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MICROSTRUCTURAL AND ELECTRICAL CHARACTERIZATION OF Ti AND Mg DOPED Cu-CLAD MgB_2 SUPERCONDUCTING WIRES

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The recent studies on Ti doping effect on the critical current density (J_c) of MgB_2 composite superconductors prepared under ambient pressure has shown an important enhancement at 20 K. In the present work, we have fabricated Ti and Mg doped superconducting MgB_2 wires by packing reacted MgB_2 and Ti or Mg powders together inside Cu tubes with a diameter of 6 mm. The tubes were then cold worked by rolling or drawing to smaller diameters. The prepared Cu-clad Ti and Mg added MgB_2 superconducting wires were annealed at various temperatures to enhance the grain connectivity of the MgB_2 bulk materials. The effect of the sintering time has been investigated for high performance characteristics of superconducting Cu-clad Ti and Mg added MgB_2 wires. The microstructural evaluation of the superconducting wires has been carried out using XRD and SEM equipped with EDX analysis system. The interfacial properties between Cu sheath and superconducting core was characterized using SEM-EDX. Furthermore, the influence of the presence of Ti and Mg on T_c has been investigated to understand the structural and electronic properties of superconducting Ti and Mg doped MgB_2 wires.

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Keywords: MgB_2, Superconducting wire, Powder in tube method

1. Introduction

Recently, very high transport critical current densities (J_c), around 10^6 A/cm^2, have been reported at the temperature of 20 K in bulk superconducting MgB_2 samples [1], after the discovery of superconductivity of MgB_2 at 39 K in 2001 [2]. Several techniques have been used to obtain high J_c values in MgB_2 wires [3]. The powder-in-tube (PIT) method [4-6] appears to be the most practical and advantageous technique, since MgB_2 itself is mechanically hard and brittle to form a wire without a suitable, non-reactive sheath material, such as Fe [4], Cu [5], Ag [6]. Among these materials Fe also provides magnetic screening to external applied magnetic fields in the superconducting core. Copper is one of the most suitable sheath materials for the fabrication of MgB_2 composite wires due to its low cost and high ductility. The grain size is also an important parameter for grain connectivity. A poor connection between grains and lack of flux pinning centers in the materials affects current density of superconducting wires. Doping materials as matrix element such as Ti [7], Al [8] inside MgB_2 is the best way in order to enhance the connection between grains. Ti has hexagonal crystal structure similar to MgB_2. It can fill the voids and connect grain boundaries since Ti has less molecular volume than MgB_2. Ti is a good electrical conductor and has large melting point. Mg is a ductile material with low melting point in MgB_2 provides infiltration into the voids in superconducting phase below the decomposition temperature of MgB_2. It improves toughness and connects grains boundaries [9]. The addition of excess Mg prevents the degradation of MgB_2 superconducting core during the formation of $MgCu_2$ layer due to diffusion of Mg from superconducting core. Annealing is another way to increase the grain connectivity and to reduce the porous structure and provide the more homogeneously MgB_2 and Mg/Ti mixture. In this study, the superconducting properties of

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copper-clad Mg and Ti doped MgB_2 wires were fabricated by conventional powder-in-tube techniques (PIT) and ex-situ reaction procedure was used. The samples were annealed at various temperatures between 400 °C and 800 °C. The annealing results on the superconducting properties of wires are discussed.

