RRR and thermal conductivity of Ag and Ag0.2wt%Mg alloy in Ag/Bi-2212 wires

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Abstract. The residual resistivity ratio (RRR) and thermal conductivity of metal matrix in metal/superconductor composite wires are important parameters for designing superconducting magnets. However, the resistivity of silver in reacted Ag/Bi-2212 wires has yet to be determined over temperature range from 4.2 K to 80 K because Bi-2212 filaments have a critical transition temperature T_c of ~ 80 K, and because it is unknown whether the RRR of Ag/Bi-2212 degrades with Cu diffusing from Bi-2212 filaments into silver sheathes at elevated temperatures and to what degree it varies with heat treatment. We measured the resistivity of stand-alone Ag and AgMg (Ag-0.2wt%Mg) wires as well as the resistivity of Ag and Ag-0.2wt%Mg in the state-of-the-art Ag/Bi-2212 round wires reacted in 1 bar oxygen at 890 °C for 1, 8, 24 and 48 hours and quickly cooled to room temperature. The heat treatment was designed to reduce the critical current I_c of Bi-2212 wires to nearly zero while allowing Cu loss to fully manifest itself. We determined that pure silver exhibits a RRR of ~ 220 while the oxide-dispersion strengthened AgMg exhibits a RRR of ~ 5 in stand-alone samples. A surprising result is that the RRR of silver in the composite round wires doesn't degrade with extended time at 890 °C for up to 48 hours. This surprising result may be explained by our observation that the Cu that diffuses into the silver tends to form Cu_2O precipitates in oxidizing atmosphere, instead of forming Ag-Cu solution alloy. We also measured the thermal conductivity and the magneto-resistivity of pure Ag and Ag-0.2 wt%Mg from 4.2 K to 300 K in magnetic fields up to 14.8 T and summarized them using a Kohler plot.

Introduction

Silver-sheathed $Bi_2Sr_2CaCu_2O$ (Ag/Bi-2212 hereafter) multi-filament round wire has long been considered as a promising candidate for building high field magnets generating fields beyond 20 Tesla. Recently, the critical current density of commercial powder-in-tube (PIT) Ag/Bi-2212 wires were significantly improved, with the best engineering critical current density J_E and the critical current density J_c at 4.2 K and 20 T exceeding 700 A/mm^2 and 2800 A/mm^2, respectively [1], [2]. In comparison, the best commercial RRP Cu/Nb_3Sn wires exhibit J_c of 3000 A/mm^2 at 4.2 K and 12 T, which decreases rapidly with increasing magnetic fields to 1500 A/mm^2 at 4.2 K and 15 T. The record J_c in Ag/Bi-2212 was achieved by removing porosity in the Bi-2212 filaments in PIT superconducting wires, through densification treatment [1]-[3]. Importantly, such high J_c can be achieved in long-length Bi-2212 wires through an overpressure partial melt processing so Ag/Bi-2212 round wire is becoming a magnet-grade conductor [2].

In additional to using pure silver as a stabilizer, commercial Bi-2212 wires use oxide-dispersion strengthening silver alloys to improve their mechanical strength [4], [5]. Popular silver alloys used include Ag-0.2 wt%Mg, AgAl, AgMn, and AgMgSb [6] and they typically occupy 25% of the total volume of the conductor. Resistivity ρ and thermal conductivity κ of both silver and silver alloys

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Operated by Fermi Research Alliance, LLC under Contract No. DE-AC02-07CH11359 with the United States Department of Energy

are important materials properties. For example, they are important for designing the quench protection circuitry [7], [8] and affects the design of the entire magnet system. During a magnet quench, the power generation density in a normal zone is given by $(1-\lambda)J_m^2(t)\rho(T,B)$, where λ is the volumetric ratio of superconductor in the metal/superconductor composite, J_m the current density in the metal matrix, and $\rho(B,T)$ the effective resistivity of the metal matrix. Both J_m and $\rho(B,T)$ would depend on the magneto-resistivity of pure silver and Ag-alloys.

