgB$_2$, x-ray diffraction (XRD) patterns were recorded at room temperature. Figure 1(a) shows the XRD patterns for all the n-SiC doped samples along with pristine MgB$_2$ synthesized at $700$, $750$, $800$ and $850$ $^\circ$C. 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 $P6/mmm$. Powder XRD analysis revealed that nearly single-phase MgB$_2$ bulks containing only a minor fraction of MgO (marked by ‘o’ in figure) were obtained for all the samples heated at above $700$ $^\circ$C, while the samples heated at $700$ $^\circ$C showed strong diffraction peaks due to unreacted magnesium (marked by ‘$’ in figure 1(a)) in the sample. The volume fraction of unreacted Mg is nearly $25\%$ in the pure MgB$_2$ sample synthesized at $700$ $^\circ$C. The MgO fraction is almost the same in all the samples irrespective of SiC content and synthesis temperature. It is to be clarified that Mg remains un-oxidized at all temperatures because all the samples were synthesized in an inert atmosphere of argon gas.

Samples doped with SiC showed a considerable amount of Mg$_x$Si (marked with * in the figures) and minor quantities of unreacted SiC (+). In particular for both MgB$_2$ + n-SiC$_x$, the $\{hkl\}$ planes $\{111\}$, $\{200\}$, $\{220\}$, $\{311\}$ and $\{400\}$ of the Mg$_x$Si are noticed clearly in figure 1. At a doping level of $x = 5$ wt$\%$ the samples consist of a major phase of MgB$_2$ with a minority phase of Mg$_2$Si; increasing the doping level of n-SiC at $x = 10$ wt$\%$, the amount of this non-superconducting phase increases. The formation of Mg$_2$Si in SiC doped samples indicates the dissociation of the SiC and the reaction of Si with Mg (SiC starts to react with Mg at a temperature as low as $600$ $^\circ$C). In fact, this decomposition of SiC and the formation of the Mg$_2$Si phase are reported in almost all the SiC doping studies [3, 4, 6, 17]. No other impurity phases like MgB$_4$, Mg$_2$B$_7$, Mg$_2$C$_3$ or MgB$_2$C$_2$ are detected in any of the samples.

As far as the majority MgB$_2$ phase is concerned, the peak $\{100\}$ situated between $2\theta = 33^\circ$ and $34^\circ$ shifts towards the higher angle with increasing doping content of SiC, 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$_2$ are calculated using these peak shifts, and their variation is reported in table 1. The change in $c$ with increasing $x$ is relatively small compared to the $a$ parameter. The $a$-axis parameter shows a larger drop with $x$ for all the temperatures. The decrease in $a$ indicates the effective partial substitution of B by C [3–13, 17, 18]. The substituent C atoms are readily available from the SiC. The actual C substitution level for our MgB$_2$ + (SiC)$_x$ samples can be estimated indirectly from the change in lattice parameters using the formula $x = 7.5\Delta(c/a)$, where $\Delta(c/a)$ is the change in $c/a$ compared to the pure sample [18, 19]. Figure 1(b) depicts (from the bottom to the top) the variation in the $a$-axis lattice parameter, the $c/a$ value, the actual C substitution level ($x$) in Mg$(B_{1-x}C_x)$$_2$ and the FWHM of the $(110)$ peak with synthesis temperature.

### Table 1. Lattice parameters ‘$a$’ and ‘$c$’ calculated from the peak shifts in XRD patterns for undoped and SiC doped samples of all the four series synthesized at different temperatures.

