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Abstract

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Keywords

carbon, homogeneous, nano, density, current, critical, enhanced, temperature, low, doping, formed, significantly, rapidly, grains, mgb2

Disciplines

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Significantly enhanced critical current density in nano MgB₂ grains formed at low temperature with homogeneous carbon doping

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Abstracts

High performance MgB₂ bulks using carbon-coated amorphous boron as boron precursor were fabricated by Cu-activated sintering at low temperature (600°C, below the Mg melting point). Dense nano-MgB₂ grains with a high level of homogeneous carbon doping were formed in these MgB₂ samples. This type of microstructure can provide a stronger flux pinning force, together with depressed volatility and oxidation of Mg owing to the low-temperature Cu activated sintering, leading to the significant improvement of critical current density (J_c) in the as-prepared samples. In particular, the value of J_c for the carbon-coated (Mg_{1.1}B₂)Cu_{0.05} sample prepared here is even above 1×10^5 A/cm² at 20 K, 2 T. The results herein suggest that the combination of low-temperature Cu activated sintering and employment of carbon-coated amorphous boron as precursor could be a promising technique for the industrial production of practical MgB₂ bulks or wires with excellent J_c , as the carbon-coated amorphous boron powder can be produced commercially at low cost, while the addition of Cu is

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very convenient and inexpensive.

Keywords: carbon coated boron; MgB₂; critical current density

1. Introduction

The intermetallic compound MgB₂ with the transition temperature (T_c) of 39 K has been the focus of worldwide attention, due primarily to its potential for practical applications [1]. Its electrical application is largely determined by the current carrying capability, i.e. the critical current density (J_c) of the superconductor at the application temperature. Although considerable progress has been made in the fabrication and performance of MgB₂ to date [2], the critical current density in MgB₂ is still below optimized material [3].

As is well known, flux pinning and grain connectivity are the critical factors determining the performance of J_c in the Type II superconductors. A significant improvement might be achieved in J_c of MgB₂ if one technique could enhance the flux pinning strength and increase the grain connectivity at the same time. Low-temperature (below the melting point of Mg) sintering, which was developed in recent years, is potentially such a technique [4-6]. Low sintering temperature can significantly depress volatility and oxidation of Mg, which leads potentially to improved connectivity between the MgB₂ grains. In addition, sintering at low temperature can also prevent MgB₂ grain coarsening, allowing refined grains to be obtained, which enhances grain-boundary pinning. Both factors are responsible for the improvement of critical current density in samples sintered at low temperatures

compared to those processed above the melting point of Mg. The reaction between magnesium and boron at low temperature, however, generally takes a very long time to form the complete MgB_2 phase due to the low diffusion rate of atoms in the solid state reaction type below the melting point of Mg [4, 7]. Many efforts have been made, including ball milling, the usage of nano-Mg precursor, and metal doping, to lower the formation temperature and shorten the processing time of MgB_2 [8-16]. Among these methods, metal doping as Ag, Sn, Bi, Se, Te or Mg_2Cu were used [11, 14, 13 and 15 (Mg_2Cu), 16], as well as minor Cu doping [12, 17], was proved to be the most convenient, effective, and inexpensive way to improve the formation of MgB_2 during the low-temperature reaction. In our previous studies [18-20], the mechanism behind the accelerated phase formation of MgB_2 by Cu addition was also investigated based on the activated sintering theory [21].

Although Cu addition is the most effective activator during the low-temperature sintering of MgB_2 superconductor, the improvement in J_c (in particular, at high magnetic fields) for MgB_2 samples prepared by Cu-activated sintering at low temperature still cannot meet the requirements of applications, and more efforts are needed to further enhance J_c . On the other hand, it is now well established that carbon doping can obviously improve the J_c performance of MgB_2 at high fields by the substitution of carbon onto boron lattice sites [22, 23]. Based on this background, a low-cost and practical method for fabricating MgB_2 superconductors with significantly improved J_c may be obtained potentially by combining the advantages of Cu-activated sintering at low temperature and carbon doping. Evidently, choosing the

appropriate approaches that can effectively introduce carbon doping during the low temperature sintering is fundamental to the successful application of this method. Based on previous studies [2, 24-28], not all carbon doping techniques that are effective in the high-temperature synthesis process of MgB_2 are still available in their low-temperature synthesis process. It is proposed that only those approaches that are able to release highly active C before the commencement of solid-solid reaction between Mg and B can lead to the effective carbon substitution for B during the low-temperature synthesis.