One would think that the task is rather simple as one just needs to measure $\rho(B,T)$ of silver and silver alloys used in the production of Ag/Bi-2212 wires. This, however, ignores the influence of Bi-2212 filaments on transport properties of silver and silver alloys. Bi-2212 filaments are embedded in a silver matrix, which again is encased inside a Ag-alloy external sheath, without a reaction barrier. During the partial melt processing, the elements inside Bi-2212 filaments can diffuse into silver, introducing a small amount of impurity atoms and lattice defects to enhance the scattering of electron at low temperatures and therefore raising the residual resistivity at low temperatures. Among all the elements forming Bi-2212, Cu has the highest solubility and a diffusion coefficient of ~2-3x10^{-11} cm^2/s in Ag at ~ 890 °C [9]. However, it is not easy to determine resistivity and thermal conductivity of silver and silver alloys in a reacted Ag/Bi-2212 wire because Bi-2212 filaments in reacted Bi-2212 wires have a T_c of ~82 K and an I_c of several hundred Ampere [9]-[12].

In this paper, we report the electrical resistivity and thermal conductivity of Ag and Ag-0.2wt%Mg (AgMg hereafter) alloy used in real production of Ag/Bi-2212 conductors. These properties are tested in temperature from 4.2 K to 300 K and in magnetic field up to 14.8 T. We also developed a new protocol for determining RRR of Ag/Bi-2212 wires and its dependence on Cu-loss and heat treatment parameters.

Experiments

2.1. Magneto-resistivity and thermal conductivity measurement of stand-alone Ag and AgMg alloy

As the first step, this study determined the $\rho(T, B)$ $\rho(B,T)$ of silver and silver alloys used in the production of Ag/Bi-2212 wires. Samples of the silver and silver-magnesium alloy (Ag with 0.2 wt% Mg) were supplied by Oxford Superconducting Technology (OST) as round wires with a diameter of 0.55 mm. Samples were heat-treated using a standard partial-melt-processing in 1 bar flowing pure O_2 to anneal the silver for removing the influences of cold deformation and to introduce the MgO precipitates. The resistivity of the heat-treated Ag and AgMg alloy samples were measured in a Quantum Design Physical Property Measurement Systems (PPMS) using a standard four-probe method with activation current up to 100 mA as a function of temperature from 4.2 K to 300 K and of magnetic field up to 14.8 Tesla. The thermal conductivity of the heat-treated Ag and AgMg wires were measured from 300 K to 4 K using the thermal-transport-option (TTO) of PPMS. The measurement was calibrated using a nickel sample from Quantum Design.

2.2. Resistivity measurement of silver in heat-treated Ag/Bi-2212 wires

We also determined the resistivity of Ag and Ag-0.2 wt%Mg in Ag/AgMg/Bi-2212 wires using a new protocol, which takes into consideration of possible effects of Cu loss on resistivity of silver. Samples were reacted at 890 °C, at which Bi-2212 filaments are in melt state and contain a mixture of an amorphous liquid and two solid crystalline phases (a Cu-free phase (CF) and an alkaline-earth cuprate phase (AEC)), and then rapidly cooled down to room temperature. The majority of Bi-2212 filaments in these samples are expected to be filled with liquid, AEC, and CF, and contain a few Bi-2212 whiskers, and therefore the I_c of these samples is close to zero. The dwelling time at T_{max}=890 °C was varied from 1 hour to 48 hours to amplify the possible effect of Cu-loss on sheath resistivity, as Cu-loss is expected to be most active when Bi-2212 filaments are in the melt state. Two types of wires were studied. The first wire is 0.8 mm diameter, PMM101108-1 fabricated by OST with a Ag:AgMg:Bi-2212 ratio of 0.5:0.25:0.25; this wire represents the widely fabricated commercial Ag/Bi-2212 wires. The second wire, 0.8 mm diameter, PMM140721, has a Ag:AgMg:Bi-2212 ratio of

0.33:0.42:0.25 and represents wires with higher mechanical strength with a larger volume of AgMg. After a standard partial melt processing in 1 bar flowing O_2, the I_c of PMM101108-1 at 4.2 K, self-field is 425 A whereas the I_c of PMM140721 is 450 A. For simplicity, PMM101108-1 and PMM140721 are named type "A" and "B" in the rest of this paper.

