In-situ synchrotron x-ray study of MgB$_2$ formation when doped by SiC

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Abstract. We have studied the evolution of the reaction $x$Mg + $2B + y$SiC $\rightarrow x$Mg$_{1-x}$(B$_{1-y}$C$_y$)$_2 + y$Mg$_2$Si in samples of 1, 2, 5 and 10 wt% SiC doping. We found a coincident formation of MgB$_2$ and Mg$_2$Si, whereas the crystalline part of the SiC nano particles is not reacting at all. Evidence for incorporation of carbon into the MgB$_2$ phase was established from the decrease of the a-axis lattice parameter upon increasing SiC doping. An estimate of the MgB$_2$ lower limit grain size was found to decrease from $L_{100} = 795$ Å and $L_{002} = 337$ Å at 1 wt% SiC to $L_{100} = 227$ Å and $L_{002} = 60$ Å at 10 wt% SiC. Thus superconductivity might be suppressed at 10 wt% SiC doping due to the grain size approaching the coherence length.

1. Introduction

The challenges of incorporating the MgB$_2$ superconductor into metal sheath materials in order to provide mechanically stable wires or tapes are still being faced and effort is focused on reducing the reaction with the metal sheath and on improving the intrinsic properties of the MgB$_2$ by doping. This work represents a model study of the role of SiC doping in pressed powder pellets of Mg and B wrapped in a thin Fe foil to prevent evaporation of the Mg during the in-situ reaction. This configuration is similar to Powder In Tube produced MgB$_2$ in Fe wires, but the heavy texture of especially Mg is avoided.

2. Experimental details

2.1. Samples

Powders of Mg(Goodfellow, 99.8 %), B(Fluka 95-98 %) and 1, 2, 5 and 10 wt% nanoparticle SiC(Alfa Aesar 95 %, 30 nm) were mixed by mechanically alloying using ball milling for 50 hours. Disk shaped pellets with a diameter of $3.2 \pm 0.1 mm$ and thickness of $2.2 \pm 0.2 mm$ were pressed by isostatic pressing at $T = 20$ °C and $P = 640$ MPa in vacuum. A 99.5 % Fe foil from Goodfellow and of thickness $t = 0.05$ mm was wrapped around the samples and closed as an envelope in order to reduce the Mg evaporation during the in-situ experiment.
Figure 1. Summary plot of an in-situ study of a Mg + 2B + 10 wt % SiC sample. Left: The scattered intensity is showed by the color scaling as function of the d-spacing (horizontal) and time (vertical). Right: The temperature history is plotted as function of time and the melting point of Mg is indicated by the red line.

2.2. Synchrotron setup

The in-situ experiments were performed at the BW5 high energy beamline at HASYLAB using a high temperature furnace holding a sample stick inside a quartz tube for control of the atmosphere and capton windows in the outer wall to reduce the background. A MAR345 image plate detector was used to collect the scattered intensity from the samples mounted inside the furnace. Since Fe is scattering much more than the elements in the superconductor a lead ring was mounted in front of the detector to damp the Debye-scherrer cone coming from the Fe(110) reflection of the Fe foil wrapped around the samples. The dimensions of the lead absorber ring and the sample to detector distance determines the photon wavelength, which was set to $E = 77.02$ keV giving a factor $10^2$ absorption of Debye-scherrer cones in the range of $d = 2.00 - 2.08$ Å [1]. A square beam of 0.5 mm x 0.5 mm was defined by a WC slit before a gradient Si/Ge monochromator crystal. Two slits of 1.0 mm x 1.0 mm and 3.0 mm x 3.0 mm opening was mounted together with a beam monitor and a camera shutter for controlling detector exposure time. The furnace was mounted on a motorized sample table and a Ø15 mm length 30 mm lead beamstop was mounted in front of the image plate detector. A diode monitor was embedded in the front of the beamstop and measured the transmitted direct beam, which was used to normalize the scattered intensity. The image plate was typically exposed for 60 sec and a 68 second data readout period then followed. The diffraction patterns of the setup was stored on a computer and processed with log-files holding beamstop monitor, temperature and time information. A flow of argon gas was maintained trough the quartz tube of the furnace and bubbled through a bottle of water before leaving the gas system.
Figure 2. Phase evolution of the Mg + 2B + 10 wt% SiC → MgB$_2$ reaction illustrated by the integrated intensity of central reflections as seen in figure 1. The fitting was performed in several time intervals due to the changes in the peak overlap.