In the present work, carbon-coated amorphous boron powder prepared by Pavezyum company was employed as the boron precursor, with hope of providing sufficient homogeneous carbon doping for low temperature Cu-activated MgB_2 synthesis. Combining thermal analysis of the synthesis process, phase composition identification, detailed microstructure observations, and superconducting properties measurements, it was found that dense nano- MgB_2 grains with a high level of homogeneous carbon doping were formed in these MgB_2 samples using carbon-coated boron as a precursor that were prepared by Cu-activated sintering at low temperature. This synthesis method is responsible for the significantly improved J_c of the present samples compared to MgB_2 samples chemically doped with nano-SiC and other carbon-based dopants, with sintering at either low temperature or high temperature in previous studies [23-29].

2. Experimental

Commercial carbon-coated amorphous boron powders used in present work were from Pavezyum Advanced Chemicals (PAVEZYUM) [30]. These powders were produced through pyrolysis of a mixed gas consisting of diborane gas (B_2H_6), hydrogen, and hydrocarbon (C_xH_y) under inert conditions. There is always hydrogen gas present in the gas stream, which enables a reducing atmosphere and provides protection against oxidation. At the same time, it can enhance the thermal conductivity during the pyrolysis. The carbon addition is based on the simultaneous decomposition or pyrolysis of gaseous hydrocarbon (C_xH_y) in the furnace with the B_2H_6 . The temperature interval is enough to paralyze both gases, and it is thought that freshly formed spherical boron particles are coated at this stage with again freshly formed active carbon.

According to the elemental analyzers from Laboratory Equipment Corporation (LECO), the C percentage in the carbon-coated amorphous boron powder used in present work is about 2.30 wt. %. We also investigated the microstructure of this powder by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) and found that the nanosize amorphous boron particles (about 50 nm in size) were homogeneously coated by thin layers of carbon (see Fig. 1) within the observed area. Herein, the advantage of employing this kind of carbon-coated boron as a precursor is that this thin carbon layer on the surface of the boron particle is highly active and could introduce sufficient carbon doping at low sintering temperature. Moreover, carbon doping introduced in this way should be very

uniform.

Bulk samples of MgB_2 were prepared by a Cu-activated sintering method at low temperature. Carbon-coated amorphous boron powder, Mg powder (99.5% purity, 100 μm in size), and Cu powder (99.7% purity, 3 μm in size) were mixed in a molar ratio of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05). Herein, the amount of Cu addition was determined according to a previous study [15, 18], and the excess amount of 0.1 Mg was introduced to compensate for the oxidation of Mg as well as the formation of Mg-Cu alloy during the sintering process. Then the mixed powder was pressed into cylindrical pellets ($\phi 8 \times 1.5$ mm) under a pressure of 10 MPa.

In order to acquire kinetic information during the low-temperature sintering process for the Cu-added MgB_2 using carbon-coated boron precursor, all pellets were firstly heated and analyzed simultaneously using a high-resolution Netzsch DSC 404C Differential Thermal Analysis (DTA) apparatus under protection of argon gas. A heating rate of $10^\circ\text{C}/\text{min}$ was applied from room temperature to 800°C .

According to the differential scanning calorimetry (DSC) curves of all samples, one temperature, 600°C , was generally selected as the sintering temperature for all the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ samples to fabricate the MgB_2 bulks. All the samples were isothermally sintered at this temperature for 5 h. The microstructure and phase composition of the sintered samples were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Based on XRD data, the lattice parameters of these prepared samples were determined by Rietveld refinement using FullProf software. The magnetization of the sintered samples was measured using a physical properties

measurement system (PPMS). The measured cuboid samples are cut from the sintered bulks and their corresponding size is about $4 \times 2 \times 1$ mm. Then, the T_c was obtained from the temperature dependence of the normalized zero-field-cooled (ZFC) magnetization (the applied magnetic field is 50 Oe), and the J_c was calculated from the width of magnetization hysteresis loops (ΔM), based on the extended Bean model.

3. Results and discussion

The DSC curves of pure and Cu doped MgB_2 samples with carbon coated amorphous boron are presented in Fig. 2 as a function of the sintering temperature. It can be seen that the sintering process for the MgB_2 bulk with carbon-coated amorphous boron features two distinct exothermic peaks from room temperature to 800°C , which is slightly different from the case of MgB_2 bulks with amorphous boron in previous studies [2, 19]. In the case of MgB_2 bulks with amorphous boron, there are generally three orderly exothermic peaks corresponding to the solid-solid reaction, the melting of Mg, and the solid-liquid reaction. Moreover, one can also see that the intensity of the first exothermic peak in these carbon-coated samples is stronger than that of a sample made with amorphous boron, accompanied by a decrease in the peaking temperature of the second exothermic peak. The explanation is that carbon-coated amorphous boron is more active than amorphous boron and can better react with solid Mg. Consequently, most of the Mg can be consumed in the solid state before it melts, and thus, no obvious peak owing to Mg melting can be recognized in the DSC curve of the carbon-coated samples in the present work. The $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ samples with $x =$