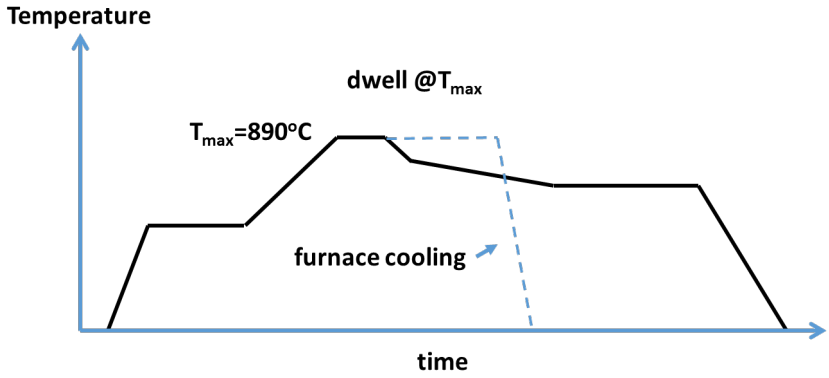

Figure 1. The heat treatment procedure used to generate I_c-depressed samples for sheath resistivity measurements. The dashed-line marks where this procedure differs from the standard partial-melt-processing (PMP): the slow cooling (10 ºC/hr from 890 ºC to 880 ºC and 2.5 °C/hour from 880 ºC to 830 ºC) is replaced with a fast furnace cooling (about 100 °C/hour in the first hour and an average rate of 50 °C/hour from 890 °C to room temperature) and the dwelling time at T_{max}=890 °C varies from 1hour to 48 hours. Refer to the text for more details.

2.3. Microscopy observation of Cu-loss

To determine at what temperatures Cu loss occurs and where Cu migrates, the surface and cross-sections of various heat-treated Ag/Bi-2212 conductors were examined using a scanning electron microscope JOEL-5900 (SEM) equipped with energy dispersive x-ray spectrometers (EDS).

Results

3.1. Resistivity and thermal conductivity of Ag and AgMg

Figure 2 presents $\rho(B, T)$ plots of Ag and Ag-0.2 wt%Mg wires heat treated using a standard partial melt processing in 1 bar flowing O_2. For pure silver wire, the measured zero-field resistivity at 300 K, ρ(300 K, 0 T), is 16.14 nΩ m and that at 4.2 K, ρ(4.2 K, 0 T), is 0.0754 nΩ m, which gives a *RRR* ratio, defined as ρ(300 K, 0 T)/ρ(4.2 K, 0 T), of 214. For Ag-0.2wt% wire, ρ(300 K, 0 T) is 19.7 nΩ m and ρ(4.2 K, 0 T) is 3.84 nΩ m, giving a RRR ratio of 5.1. Magnetic field impacts the resistivity of Ag significantly in temperature range from 4.2 K to 50 K. At 4.2 K, applying a 14.8 T field increases the resistivity of Ag by a factor of five, whereas for temperature higher than 70 K, the increase in resistivity is less than 15%. The resistivity of AgMg is not sensitive to magnetic field and only increases by 10% with field increasing from 0 T to 14.8 T at 4.2 K and the field-induced resistivity increase is negligible at higher temperatures. Using all the $\rho(B, T)$ data from this study, a Kohler plot is generated by plotting the magnetic field–induced resistivity change, $[\rho(B,T)-\rho(B=0,T)]/\rho(B=0,T)$, against $B*[\rho(B=0,273\ K)/\rho(B=0,4.2\ K)]$, as shown in Figure 2 (C). Both the Ag and AgMg results converge to the reference data reported in Ref [13] well. The thermal conductivity κ of Ag and AgMg wires is shown in Figure 2 (D). κ of Ag has a peak of ~2600 W/Km at ~15 K and has a room temperature value of ~500W/Km. κ of AgMg is much lower than Ag and slowly increases with temperature, which is common in silver with low RRR and silver alloys.

