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Physica C 412–414 (2004) 1174–1178
PHYSICA C
www.elsevier.com/locate/physc

Microstructure and superconductivity of MgB_2 synthesized by using Mg-based compound powders

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Received 29 October 2003; accepted 25 November 2003
Available online 1 June 2004

Abstract

MgB_2 can be synthesized through a new route using Mg_2Cu instead of pure Mg. When the temperature is elevated to around the melting point of Mg_2Cu (568 °C), the T_c for Mg_2Cu/B Fe-sheathed wires increases rapidly to about 37.5 K. Mg_2Cu with its low melting point promotes the diffusion reaction to form a high T_c MgB_2 at low temperatures. A lot of second phases forms with small amounts of MgB_2 in the core of the wires. However, the transport J_c value, which is greater than 10^5 A/cm^2 at 4.2 K in ambient fields, is rather high. Since the J_c value is estimated from a net-cross-sectional area of MgB_2 it is expectedly high. Moreover, Mg_2 Cu/B/metal-substrate layered composites were also prepared in this study. After a heat treatment at 600 °C for 10 h in a vacuum, a 50 μm thick MgB_2 diffusion layer forms with a high-density microstructure. Cu is released from Mg_2Cu, and collects on the surface of the diffusion layer. This behavior of Cu is similar to that of the bronzed process used for Nb_3 Sn practical conductors.

PACS: 74.72.Yg; 74.62.–c
Keywords: MgB_2 compound; Superconducting wire; Diffusion process; Thick layer

1. Introduction

The discovery that MgB_2 exhibits superconductivity [1] sparked new interests into the practical conductor research because of its high critical temperature T_c of 39 K, simple binary chemical composition and relatively low material costs.

In order to achieve a reaction between Mg and B powders during the fabrication of MgB_2, the starting powder characteristics such as particle size and surface condition should be important. It is best to start with powders that have a fine particle size and are resistive to surface oxidization. In addition, it is desirable that the heat treatment be carried out at low temperatures because of the formation of fine MgB_2 grains. We investigated the synthesis of in situ MgB_2 wires and thick-film coated layers through the liquid–solid diffusion reaction between Mg_2Cu and amorphous B. Mg_2Cu is an intermetallic brittle compound so it is easy to fabricate Mg_2Cu fine particle powders by mechanical grinding. Moreover, Mg_2Cu has a lower melting point (568 °C) than that of pure Mg

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doi:10.1016/j.physc.2003.11.080

(650 °C), thus Mg_2Cu is expected to promote a diffusion reaction at low temperatures.

2. Experimental

Mg_2Cu ingot was made in an Ar atmosphere with a Tammann furnace. The ingot was then crushed and mechanically ground into a coarse powder of about 50 μm in average diameter. Phase identification was carried out with X-ray diffraction (XRD) analysis using Ni-filtered CuKα radiation for the coarse Mg_2Cu powder. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were also carried out for the coarse Mg_2Cu powder. Both TGA and DTA were carried out with an auto simultaneous instrument (Shimadzu: TGA-60H) in open air. The Mg_2Cu powder was mixed with amorphous B powder using an atomic ratio of Mg:B = 1:2. The average size of the amorphous B powder was a few tens of microns in diameter. The Mg_2Cu and B mixture was tightly packed into Fe tube (99.99% purity) with an outer diameter and inner diameter of 10 and 6 mm, respectively. Wire drawing was carried out using a grooved-roller and cassette-roller-dies. Precursor wires had a diameter of 0.72 mm. Normal precursor wires using pure Mg and amorphous B powders were also made for comparison. For the other study, a thick MgB_2 layer on a metal substrate was fabricated. Amorphous B layer (200 μm thick) was formed on the pure Nb substrate-tape by using a plasma spraying technique. Then, Mg_2Cu slurry using ethyl alcohol as a solvent was coated on the surface of the plasma-sprayed amorphous B layer creating Mg_2Cu/B/metal-substrate layered composites. Both the PIT Fe-sheathed wires and layered composites were heated to between 550 and 650 °C in a dynamic vacuum under a pressure of less than 10^{-3} Pa.