0.03 and 0.05 experience a similar process to the sample without Cu addition, except that the peaking temperature of both exothermic peaks decreases dramatically with increasing Cu addition, which indicates that Cu addition can also accelerate the reaction between Mg and carbon-coated amorphous boron to form MgB_2 phase, just as in the case of MgB_2 with amorphous boron, following the activated sintering mechanism [19]. This conclusion can be further confirmed by the XRD results on the corresponding MgB_2 samples sintered at low temperature.

According to the DSC curves, one characteristic temperature, 600°C , was selected as the reaction temperature to synthesize the bulk MgB_2 , which guarantees that MgB_2 phase can form as rapidly as possible in the Cu-added samples, while the volatility of Mg can be minimized. Fig. 3 shows the XRD patterns of the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03, \text{ and } 0.05$) samples with carbon-coated boron prepared by sintering at 600°C for 5 h. It is found that the MgB_2 sample without Cu addition consists of Mg as the main phase and MgB_2 as the minor phase. This result indicates that the reaction between Mg and carbon-coated boron is still very slow at such a temperature, and only a small amount of MgB_2 can be formed in the carbon-coated sample without Cu addition. On the other hand, in the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0.03 \text{ and } 0.05$) samples sintered at the same temperature, MgB_2 is present as the main phase with MgCu_2 phase as the minor phase. Moreover, as the amount of Cu addition increases, the intensity of the MgB_2 peaks becomes stronger. This result, consistent with the DSC results shown above, suggests that the formation of MgB_2 phase in the samples where carbon-coated boron is used as precursor can be accelerated as well by Cu addition during the sintering process.

Generally, carbon doping decreases the lattice parameter a , while it has no obvious influence on lattice parameter c in the MgB_2 lattice. In order to verify whether carbon doping was introduced effectively into the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0.03$ and 0.05) samples with carbon-coated boron prepared in the present work, their MgB_2 lattice parameters were calculated based on the XRD data. It is found that lattice parameter a of these two samples is obviously decreased to $3.0731 \text{ \AA}$ and $3.0712 \text{ \AA}$, respectively, which are both smaller than that of standard MgB_2 bulks with amorphous boron, while lattice parameter c remains almost unchanged. According to Avdeev et al.'s study [31], the level of C substitution, x in the formula $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$ can be estimated as $x = 7.5 \Delta(c/a)$, where $\Delta(c/a)$ is the change in c/a compared to a pure MgB_2 sample. In the present case, the actual amount of carbon doping in the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.03}$ and $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ samples is 0.023 and 0.026 , respectively, which indicates that usage of carbon-coated boron as precursor can effectively introduce carbon doping at low temperature and that Cu addition can promote this process to a certain extent. Compared to other approaches that introduce carbon doping at low sintering temperature (see table 1) [24, 27, 28, 32], the level of carbon doping introduced by carbon-coated boron in present work is higher, which must be attributed to the higher activity of the carbon layer on the surface of the boron particles.

Fig. 4 shows SEM images of the microstructures of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05) samples after sintering at 600°C for 5 h. It is observed that the MgB_2 sample without Cu addition that was sintered at low temperature is porous, and no regular MgB_2 grains can be easily recognized (see Fig. 1a), even though highly active

carbon-coated amorphous boron was employed as precursor. On the other hand, the MgB_2 samples with Cu addition sintered under the same conditions consist of large amounts of uniform refined MgB_2 grains. These samples are also denser than the samples without Cu addition because all those MgB_2 grains were formed as the major component and in better connection with each other (see Fig. 4b, 4c, and 4d). Even compared to the Cu-doped MgB_2 samples with amorphous boron, or Cu and other carbon-based chemically co-doped MgB_2 samples sintered at low temperature in previous studies [14, 27-29], the MgB_2 grains in the samples prepared herein are much smaller (about 100–200 nm, see Fig. 4d) and more homogeneous. Actually, this kind of nanosize MgB_2 grain can only be observed in previous studies in MgB_2 samples fabricated after long ball-milling treatment of precursors and subsequent sintering [33-35]. Since the grain size of the MgB_2 as it is formed depends on the particle size of the boron powder precursor [36, 37], it is easy to understand this result, given that the boron precursor in the present work, carbon-coated boron particles prepared by pyrolysis of mixed diborane (B_2H_6), hydrogen, and hydrocarbon (C_xH_y) gas, is more refined and homogeneous than amorphous boron (see Fig. 1). Moreover, the low sintering temperature in the present case can also prevent the MgB_2 grain coarsening that always occurs during high temperature sintering.

