Key Engineering Materials Vols. 264-268 (2004) pp. 1197-1200
online at http://www.scientific.net

Electrical and Microstructural Properties of Superconducting MgB_2/Mg Composites

M. Egilmez[1], A. Gunel[1], S. Okur[1], M. Tanoglu[2] and L. Ozyuzer[1]

[1]Department of Physics, Izmir Institute of Technology, Izmir, Turkey

[2]Department of Mechanical Engineering, Izmir Institute of Technology, Izmir, Turkey

Keywords: Superconductivity, Composites, MgB_2, Superconducting wire.

Abstract. MgB_2/Mg composites were prepared to improve mechanical properties of brittle superconducting MgB_2. MgB_2 and Mg powders were mixed at different weight ratios and uniaxially pressed in a cylindrical dye at 0.5 GPa and at various temperatures for two hours to prepare MgB_2/Mg composites. X-ray diffraction, SEM and EDX were used for phase identification and microstructural characterization. In addition to the main MgB_2 and Mg phases, the microstructural studies have indicated the presence of a minor amounts of second phases, namely MgO and B-rich compounds. The surface morphology, grain size and porosity ratio of the samples prepared under various temperatures were also investigated. The resistivity measurements were performed in the range of room temperature to 15 K. The effect of excess Mg and secondary phases on critical temperature of MgB_2/Mg composites were studied.

Introduction

It has been only two years passed after the discovery of superconductivity in MgB_2 at 39 K. The theoretical studies are in agreement for the mechanism behind superconductivity in MgB_2 [1,2] while there is no consensus on theory of high temperature superconductors (HTS) in past 16 years of their breakthrough [3]. On the application point of view, the small scale applications of MgB_2 are not promising due to two band superconductivity with a dominant small energy gap [4,5]. On the other hand, the large scale applications are promising and the MgB_2 superconductor wire technology is getting mature to be available in the market to replace Nb-Ti and Nb_3Sn [6]. The brittleness of MgB_2, as in Nb_3Sn and HTS, does not allow it to be used as a stand alone material. The novel methods have to be used to improve mechanical properties while maintaining its critical temperature (T_c) and critical current (J_c). One of the way to overcome this difficulty is to use a ductile metallic sheath, namely powder in tube (PIT) method [7-10]. This is the most studied method for former conventional superconductors and HTS [12-14]. Since silver is the only suitable cladding material for HTS, addition of some other materials in HTS strongly affects T_c and J_c of the superconductor. In addition, if the materials other than Ag are used for cladding, the diffusion of sheath degrades the superconducting properties of wire. PIT MgB_2 wires have also been fabricated using various cladding materials such as Fe, Cu, Ni, etc. Perhaps, the most important one is the cladding of MgB_2 with steel tube and observation of relatively high T_c and J_c values without any heat treatment. Recently, the metal composites are gaining popularity because of less reactivity of certain materials on MgB_2 [11]. In this study, MgB_2/Mg composites were prepared to investigate the effects of various sample preparation conditions on the electrical and microstructural properties. Here, Mg was employed as the matrix materials not only due to its ductility, but also the possibility of the compensation of any Mg loss from MgB_2 during composite preparation. Mechanical properties of prepared metal matrix composites are deferred to another article.

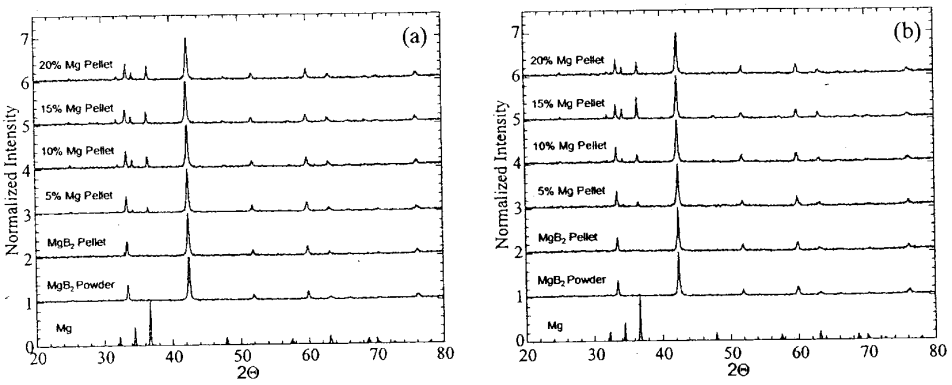

Figure 1(a) and 1(b). Powder x-ray diffraction patterns of Mg, MgB_2 powder, MgB_2 pellet and MgB_2/Mg composites with various Mg ratio pressed at 400 °C and 500 °C, respectively.