After heat treatment, T_c and transport critical current I_c (4.2 K) were measured by a DC four-probe method. I_c (4.2 K) measurements were made under magnetic fields up to 10 T using a superconducting magnet. J_c for the PIT Fe-sheathed wires is defined as the I_c divided by a total cross-sectional area of the powder filled core. Magnetic transition curves were also measured using a SQUID magnetometer (Quantum Design: MPMS-5). X-ray diffraction (XRD) analysis for the phase identification was made for both specimens, and microstructures were observed using a field-emission scanning electron microscope (FE-SEM). Elemental mapping and quantitative composition analysis were carried out with an energy dispersive X-ray (EDX) spectrometer.

3. Results and discussion

Fig. 1 shows the TGA–DTA results for Mg_2Cu and pure Mg. The Mg_2Cu melting point (568 °C) is lower than that of pure Mg (650 °C). Both weight ratios, Mg_2Cu and pure Mg, increase with increasing temperature, which indicates that both powders oxidize at high temperatures. However, the weight ratio for Mg_2Cu is smaller than that of pure Mg, therefore, Mg_2Cu should be more resistive to oxidation compared to pure Mg.

Fig. 2 shows the relationship between T_c versus temperature for Mg_2Cu/B/Fe and Mg/B/Fe wires. When the temperature is elevated to around the melting point of Mg_2Cu (568 °C), the T_c for Mg_2Cu/B Fe-sheathed wire specimens rapidly increased and reached about 37.5 K due to the formation of the MgB_2 phase through the liquid (Mg_2Cu)–solid (B) diffusion reaction. The T_c values are comparable to the reported values for

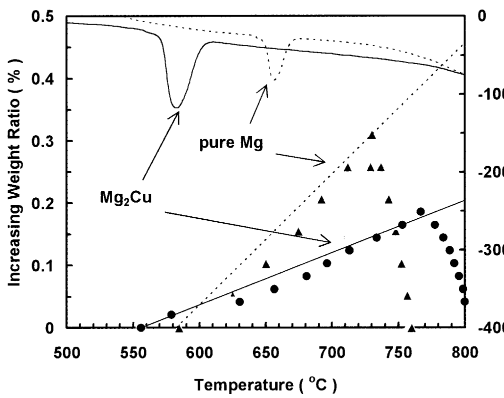

Fig. 1. Comparison of TGA–DTA results for Mg_2Cu and pure Mg. Solid circles and triangles represent increasing weight ratios calculated from TGA data for the Mg_2Cu and pure Mg, respectively.

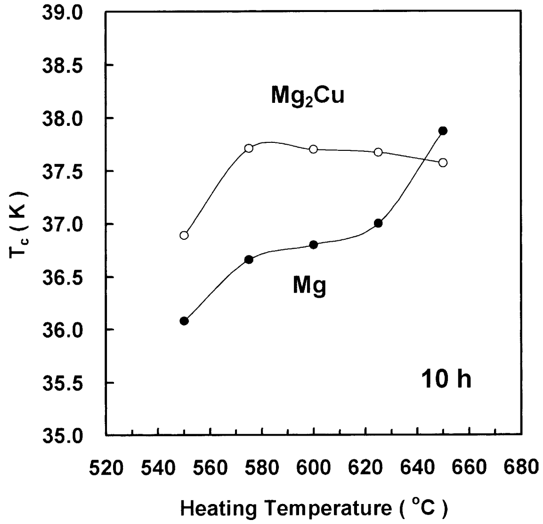

Fig. 2. T_c versus heating temperature for Mg_2Cu/B (open circle) and Mg/B (solid circle) Fe-sheathed wires. Heating time is fixed for 10 h.