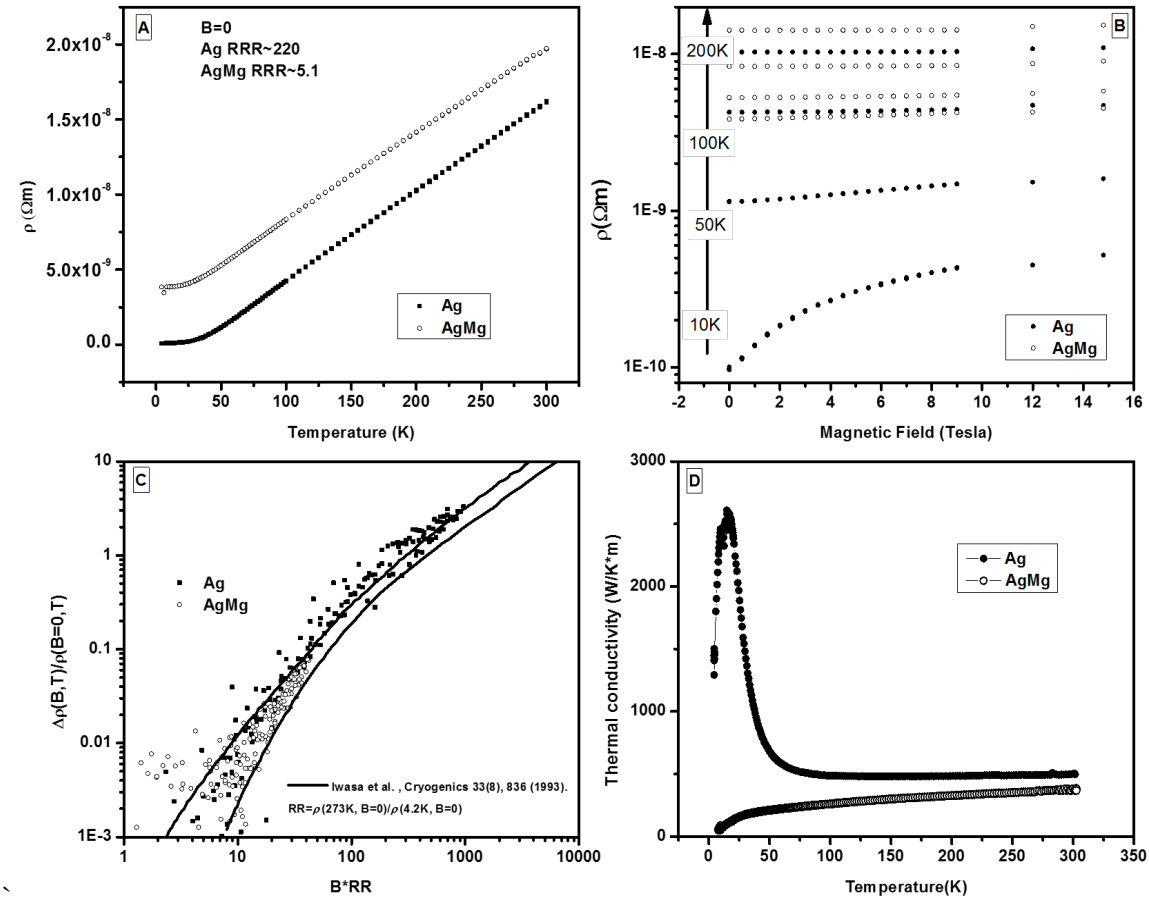

Figure 2. Resistivity and thermal conductivity of heat-treated Ag and AgMg (0.2wt% Mg). A. $\rho(T)$ of pure Ag and Ag-0.2wt%Mg in zero magnetic field over 4.2 – 300 K. (B): Dependence of ρ_{Ag} and $\rho_{Ag\text{-}0.2wt\%Mg}$ on magnetic fields at 4.2 K, 50 K, 100 K and 200 K. (C): Kohler plot generated from all the $\rho(B, T)$ data from this study. The $\rho(B,T)$ behavior of both Ag and AgMg alloys are consistent with the reference data reported in Ref [13]. (D): Thermal conductivity of Ag and AgMg in zero field.

3.2. Observation of Cu-loss in Ag/Bi-2212 conductors

We have observed clear evidences of Cu loss in two types of conductors. Figure 3 shows the back-scattering electron images of the surfaces of heat-treated Ag/Bi-2212 dip-coated tapes whereas the Figure 4 for heat-treated Ag-0.2 wt%Mg/Ag/Bi-2212 round wires. The sheath of dip-coated tapes is pure silver and the outmost sheath of round wires is Ag-0.2 wt%Mg. On the surfaces of all these conductors, Cu_2O particles are found. Meanwhile, EDS was not able to detect Cu signal in the Ag matrix, within the detection limit 0.1% of EDS. It is important to note that these Cu-rich particles can appear even without heating Ag/Bi-2212 above the partial melting point of Bi-2212. As shown in Figure 4, such Cu-rich particles can be found on round wires heated to 800 °C and dwelled for 70 hours.