2. Experimental

Mg (-200 mesh) or Ti (-200 mesh) powder was mixed with pure MgB_2 (-325 mesh from Alfa Aesar) with various weight percentages from 0 to 20%. Then the powder mixture was filled into a Cu tube with a wall thickness of 1 mm and outer diameter of 6 mm in air. Only hand pressing was applied to increase the density of MgB_2 powder or Mg/MgB_2 mixture in Cu tube. The filled tube was cold drawn in a number of steps with about 5% of section reduction up to 3 mm outer diameter then two-axial rolling method was used to prepare a rectangular Cu-clad MgB_2 wire with a core diameter of 0.7-0.8 mm and with an outer diameter of 1.5 mm, while the superconducting fill factor corresponds to about 25%-30% for the whole conductor volume. The samples were then annealed in a tube furnace in a high purity Ar gas flow under ambient pressure at 800 °C for 3 minutes for Mg doped samples and at 800 °C for 1 hour for Ti doped samples and quenched to air. For longer annealing process, the Mg doped samples were annealed at 400 °C for 2 hours and kept in Ar gas flow until room temperature under ambient pressure. The microstructure of the Cu-clad MgB_2 filaments was analyzed by x-ray diffraction technique using Philips Expert Plus with Cu-K$\tilde{\alpha}$, a scanning electron microscope (SEM), Philips XL 30S Feg and energy dispersive x-ray diffraction (EDX) technique. The resistivity of the composite wires was measured in an Oxford cryopump system in a temperature range from 300 K to 20 K.

3. Results and discussion

The SEM picture of a %5 Mg doped Cu clad MgB_2 superconducting composite wire is given in Fig. 1a after annealing at 800 °C for 3 min. The diameter of the composite core was measured about 0.8 mm and outer diameter of 1.5 mm from SEM picture. Fig. 1b shows EDX intensity taken at the interface between Cu sheath and MgB_2/Mg core while moving from Cu sheath to the MgB_2 + 5%Mg superconducting core about 250 μm along the radial direction as marked in Fig. 1a. In the interface region (from 100 μm to 150 μm), the amount of Cu ratio decreases and Mg and B ratio starts to increase.

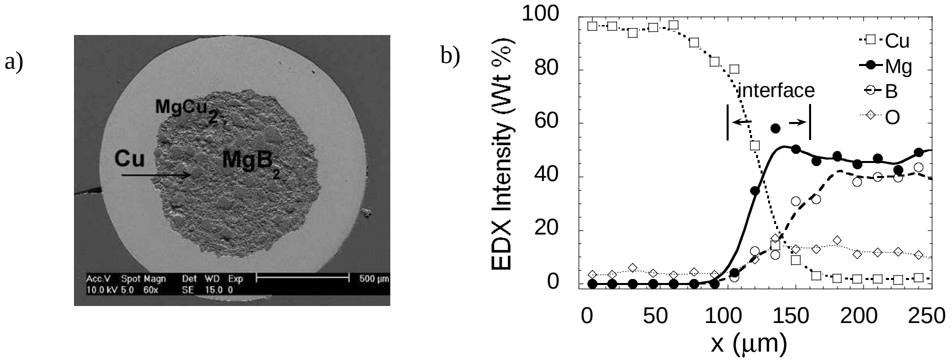

Fig. 1. a) SEM pictures of %5 Mg doped Cu clad MgB_2 superconducting composite wire, b) EDX Intensity taken at the interface between Cu sheath and MgB_2 + 5% Mg core while moving along the radial direction toward to the core center as shown in (a).

It is clear that the stoichiometry of MgB_2 is not maintained and excess Mg and Cu are more pronounced. Then inside the superconducting core the Mg and B ratio is close to the MgB_2 stoichiometry. X-ray diffraction patterns of the Mg doped MgB_2 filament after removing the Cu sheath mechanically before annealing and after annealing at 400 °C for 2h and 800 °C for 3 min in argon atmosphere are given in Fig. 2a, and in Fig. 2b respectively. For nonannealed wires in Fig. 2a the Mg peaks are increasing with increasing doping level. The unreacted excess Mg peaks are still visible after annealing at 400 °C as seen in Fig. 2b. However, the excess Mg peaks disappear and new intermetallic $MgCu_2$ peaks become visible after a short annealing at 800 °C for 3 minutes probably due to interaction between Cu sheath wall and MgB_2+5% Mg superconducting composite core. Similar XRD results have been observed for Ti doped MgB_2 composite wires as shown as shown in Figs. 3a and 3b. The Ti peaks are increasing with increasing doping level before annealing (Fig. 3a). However the excess Ti peaks disappear and new intermetallic $MgCu_2$ and $CuTi_2$ peaks become visible after a long annealing process at 800 °C for 1 hour due to interaction between Cu sheath wall and MgB_2+Ti composite core. The superconducting MgB_2 peaks also disappear due to diffusion of Mg from the superconducting core into the interface between sheath and core to form intermetallic $MgCu_2$ layer on the tube walls after the long annealing process.

