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Role of silver addition in the synthesis of high critical current density MgB_2 bulk superconductors

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Abstract

Ag-doped MgB_2 bulk superconductors have been prepared using a standard solid state processing. The addition of Ag to MgB_2 powders during the sintering process has been found to result in an important advantage, namely, the prevention/reduction of loss of Mg, a problem most commonly observed in the sintering of MgB_2 bulk samples at elevated temperature and ambient pressures. The Ag-doped MgB_2 sample has a distinct superconducting transition temperature around 39 K, while the undoped MgB_2 undergoes only a very feeble transition to a diamagnetic superconducting state at around 39 K. The normal conducting silver regions in the MgB_2 matrix act as pinning centres resulting in the realization of high critical currents in the presence of magnetic fields.

1. Introduction

Magnesium diboride (MgB_2) with its superconducting transition temperature at 39 K has generated tremendous interest because of its potential for formability into wires and tapes for applications ranging from power transmission to motors and generators [1–6]. The primary advantage of MgB_2 over high-temperature yttrium and bismuth-based materials is derived from its large coherence length (∼50 Å) compared to 3–5 Å for high-temperature superconductors (HTSCs) [7]. In addition to its simple chemical composition and crystal structure, MgB_2 has the ability to carry high transport currents at temperatures (10–20 K) accessible easily to cryocoolers. While the compound is simpler than HTSCs in terms of chemical composition and crystal structure, new problems are encountered in the synthesis of MgB_2, namely loss of Mg and low density. To avoid these problems the sintering is usually carried out at high pressures with additional sources of Mg [3–6]. Also, the current carrying capability of MgB_2 in the presence of high fields is poor due to weak flux pinning. The mass density of the material can, of course, be increased by sintering at high temperatures, but this alone is not sufficient to enhance the current carrying capability of this material. The key applications of MgB_2 superconductors will be for wires and tapes. It is highly desirable that synthesis of a highly dense, high critical current capacity phase is possible at ambient pressures to enable large-scale applications. In this paper, we show that these desirable properties are achieved by the addition of silver in MgB_2 bulk superconductors.

2. Experimental

Undoped and 5 wt% silver added MgB_2 powders were first cold pressed into a pellet form. The pellets were then wrapped in tantalum foil separately and were sealed in a single quartz tube after evacuation by a rotary pump. The sealed pellets were sintered at 850 °C for six hours, and then diced into small rectangular bars or circular discs using a diamond wire. Small amounts of powders were scraped from each pellet for x-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. The superconducting transition temperature and critical current density were determined using magnetization versus temperature (*M–T*) and magnetization versus field (*M–H*) data recorded using a superconducting quantum interference device (SQUID) magnetometer.

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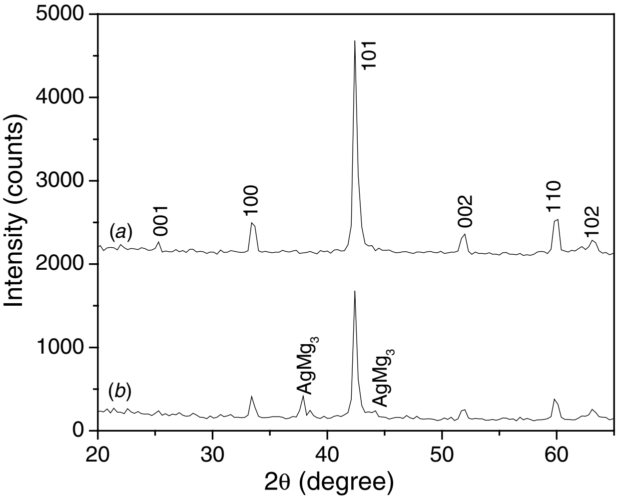

Figure 1. X-ray diffraction patterns recorded from (*a*) undoped and (*b*) silver-doped MgB_2 powders.