Experiment

Commercial MgB_2 powder (Alfa Aesar) and Mg powder (-270 mesh and 99.9% purity) were used for the fabrication of MgB_2/Mg composites. MgB_2 and Mg powders are mixed homogenously and uniaxially pressed under pressure of 0.5 GPa in a metallic dye. The dye was heated to 400 and 500 °C after the pressure applied. The decomposition temperature of MgB_2 and melting point of Mg are 950 °C and 654 °C, respectively. Therefore no reaction between MgB_2 and Mg is expected at the selected pressing temperatures. During pressing, the temperature was kept constant for two hours while maintaining the pressure and leaved to cool down to room temperature. The weight ratio of Mg to MgB_2 was 0, 5, 10, 15, and 20% for different batch of samples. The resulting pellets were about 0.9 mm thick and 15.6 mm in diameter. The phase identification of MgB_2/Mg composites was performed by an X-ray diffraction (XRD) and microstructural observations were carried out by SEM coupled with an energy dispersive x-ray (EDX) spectroscopy. The rectangular samples, 15.6x3.0x0.9 mm^3 in size, are diced from pellets and silver paint is used to attach current and voltage leads. The resistivity measurements were conducted in closed-cycle He cryostat using four-point probe method.

Results and Discussions

Fig. 1(a) and 1(b) show the XRD pattern of MgB_2/Mg composites prepared at 400 °C and 500 °C, respectively. We have also included patterns of Mg and MgB_2 powder. For clarity, the intensity of each spectrum is normalized at 2Θ value which shows maximum intensity. As the concentration of Mg increases within the composites, Mg peaks become detectable in the spectrum. The existence of Mg peaks indicate that there is no observable reaction between MgB_2 and Mg. Although the visible major phases are Mg and MgB_2, the close examination of XRD results indicates the possible presence of MgB_4 and MgO. The presence of secondary phases was also examined with EDX analysis which does not lead precise results for the secondary phases, i.e. existence of Mg and B with a weight ratio that suits the MgB_4, the stoichiometry does not always indicate the presence of MgB_4. In such a circumstance, one is not able to state the formation of MgB_4 by only relying on the EDX results which can refer the any combination of the Mg, B, MgB_2 and MgB_4. EDX results based on the relative atomic weights may be misleading especially for light substances or for substances with close atomic weights.On the other hand, the search match results of XRD data confirm that the amount of MgB_4 does not increase during the sample preparation

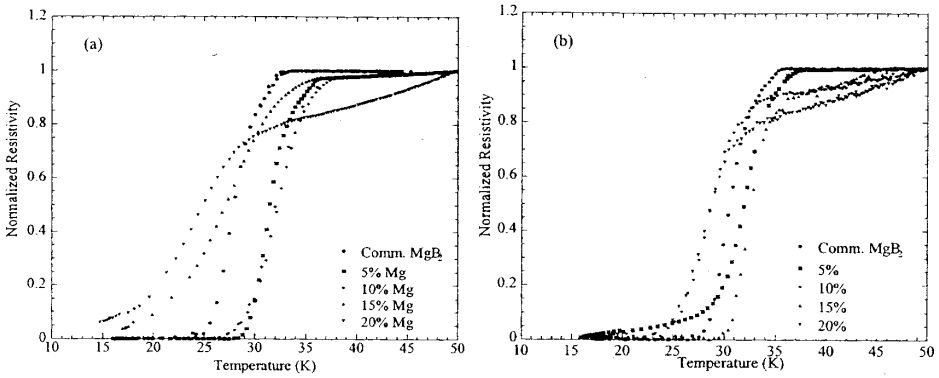

Figure 2(a) and 2(b) Normalized resistivity of MgB_2/Mg composites prepared at 400 °C and 500 °C respectively.

The presence of MgB_4 is undesirable in superconductor composite wire, since it is generally situated around grain boundaries with large mismatch in the crystal structures. As a result, the presence of MgB_4 causes a loose connection between grain boundaries. Excluding MgO, the secondary structures are observed in all of our samples and they probably originate from commercial powder. There is a slight increase of MgO phase, which might be occurred during the heat treatment. It is shown that the presence of MgO particles may enhance the superconducting properties by acting as pinning center. The MgO and MgB_4 were also detected in the XRD analysis of a similar study on hot isostatically pressed MgB_2 pellets of the same commercially available MgB_2 powders prepared around 900 °C [15]. Since our temperature range is relatively low for the formation of MgB_4, and the excess Mg prevents the formation of this phase, we do not expect an increase in the concentration of these impurities in the samples after the heat treatment. This is favorable, because any new phases degrade superconductivity of MgB_2.

SEM images of prepared samples show that the grain sizes of MgB_2 are around 0.3-5.0 μm for 400 °C heat treated samples, and around 0.2-5.0 μm for 500 °C heat treated samples. Even at first glance this impression is gathered from our SEM images and it is hard to state the result with great precision. We have been only able to study fractured surfaces because of the practical difficulties to prepare polished surfaces. The observation of actual grain spacing, sizes, distribution of grains and empty spaces was not obvious due to the complexity of the fractured surfaces. The grain size refinement generally observed either by drawing and rolling of metal-sheathed tubes [7] or addition of some impurities such as Ti and Zr [16].