| Sample name     | $T_c$ ($^\circ$C) | ‘$a$’ (Å) | ‘$c$’ (Å) | ‘$a$’ (Å) | ‘$c$’ (Å) | ‘$a$’ (Å) | ‘$c$’ (Å) |
|-----------------|------------------|----------|----------|----------|----------|----------|----------|
| Pure MgB$_2$    | 700              | 3.0844(92)| 3.5208(40)| 3.0829(96)| 3.5203(83)| 3.0803(47)| 3.5191(89)| 3.0854(58)| 3.5253(91)|
| MgB$_2$ + 5% n-SiC | 750              | 3.0844(13)| 3.5210(66)| 3.0774(54)| 3.5259(60)| 3.0712(60)| 3.5176(88)| 3.0796(91)| 3.5293(83)|
| MgB$_2$ + 10% n-SiC | 800             | 3.0799(42)| 3.5227(44)| 3.0685(26)| 3.5209(52)| 3.0672(17)| 3.5206(93)| 3.0720(07)| 3.5299(99)|
| MgB$_2$ + 15% n-SiC | 850             | 3.0799(42)| 3.5227(44)| 3.0685(26)| 3.5209(52)| 3.0672(17)| 3.5206(93)| 3.0720(07)| 3.5299(99)|
Figure 1. (a) Powder XRD patterns for 5 and 10 wt% n-SiC doped samples along with a pristine MgB$_2$ sample synthesized at 700, 750, 800 and 850$^\circ$C. (b) Variation of $a$-axis lattice parameter, $c/a$, actual C substitution level ($x$) in Mg($B_{1-x},C_x$)$_2$ and FWHM of (110) peak with synthesis temperature.

Figure 1(b) shows an increase in the $c/a$ value at a particular synthesis temperature as we add the n-SiC to MgB$_2$; this clearly indicates the presence of lattice strain in doped samples. The lattice strain can be attributed to the C substitution in the structure and unreacted C inside the grains [20]. It is observed that the $c/a$ and $x$ values are changed moderately for 750, 800 and 850$^\circ$C samples in comparison to 700$^\circ$C samples. Except for 700$^\circ$C, the low temperature synthesis causes larger values of FWHM, suggesting a smaller grain size and imperfect crystallinity. Figure 1(b) reveals that change in the $a$-axis parameter, $c/a$ values, FWHM values and actual C substitution level for 700$^\circ$C samples is smaller than for other samples, which are heated at a relatively higher temperature; hence it seems that a synthesis temperature of 700$^\circ$C is a comparatively low temperature for partial substitution of C at the B site in the MgB$_2$ matrix.
3.2. DC and AC susceptibility measurements

Figure 2(a) depicts the DC susceptibility versus temperature $\chi(T)$ plots in the FC and ZFC case for an applied field of 1 mT for the series of samples prepared at 750 °C. It is evident from the figure that pure MgB$_2$ undergoes a sharp superconducting transition with an onset at 38.6 K within a 1 K temperature interval. All the samples exhibit a one-step transition from the normal state to the superconducting state; however, the transition width increases a bit by increasing the amount of dopant.

The temperature dependence of the real ($X'$) and the imaginary ($X''$) parts of the AC susceptibility is illustrated in figure 2(b) for all three samples realized at 750 °C. For these AC susceptibility measurements, an AC magnetic field of 1 mT rms value with frequency $f = 33$ Hz was used in the absence of a DC field. Below the critical temperature, a sharp decrease in the real part of the AC susceptibility occurs, which reflects the diamagnetic shielding. In addition, below $T_c$, a peak appears in $X''$, reflecting losses related to the flux penetrating inside the grains. No evidence of a two-peak behavior (granularity) was detected. As the SiC content increases, the onset of diamagnetic shielding in $X'$ and the peak position in $X''$ shift towards lower temperatures.

Figure 3 shows the variation of transition temperature ($T_c$) with synthesis temperature ($T_s$) for the undoped and doped samples. $T_c$ is deduced from the onset temperature of the diamagnetic transition ($T_{dc}$) in the DC susceptibility measurements. For the undoped sample $T_c$ shows an increase with increasing preparation temperature, which can be attributed to the improvement of crystallinity due to higher temperatures. The $T_c$ for the doped samples also depends on the C substitution level: the competitive behavior of these two factors produced the curves of figure 3.