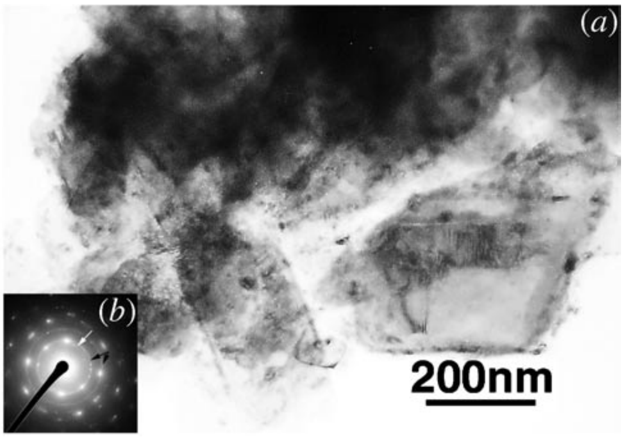

Figure 2. (*a*) Transmission electron micrograph of an Ag-doped MgB_2 bulk sample and (*b*) the diffraction pattern containing a ring structure corresponding to a polycrystalline structure of MgB_2 and $AgMg_3$ phases.

3. Results and discussion

The XRD patterns recorded from undoped and silver-doped powders are shown in figure 1. As seen in this figure, all the peaks are attributed to pure MgB_2 compound in the case of undoped MgB_2 sample, while the silver-doped MgB_2 powder has additional peaks at angles (2θ) of 35.87°, 37.87° and 44.16°. These additional peaks have been indexed to the $AgMg_3$ compound. Scanning electron microscopy (SEM) studies carried out in conjunction with energy dispersive x-ray (EDX) analysis have indicated that silver is mostly present in intergranular spaces and grains are mostly devoid of silver. The TEM analysis of Ag-doped MgB_2 bulk samples also shows the presence of an Ag-rich phase as precipitates outside the MgB_2 grains (figure 2(*a*)). The diffraction pattern of this region (shown in figure 2(*b*)) contains a ring structure corresponding to a polycrystalline structure. These rings were indexed as MgB_2 and $AgMg_3$ phases. The diffraction rings for MgB_3 are clearly marked. The presence of $AgMg_3$ in the form of small

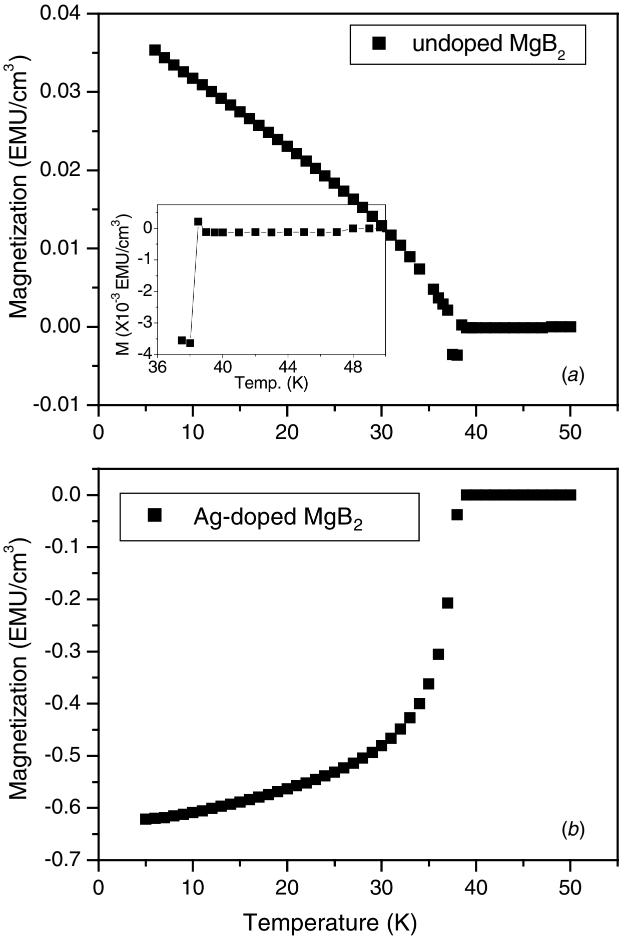

Figure 3. Zero field cooled *M–T* plots for (*a*) undoped and (*b*) Ag-doped MgB_2 bulk samples. The plot displayed in the inset is used to reveal weak but distinct superconducting transition of non-silver containing MgB_2 sample.

~10–20 nm precipitates is quite significant, as they can act as flux pinning centres, thus stabilizing superconducting flux line lattice against the applied magnetic field.

