Microstructural and Electronic Characterization of Ti and Mg doped Copper-Clad MgB_2 Superconducting Wires

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ABSTRACT: The recent studies on Ti doping effect on the critical current density (J_c) of MgB2 composite superconductors prepared under ambient pressure has shown an important enhancement at 20 K [1]. In the present work, we have fabricated Ti and Mg doped superconducting Mgl$2 wires by packing reacted MgB2 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 Copper-Clad Ti and Mg added Mgl$2 superconducting wires were annealed at various temperatures to enhance the grain connectivity of the Mgl$2 bulk materials. The effects of the sintering time have 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.

ÖZET: Son zamanlarda yapılan çalışmalar normal atmosfer basıncı altında yapılan Ti katkılamanın MgB2 kompozit üstüniletken tellerin kritik akım yoğunluğunu (Jc) artırdığım göstermektedir [Fu, 2003]. Bu çalışmada ise Ti veya Mg, MgB2 ile karıştırılıp 6 mm çapında Cu boruların içerisinde paketlendikten sonra çekerek veya merdane ile ezerek daha küçük çaplarda Ti ve Mg katkılı üstüniletken teller haline getirilmiştir. Hazırlanan Cu kılıflı Ti ve Mg katkılı MgB2 üstüniletken teller MgB_2 tozlan arasındaki bağlantıyı artırmak için değişik sıcaklıklarda tavlanmıştır. Tavlama sıcaklığının Ti ve Mg katkılı Cu kılıflı üstüniletken MgB_2 nin kritik sıcaklığa (T_c) olan etkisi incelenmiştir. Üstüniletken tellerin micro yapısal analizleri XRD ve EDX analiz sistemine sahip SEM cihazı ile yapılmıştır. Üstüniletken MgB_2 çekirdek ile Cu kılıf arasında kalan bölgenin özellikleri SEM-EDX ile karakterize edilmiştir. Böylece Cu kılıflı MgB_2 tellerin yapısal ve elektronik özelliklerini anlamak için Ti ve Mg katkılamanın kiritik sıcaklığa olan etkisi araştırılmıştır.

1. INTRODUCTION

Magnesium diboride, MgB_2, was announced as a superconductor with a critical temperature, T_c of 39 K in 2001 [Nagamatsu, 2001]. It has higher critical temperature than NbaSn at 18 K, which is used widespread in superconducting technological applications today such as high power transformers, super current carrying transmission wires, MIR, NMR, SMES magnets [Glowacki, 2002] Superconducting MgB_2 wires can carry large electrical currents as much as millions of amperes per centimeter square without energy loss while cupper can carry only 400 A/cm^2 with energy consumption. The critical temperature of MgB_2 is much lower than high temperature superconductor, ($HgBa2Ca_2Cu30g$ at 135 K) but fabrication costs of HTS is higher comparing with MgB_2 and the performance of MgB_2 is better than NbTi and Nb_3Sn [Machi, 2003]. MgB_2 with higher critical temperature at 39 K promises many advantages, mainly for superconducting magnets running around 20 K, that economical cryopumps can easily maintain. MgB_2 has good grain connectivity and absence of weak links. MgB_2 has hexagonal crystal structure. It is less anisotropic than HTS and convenient material for practical applications [Larbalestier, 2001].

MgB2 has a brittle nature and low strength. But the powder-in-tube (PIT) method is the most popular in achieving good quality wires. The selection of suitable clad, giving thermal, electrical and mechanical stability without deterioration of the superconductor is important. The clad material should be hard but ductile and malleable metals. Also, it is important to find a suitable clad material which does not tend to react with Mg and MgB2 and not to decrease the superconductivity (Eğilmez, 2004). Many cladding metarial has been used to fabricate metal - clad MgB2 wires such as Cu [Martinez, 2003], Fe [Fu, 2003], stainless steel SS, Cu - Ni [Kumaraka, 2001], Ag [Soltanian, 2002], Ag / SS [Glowacki, 2001], and Ta / Cu / SS [Fu, 2002]. There are small numbers of metals, which are not soluble or do not form intermetallic compounds with Mg such as Mo, Nb, Ta, V, Hg, W [Jin, 2001]. The ductility of these metals is not good like copper or iron. During the annealing process, some of the metal clad can easily cause to vanish superconductivity by reacting with the MgB2 core.

