Beneficial Impact of Excess Mg on Flux Pinning in Bulk MgB\(_2\) Synthesized with Ag Addition and Carbon Encapsulated Boron

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Silver addition has been known to improve mechanical and superconducting performance of bulk magnesium boride (MgB\(_2\)) superconductor synthesized via solid state sintering. While formation of pinning phases and impurities such as Ag–Mg phases and MgO, respectively, responsible for high performance, part of the Mg in initial mixture will be expected to be consumed by silver. In this work, the authors add varied amounts of Mg systematically such as \(x = 2\) (while \(x = 1.05, 1.075, 1.1, 1.125, 1.15\)) ratio of Mg:B instead of usual stoichiometric ratio of 1:2. To obtain high superconducting properties, the authors use carbon encapsulated boron (1.5% carbon) along with 4 wt\% Ag. X-ray diffraction analysis shows the presence of Ag–Mg phases and minute amount of MgO. Superconducting quantum interference device (SQUID) measurements indicate that high irreversibility field (4.76 T) and large \(J_c\) of 520, 440, and 347 kA cm\(^{-2}\) at 10, 15, and 20 K, respectively, at self-field was exhibited in sample with \(x = 1.075\). Flux pinning force studies are done to analyze the effect of secondary phases formed. All results analyzed explain the improved critical current performance based on nanometer-sized Ag–Mg particles in the final product.

1. Introduction

Despite the emerging high temperature superconducting (HTS) materials (\(T_c > 77\) K) till recent times, magnesium diboride (\(T_c \approx 39\) K) caught immediate attention of many researchers since its discovery by Jun Akimitsu group in 2001.\(^1\) For example, the superconducting transition temperature of MgB\(_2\) is significantly lower than that of YBa\(_2\)Cu\(_3\)O\(_7\) “Y-123,” however, MgB\(_2\) benefits from some BCS-like superconducting features, e.g., a large coherence length and weak magnetic relaxation. Apart from that, the other vital reasons for MgB\(_2\) being one of the trending bulk superconductors because of its attractive physical properties, such as simple hexagonal crystal, light weight as the elements Mg and B are low atomic numbered, low coherence length, no weak link issue,\(^2\) and finally the most important advantage which is easy synthesis (solid state sintering). Hence mainly focused on working toward high trapped field applications at 20 K. Extensive research has been carried on its characterization\(^3\) and applications\(^4\) as MgB\(_2\) can be fabricated in many forms as crystals, powder, thin films, macroscopic wires, nanowires, and tapes. These multiple forms and various intricate-shaped bulks can be fabricated but not only solid state sintering but also various approaches such as mechanical alloying, sol–gel, and vapor-transport process.\(^5\) MgB\(_2\) offers the possibility of wide-ranging engineering applications\(^6\) in a temperature range of 20–30 K, where traditional superconductors such as Nb\(_3\)Sn\(^7\) and Nb–Ti alloys, cannot play any role due to their low \(T_c\) (\(\approx 10\) K, operating temperatures are around 4.5 K). MgB\(_2\) is superior because of ability to exhibit superconductivity in sintered form unlike most of the HTS materials, as it does not have any weak link issues. The main feature of this material is that its superconducting properties will not be deterred because of its grain boundaries; in contrary, these hindrances act as pinning centers there by enhancing the superconducting critical current density (\(J_c\)). This is mainly due to its peculiar inherent feature of the material of not being negatively affected by weak links caused by grain boundaries as mentioned earlier. Comparing the group of present intermetallic superconductors, the critical temperature of MgB\(_2\) is rather high, which helps to lower the cooling costs. Because of the above mentioned advantages, MgB\(_2\) is a promising material for several applications such as in power industry (superconducting wires, etc.), magnetic resonance imaging (MRI), fault current limiters (FCL), SQUID devices, high energy storage, levitation-based devices, and powerful super-magnets operating at around 20 K.\(^8\) When aiming at superconducting super-magnet applications, it is necessary to produce a good quality and high performance bulk MgB\(_2\) material with high \(J_c\) and low-production cost. For improving superconducting properties such as trapped field of the superconducting material, one has to improve the critical current density as well as the volume parameter as trapped field is proportional to \(J_c\) and volume. In case of MgB\(_2\) bulk, as the synthesis