Most evident effect of increasing Mg constituents is an increase in slope of the resistivity curve above the transition temperature as illustrated in Figs. 2(a) and (b). As we expected, the normal state conductivity of composites are increased with increasing Mg ratio. These restrict us to plot normalized resistivity in spite of resistivity. The resistivity in the Figs. 2(a) and (b) are normalized at their vale at 50 K. In normal state, the resistivity versus temperature graphs of samples including excess Mg has a slope strongly depends on the Mg concentration and when the superconducting transition begins the slope suddenly increases. The change in the slope above the T_c^{onset} results from temperature dependence of Mg resistance. Since Mg has relatively lower resistivity (1.6 μΩcm at 300 K) compared to MgB_2 (4.5 μΩcm at 300 K), the increasing concentration of Mg decreases resistivity of MgB_2/Mg composites in the normal state. Under the T_c^{onset}, the current percolate through superconducting MgB_2 phases and the slope in this part mainly determined by superconducting MgB_2 phases and consequently by their grain connectivity, grain size, porosity and purity. The broadening of superconducting transition is an undesired effect especially when the T_c^{zero} decreases considerably. As revealed Fig. 2, an increase of 100 °C in heat treatment in the applied temperature range leads to an improvement in T_c^{onset} values. This is probably due to increase

in grain connectivity and better fuse of Mg in empty spaces by decreasing porosity of the sample. For samples heat-treated at 400 °C, the increase in T_c^{onset} continues up to 10% Mg addition (T_c^{onset} =38.3 K). The value of the improvement is around 4.4 K relative to unsubstituted sample. On the other hand, T_c^{onset} for 15% Mg addition is still higher than unsubstituted sample. The amount of increase in T_c^{onset} for 10% Mg and 400 °C pressed samples relative to that of unsubstituted samples is 5.2 K. Similar case is also valid for samples prepared by 500 °C heat treatment with some exceptions. For these samples, T_c^{onset} continues to increase up to 15% Mg addition (T_c^{onset} =36.2 K). The maximum magnitude of the increase in the T_c^{onset} is obtained for 15% Mg and 500 °C pressed samples and that in the T_c^{onset} is reached for 5% Mg and 500 °C pressed samples (T_c^{onset} =37.3 K). Although T_c^{onset} value is better for 500 °C heat treated one among the pure samples, in the case of Mg substitution a best value is obtained for the sample of 10% Mg and 400 °C pressed samples. While normal state to the superconducting state transition region broadens with increasing concentration of Mg for the 400 °C heat treated samples, it fluctuates with increasing Mg concentration for the 500 °C heat treated samples.

In summary, we prepared MgB_2/Mg composites using uniaxial hot pressing. XRD results illustrate that the initial excess Mg constituent is still present in the final metal matrix composite in unreacted form. Microstructural studies performed by SEM and EDX indicate the possible presence of secondary phases such as MgB_4 and MgO in minor amounts. The temperature dependence of resistivity results of MgB_2/Mg composites demonstrates that while excess Mg improves normal state properties and the superconducting transition temperature.

Acknowledgements

This research is partially supported by TUBITAK (Scientific and Technical Research Council of Turkey) project number TBAG-2031. L.O. acknowledges support from Turkish Academy of Sciences, in the framework of the Young Scientist Award Program (LO/TUBA-GEBIP/2002-1-17).

References

[1] T. Yildirim et al.: Phys. Rev. Lett. Vol. 87 (2001), p. 037001
[2] D. G. Hinks, H. Claus and J. D. Jorgenson: Nature Vol. 411 (2001), p. 457
[3] J. F. Zasadzinski et al.: Phys. Rev. Lett. Vol. 87 (2001), p. 067005
[4] H. Schmidt et al.: Phys. Rev. Lett. Vol. 88 (2002), p. 127002
[5] M. Iavarone et al.: Phys. Rev. Lett. Vol. 89 (2002), p. 187002
[6] D. Larbalestier et al.: Nature Vol. 414 (2001), p. 368
[7] S. Jin et al.: Nature Vol. 411 (2001), p. 563
[8] S. Zhou et al.: Supercond. Sci. Technol. Vol. 15 (2002), p. 236
[9] G. Grasso et al.: Appl. Phys. Lett. Vol. 79 (2001), p. 230
[10] H. Kumakura et al.: Appl. Phys. Lett. Vol. 79 (2001), p. 2435
[11] T. He, R. J. Cava and J.M. Rowell: Appl. Phys. Lett. Vol. 80291 (2001)
[12] D. C. Dunand: Appl. Phys. Lett. Vol. 79 (2001), p. 4186
[13] A. Sharoni et al.: J. Phys. Condens. Matter Vol. 13 (2001), p. L503
[14] J. A. Wilson et al.: J. Mater. Sci. Vol. 36 (2001), p. 67
[15] T. C. Shields et al.: Supercond. Sci. Technol. Vol. 15 (2002), p. 202
[16] Y. Zhao et al.: Physica C Vol. 378-381 (2002), p. 122