2.3. Data reduction
The two dimensional scattering data from the MAR345 image plate are integrated radially by the fit2d programs and represented as function of the d-spacing of the crystallographic planes causing the diffraction signal, as described by the Bragg law $\lambda = 2d\sin(\theta)$, where $\lambda$ is the photon wavelength and $\theta$ is the scattering angle. An Al$_2$O$_3$ ceramic plate wrapped in Fe foil is used to calibrate the sample detector distance of the setup in order to calculate the scattering angle. The radial data is subsequently normalized by the beamstop monitor and the exposure time of the image plate. A normalized Fe foil background measured beside the Al$_2$O$_3$ sample is subtracted from the in-situ data before fitting is done using MATLAB scripts.

3. Measurements
Figure 1 shows the scattered intensity from the 10 wt% SiC doped Mg + 2B sample during an in-situ experiment, where the sample was heated by a ramp of 20 °C/min to 700 °C followed by a 30 minutes dwell time and cooling towards room temperature. The Mg(100), Mg(002) and Mg(101) reflections are dominating in the initial stage as well as some crystalline boron reflections corresponding to the $\beta$ rhombohedral phase, which is present in the primarily amorphous boron powder. The crystal lattice of Mg is expanding during the heating ramp and the Mg reflections are shifted towards larger d-spacings. Mg$_2$Si is already formed around $T = 300$ °C, whereas the crystalline boron signals disappears at $T = 500$ °C and the Mg melts at $T = 649$ °C where the majority of the MgB$_2$ phase is formed on a time scale of 10 minutes. Similar experiments were performed on the samples with lower SiC doping level.
3.1. Reaction of MgB$_2$ doped with SiC

From figure 1 one can see that the primary secondary phase due to the presence of the SiC is Mg$_2$Si and this might lead to a Mg deficiency in the final MgB$_2$ phase. The incorporations of carbon into the MgB$_2$ phase has been shown to improve the properties of the superconductor by increasing the upper critical field[2]. In the case of SiC doping the maximum available carbon is proportional to the Si contents and one can therefore propose an ideal reaction equation for the SiC doping of MgB$_2$.

\[ xMg + 2B + ySiC \rightarrow zMg_{1-p}(B_{1-q}C_q)_{2} + yMg_2Si \]  

(1)

where x represent the starting Mg and y is the amount of SiC which is transformed during the reaction. The factors p and q indicates the Mg deficiency and the carbon doping of the final MgB$_2$ phase, whereas the factor z is the fraction of MgB$_2$ formed. One can balance the equation above with respect to the elements and by solving for the factors on the right side of 1 one gets

\[ z = \frac{y}{2} + 1 \quad p = \frac{5y - 2x + 2}{y + 2} \quad q = \frac{y}{y + 2} \]  

(2)

Thus the Mg deficiency and the carbon doping of the resulting superconducting phase can in principle be determined from the starting composition of the powder mixture and the amount of Mg$_2$Si formed as observed in the in-situ experiment. However the scattered x-ray signal is primarily caused by crystalline phases in the sample and amorphous phases such as the majority of the initial boron powder are hard to detect with x-rays.

In the following we will examine if equation 1 is supported by the in-situ data of the SiC doping series. Figure 2 shows the integrated intensity of selected reflections determined by fitting Lorentz functions to the data. The intensity ratios between Mg(100) and Mg(002) and the Mg(101) are 35% and 37%, which are somewhat close to the ideal powder ratios of 25% and 35 % as given by the PDF card 35-821 and the deviation might be caused by a weak texture induced during the pressing of the pellets. It is interesting that the SiC signal remains constant during the entire experiment, which indicates that the crystalline part of the SiC is not reacting at all, whereas the amorphous or nano crystalline SiC is transformed into the Mg$_2$Si. The peak of the SiC signal at the Mg melting on figure 2 is an artifact of the fitting of overlapping functions, but the fits are reliable at the start and end of the experiment. The MgB$_2$(101) signal is correlated with the Mg$_2$Si, which leaves the possibility of incorporation of carbon into the superconductor.

Figure 3 and 4 shows the d-spacing of the MgB$_2$(002) and MgB$_2$(100) reflections at T = 700 °C and at the end of the dwell period, where the formed MgB$_2$ is expected to be strain free compared to the contracted room temperature state at the end of the in-situ experiments. It is seen that the a-axis of the formed MgB$_2$ is decreasing with increasing SiC contents, whereas the c-axis remains almost constant. This is an indication of the incorporation of carbon and figure 5 shows the relative change of the a-axis and the c-axis. The d-spacing of the Fe foil around the 4 samples was used to correct for small differences in the sample-detector distances. A ∆d/d = −0.0055 at 10 wt % SiC correspond to a doping of q = 0.06 according to [3]. Another interesting feature of figure 3 and figure 4 is that the peaks broaden as the SiC doping is increased and this indicates that the formed MgB$_2$ becomes more nano-crystalline or that the MgB$_2$ is doped in-homogenous giving a broader d-spacing distribution. By assuming a pure grain size broadening one can estimate a lower limit of the grain size using the Scherrer equation

\[ B(2\theta) = \frac{0.94\lambda}{L\cos(\theta)} \]  

(3)

where B is the Full Width at Half Maximum of a diffraction peak, L is the size of the crystal lattice in the direction of the reflection analyzed and θ is the scattering angle [4].
width is increasing at doping levels above 2 wt%.