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2. Experimental Section

To study the optimum amount of excess Mg precursor required for balancing the loss from Ag–Mg phases formation or obtaining best \( J_c \), a series of bulk MgB\(_2\) is synthesized by an in situ solid state reaction. Several amounts of Mg had been varied such as \( x = 1.05, 1.075, 1.1, 1.125, 1.15 \) in MgB\(_2\). The precursors used were commercial powders (Furu-uchi Chemical Corporation) of amorphous Mg powder (99.9% purity, 200 meshes), carbon encapsulated boron powder (1.5% carbon) and 4 wt% Ag. In general, to make 1 g of MgB\(_2\) without Ag we use 0.529 g of Mg powder and 0.471 g of Carbon coated/encapsulated boron (CCB) (1.5% carbon) powder, which is 1:2 molar ratio of Mg:B. These powders were rigorously mixed and ground in a glove box to avoid oxide formation. This mixture is then pressed into 20 mm diameter, 7 mm thick pellets using a uniaxial hydraulic press with a force of approximately 20 kN. These pellets were immediately wrapped in titanium (Ti) foils and heat treated at 775 °C for 8 h in a tube furnace in Ar atmosphere. The constituent phases of the samples were identified with a high-resolution automated X-ray powder diffractometer (RINT2200) with a step size of 0.01° from 10° to 90°, using Cu-K\(_\alpha\) radiation generated at 40 kV and 30 mA. Rietveld analysis was done to find out the phase fraction of all constituent phases detected from XRD. The microstructure of these samples was later studied with Field emission scanning electron microscope (FE-SEM).

SQUID specimens with dimensions of approximately 1.5 × 1.5 × 0.75 mm\(^3\) were made from MgB\(_2\) bulk samples. Critical temperature (\( T_c \)) and critical current density (\( J_c \)) are measured using SQUID Magnetometer (Quantum Design, model MPMS5). \( J_c \) is calculated from magnetization hysteresis loops (M–H) using extended Bean critical state model formula, mentioned below as Equation (1)

\[
J_c = 20\Delta m/[a^3c(b - a/3)]
\]

In this equation, \( a \) and \( b \) are cross sectional dimensions, \( b > a \), and \( c \) is thickness of the specimen (\( a, b, c \) in mm) and \( \Delta m \) (in emu units, 1 emu = \( 10^{-3} \) Am\(^{-1}\)) is the difference in magnetic moments during increasing and decreasing field in the M–H loop.

3. Results and Discussion

The X-ray diffractograms (XRD) (see Figure 1) of the Mg excess samples (best sample and highest Mg excess doped) are compared with pure sample. Formation of Ag–Mg phases along with small amounts of MgO, while MgB\(_2\) being the main phase can be observed. From this systematic increase in Mg, \( x = 1.075 \) seems to have the highest Ag–Mg phase fraction which can be seen by peak intensity of Ag–Mg phase. However, in other samples where \( x < 1.075 \), the excess Mg is forming Ag–Mg phase but only minute amount and for sample where \( x > 1.075 \), the excess Mg seems to be contributing to other phases such as MgO which there by reducing the effecting the amount of Ag–Mg phase as the peak intensity of MgO keeps increasing.

![Figure 1. XRD of MgB\(_2\)-CCB 1.5%Ag 4 wt% which shows the optimum Ag–Mg phase (high peak intensity) formation at \( x = 1.075 \). Unidentified peaks correspond to MgB\(_2\).](image-url)
with extra Mg addition. It is also important to note that the MgO phase is minute in all the samples, which is similar to our earlier reports.\(^{[11]}\) In order to bolster the above-mentioned conclusions, we did Rietveld refinement followed by phase fraction analysis using materials analysis using diffraction (MAUD) software (see Figure 2). Crystallographic information of MgB\(_2\), MgO, and AgMg used to analyze the phase fraction are P6/mmm (CIF ref: 1000026), Fm-3m (CIF ref: 1000053), and Pm-3m (CIF ref: 1509457), respectively. We found that highest AgMg phase fraction percentage of around 2\% is observed in \(x = 1.075\) sample while in the highest excess Mg added sample showed only 0.3\% AgMg phase.

To study the effect of this excess Mg addition on the superconducting properties of bulk Mg\(_x\)B\(_2\). Coming to the superconducting transition temperature \(T_c\), for clear understanding, we have plotted the first derivative of DC magnetic moment against temperature (see Figure 3). All the samples have a sharp superconducting transition, which shows that \(\Delta T_c\) is approximately 1 K. However, the \(\Delta T_c\) is increasing with the increase in excess Mg addition; this is probably because of the formation of more MgO. \(T_c\) of all samples is near to 37.5 K (slightly lower than 39 K), which is expected from a carbon doping in form of carbon encapsulated boron.\(^{[12,10]}\) This reduction is mainly due to carbon but not Ag because, Ag substitution is only possible when added in very less wt\% and given a lot of sintering duration.\(^{[12,11]}\) Hence, it is difficult for Ag to be substituted in MgB\(_2\) lattice in our case. \(T_{c\text{onset}}\) increase with increase in excess Mg concentration which might imply that Mg is sufficient enough to form high percentage of MgB\(_2\) superconducting phase. The detailed information on superconducting critical temperature onsets \((T_{c\text{onset}})\) and \(\Delta T_c\) can be found elsewhere.\(^{[20]}\)