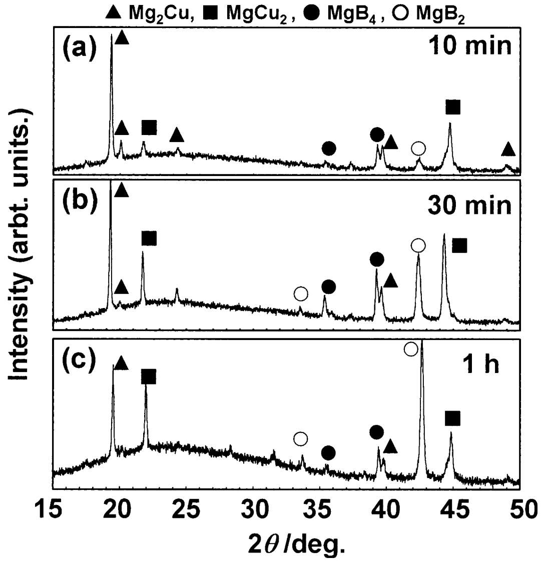

Fig. 3. XRD patterns of the Mg_2Cu/B Fe-sheathed wire reacted at 600 °C as a function of heating time. (a), (b) and (c) are for wires reacted at 10 min, 30 min and 1 h, respectively.

MgB_2 single crystal [2]. This result indicates that the MgB_2 superconducting phase can be synthesized through a new route using Mg_2Cu instead of pure Mg. At the same temperatures, MgB_2 also formed in the Mg/B Fe-sheathed wires. In this case, MgB_2 was synthesized by a solid (Mg)–solid (B) diffusion reaction through rather slower reaction.

Fig. 3(a), (b) and (c) show XRD patterns for Mg_2Cu/B Fe-sheathed wires reacted at 600 °C for 10 min, 30 min and 1 h, respectively. As the reactions progressed the Mg_2Cu decomposed and released Mg, thus changing the phase composition into $MgCu_2$. The Mg that was released reacted with amorphous B and formed the MgB_2 superconducting phases. These chemical reactions occurred within 10 min at 600 °C. No diffraction peaks for MgO were observed in Fig. 3. The intensity of diffraction peaks for MgB_2 became stronger with increasing heating time, however the volume fraction of MgB_2 was still small and a lot of second phases such as $MgCu_2$ remained in the core even though the specimens were heat treatment for 10 h. According to SEM observation, the second phases are as large as a few tens of microns in diameter and may become obstacles to the superconducting current flow. The transport current must flow like a percolation due to the weak linkage between MgB_2 grains. However, Mg_2Cu/B Fe-sheathed wire that reacted at 600 °C for 1 h shows a high transport J_c which was greater than 10^5 A/cm^2 at 4.2 K in a ambient field as shown in Fig. 4. The J_c (4.2 K)-B curve for the Mg_2Cu/B Fe-sheathed wire is comparable with a result reported by Goldacker et al. [3]. As expected, the J_c of the present Mg_2Cu/B wire should be very high since it is estimated from the net-cross-sectional area of MgB_2. An improvement in J_c for the PIT in situ wires using Mg_2Cu is promising if the volume fraction of second phases can be reduced by optimizing wire-fabrication conditions, such as the size of starting powders and the powder mixture ratio, etc. When fine second phase particles are dispersed in the wire core, it can also be expected that they will behave as effective flux pinning centers.

Fig. 5 shows the SEM image and EDX element mappings of the cross-section of Mg_2Cu/B/Nb tape-substrate composite reacted at 600 °C for 10 h in a dynamic vacuum. The diffusion layer that formed near the surface of the specimen was about 50 μm thick and showed a high-density microstructure. On the other hand, the plasma-sprayed

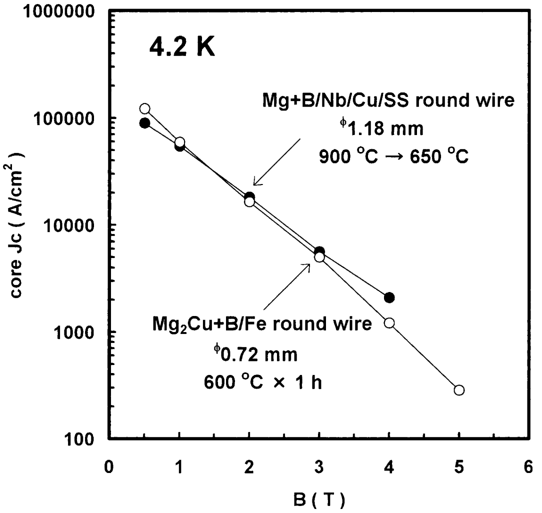

Fig. 4. J_c(4.2 K)-B curves for Mg_2Cu/B/Fe wire reacted at 600 °C for 1 h. Data reported by Goldacker et al. is attached for a comparison.

