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Effects of sintering atmosphere on the superconducting properties of SiC doped bulk MgB₂ superconductor

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Abstract. A study was conducted to investigate the effects of the sintering atmosphere on the superconducting properties of SiC doped MgB₂ superconductors. Four different purity Ar gases were chosen as the sintering atmosphere for making bulk samples. It was found that the impurities in the Ar gas resulted in different levels of MgO in the resultant MgB₂ superconductors. Superconducting properties, such as the critical temperature (Tc), critical current density (Jc) and upper critical field (Hc₂) were affected by the impurity phase inside the samples. Sample phase composition and morphology were analyzed to explain the effect of the sintering atmosphere on the sample properties.

Introduction

The discovery of superconductivity in MgB₂ in 2001 has drawn great interest from researchers all over the world [1]. This superconductor has a Tc of 39 K, a temperature which existing metallic superconductors such as NbTi and Nb₃Sn can not reach. People expect MgB₂ to be a strong candidate for applications around the temperature of 20 K. The subsequent research found that weak-links, such as impurity phase and grain boundaries in the MgB₂ superconductor are not as harmful as in high temperature superconductors, meaning that no special treatments are needed to achieve texture or preferential grain orientation when making MgB₂ superconductors [2]. This tolerance to weak-links also provides the possibility of doping MgB₂ with tiny particles so as to pin flux at high magnetic field without suffering critical current density loss, which is a great advantage of MgB₂ over the high Tc superconductors.

For applications in magnetic field, the MgB₂ superconductor must possess a high current density at high magnetic field. Over the past several years, the magnetic field dependence of the critical current of MgB₂ has been improved via doping with materials such as SiC, or carbon in the form of nano particles or nano carbon tubes [3, 4, 5, 6].

The fabrication process for the doped MgB₂ has been optimised by many groups. High Jc as well as high irreversibility field (Hₘₙ) have been achieved [3-7]. The sintering temperature and duration play an important role in determining the superconducting properties. Usually, the sintering process is carried out under high purity Argon gas. The use of Argon can protect the MgB₂ from oxidization; however, there are two factors that need to be considered for the use of high purity Ar gas. One factor is that an impurity such as oxygen from the Ar gas may be necessary for improving the high magnetic field Jc. In the case of oxygen this is due to the oxygen alloying with MgB₂. The oxygen may

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substitute for B, or form tiny particles with Mg or B, with both outcomes offering possible beneficial properties. There are also economic considerations due to the high cost of the high purity Ar gas, since the lower purity Ar gas is much cheaper. Recently it was found that the ball milling atmosphere exerted a strong effect on MgB$_2$ superconducting properties, in the case of MgB$_2$ tapes made from mature MgB$_2$ via an ex-situ process. [8]. The in-situ process is more influenced by the sintering atmosphere than the ex-situ process, in that MgB$_2$ forms from elemental B, Mg and other components in this case. It is necessary to study the effects of the Ar purity on the MgB$_2$ superconducting properties in the in-situ process. In this paper, SiC doped MgB$_2$ pellets were sintered in Ar gas with different impurity levels, and effects of the impurity level are discussed.

**Experimental**

A combination of 99% pure boron powder from Alfa Aesar, 99% pure Mg powder with a size of 325 mesh and SiC powder with a 30 nm size were mixed with a mortar and pestle for 30 minutes. The mixed powders were put into a pressing die and pressed into pellets 12mm in diameter. The pellets were placed on iron boards; the iron boards with the MgB$_2$ samples were put into a tube furnace, which was evacuated and Ar gas of different purities was introduced. The samples were sintered in the tube furnace at 700°C for 30 minutes with the protection of the Ar gas. Four different levels were used: ultra high purity (UHP), high purity (HP), welding grade (WGP) and 0.1% Oxygen mixed with high purity Ar gas (01O). In these gases, the main impurities include O$_2$, H$_2$O, and N$_2$. The manufacturer provided compositions of these four gases are listed in Table 1.