Shown in figure 3 are zero field cooled *M–T* plots for undoped and Ag-doped MgB_2 bulk samples. The *M–T* data were recorded in a field of 10 Oe. It is interesting to note that while the Ag-doped MgB_2 sample has a distinct superconducting transition temperature around 39 K, the undoped MgB_2 undergoes a very feeble transition to diamagnetic superconducting state at around 39 K (see the inset of this figure). When the temperature is lowered further, the silver-doped MgB_2 sample remains diamagnetic but the undoped MgB_2 sample turns paramagnetic below ~36 K. The presence of such a weak superconducting phase in undoped MgB_2 sample is thought to be associated with either the loss of Mg or the dissociation of MgB_2 compound at 850 °C (the temperature of sintering in the present study) into non-stoichiometric non-superconducting compounds. In this situation, the vortex current might be circulating around the non-superconducting phase with a sense of rotation opposite to that of the diamagnetic screening surface current resulting in the realization of positive magnetization signal as seen in figure 1(*a*). We want to make it clear that although there are plenty of reports available in the literature claiming

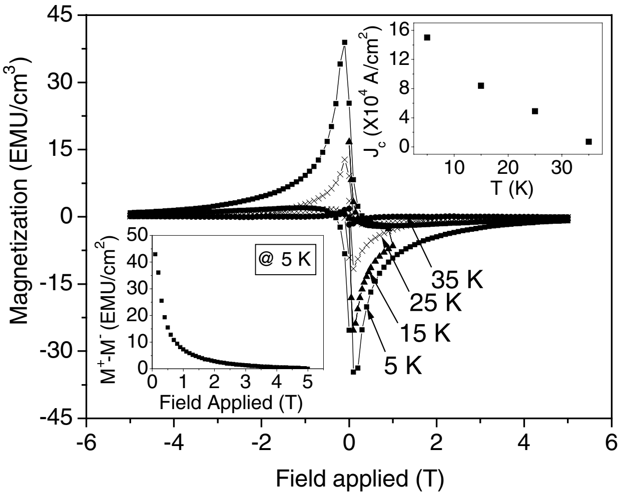

Figure 4. *M–H* loops recorded from Ag-doped MgB_2 bulk samples at 5, 15, 25 and 35 K. The critical current density is plotted against the temperature in the top inset of this figure. The bottom inset shows the variation of the residual magnetization as a function of applied field.

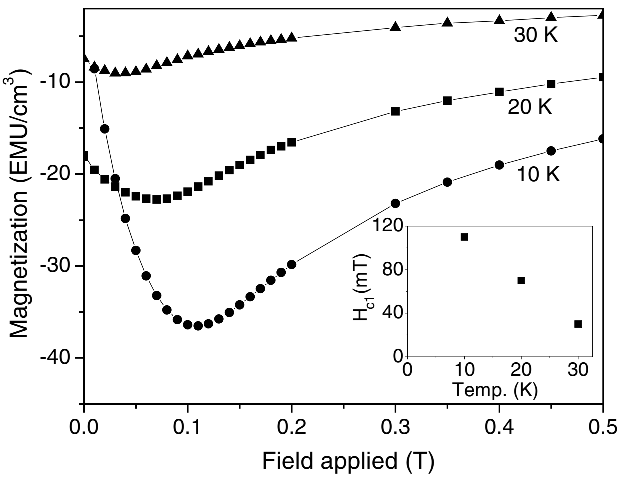

Figure 5. *M–H* curves recorded close to zero field to estimate the lower critical field (H_{c1}). The $H_{c1}(T)$ are plotted in the inset of this figure as a function of temperature.

the synthesis of MgB_2 bulk superconductors with high critical temperature and high critical current density, none of these papers [1–6] report the synthesis of MgB_2 bulk materials without either high pressure, or using additional source of Mg or the combination of both. It is in this context that our work on Ag doping assumes an interesting importance.

The XRD data for undoped MgB_2 samples indicate that there are no decomposed phases present and we believe that the loss of superconductivity is most likely due to loss of Mg resulting in the formation of a magnesium deficient non-superconducting $Mg_{1-x}B_2$ phase. The presence of silver seems to have prevented the loss of Mg due to high affinity of silver atoms for Mg. We believe the silver acts as a temporary trap for Mg atoms by forming some intermediate compounds with high Mg content. The intermediate compound may subsequently release Mg atoms back to non-stoichiometric $Mg_{1-x}B_2$ compound assisting in the formation of stoichiometric MgB_2 material with good superconducting properties. The proposed mechanism can be described as follows:

$$n\mathrm{MgB}_2 \xrightarrow{850\ ^\circ\mathrm{C}} \mathrm{Mg}_{1-x}\mathrm{B}_2 + (n-x)\mathrm{Mg}$$

$$(n-x)\mathrm{Mg} + \mathrm{Ag} \rightarrow (\mathrm{AgMg}_{n-x})^*$$

$$(\mathrm{AgMg}_{n-x})^* + n\mathrm{Mg}_{1-x}\mathrm{B}_2 \rightarrow n\mathrm{MgB}_2 + \mathrm{Ag}$$