3.3. Irreversibility field ($H_{irr}$) and critical current density ($J_c$)

The magnetic hysteresis loops for the undoped and doped samples prepared at 750 °C are shown in figure 4 at $T = 5, 10, 20$ K and under up to 14 T applied field. This figure clearly demonstrates that at $T = 5$ K the closing of the $M(H)$ loop for pure samples is at $\sim 9$ T, which becomes $\sim 12$ T for the $x = 5$ wt% n-SiC doped sample and the $M(H)$ loop is still open at 14 T for $x = 10$. This indicates that there is quite significant improvement in irreversibility field values with addition of n-SiC in the parent compound at the reaction temperature of 750 °C. 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$^{-2}$ [21]. To find out the effect of synthesis temperature along with doping level of n-SiC on $H_{irr}$ values a plot is drawn in $H_{irr}$ versus $T_s$ and it is shown in figure 5(a) for all the three samples ((i) undoped, (ii) 5 wt% and (iii) 10 wt% n-SiC doped) at 5, 10 and 20 K. A careful look at figure 5(a) implies that doping with n-SiC has significantly improved the irreversibility field ($H_{irr}$) for all synthesis temperatures. Among all the synthesis temperatures 750 °C gives the best value of $H_{irr}$, which can be attributed to grain boundary pinning due to a smaller grain size at low synthesis temperatures. Therefore, we plotted the variation of
Figure 4. Magnetization loop $M(H)$ for $\text{MgB}_2 + n$-SiC, ($x = 0\%$, 5 wt% and 10 wt%) samples of the second series (synthesized at 750°C) up to 14 T field at 5, 10 and 20 K.

$\mu_0H_{irr}$ with n-SiC concentration for 750°C samples separately in figure 5(b). The 10 wt% n-SiC doped samples have the highest values of $H_{irr}$ at $T_s = 750°C$. The values of $\mu_0H_{irr}$ for the 10 wt% n-SiC added sample reached 14, 11.8 and 6.5 T, compared to 8.9, 7.9, 5.0 T for the pure one at 5, 10 and 20 K, respectively. The spectacular enhancement in $\mu_0H_{irr}$ values being seen in figures 5(b) is definitely due to improvement in flux pinning in $\text{MgB}_2$ by the n-SiC doping and low temperature synthesis.

The magnetic $J_c$ for all the samples was calculated using Bean’s critical state model from the $M(H)$ loop at 5, 10 and 20 K and the results are plotted in figure 6(a). We used the formula:

$$J_c = \frac{20 \times \Delta M}{\alpha(1 - \frac{a}{b})}$$

where $a < b$.

Here $\Delta M = |M_+| - |M_-|$ which comes from the $M(H)$ loops and $a$ is the thickness and $b$ the width of the bar shaped sample. Figure 6(a) shows the magnetic $J_c$ versus $\mu_0H$ for all the samples for all four reaction temperatures at 20 and 5 K. We found from the XRD and phase analysis that the 700°C samples are not very phase pure and also there is no appreciable value of actual C substitution level in the doped samples at this reaction temperature. Accordingly the first figure of figure 6(a) also represents a very small improvement in 5 wt% doped samples in comparison to the pure $\text{MgB}_2$ sample. For the other reaction temperature, among all the doped samples the 10 wt% n-SiC doped sample gives the best $J_c(H)$ performance. The samples reacted at 800 and 850°C show the almost similar behavior of $J_c(H)$ performance. In these two series of samples, for undoped $\text{MgB}_2$, $J_c$ drops rapidly in the presence of magnetic field and for both is almost negligible above 4 T and around 7 T at 20 K and 5 K, respectively; for the 10 wt% n-SiC doped samples $J_c$ becomes negligible at around 5 and 11 T, respectively. Among all the four series the one at 750°C demonstrates the best $J_c(H)$ performance. The $J_c$ is 16 times higher than the pure one in the case of the 5 wt% n-SiC doped sample and 30 times higher for the 10 wt% n-SiC doped sample at 5 K in a field of 8.5 T. The $J_c$ values are $1.1 \times 10^3$ A cm$^{-2}$ and $1.3 \times 10^3$ A cm$^{-2}$ at 5 K in the high field of 12 T for 5 wt% and 10 wt% n-SiC doped samples, respectively.