Figure 3. MgB$_2$(002) diffraction peak as function of the SiC doping at $T = 700 \, ^\circ C$ and after 30 minutes dwell. It should be noted that the peak width is increasing at doping levels above 2 wt% indicating that the grain size of the formed MgB$_2$ is decreasing.

prefactor 0.94 may be different for different crystallographic directions, but should be of the order unity. However the deconvolution of the instrumental resolution must be performed before the Scherrer equation can be applied. Lorentz functions were fitted to the Al$_2$O$_3$ diffraction peaks of the ceramic plate used to calibrate the sample detector distance. The grains of the Al$_2$O$_3$ are large and the Lorentz widths therefore probe the resolution function of the instrument. The width of two Lorentz function convoluted is just the sum of the widths, whereby $B(2\theta)_{\text{Real}} = B(2\theta)_{\text{measured}} - B(2\theta)_{\text{resolution}}$. The right hand axis of figure 5 shows the MgB$_2$ lower limit grain size along the (100) and (002) direction as determined from the Scherrer equation 3.

4. Discussion

The critical current density vs magnetic field $J_c(B)$ of the SiC doped samples has been determined in a previous study and it was concluded that the $J_c(B)$ line was increasing for 5 wt% SiC, but it is falling under the un-doped sample when increasing the doping to 10 wt% [5]. Additional SEM and TEM analysis suggested a MgB$_2$ grain size in the range $d = 20$-$50$ nm for the undoped samples and this is in agreement with the lower limit of the particle size found from the synchrotron measurements, which reflects the bulk grain size distribution in 0.55 mm$^3$ of the sample due to the transmission geometry of the experiment. The synchrotron data also suggest that the MgB$_2$ grains formed are like flakes with a larger extend in the ab plane than along the c-axis. The data indicates that the extent of the grain is becoming comparable to the coherence length $\xi_c = 2.3$ nm and $\xi_{ab} = 10.2$ nm of undoped single crystals [6]. Thus the reduced $J_c(B)$ at the 10 wt% SiC doping level might be caused by a suppression of superconductivity in the grains, which were not doped by carbon and therefore have the coherence length of the undoped MgB$_2$.

5. Conclusion

We have determined the evolution of the reaction $xMg + 2B + ySiC \rightarrow zMg_{1-p}(B_{1-q}C_q)_2 + yMg_2Si$ in samples doped with 1, 2, 5 and 10 wt% SiC and found that the MgB$_2$ and Mg$_2$Si...
Figure 5. Left: Relative peak positions of the MgB$_2$(100) and MgB$_2$(002) reflections as function of the SiC doping ranging from 1-10 % at T = 700 °C after 30 minutes of dwell in the temperature history. The contraction of the in-plane lattice spacing with a almost constant c-axis indicates that carbon is incorporated into the superconductor, which we propose to write as $Mg_{1-p}(B_{1-q}C_q)_2$, where p and q are measures of the Mg deficiency and carbon doping. Right: Lower limit of MgB$_2$ grain size as determined from the broadening of the MgB$_2$ reflections and using the Scherrer equation in a strain free MgB$_2$ state formation are coincident, but that the crystalline part of the SiC nano particles does not react at all. The shift of the MgB$_2$(100) and MgB$_2$(002) peaks provide evidence for incorporation of carbon into $Mg_{1-p}(B_{1-q}C_q)_2$, but the broadening of the peaks indicate that the MgB$_2$ becomes more nano-crystalline by increasing SiC doping. By fitting the peak widths at T = 700 °C in a strain free state lower limit estimates of the grain size was derived from the Scherrer equation. $L_{100} = 795$ Å and $L_{002} = 337$ Å at 1 wt% SiC and $L_{100} = 227$ Å and $L_{002} = 60$ Å at 10 wt% SiC were obtained and might explain that superconductivity is suppressed at 10 wt% SiC doping, because the grain size becomes comparable to the superconducting coherence length.

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