**TABLE 1. Composition of Ar gas.**

| Gas                | Purity minimum % | Max impurity (ppm) | O$_2$ (ppms) |
|--------------------|------------------|--------------------|-------------|
| Ultra high (UHP)   | 99.999           | 10                 | 1           |
| High purity (HP)   | 99.997           | 30                 | 5           |
| Welding grade (WGP)| 99.99            | 100                | <25         |
| 0.1% O$_2$ (01O)   | 99.9             | 1030               | 1000        |

The sintered pellets were polished down to size of $1 \times 2 \times 3$ mm rectangular shaped pieces. The samples were measured with a Quantum Design Physical Properties Measurement System (9 Tesla PPMS) with the magnetic field parallel to the longest dimension of the samples. The critical current density was derived from the M-H loop by using the Bean critical state model $J_c = 12\Delta M d / (3b-d)$, where b and d are the dimensions of the sample perpendicular to the applied field and b > d. $\Delta M$ is the width of the hysteresis loop between the descending and ascending branches of the M-H loop. Resistivity measurements were carried out using the Quantum Design PPMS system on 1-cm-long samples obtained from the same batch. The upper critical field $H_{c2}$ and irreversibility field $H_{irr}$ for the samples were evaluated from the $\rho$-$T$ curves by standard of 90% and 10% points on the curve respectively. A Jeol 6460A Scanning Electron Microscopy (SEM) was used to watch the morphology and Philips PW1730 X-ray diffraction (XRD) was used to analyze the phase composition with Cu Kα radiation. Continuous scanning was used with scanning rate of 2°/min and step size of 0.02°.

**Results and discussion**

**Superconducting properties**

The superconducting transition temperature was determined from magnetic moment measurements performed as a function of temperature in a 50 Oe, 117 Hz AC field in zero field cooling (ZFC) mode. The results for all the samples are plotted in Figure 1. The three samples sintered under higher purity Ar gas show $T_c$ at a temperature of around 33K which is lower compared with pure MgB$_2$ samples.
The $T_c$ decrease is due to SiC doping. The transition temperature width for these three samples is also similar. However, the $T_c$ of the sample sintered under 0.1% O$_2$ mixed argon gas showed different behaviour to the other samples in that the transition for the 0.1% O$_2$ argon gas treated sample contains two steps. The transition starts at 34 K with another step at 30.5K. This two step transition probably is a result of the disorder introduced by impurity phases such as MgO. It may also be a result of deficiency of Mg caused by excessive O$_2$ to react with Mg to form MgO.

Figure 1. AC magnetization of MgB$_2$ sintered under different atmosphere. Inset shows the enlarged part of the onset transition temperature area

The $J_c$ of the samples derived from the M-H loops is shown in Figure 2. We can only measure $J_c$ at fields lower than 8 T due to the limitation of the equipment, so the $J_c$ at magnetic fields higher than 8 T is unknown. The $J_c$-H performance of the samples is ranked differently at 20K and 5K. At 5 K, all the samples show a similar level of $J_c$, with the 0.1% O$_2$ argon treated sample having a slightly higher $J_c$. At 20 K, however, the 0.1% O$_2$ argon treated samples show the lowest $J_c$ compared with the other samples. The inconsistent performance for the 0.1% O$_2$ containing Ar at 5K and 20K may be
explained as follows: At 5K, the superconducting current is carried by the higher $T_c$ (34K) component as well as the lower $T_c$ component; the $J_c$ contribution from the lower $T_c$ component somehow weakens at 20 K and results in the $J_c$ decrease. At 20K, the ultra-high Ar treated samples had lower $J_c$ at higher field, which could be a result of lack of pinning sites because the higher purity level Ar gas meant less impurity in the resultant MgB$_2$. It is suggested the sintering Ar atmosphere does not necessarily have to be ultra high-purity, but should not contain higher than 0.1% O$_2$ in the Ar in order to maintain a high $J_c$ at 20 K at higher magnetic field.

The temperature dependence of the resistivity under different magnetic fields was measured using the PPMS. The values of $\rho$ at $T = 40$ K and the residual resistivity ratio, RRR= $\rho_{300}$ / $\rho_{40}$, were calculated from the set of R-T curves at different magnetic fields, and the results for the measured samples are shown in Table 2. The higher resistivity compared to pure MgB$_2$ could be a result of SiC doping and the effect of the Ar impurity level. When the impurity level of the Ar increases, the resistivity also increases, which hints that there has been an increase of the impurity level inside the MgB$_2$ samples. $1/F$ is the fractional area of the sample that carries the supercurrent, and $1/F$ for the different samples was calculated from the expression $\Delta \rho = F[\Delta \rho_{sc}]$ [9], where $\Delta \rho$ is the change in resistivity from 300K to 40K for single crystal MgB$_2$, typically 4.3 $\mu$Ω cm [10], $\Delta \rho_{sc}$ is the change in resistivity from 300K to 40K for our samples. $1/F$ for our samples is shown in Table 2. Note that as the impurity level of Ar gas increases the $1/F$ decreases.