Figure 5. (a) Effect of synthesis temperature ($T_s$) on the irreversibility field ($H_{irr}$) for pure, 5 and 10 wt% doped $\text{MgB}_2$ samples at 5, 10 and 20 K. (b) Variation of irreversibility field ($H_{irr}$) with respect to n-SiC concentration at 5, 10 and 20 K for $T_s = 750°C$. 
Figure 6. (a) The critical current density versus magnetic field $J_c(H)$ plots at 20 and 5 K for SiC doped and undoped samples synthesized at 700, 750, 800 and 850 °C. (b) Dependence of $J_c$ on synthesis temperature at 5 K and 6 T for pure MgB$_2$ and at 5 K and 9 T for doped samples.

Figure 6(b) shows the dependence of magnetic $J_c$ on synthesis temperature at 5 K and 6 T for the undoped one and at 5 K and 9 T for the doped samples. Both pure and SiC doped samples have the best $J_c$ for a lower synthesis temperature. The $J_c$ values decrease gradually with increasing synthesis temperature for the SiC doped and undoped samples. These $J_c$ values are quite competitive with reported literature values [5, 21, 22] and little bit higher than in [16, 23, 24].

The observation of the dependence of $J_c$ on SiC concentration and on synthesis temperature strongly suggests that the following two parameters affect $J_c$: (i) enhancement of grain boundary pinning by growing small crystals at lower synthesis temperature and (ii) introduction of defects/dislocations by C substitution. We observed that lower synthesis temperature, i.e. 750 °C, is best for the better $J_c(H)$ performance for undoped MgB$_2$ as well as for the n-SiC doped MgB$_2$. As opposed to n-C doping, n-SiC doping does not require high-temperature synthesis to obtain the higher $J_c(H)$ values [25].

3.4. Magneto-transport and upper critical field ($H_{c2}$)

Since the 750 °C series of samples show the best values of $J_c(H)$ and therefore $H_{irr}$, we are presenting the magneto-transport measurement up to 14 T applied field for these samples. Figure 7(a) shows the superconducting transition region of magneto-transport measurement up to 14 T for (I) pure, (II) 5 wt% and (III) 10 wt% n-SiC doped samples.
Figure 7. (a) Superconducting transition zone of resistivity vs temperature plot under applied magnetic field $\rho(T)H$ up to 14 T for (I) pure, (II) 5 wt% and (III) 10 wt% n-SiC doped samples synthesized at 750°C. (b) Variation of resistivity with temperature $\rho(T)$ for pure, 5 and 10 wt% n-SiC doped samples synthesized at 750°C. (c) Upper critical field ($H_{c2}$) versus reduced temperature ($T/T_c$) plot for pure, 5 and 10 wt% n-SiC doped samples synthesized at 750°C. (d) Theoretical fitting by the GL equation of upper critical field ($H_{c2}$) values for undoped, 5 and 10 wt% n-SiC doped samples of the second series. The symbols denote the experimental data and solid lines are the best-fit curve according to the GL equation.

Here, we note that the transition is very sharp at zero field for all the samples, but the transition width increases with the increase in field value. At low fields, behavior of pure samples is better than that of doped samples. The transition temperature ($T_c$) (where $\rho \to 0$) for the pure sample is 38.4 K in zero applied field. For the 10 wt% n-SiC added sample $T_c$ decreased to 34.5 K in zero applied field due to B site C substitution. Further, it is noted that the $\rho(T)$ curves for the doped samples shifted with increasing magnetic field much more slowly than the pure one. The $T_c$ value for the pure MgB$_2$ is 7.4 K for 14 T applied field, while is 14.8 K for the 10 wt% n-SiC doped sample under the same field. Thus, the addition of n-SiC clearly improves the superconducting performance of the bulk MgB$_2$ sample at elevated fields.