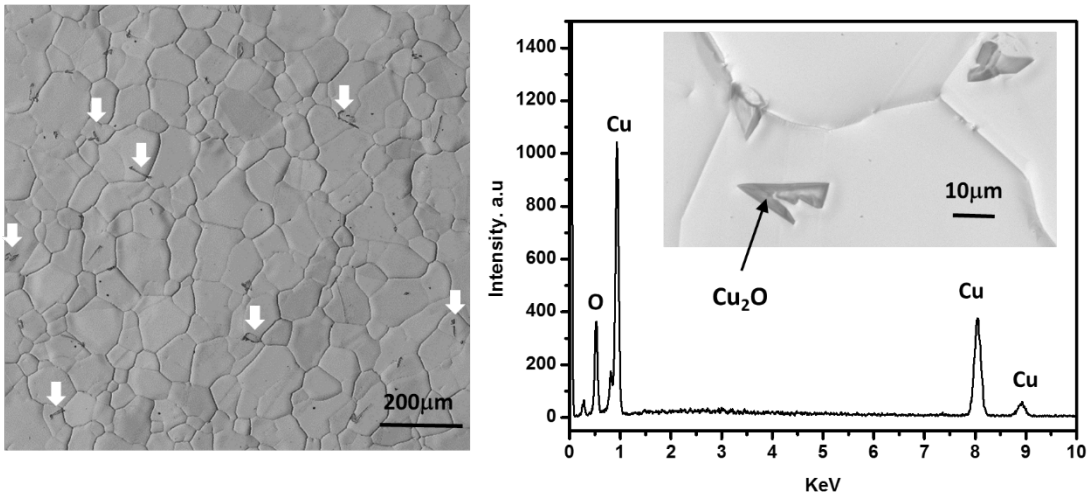

Figure 3. Left: SEM image of the Ag sheath surface of Bi-2212 dip-coated tape after PMP heat treatment. Cu-rich particles are observed and some of them are marked by the arrows. Right: high magnification image of several Cu-rich particles (the dark grey particles in the image) and the EDS elemental analysis from one of them, showing its composition to be Cu_2O.

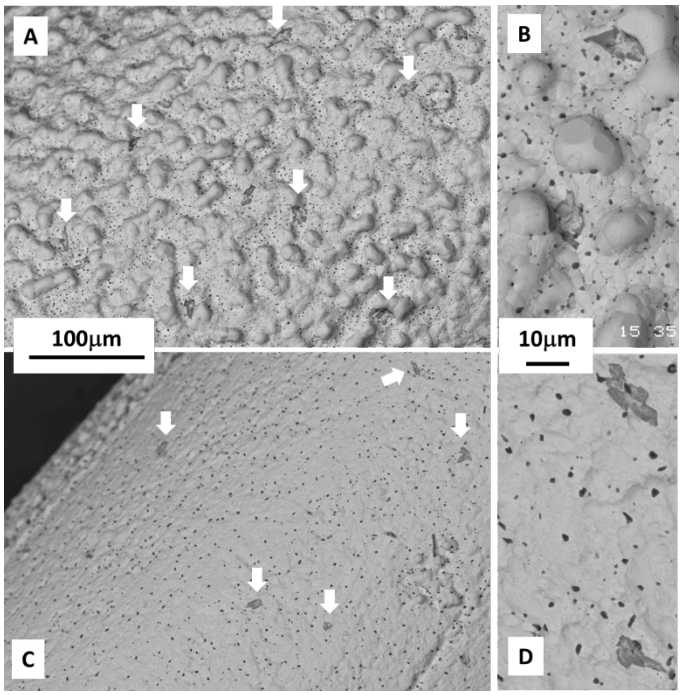

Figure 4. Surface of heat-treated Ag/Bi-2212 round wires. These wires use AgMg as outer sheath with Ag:AgMg:Bi-2212=0.5:0.25:0.25. (A) and (B): the wire was fully heat-treated. Some Cu-rich particles are marked by the arrows in (A) and (B) shows two Cu-rich particles (dark grey) with high magnification. The smaller, black particles are MgO. (C) and (D): this sample was heated to 800 °C and held for 70 hours. Cu-rich particles can also be observed on sample surface, indicating that the partial melt of Bi-2212 is not necessary for Cu-loss to occur.

3.3. Sheath resistivity of I_c-depressed wires

We measured the *V-I* curves of samples reacted at 890 °C for 1, 8, 24, and 48 hours and fast cooled to room temperature using the standard four-probe method at 300 K, 77 K, and 4.2 K. The results are summarized in Table 1. At 4.2 K, all samples exhibited a rather linear V-I characteristics with *I* going up to 30 A, indicating that the Bi-2212 filaments carried I_c of less than 1-3 A. Interestingly, the resistivity of the sheathes, including both that of Ag and that of Ag-0.2wt%Mg, didn't significantly increase with the time at 890 °C; rather it decreases by 17% and 29% for the conductor A and the conductor B, respectively.