In this study, copper was chosen as clad metal since copper has high thermal and electrical conductivity. It is a low cost and ductile metal. Therefore it is suitable for the PIT method to fabricate MgB_2 composite wires.

In PIT method, MgB_2 reacted powders (ex-situ reaction) or Mg+2B mixtures (in-situ reaction) are packed in various clad materials [Pan, 2003]. These clads are deformed by drawing or two-axial rolling [Kovac, 2004] into wires, then optionally heat treatment is applied between 400°C - 800°C.

In the in-situ reaction technique, the precursor, unreacted Mg and B powders, are packed inside a tube and then heat treatment at 950°C is applied to provide formation of MgB_2. However, deformation and solid-liquid diffusion processes can be observed in this method. It can be used for Cu, Ag, and Ni metals which have low melting point. Cu/MgB_2 composite wires has been made by using in-situ reaction technique annealed at temperatures below 660°C to prevent formation of Mg-Cu alloy [Martinez]. Heat treatment at lower temperatures or using buffer layers such as Ni [Kumakura], Ta [Fu, 2002] or Fe [Jin, 2001] can prevent reaction between core and walls of the superconducting wires. On the other hand, in the ex-situ reaction technique, metal tubes were filled with precursor pre-reacted MgB_2 powder and deformed. This technique is suitable „ for hard clad materials. Because it provide chemical compatibility and possibility of high core densities inside the clad [Pan, 2003]. Ex-situ reaction technique is suitable for smaller and more homogeneous microstructures. On the other hand, 1% additional impurity of C atom can destroy the superconductivity of MgB_2.

The grain size is an important parameter for grain connectivity. A poor connections between grains and lack of flux pinning centers in the materials affects current density of superconducting wires. Doping materials as matrix element inside MgB_2 best way in order to enhance the connection between grains. Several metals have been used as a doping material in the literature such as titanium [Zhao, 2002; Fu, 2003; Kramer, 2003], aluminum [Xiang, 2002], zinc, copper.

Ti and Mg have been chosen in this study since Ti has hexagonal crystal structure similar to MgB_2. The molecular volume of Ti is less than MgB_2. So it can fill the voids and connect grain boundaries. Ti is a good electrical conductor and has large melting point so it is suitable for annealing process. 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 (Eğilmez, 2004)
The purpose of annealing process is to increase the grain connectivity, reduce the porous structure and provide the more homogeneously MgB_2 and Mg/Ti mixture. As the annealing temperature increased, the connectivity of each grain increased and porous structure is reduced. As a result of this process, critical current density is increased [Matsumoto, 2002]. In this study, the superconducting properties of 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 WORK

2.1 Sample Preparation

Commercial MgB_2 powder (Alfa Aeaser) Mg and Ti powder were used for the fabrication of MglV Mg and MgBi/Ti wires. The weight ratio of Mg and Ti to the MgB_2 composite was chosen as 0, 5, 10, 15, and 20 %. The total initial weight of each composite to fill into a Cu tube was chosen to be 2 grams. We have applied the ex-situ reaction PIT method. MgB2 and Ti or Mg powders were mixed homogeneously and filled into a Cu tube with a wall thickness of 1 mm, outer diameter of 6 mm and length of 10 cm in air. Only hand pressing was applied to fill the MgB^Mg and MgB_2/Ti mixture in Cu tube. After the tube was filled, wires were prepared in two steps: drawing and using two-axial rolling method as shown in Figure 1. First, wires were drawn, until the diameter drops to 3 mm and then rectangular wires (1.5 mm x 1.5 mm) made by two-axial rolling as shown. Finally wires were annealed at 400, 600, and 800°C, in argon. 25 samples were prepared and cut into the length of 1.5 cm for measurements. The microstructure and superconducting properties were investigated by the X-ray diffraction and resistivity versus temperature measurements.

In order to determine critical temperature and critical current, the DC resistance of a sample is measured with a computer controlled Oxford Edward 1.5 cryopump system. The resistivity of

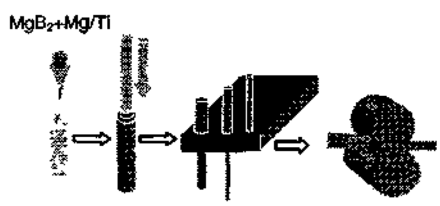

Figure 1. Fabrication steps of Superconducting Cu-clad Ti and Mg added MgB2 wires using PIT method

samples can be directly measured by decreasing temperature from room temperature (296 K) to 15 K. Each samples were measured for different probe currents, 10 mA, 20 mA, 50 mA and 100 mA not to heat up the superconducting MgB_2 wires during the measurement by using four point probe method. Four point probe method is the most common method of determining the T_c and J_c of a superconductors. Copper wires were soldered to the samples at four different positions. Current is given through the edge of wires. Then voltage is measured from any other two points between them to be able to calculate the resistance of the wires using Ohm's law. The resistance drops to zero and no voltage appears across the second set of points, if the temperature is below the critical temperature of MgB_2 wire in superconductive state.