The temperature dependence of the normalized ZFC magnetization for the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05) samples after sintering at 600°C for 5 h is presented in Fig. 5. The sample without Cu addition exhibits weak superconductivity due to the minor MgB_2 phase. The T_c values of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.03}$ and $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$

sintered at low temperature both appear similar to that of a traditional MgB_2 sample with amorphous boron sintered at high temperature, except that there is a slight depression in T_c . This might be attributed to the C substitution for B. With Cu addition increasing from 3at% to 5at%, one can see that the T_c is slightly decreased, which should result from more C substitution for B, as well as more MgCu_2 impurity, existing in the 5 at% Cu doped sample. The measured J_c - H characteristics of the low-temperature sintered $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0.03$ and 0.05) samples are shown in Fig. 6. As references, the J_c - H characteristics of a Cu-doped MgB_2 sample and of a Cu and nano-SiC multi-doped MgB_2 sample are presented in Fig. 6 as well. (The multi-doped sample exhibited the best reported J_c performance among all the low temperature sintered MgB_2 samples in previous studies [29].) Both of these reference samples were made from amorphous boron precursor and subjected to low temperature sintering under the same conditions as the present Cu-added samples made from carbon-coated amorphous boron precursor. The sample without Cu addition sintered under the same conditions (not shown) exhibits lower J_c values (less than 1×10^3 A/cm²), mainly due to the small fraction of MgB_2 phase, and thus, the corresponding J_c - H curve is not presented here. Although there some MgCu_2 impurity exists in the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.03}$ and $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ sintered at low temperature, these samples exhibit excellent J_c (above 1×10^5 A/cm² in the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ sample at 2 T, 20 K). Especially at high fields, the level of enhancement in J_c of these two samples is much higher than those of the Cu and the Cu + nano-SiC co-doped samples, and also other carbon-based chemically doped samples sintered at low temperature [27-29, 32].

According to our previous studies [2, 14, 19], MgCu_2 impurity mainly concentrates around the voids and is seldom embedded in the MgB_2 matrix, which hardly degrades the grain connectivity of MgB_2 phase and thus has no negative effect on the performance of J_c for these two samples. Besides, higher density and less MgO impurity in our prepared samples due to low temperature sintering can obviously enhance the grain connectivity and thus further improve J_c , especially at low fields [2, 14]. More importantly, as discussed above, the level of carbon doping introduced by carbon-coated boron in present work is higher and more homogeneous than for other types of carbon-based chemical doping. Meanwhile, using carbon-coated boron as precursor can also lead to more refined MgB_2 grains, which are supposed to provide more grain boundary pinning. Both factors contribute to the significantly improved J_c at high fields. Further analysis of the flux pinning behavior in terms of flux pinning force can provide us with deeper insights. Fig. 7 shows the normalized pinning force F_p/F_{pmax} as a function of reduced magnetic field h in the as-prepared samples with $h = H/H_{irr}$, where H_{irr} is the irreversibility field. Flux pinning force per unit area, or pressure, $F_p = -J_c \times B$, defines J_c in Type II superconductors and is determined by the microstructure and nanostructure of the sample. The irreversibility field (H_{irr}) has been estimated by extrapolating the $J_c^{1/2}H^{1/4}$ vs. H curve to the horizontal axis, also called the Kramer extrapolation. According to the Hughes' study [38], if the grain boundary pinning is predominant, the peak of the F_p/F_{pmax} is expected to be located at $h = 0.2$. In the present study, the peak of F_p/F_{pmax} in the Cu-doped MgB_2 sample with amorphous boron precursor fabricated at low temperature is located at about $h = 0.2$,

which indicates that the grain boundary pinning is the predominant pinning mechanism in this sample. On the other hand, the peak of the pinning force curves in both the nano-SiC and Cu co-doped MgB_2 sample and the Cu-doped MgB_2 sample with carbon-coated boron sintered at low temperature are shifted towards high field, which reveals the additional pinning centers supposed to result from carbon doping. Besides, more refined MgB_2 grains and nano impurities in these two samples may also contribute to the additional pinning centers. The peak in the pinning force curve for the Cu-doped MgB_2 sample with carbon-coated boron is shifted towards even higher field than that of the nano-SiC and Cu co-doped sample, indicating more carbon doping in this sample.