A further important point is that the nominal resistivity of these samples is very different, $\rho$ (40 K) being 35 $\mu$Ω cm for the undoped sample, 84 $\mu$Ω for 5 wt% and 155 $\mu$Ω for the 10 wt% n-SiC doped sample. This is because the scattering increases with increasing n-SiC content. In figure 7(b) the temperature dependence of normalized resistivity $R(T)/R(300 K)$ is shown for pure, 5 and 10 wt% SiC doped samples. The residual resistivity ratio (RRR = $R_{300 K}/R_{T_{onset}}$) values for the pure, 5 wt% and 10 wt% SiC doped samples are 3.0, 1.75 and 1.5, 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 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 C substitution at B sites. This is in agreement with previous studies on MgB$_{2-x}$C$_x$ systems [26, 27].

The variation of upper critical field with respect to reduced temperature $H_{c2}(T)$ is shown in figure 7(c). The upper critical field is determined from the resistive transitions shown in figure 7(a) using the criterion of 90% of the $\rho_N$ value, where $\rho_N$ is the normal resistivity at about 40 K. Both the doped samples show the higher values of critical field in comparison to the pure sample but the 10 wt% n-SiC doped sample has the best values. At about 20 K (or at $T/T_c$ $\sim$ 0.54) the $H_{c2}$ value for the undoped sample is $\sim$10 T and the same is enhanced to 14 T for the 10 wt% n-SiC doped sample. The C substitution into B sites in the lattice is responsible for increase in $H_{c2}$ due to the disorder on the lattice site of B. We argue that n-SiC reacting with Mg, releases highly reactive free C on the atomic scale at that temperature where 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 substituted into B sites [4].

Some theoretical models need to be applied to determine the upper critical field values at low temperatures. The experimental data for the $H_{c2}$ of MgB$_2$ can be described with high accuracy by the Ginzburg–Landau (GL) equation [28]:

$$H_{c2}(T) = \frac{H_{c2}(0)\theta^{1+a}}{1 - (1 + \alpha)\omega + t\alpha^2 + m\omega^3}$$

with $\omega = (1 - \theta)^{1+a}$ and $\theta = 1 - T/T_c$. (1)

In figure 7(d), we plot the experimental data of $H_{c2}$ as symbols for the second series of samples. We also show the theoretical fitting to these data by the above GL equation (shown by solid curves). As shown in figure 7(d), there is reasonable agreement between theory and experiment. We obtained the fitting parameters $\alpha = 0.41$, $t = 2.5$ and $m = -0.95$ for 5 wt% n-SiC doped sample; these values match well with those of Askerzade et al [28]. The small deviation between the data and theory may suggest some additional effective bands which should be considered in the GL theory in order to get an exact temperature dependence for $H_{c2}$. From the fitting, we can clearly see that, initially, the behavior of $H_{c2}$ with $T$ is linear near $T_c$ and extends up to a temperature of $\sim$10 K and after that it saturates in the range 3–10 K. Below 3 K the $H_{c2}$ line has a negative curvature. The $H_{c2}(0)$ for the 5 wt% n-SiC doped sample is found to be about 33.2 T, while it is just nearly 17 T for the pure MgB$_2$ sample. Thus, GL theory also confirms the enhancement of the $H_{c2}$ value. The $H_{c2}(0)$ values determined by us are also in agreement with other reported literature [11, 29, 30].
3.5. Structure–microstructure and interface analysis by high-resolution TEM