3. RESULTS AND DISCUSSION

Figure 2 shows SEM pictures of a) %5 Mg and b) %5 Ti doped Cu clad MgB_2 superconducting

Figure 2. SEM pictures of a) %5 Mg and b) %5 Ti doped Cu clad MgB_2 superconducting composite wires annealed at 400 °C 1 hour.

composite wires annealed at 400 °C for 1 hour. The diameter of the %5 Mg + Cu clad MgB_2 superconducting composite core produced by cold drawing technique was measured about 0.8 mm and outer diameter of 1.5 mm from SEM picture. On the other hand the inner diameter was 0.6 mm and the outer diameter was measured 1 mm for %5 Ti + Cu clad MgB_2 superconducting composite wire produced by cold drawing technique up to 3 mm then two-axial rolling technique up to 1 mm. The shape of Ti added wire is rectangular due to shape of the grove of the cylinders used in the two-axial roller machine.

The effect of cold working and annealing temperature and annealing time on the microstructural development of Cu-sheathed tapes on the MgB_2 phase was analyzed by x-ray diffraction measurements as shown in Figure 3. The comparison of Figure 3c and Figure 3b shows Mg diffusion from pure MgB2 superconducting core after short annealing of Cu-clad MgB_2 wire at 800 °C for 3 minutes. As a result, x-ray diffraction pattern in Figure 3c is seen blur due to excess amorphous B in the core due to the loss of Mg during the formation of mtermetallic $MgCu_2$ in the Cu sheath wall. After adding 5% excess Mg, unreacted Mg peaks become visible before annealing as shown in Figure 3d. After annealing, the excess Mg peaks disappear and $MgCu_2$ peaks can be seen in Figure 3e. This shows that most of the excess Mg was spent for the formation of $MgCu_2$ layer on the interface between Cu and MgB_2/Mg superconducting composite core. Similar peaks were observed for 10% Mg added composite wires except that the excess Mg peaks are more pronounced before annealing as seen in Figure 3f. They disappear after annealing at 800 °C for 3 minutes as seen in Figure 3g and there is no sign of Mg saturation since none of the Mg is visible. This means $MgCu_2$ layer formation is still active. There is no sign of evident,peak broadening or shifting that could be associated with molecular structural parameters of the MgB_2 phase inside Cu sheath.

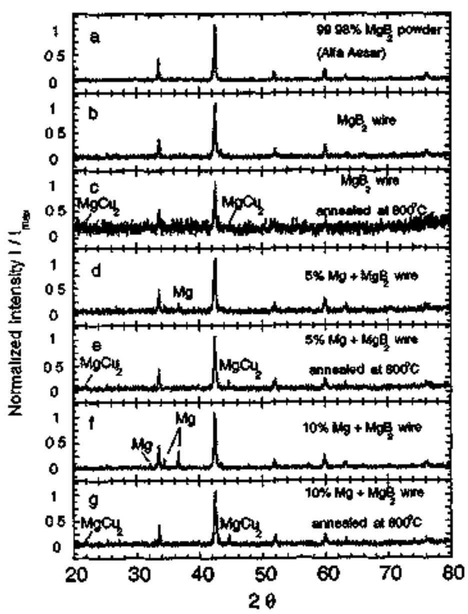

Figure 3. X-ray diffraction patterns of the MgB_2 powders, a) before packing, b) of the MgB_2 filament after removing the Cu sheath mechanically after the cold drawing process to a wire with outer diameter of 1.5 mm, c) after annealing at 800 °C for 3 min., d) of the mixed MgB_2 filament with 5% Mg before annealing, e) of the 5% Mg added filament after annealing at 800 °C for 3 min., f) of the mixed MgB_2 filament with 10% Mg before annealing, and e) of the 10% Mg added filament after annealing at 800 °C for 3 min.