M–H loops are studied to estimate the \(H_{\text{irr}}\) (Irreversibility field) and later are used to calculate superconducting critical current density \((J_c)\). \(H_{\text{irr}}\) is value field strength at \(J_c\) equivalent to 100 A cm\(^{-2}\). It is surprising to see the \(H_{\text{irr}}\) and \(J_c\) to be in accordance with the phase fraction of Ag–Mg phase. The highest \(H_{\text{irr}}\) is for sample \(x = 1.075\) which is 4.76 T at 20 K, while that of a normal pristine sample is around 4.3 T\(^{[21]}\). Additional details for other samples can be found in Figure 4. This indicates that addition of excess Mg along with usage Ag and CCB can ascend the usage of MgB\(_2\) up to high field applications. Simultaneously,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Phase fraction analysis of best sample (Mg\(_{1.075}\)B\(_2\)-CCB 1.5 wt \%Ag 4 wt\%) using MAUD. Maximum AgMg phases fraction is detected in this sample of all samples.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Magnetization loops of systematically excess Mg added samples (Mg\(_x\)B\(_2\)-CCB 1.5%-Ag 4 wt\%). Sample \(x = 1.075\) shows high critical field or \(H_{\text{irr}}\).}
\end{figure}

the highest \(J_c\) is seen in \(x = 1.075\) sample. 347 kA cm\(^{-2}\) at self-field, 244 kA cm\(^{-2}\) at 0.5 T and 136 kA cm\(^{-2}\) at 1 T, while the values of pure sample is around 220 kA cm\(^{-2}\) at self-field. \(J_c\) trends for other samples can be seen in Figure 5. It can be concluded that the excess Mg addition along with defects and
other high field pinning centers is a contributing factor for improving the high field \( J_c \). Similar effects have been observed in previous research such as optimizing Ag addition in MgB\(_2\). It was reported that AgMg\(_2\) phases formed acts as flux pinning centers in MgB\(_2\) responsible for the improved \( J_c \).\(^{[16,22,23]}\) Also, formation of tiny MgB\(_2\) grains because of Ag addition was shown by AFM studies and the density improvement was also observed as the Ag–Mg particles fill in the voids.\(^{[24]}\) In addition, mechanical properties are also enhanced because of the Ag–Mg alloy particles distribution in the matrix.\(^{[16]}\) Later it was also considered that Ag addition that results in Ag–Mg alloys phase that has high thermal conductivity and will aid in suppressing flux jumps.\(^{[19,25]}\) Furthermore, this scenario of additive reacting with Mg in matrix is observed even in SiC doping where Mg\(_2\)Si, an Mg–Si based compound is formed which is responsible for the \( J_c \) improvement.\(^{[26]}\) These \( J_c \) trends are also in congruence with X-ray and phase fraction analyzed data. This accordance is as per our assumption that when excess Mg is beyond \( x = 1.075 \), formation of MgO is favored over AgMg phase, thereby diminishing the superconducting performance there by resulting in low \( J_c \).

To evaluate the normalized pinning force density for a material, we used Dew–Hughes general expression

\[
F_p / F_{p,max} \propto 1 - h^q
\]

In the above Equation (2), \( p \) and \( q \) are dimensionless parameters that vary with flux pinning mechanism. Based on this evaluation, different types of pinning centers as well as mechanisms are attributed for different values of \( p \) and \( q \). Usually, if the peak position or \( h_{max} \approx 0.2 \) the dominant pinning is from grain boundary, if \( h_{max} \approx 0.33 \) pinning is from normal conducting inclusions and if \( h_{max} \approx 0.5 \) the pinning is from weak superconducting areas.\(^{[27]}\) In order to understand the flux pinning characteristics in our sample, we have plotted and studied the normalized flux pinning force curve against reduced magnetic field. In this curve \( F_p = F_p / F_{p,max} \) is plotted against

**Figure 5.** Superconducting critical current density of various excess Mg added samples (Mg\(_{x}\)B\(_2\)-CCB 1.5%-Ag 4 wt%) at various magnetic fields. At high fields and low fields \( x = 1.075 \) sample shows best performance.

**Figure 6.** Flux pinning diagrams calculated from the M–H loops using Dew–Hughes model. Peak position lies at approximately 0.2 which indicates the primary pinning mechanism is grain boundary pinning.