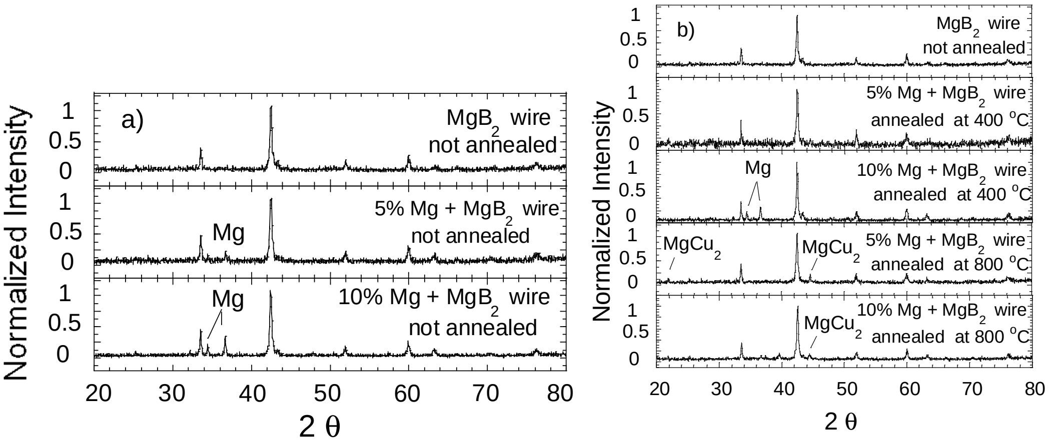

Fig. 2. X-ray diffraction patterns of the Mg doped MgB_2 filament after removing the Cu sheath mechanically a) before annealing, b) after annealing at 400 °C for 2h and 800 °C for 3 min in argon atmosphere.

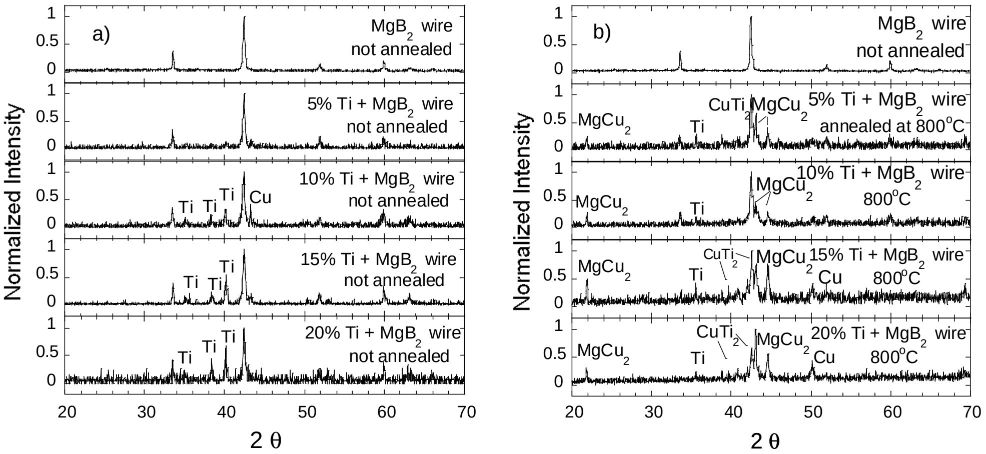

Fig. 3. X-ray diffraction patterns of the Ti doped MgB_2 filament after removing the Cu sheath mechanically a) before annealing, b) after annealing at 800 °C for 1 h in argon atmosphere.