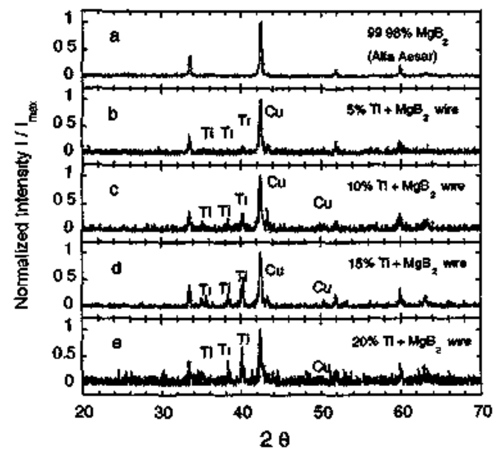

Figure 4. X-ray diffraction patterns of the MgB_2 powders, a) before packing, b) 5% Ti added, c) 10% Ti added, d) 15% Ti added, e) 20% Ti added MgB_2 filament after removing the Cu sheath mechanically after the two-axial rolling process to a wire with outer diameter of 1 mm before annealing.

We have not observed any evident peak for the $MgCu_2$ formation in the x-ray diffraction pattern of the MgB_2/Mg composite wires annealed at 400 °C for 2 hours. This means that there is no reaction between Mg and Cu sheath wall below the melting point of Mg, since the Mg peaks of the 10% Mg added filament still remain unchanged after annealing at 400 °C for 2 h (not shown here).

Figure 4 shows X-ray diffraction patterns of the MgB_2 powders, a) before packing, b) 5% Ti added, c) 10% Ti added, d) 15% Ti added, e) 20% Ti added MgB_2 filament after removing the Cu sheath mechanically after the two-axial rolling process to a wire with outer diameter of 1 *mm* before annealing. The characteristic XRD Intensity of Ti peaks is increasing with increasing doping level of Ti for the Ti added MgB_2 wire filaments after removing the Cu sheath mechanically after the two-axial rolling process to a wire with outer diameter of 1 mm before annealing as shown in Figure4. In Figure5, XRD Intensities of Ti added MgB_2 wire filaments annealed at 600 °C are given. The magnitude of Ti peaks is smaller comparing with the XRD results for nonannealed wires shown in Figure 4. The reason for this is not clear. But it is possible a chemical reaction of Ti with superconducting core or Cu wall, even though there is no sign of either argument in the XRD result. Figure6 shows XRD patterns of the Ti added MgB2 wire filaments annealed for 1 h at 800 °C. The excess Ti peaks disappears after annealing at 800 °C and intermetallic $MgCu_2$ layer forms in the interface between Cu clad and MgBj/Ti superconducting composite core.

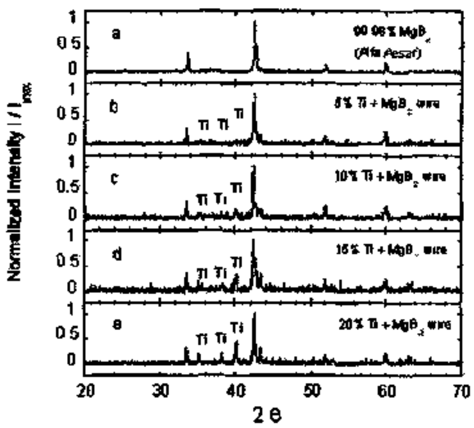

Figure5. XRD Intensities of Ti added MgB_2 wire filaments annealed for 1 h at 600 °C.

An important results of XRD analysis is MgB2 peaks disappear at 800 °C and superconductivity is destroyed due to overheating, which causes to form another phases of the material.

Figure 7 demonstrates resistance versus temperature characteristics of sintered and un-sintered tapes made of MgB2/Mg composite wires with outer diameter of 1.5 mm with Cu sheath at a driven current of 50 mA. T_c of the unsintered Cu-clad Mgl^Mg composite tapes increases from 26 K to 27 K by adding 5% Mg while it decreases to 25 K with 10% excess Mg. The change in T_c is approximately 5-6 K. Similar improvements in T_c and J_c have been seen after annealing at 400 °C for 2 hours or at 800 °C for 3 minutes as the amount of excess Mg are increased in the MgB_2 core. T_c of the Cu-clad MgB_2 tape with 5% Mg increases from 27 K to 33.5 K with relatively sharp transition. T_c of the Cu-clad MgB_2 tape with 10% Mg shows better result and it increases from 25 K to 34.5 K, while T_c of the pure Cu-clad MgB_2 tape without Mg decreases from 26 K to 23 K. These confirm the XRD and EDX results discussed above.