**Figure 7.** Low magnification SEM analysis of Mg rich MgB\(_2\) samples. AgMg phase (white) in the MgB\(_2\) matrix (black); SEI image (left), comp image (right).
$h = H_{irr}/H_{Ic}$ at 20 K, where $H_{Ic}$ is the irreversibility field obtained from M–H loops. Here we determined $H_{Ic}$ criterion as field where $J_c \approx 100 \text{ A cm}^{-2}$.[26] Similar to our previous literature,[11,16,20,27] in our system, the peak position is located at $h_{max} = 0.2$ (see Figure 6), which indicates that the dominant mechanism for the pinning is grain boundary pinning ($\delta l$ pinning). This result is in accordance with previous studies for which normal and surface pinning dominate with in grains. Precisely the grain boundaries within Ag–Mg nanoparticle layer are contributing to the pinning at self-field. In our previous work, the $J_c$ vs $h$ peak was at 0.17 when we used nano amorphous boron without any additives or dopants used.[11] The fact that peak shifted from 0.17 to 0.2 means that the contribution of 3D-defect pinning or $\delta T_c$ pinning has improved, although the primary pinning is from grain boundaries.[21] Presence of Ag–Mg phases along with lattice distortion from CCB addition is responsible for this shift in the flux pinning peak position.

To confirm the mechanisms responsible for the $J_c$ improvement we have done microstructural analysis by scanning electron microscopy (SEM). It can be observed from high magnification SEM images (left) and back scattered images (right) in Figure 7 that secondary phases, mostly Ag–Mg based (white) are formed inside the matrix (black) and seem to be contributing for the flux pinning. The white colored secondary phases are most likely Ag–Mg, while the matrix being MgB$_2$. On the other hand, high magnification images tell us that nano-particle layers of Ag–Mg phases are formed in grain boundaries (see Figure 8). To confirm the presence of these layers throughout the sample, we tried performing elemental mapping using energy dispersive X-ray spectroscopy (EDX) in FE-SEM. The mapping (see Figure 9) shows uniform distribution of Ag, which thereby tells us that these Ag–Mg layers...
are formed throughout the sample. In addition, uniform carbon distribution can also be observed since we have used carbon encapsulated boron as precursor. These can clarify upon any suspicion over non-uniform distribution of dopants in the sample. These layers have Ag–Mg nanoparticles around 20–30 nm, which increase the number of grain boundaries might be contributing to the zero field critical current density. Flux pinning diagrams are calculated to determine the dominant pinning mechanism. To deeply study the best sample’s behavior we tried to measure the M–H loops at various temperatures (10, 15, 20, 25, 30, and 35 K) and calculated the $J_c$ and flux pinning diagrams to observe the change in mechanisms with temperature. High $J_c$ such as 521 kA cm$^{-2}$ was observed at 10 K, while it dropped steadily with increase in temperature, $J_c$ of 441, 350, 250, 141, and 27 kA cm$^{-2}$ was noted at 15, 20, 25, 30, and 35 K, respectively (see Figure 10). Flux pinning diagram reveals that at high temperatures the peak is at $h \approx 0.3$, while low temperatures it is at $h = 0.22$ (see Figure 11) which shows that the dominant pinning mechanisms slightly changes with temperature, this is in accordance with previous research.[27] Therefore, we think that slightly excess Mg addition is necessary and beneficial in obtaining optimum pinning effect from Ag addition in solid-state sintered bulk MgB$_2$ system.

4. Conclusion

Bulk MgB$_2$ samples with variation in excess Mg precursor has been synthesized in argon atmosphere via solid-state sintering process at 775 °C. XRD analysis shows that peak corresponding to Ag–Mg phase is strong when $x = 1.075$ (in Mg$_x$B$_2$), which also reflected in phase fraction analysis. Critical temperatures of all the samples is close to 37.5 K, because of usage carbon-encapsulated boron, but have sharp transitions, $\Delta T \approx 1$ K. M–H loops show that the sample with 7.5 wt% excess Mg or Mg$_{1.075}$B$_2$ (best sample) has high irreversibility field ($H_{irr}$) such as 4.76 T. In correspondence with XRD, the best sample showed the highest $J_c$ such as 520, 440, and 347 kA cm$^{-2}$ at 10, 15, and 20 K, respectively. SEM analysis confirmed the presence of secondary Ag–Mg phases and improved microstructural changes such as particle refinement, up to 20–40 nm. Hence, the results suggest that using 1.075:2 ratio of Mg:B is crucial for development of high performance bulk MgB$_2$ material while using CCB and Ag addition.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Ag added bulk MgB$_2$, carbon encapsulated boron, excess Mg, flux pinning

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