It is worth noting that the J_c performances of the low-temperature sintered $(\text{MgB}_2)\text{Cu}_{0.03}$ and $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ samples with carbon-coated boron are even better than some of carbon-based chemically doped samples sintered at high-temperature across the whole field [22-23, 25, 39]. This can be mainly attributed to the higher density and the presence of less MgO impurity resulting from the depressed volatility and lesser tendency of Mg to oxidize, respectively, during the low-temperature Cu-activated sintering. On the other hand, the value of magnetic J_c in our prepared samples is still lower than transport J_c in the $\text{C}_4\text{H}_6\text{O}_5$ doped MgB_2 wires fabricated by low temperature sintering after cold high pressure densification (CHPD), as shown in our previous study [40]. This means that the J_c of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ bulks and wires with carbon-coated boron precursor could be further improved in future via pressure effect, such as CHPD and hot isostatic pressure (HIP).

4. Conclusions

In summary, MgB_2 bulks with carbon-coated boron used as precursor were synthesized at low temperature by Cu-activated sintering. The usage of carbon-coated boron in the present work resulted in uniform refined MgB_2 grains, as well as a high level of homogeneous carbon doping in the MgB_2 samples. These factors, combining the advantages of the carbon-coated boron with the advantages of Cu-activated sintering at low temperature, led to significant improvement of J_c . The value of J_c in the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ sample prepared here is even above $1 \times 10^5 \text{ A/cm}^2$ at 2 T, 20 K, which is higher than for other undoped and doped MgB_2 samples sintered under various conditions. These results suggest that low-temperature Cu-activated sintering combined with employment of carbon-coated amorphous boron as precursor could be a promising technique to produce practical MgB_2 bulks or wires with excellent J_c on an industrial scale. This is because the carbon-coated amorphous boron powder can be produced commercially at low cost, while the addition of Cu is very convenient and inexpensive.

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Table and Figure captions

Table 1 Comparasion of actual carbon doping level and J_c among low temperature sintered MgB_2 samples using various carbon doping methods.

Fig. 1 TEM images of carbon-coated nanosize amorphous boron particles prepared by the pyrolysis technique.

Fig. 2 DSC curves of pure and Cu-doped MgB_2 samples with carbon coated amorphous boron. The DSC curve of undoped MgB_2 samples with amorphous boron was also present as a reference.

Fig. 3 XRD patterns of the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05) samples with carbon-coated boron prepared by sintering at 600°C for 5 h.

Fig. 4 SEM images of the microstructures of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05) samples with carbon-coated boron after sintering at 600°C for 5 h, with (a) $\text{Mg}_{1.1}\text{B}_2$, (b) $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.03}$ and (c) $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$. High-resolution SEM image of $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ sample is also presented in (d) to allow better observation of MgB_2 grains in the Cu-doped sample.

Fig. 5 Temperature dependence of normalized ZFC magnetization for the $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0, 0.03$ and 0.05) samples with carbon coated boron after sintering at 600°C for 5 h.

Fig. 6 Measured J_c - H characteristics of the low-temperature sintered $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_x$ ($x = 0.03$ and 0.05) samples with carbon coated boron at 20 K. The inset is J_c - H characteristics of these two samples measured at 4.2 K. Besides, the J_c - H characteristics of a both Cu and nano-SiC multi-doped MgB_2 sample and of a solely

Cu doped sample, both made with amorphous boron precursor and sintered under the same conditions, are also presented here as references.

Fig. 7 Normalized pinning force F_p/F_{pmax} as a function of reduced magnetic field h for the low-temperature sintered $(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.03}$ sample, with $h = H/H_{irr}$. The corresponding F_p/F_{pmax} curves of both the Cu and nano SiC multi-doped MgB_2 sample and the solely Cu doped sample, both with amorphous boron precursor sintered under the same conditions, are also presented as references.

Table 1

samples	sintering condition	x in $\text{Mg}(\text{B}_{1-x}\text{C}_x)_2$	J_c (20K, 2T) A/cm^2
MgB_2 + 8 at% graphene Solid state mixing [24]	650°C, 5 h	0.023	8.7×10^4
MgB_2 + 3 wt% SiC Solid state mixing [32]	650°C, 1 h	0.010	5.5×10^4
MgB_2 + 10 at% $\text{C}_4\text{H}_6\text{O}_5$ Chemical solution [27]	600°C, 4 h	0.023	4.5×10^4
$(\text{MgB}_2)_{0.97}\text{Cu}_{0.03}$ + 3 wt% Gly Chemical solution [28]	600°C, 15h	0.019	3.9×10^4
$(\text{Mg}_{1.1}\text{B}_2)\text{Cu}_{0.05}$ with carbon coated boron precursor this work	600°C, 5h	0.026	1.02×10^5

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7