The resistivity versus temperature characteristics normalized at 50 K at a driven current of 50 mA for nonannealed and annealed MgB_2/Mg and MgB_2/Ti composite wires are given in Fig. 4a and Fig. 4b respectively. There is a slight increase in T_c for nonannealed Cu-clad MgB_2/Mg composite wires. However after annealing at 400 C for 2 h, T_c increases from 25 K to 34.5 K with relatively sharp transition for 10% doped samples, while T_c of the pure Cu-clad MgB_2 wire decreases from 26 K to 23 K. Similar increase in T_c have been observed for the nonannealed Ti doped superconducting composite wires. But after annealing at 800 °C, superconducting transition has not been observed for Ti doped superconducting composite wires. These confirm the XRD and EDX results discussed above. This means that there is degradation for the pure MgB_2 wires after annealing due to the loss of Mg from the superconducting core, while excess Mg helps to maintain the stoichiometry of MgB_2 compound. For shorter sintering process, 3 minutes at 800 °C is sufficient enough to connect grains inside MgB_2/Mg or MgB_2/Ti composite wires without destroying the superconductivity.

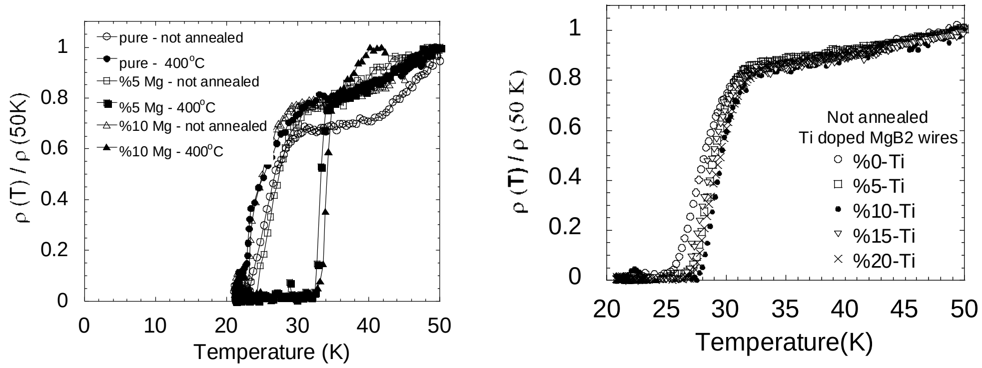

Fig. 4. The normalized resistivity versus temperature plot, a) for annealed and nonannealed Cu-clad Mg doped MgB_2 wires, b) for nonannealed Cu-clad Ti doped MgB_2 wires.

4. Conclusion

Formation of intermetallic $MgCu_2$ and $CuTi_2$ layer, and diffusion of Mg from the superconducting core into the interface between sheath and core was observed for the Cu-clad MgB_2/Mg and MgB_2/Ti composite wires after annealing at 800 °C respectively. Temperature dependence of resistivity measurements show that excess Mg gives better results at annealing at 400 °C for 2 hours for longer sintering process. For shorter sintering process, 3 minutes at 800 °C is sufficient enough to connect grains in MgB_2/Mg and MgB_2/Ti composite wires. Excess Mg prevents the degradation of MgB_2 superconducting core during the formation of $MgCu_2$ layer, which might prevent the diffusion of Mg from the superconducting core so that the stoichiometry of the MgB_2 is maintained. It was found that electronic properties of superconducting MgB_2 wires are improving with Mg and Ti doping. The critical temperature of Ti doped wires increases with increasing Ti doping ratio. However the superconductivity is destroyed for type of samples, if the samples are annealed at 800 °C for longer than 1 h.

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