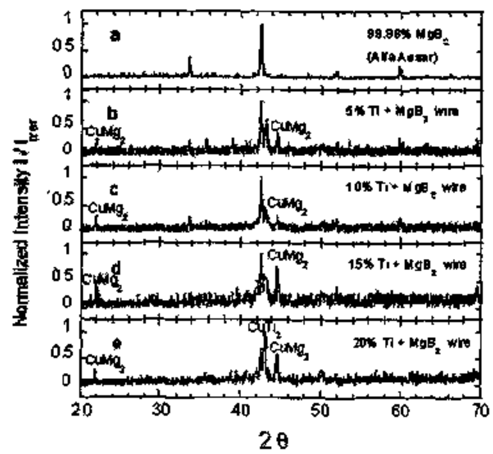

Figure 6. XRD patterns of the Ti added MgB_2 wire filaments annealed for 1 h at 800 °C.

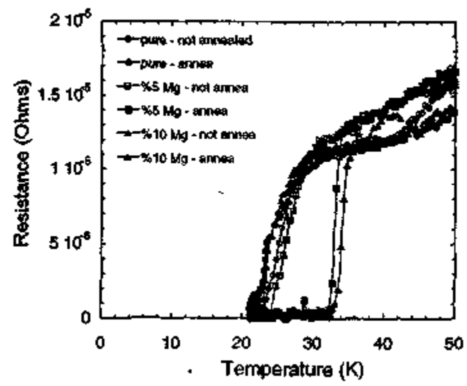

Figure 7. The Resistance of all the annealed and nonannealed Cu-clad Mg doped MgB_2 vires as function of temperature using PIT method

This means that there is a 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, to decrease the formation of MgCu2 layer in the interface, 3 minutes at 800 °C is sufficient enough to reach to the same annealing effect on the MgB2/Mg composite wires.

The normalized resistivity of all the Ti doped MgB_2 vires is given as function of temperature in Figure 8. The resistivity was measured for nonannealed samples with 50 mA applied current. When Ti doping levels are increased, the value of T_c

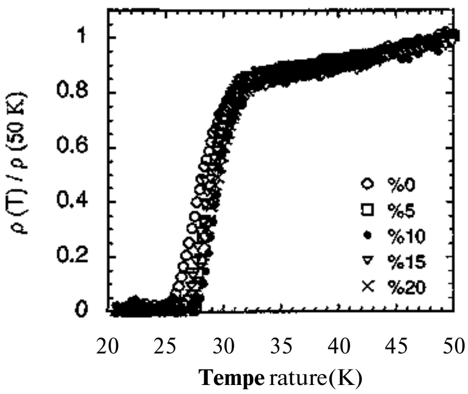

Figure 8. The normalized resistivity of all the nonannealed Cu-clad Ti doped MgB2 vires as function of temperature using PIT method

increases as shown in Table 1. In order to determine the critical temperature at the tangential line to the part of resistivity curve in the normal state is drawn along the slope of the curve. Then the corresponding temperature points are chosen for TconseL when resistivity starts to decrease. T_{co}ffset was determined when the resistivity at zero. AT_C gives the differences between these points. The critical temperature of Ti doped wires is increasing from 3IK to 34 K with increasing Ti doping level. There is a sharp transition for the samples with 10%

Table 1: The T_c values for not annealed samples

Ti	TeOnset (K)	$T_c$offset (K)	AT_n(K)
0	31	24	7
5	32	23	9
10	32,5	26	65
15	33	26	7
20	34	27	7

doped MgB2 wires.

Finally, formation of intermetallic MgCu2 layer on the tube walls, and diffusion of Mg from the superconducting core into the interface between sheath and core was observed for the Cu-clad MgB2/Mg composite wires annealed at 800 °C. Temperature dependence of resistance and J_c 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 optimum value to reach to the same annealing effect on the MgB2/Mg composite wires. Excess Mg prevents the degradation of MgB_2 superconducting core during the formation of MgQfe 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 MgB2 wires are improving with excess Mg and annealing temperature and time. The critical temperature of Ti doped wires is increasing from 31 K to 34 K with increasing Ti doping level. But superconductivity is destroyed if the samples are annealed at 800C for longer time

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