The *M–H* loops recorded from Ag-doped MgB_2 bulk samples at 5, 15, 25 and 35 K are shown in figure 4. The zero field intergranular critical current density, measured using the Bean critical state model [8], has been plotted against temperature in the top inset of this figure. It should be noted that even at 35 K, the material is capable of supporting a current of 7×10^3 A cm^{-2}. It is believed that the high density of normal conducting $AgMg_3$ regions, which act as flux pinning centres, is responsible for the realization of such high critical current densities [9, 10]. The evidence in favour of this argument comes from the plot of the residual magnetization [11], $M = M^+ - M^-$, as a function of applied field (bottom inset, figure 4), where M^+ and M^- are the magnetization values corresponding to increasing and decreasing fields while recording the *M–H* loops. It is clear from this data that the residual magnetization decreases rapidly with applied field. This indicates that more flux lines are trapped in normal regions while decreasing the magnetic field (5 T to zero) than while increasing the field (zero to 5 T). This may be explained by the fact that the magnetic flux lines trapped by the vortex are larger in number under the influence of higher magnetic field and remain trapped when the field is removed or reduced. From *M–H* loops, we also have estimated the lower critical field, $H_{c1}(0)$. The $H_{c1}(T)$ is defined as the magnetic field [2, 4], where the initial slope meets the extrapolation curve of $(M^+ + M^-)/2$ (figure 5). The results obtained are plotted in the inset of this figure as a function of temperature. The extrapolation of this plot gives an $H_{c1}(0)$ value of 0.15 T. The absolute value of critical current density obtained in the present work is lower than the highest values reported mostly in the literature, and hence, suggests more work needs to be carried out to optimize the level of silver doping. Nevertheless, the values of critical current density reported here are very encouraging for MgB_2 bulk samples in light of sample preparation without using additional source of Mg and/or applying high pressure during high temperature sintering.

4. Conclusions

In summary, we have investigated the effect of silver addition to MgB_2 bulk superconductors for the first time. The presence of silver in MgB_2 bulk pellets seems to have prevented or reduces significantly the loss of Mg during sintering of the pellets at high temperatures and has allowed the formation of pinning centres resulting in high critical currents. This role of silver may be very beneficial in the fabrication of MgB_2 films using *in situ* processes.

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References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63

[2] Kambara M, Hari Babu N, Sadki E S, Cooper J R, Minami H, Cardwell D A, Campbell A M and Inoue I H 2001 *Supercond. Sci. Technol.* **14** L5

[3] Kim H J, Kang W N, Choi E M, Kim M S, Kim H P and Lee S L 2001 *Phys. Rev. Lett.* **87** 087002

[4] Takano Y, Takeya H, Fujii H, Kumakura H, Togano K, Kito H and Ihara H 2001 *Appl. Phys. Lett.* **78** 2914

[5] Serquis A, Zhu Y T, Peterson E J, Coulter J Y, Peperson D E and Mueller F M 2001 *Appl. Phys. Lett.* **79** 4399

[6] Zhao Y, Feng Y, Cheng C H, Zhou L, Wu Y, Machi T, Fudamoto Y, Koshizuka N and Murakami M 2001 *Appl. Phys. Lett.* **79** 1154

[7] Welp U, Fendrich J A, Kwok W K, Crabtree G W and Veal B W 1996 *Phys. Rev. Lett.* **76** 4809

[8] Bean C P 1964 *Rev. Mod. Phys.* **36** 31

[9] Kumar D, Sharon M, Pinto R, Apte P R, Pai S P, Purandare S C, Gupta L C and Vijayaraghavan R 1993 *Appl. Phys. Lett.* **62** 3522

[10] Kumar D, Apte P R and Pinto R 1995 *J. Appl. Phys.* **77** 5802

[11] Lee S H and Kim H C 2001 *J. Appl. Phys.* **89** 7496