B layer shows porous and granular microstructures. When the Mg_2Cu on the plasma-splayed B layer melted, liquid Mg_2Cu easily infiltrated into spaces among amorphous B particles. However, most of the Cu collected on the surface of the diffusion layer with heat treatment. This behavior is similar to that of the bronze process used for Nb_3 Sn practical conductors. Its magnetic superconducting transition measured by SQUID appeared at about 38 K. The thick, high density MgB_2 layer may be promising for applications involving magnetic-shielding tubes or in the superconducting cavity.

4. Conclusions

Mg_2Cu exhibits a stronger resistivity to oxidation than that of pure Mg resulting in a reduced amount of MgO contamination. Mg_2Cu, which has a low melting point of 568 °C promoted the formation of MgB_2. Mg_2Cu changed into $MgCu_2$ with the decomposition and release of pure Mg. The Mg that was released reacted with B and formed MgB_2 superconducting phase by a liquid(Mg_2Cu)–solid(B) reaction at low temperatures. Although a lot of second phases such as Mg_2Cu formed in the core of the Mg_2Cu/B Fe-sheathed wires, its transport J_c exhibited a rather high value, which was over 10^5 A/cm^2 at 4.2 K in ambient fields. J_c estimated from the MgB_2

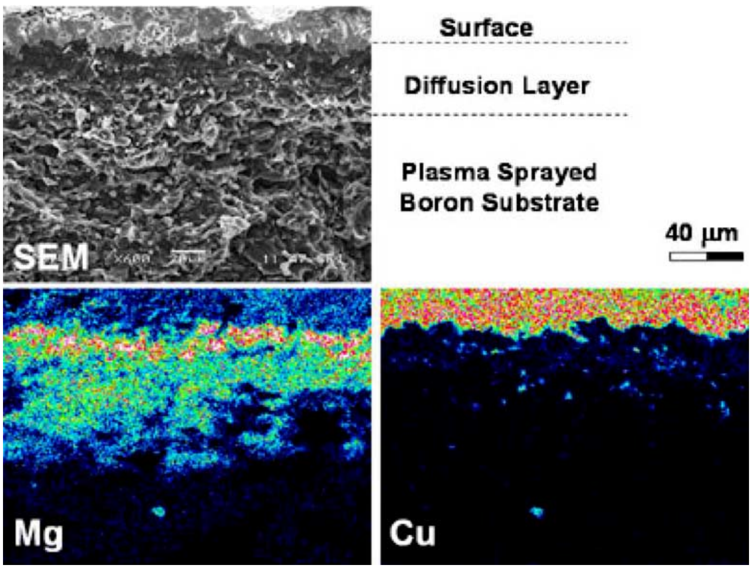

Fig. 5. SEM image and EDX element mappings of the cross-section of Mg_2Cu/B/Nb tape-substrate composite reacted at 600 °C for 10 h in a dynamic vacuum.

net-cross-sectional area should be very high. For the other study, the Mg_2Cu/amorphous B/metal-substrate layered composite that was prepared after a heat treatment at 600 °C for 10 h in a vacuum, formed a 50 μ m thick MgB_2 diffusion layer with a high density microstructure. Cu was released from Mg_2Cu, and collected on the outermost surface. This characteristic is similar to that of bronze processing for Nb_3 Sn practical conductors. A thick, dense MgB_2 layer may be promising for magnetic shielding tube or superconducting cavity applications.

Acknowledgements

The authors would like to thank Dr. A. Matsumoto of NIMS for his assistance with the 13 T superconducting magnet during J_c-B measurements. A part of this study was financially supported by the Industrial Technology Research Grant Program from New Energy and Industrial Technology Organization (NEDO) of Japan, and by the Budget for Nuclear Research of the Ministry of Education, Culture, Sports, Science and Technology.

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