We carried out microstructural investigations employing high-resolution transmission electron microscopy (HRTEM) on the 750 °C series. Figure 8 shows the HRTEM image of unreacted (bare) n-SiC particles. It can be seen that n-SiC particles are almost spherical, having a particle size of ∼20–50 nm with faceted contours on the surfaces of these nanoparticles. In figure 8, the upper inset shows the lattice scale image of an individual nanoparticle exhibiting an inter-planar spacing of 0.25 nm, which corresponds to the [111] plane of a cubic SiC (space group F43m) of lattice parameter $a = 0.43$ nm. The lower inset shows the electron diffraction (ED) pattern of the unreacted n-SiC particles. The Debye rings marked as 1–4 correspond to inter-planar spacings of 0.25, 0.22, 0.15 and 0.13 nm for \{hkl\}: \{111\}, \{200\}, \{220\} and \{311\} planes, respectively.

Figure 9(a) shows the HRTEM micrograph of pure MgB$_2$ and the corresponding electron diffraction (ED) pattern is shown as the right inset of the figure. The Debye rings of ED (right inset of figure 9(a)) correspond to inter-planar spacings of 0.27, 0.22, 0.15 and 0.12 nm for \{hkl\}: \{100\}, \{101\}, \{110\} and \{201\}, respectively. The left inset of figure 9(a) depicts the edge of an individual MgB$_2$ grain covered by a very thin layer (average size ∼9 nm), which may be attributed to the formation of MgO during synthesis. However we have not explored further any growth of such a MgO layer in the present work, but a similar effect was observed in the literature [31].

Corresponding to figure 9(a), a lattice scale image of a single grain of pure MgB$_2$ is shown in figure 9(b). It is observed that a single grain consists of several subgrains inside it with a size of about 3–5 nm. Figure 9(b) clearly reveals the random distribution of such nano-crystallites in different orientations. From this micrograph the inter-planar distances of three crystallites (marked as I, II and III in the figure) are

Figure 10. (a) Bright field HRTEM images of a MgB$_2$ + 10 wt% n-SiC sample synthesized at 750 °C; the inset shows the ED pattern of the same sample. (b) Dark field image of the MgB$_2$ + 10 wt% n-SiC sample synthesized at 750 °C; arrows show the presence of a few Mg$_2$Si particles in the sample. (c) Dark field image of the MgB$_2$ + 10 wt% n-SiC sample synthesized at 750 °C. (d) Lattice scale image of a grain of MgB$_2$ +10 wt% n-SiC sample synthesized at 750 °C. A boundary is drawn around an Mg$_2$Si particle.
calculated as 0.21, 0.15 and 0.26 nm, which correspond to the planes \{101\}, \{110\} and \{100\}, respectively, of MgB$_2$ crystals.

Figures 10(a) and (b) show the bright field and corresponding dark field HRTEM images of MgB$_2$ + 10 wt\% n-SiC sample synthesized at 750 °C respectively. Indeed, these TEM micrographs show 5–15 nm large round shaped particles of Mg$_2$Si, existing within each MgB$_2$ grain. It is to be noted that the inclusions are smaller than the SiC particles added initially, indicating that the SiC is dissolved in the parent MgB$_2$ during synthesis. Dou et al [24, 32] also observed that SiC particles could dissolve completely or up to a certain extent into MgB$_2$. The corresponding electron diffraction (ED) pattern is shown in the inset of figure 10(a). The Debye rings marked as 1–5 correspond to inter-planar spacings of 0.23, 0.22, 0.15, 0.13 and 0.12 nm for the planes \{220\} of Mg$_2$Si, the \{101\} and \{110\} planes of MgB$_2$, the \{422\} plane of Mg$_2$Si and the \{201\} plane of MgB$_2$, respectively. This clearly confirms the presence of Mg$_2$Si particles within the matrix of parent MgB$_2$. Another micrograph (figure 10(c)) exhibits a cluster of Mg$_2$Si nanoparticles in the matrix phase of MgB$_2$ grains. This image shows a large number of dislocations/defects at the interface of MgB$_2$ with the cluster of Mg$_2$Si. Dislocations are known to serve as strong pinning centers along with the nano-inclusions [33]. The lattice scale image of MgB$_2$ + 10 wt\% n-SiC in figure 10(d) clearly reveals the presence of Mg$_2$Si dispersed in the MgB$_2$ matrix. A white line boundary is marked around the Mg$_2$Si particle in the figure. The particle size of Mg$_2$Si is nearly 9 nm. In this micrograph the \{220\} plane of Mg$_2$Si is being visualized with an inter-planar distance 0.23 nm.