Table 1. Resistivity of the I_c-depressed samples. The bold numbers are from direct measurements and the other are from calculation.

Wire	Time at 890 °C(hr)	ρ_{sheath}(300K) ($10^{-8}\Omega$m)	ρ_{sheath}(4K) ($10^{-11}\Omega$m)	ρ_{Ag}(4K) ($10^{-11}\Omega$m)	RRR
"A"	1	**~1.72**	**7.23**	4.84	351
	8		**6.98**	4.67	363
	24		**6.46**	4.33	392
	48		**5.97**	4.02	436
"B"	1	**~1.80**	**18.6**	8.16	198
	8		**17.6**	7.75	209
	24		**14.2**	6.24	260
	48		**13.3**	5.85	277

Discussion

Figure 3 and Figure 4 showed that for Ag/Bi-2212 wires either in melt state or in powder state, Cu can dissolve into silver and diffuse through Ag and Ag-0.2wt%Mg to form Cu_2O particles on their surfaces, providing another strong evidence that Cu-loss is common in reacted Ag/Bi-2212 wires in additional to those presented in [6], [11], [12], [14]. This is consistent with studies of AgCu alloy [15], which shows that the Cu diffusing into silver matrix segregates and forms precipitates under oxidizing atmosphere, instead of forming a uniform solid solution alloy.

Using the resistivity of silver sheathes in two wires at 4.2 K, we calculated the resistivity of pure silver by assuming: (i) All electrical current flows in silver and Ag-Mg, with the Bi-2212 filaments' I_c being less than 3 A, and (ii) Ag and Ag-Mg form a parallel circuit, and (iii) The RRR of the Ag-0.2wt% will not be greater than 5. The results were also presented in the Table 1. The calculated ρ_{Ag}(4.2 K) was in the range of 4.02-4.84x$10^{-11}\Omega$m and 5.85-8.16x$10^{-11}\Omega$m, close to or smaller than that of the stand-alone Ag sample (7.3x$10^{-11}\Omega$m), yielding RRR ranging from 198 to 436. This is reasonably consistent with RRR=220 obtained from the stand-alone sample, suggesting that heat treatment and Cu-loss have very limited effect on the resistivity and RRR of Ag. This is perhaps because the formation of Cu_2O particles in O_2 environment minimizes the Cu atoms that stay as foreign atoms in Ag lattice, and perhaps also because the Cu content is quite low. As shown by our SEM observation, we estimated that the total amount of Cu diffusing from Bi-2212 filaments into Ag

is less than 0.1at% of Cu in Ag, based on the fact that the number density of Cu_2O particles is one or two orders lower than that of the MgO particles, shown in Figure 4.

Conclusion

We measured the $\rho(B,T)$ and $\kappa(B = 0, T)$ of Ag and Ag-0.2wt%Mg over the temperature range from 4.2 K to 300 K and over the magnetic field range from 0 T to 14.8 T. We found strong microstructural evidences that Cu in Bi-2212 filaments dissolves into silver and diffuses through Ag and Ag-0.2wt% either when Bi-2212 filaments is in melt state or when they are in powder state. We proposed a simple protocol for determining the RRR of Ag in the Ag/Bi-2212 wires, which involves calculating the resistivity of Ag after measuring the *E-J* curves at 4.2 K of Ag/Bi-2212 wires reacted at 890 °C for 48 hours and cooled to room temperature; such heat treatment allows to suppress the I_c of Bi-2212 filaments while maintaining or increasing Cu loss. The measurement and analysis indicated that the RRR of Ag doesn't, surprisingly, degrade with an extended heat treatment of 48 hours at 890 °C. This is perhaps explained by the fact that Cu diffuses through Ag to form Cu_2O precipitates on the surface. The RRR of Ag-0.2wt% is determined to be ~5 and the RRR of Ag is determined to be 200-440.

Acknowledgement

This work was supported by the U.S Department of Energy, Office of High Energy Physics through a FY12 early career award. We thank Dr. Hanping Miao and Dr. Yibing Huang with Oxford Superconducting Technology for supplying us the Ag and Ag-0.2wt%Mg samples used in this study, and Dr. Jun Lu with National High Magnetic Field Laboratory for discussion.

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