**TABLE 2. Properties of samples sintered under different atmosphere.**

|          | $T_c$ (K) | $\rho_{40}$ (µΩcm) | $\rho_{300}$ (µΩcm) | RRR | $\Delta \rho$ (µΩcm) | $H_{irr}(20k)$ (T) | $1/F$ |
|----------|-----------|---------------------|---------------------|------|----------------------|-------------------|-------|
| Ultra high Ar | 33.0      | 65.9                | 95.6                | 1.45 | 29.7                 | 9.6               | 14.5% |
| Weld grade Ar  | 33.0      | 74.3                | 106.9               | 1.44 | 32.6                 | 9.8               | 13.3% |
| 0.1% O2 Ar     | 30.5      | 80.6                | 114.6               | 1.42 | 34.0                 | 7.6               | 12.6% |

The upper critical field $H_{c2}$ and irreversibility field $H_{irr}$ for the samples were evaluated from the $\rho$-$T$ measurement. Figure 3 shows that temperature dependence of $H_{c2}$ and $H_{irr}$. Note that the sample

Figure 3. Upper critical field and irreversibility field derived from R-T measurements
sintered under welding grade Ar gas has higher $H_{c2}$ and $H_{irr}$. The ultra high purity Ar sintered samples and the 0.1% $O_2$ samples show weaker $H_{c2}$.

**Phase composition and microstructure**

XRD was used to analyze the phase composition, and the results are shown in Figure 4. All the samples contain MgB$_2$ as the main phase, as well as Mg$_2$Si and MgO as impurity phases. Note that the angular positions of the (100) peaks and the (002) peaks of MgB$_2$ show no obvious shifting among all samples sintered under different Ar atmospheres, indicating that there are no crystal lattice parameter changes for either the a or c axes across all the samples. This suggests the amount of oxygen incorporated into the lattice is negligible.

The morphology of the samples was examined by using SEM, as shown in Figure 5. All the samples contain grains of about 100 nm. It is typical for the samples to possess significant pores and some micro cracks as mentioned in our previous study [11-12]. There are no observable differences in the morphology among the samples treated in different atmospheres.

Figure 4. XRD patterns for four samples

Figure 5. Microstructure of the samples

Figure 6. Correlation of $J_c$ and the amount of MgO

(a. UHP  b. HP  c. WGP  d. 01O)

Figure 6 illustrates the correlations between $J_c$ and the amount of MgO. The amount of MgO was indicated by the ratio of the MgO (220) peak intensity to the MgB$_2$ (102) peak intensity. At 5 K and 8 T, $J_c$ increases as the Ar impurity level increases. At 20 K and 4 T, the welding grade Ar and the high purity Ar treated samples show the same level of $J_c$, but the ultra-high Ar treated sample has slightly lower $J_c$, while the 0.1% $O_2$ mixed Ar sample shows the poorest $J_c$. The amount of MgO in the samples is different from one sample to another. The MgO increases with the Ar impurity level. The Energy dispersive x-ray spectroscopy analysis (not shown) for all the samples shows the same trend.
Figure 6 indicates that the 0.1% O\textsubscript{2} mixed Ar sample has the highest amount of MgO as well as the lowest J\textsubscript{c} at 20 K and 4 T but the highest J\textsubscript{c} at 5K and 8T. The J\textsubscript{c} and T\textsubscript{c} performance probably are dominated by the amount of MgO impurity.

![Figure 7. Normalized pinning force](image)

The pinning force for the four samples was calculated by using the formula $F_p = J_c(B) \times B$. The results are shown in Figure 7. The 0.1% O\textsubscript{2} mixed Ar treated samples has the lowest pinning force at high magnetic field.

**Conclusion**

The effects of the sintering atmosphere on MgB\textsubscript{2} superconducting properties were studied. It was found that the impurity level in the protective Ar atmosphere had only a slight effect on the superconducting properties when the impurity level was lower than 0.1%. Welding grade Ar is pure enough to be a protective gas, there is no need to use Ultra high purity Ar gas. When the samples were sintered in Ar with 0.1% oxygen impurity, the J\textsubscript{c} at higher temperature (20K) and high field decreased. An excessive amount of MgO in the sample is blamed for the deterioration of the superconducting properties.

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