In some instances the unreacted (undissolved) traces of SiC are also found to be visible during the HRTEM examination of these samples. These SiC particles form a clear interface with the matrix phase of MgB$_2$. As an illustrative example, figures 11(a) and (b) represents a lattice scale image of the MgB$_2$ + 10 wt\% n-SiC sample and corresponding EDS (energy dispersive spectrum) pattern, respectively. Lattice planes of MgB$_2$ and SiC particles (which are embedded in the parent MgB$_2$ matrix) can be clearly resolved in figure 11(a). The inter-planar distances are marked as 0.26 nm and 0.22 nm, respectively, for MgB$_2$ and SiC in the image, which corresponds to the planes \{100\} of MgB$_2$ and \{200\} of SiC, respectively. A corresponding EDS analysis of the microstructure delineated the presence of Mg, B, C, Si and O peaks in the sample.

This, and the results of XRD, infers that the inclusions of nanoparticles were primarily made of Mg$_2$Si with traces of unreacted SiC. Therefore, it can be concluded that the first reaction of n-SiC with Mg forming Mg$_2$Si and the second of free C being incorporated into MgB$_2$ both help in pinning of vortices and improved superconducting performance. Mg$_2$Si and excess C can be embedded within the grain of MgB$_2$ as nano-inclusions. It must be noted that these nano-inclusions with dimension smaller than 10 nm are of the right dimension to fit with the coherence length in magnesium diboride and, therefore, are suitable to act as additional pinning centers. In neutron irradiated polycrystalline samples the correlation between defects on a nano-metric scale observed by TEM and $J_c$ enhancement was clearly demonstrated [34]; here we suggest that the $J_c$ enhancement at high field can be due to a similar effect. Naturally the better $J_c$ in-field behavior takes advantage of the increased critical field. Our results suggest that a combination of substitution-induced defects and highly dispersed additives is responsible for the enhanced flux pinning in the doped samples.

4. Conclusions

In summary, a systematic study of the effect of synthesis temperature on the phase formation, lattice parameters, FWHM, actual C content, critical current density and irreversibility field of n-SiC doped MgB$_2$ is presented in this paper. We observed that the optimal doping effect of n-SiC was achieved for a synthesis temperature of 750 °C. We can say that two factors are responsible for the best performance of the relatively low temperature (750 °C) synthesized n-SiC doped MgB$_2$ studied here, i.e. (a) C substitution for B
induces disorder in lattice sites with increased $H_{c2}$, and (b) the reduction in grain size, extra defects and embedded inclusions such as Mg$_2$Si and unreacted n-SiC enhances the flux pinning. To know the exact effect of increased $H_{c2}$ or the pinning induced defects etc on the $J_c(H)$ in general, one plots the flux pinning against the reduced field ($H/H_{c2}$) [3, 32–34]. Unfortunately, in the studied higher $J_c$ samples of MgB$_2$ doped with nano-SiC and processed at low temperature, the avalanche of flux jumps below 2 T do not permit clear observation of $J_c$ ($\rho \rightarrow 0$) of about 15 K for the studied n-SiC doped and 750 $^\circ$C synthesized MgB$_2$ under 14 T field is, to our knowledge, one of the highest values yet obtained in the literature for variously processed MgB$_2$ with added nanoparticles.

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