Abstract. 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-0.2 wt.% Mg) wires as well as the resistivity of Ag and Ag-0.2 wt.% Mg in Ag/Bi-2212 round wires reacted in 1 bar oxygen at 890 ºC 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 Ag-Mg 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 ºC for up to 48 hours. This surprising result may be explained by our observation that the Cu that diffuses into silver tends to form Cu$_2$O 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.

1. Introduction
Silver-sheathed Bi$_2$Sr$_2$CaCu$_2$O ($\text{Ag/Bi-2212 hereafter}$) 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 $J_c$ of commercial powder-in-tube (PIT) Ag/Bi-2212 wires was significantly improved, with the best engineering critical current density $J_{E}$ and the $J_c$ 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 Cu/Nb$_3$Sn wires exhibit non-Cu $J_c$ 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 treatments [1]-[3]. Importantly, such high $J_c$ can be achieved in long-length Bi-2212 wires through overpressure partial melt processing so Ag/Bi-2212 round wire is becoming a magnet-grade conductor [2].

In addition 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, Ag-Al, Ag-Mn, and Ag-Mg-Sb [6] and they typically occupy 25% of the total volume of the conductor. Resistivity $\rho$ and thermal conductivity $\kappa$ of both silver and silver alloys are important materials properties. For example, they are important for designing the quench protection
circuitry [7], [8] and affect the design of the entire magnet system, because during a magnet quench, the power generation density in a normal zone is given by \((1 - \lambda) J_m^2(t) \rho(B, T)\), where \(\lambda\) 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 industrial 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 an 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 \(\approx 2-3 \times 10^{-11} \text{ cm}^2/\text{s}\) in Ag at \(\approx 890 \text{ °C}\) [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 \(\approx 82 \text{ K}\) and an \(I_c\) of several hundred amperes [9]-[12].

In this paper, we report the electrical resistivity and thermal conductivity of Ag and Ag-0.2 wt.% Mg (AgMg hereafter) alloy used in industrial production of Ag/Bi-2212 conductors. These properties were 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 the residual resistivity ratio (RRR) of Ag/Bi-2212 wires and its dependence on Cu-loss and heat treatment parameters.

2. Experiments

2.1. Magneto-resistivity and thermal conductivity measurement of stand-alone Ag and AgMg alloy
As the first step, this study determined the \(\rho(B, T)\) of silver and silver alloys used in industrial 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 remove 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 System (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 in magnetic field up to 14.8 Tesla. The thermal conductivity of these heat-treated Ag and AgMg wires was 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 \(890 \text{ °C}\), 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 \(T_{\text{max}}=890 \text{ °C}\) 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 PMM101108-1 (37x18 architecture, \(\phi 0.8 \text{ mm}\)) 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, PMM140721 (85x6 architecture, \(\phi 0.8 \text{ mm}\)), 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 O2, the \(I_c\) of PMM101108-1 at 4.2 K, self-field is 425 A whereas the \(I_c\) of PMM140721 is 450 A whereas after 100 bar overpressure processing, the \(I_c\) at 4.2 K, self-field of PMM101108-1 increases to 870 A, producing a \(J(E,4.2\text{ K, and }20\text{ T})\) of approximately 650 A/mm². 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 beginning part of this procedure is similar to the standard partial-melt-processing (PMP): the temperature ramps from room temperature to 820 ºC at 160 ºC/hour, dwells there for 2 hours and then ramps to 890 ºC at 50 ºC/hour. The dashed-line marks where this procedure differs from the standard partial-melt-processing (PMP): the slow cooling (10 ºC/hour from 890 ºC to 880 ºC and 2.5 ºC/hour from 880 ºC to 830 ºC) and the rest of the PMP are replaced with a fast furnace cooling and the dwelling time at \(T_{\text{max}}=890\text{ ºC}\) varies from 1 hour to 48 hours.

2.3. Microscopy observation of Cu-loss
To determine at what temperatures Cu loss occurs and where Cu migrate, 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).

3. 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 O2. For pure silver wire, the measured zero-field resistivity at 300 K, \(\rho(300\text{ K, }0\text{ T})\), is 16.14 nΩ m and that at 4.2 K, \(\rho(4.2\text{ K, }0\text{ T})\), is 0.0754 nΩ m, which gives a \(\text{RRR}\) ratio, defined as \(\rho(300\text{ K, }0\text{ T})/\rho(4.2\text{ K, }0\text{ T})\), of 214. For Ag-0.2 wt. % Mg wire, \(\rho(300\text{ K, }0\text{T})\) is 19.7 nΩ m and \(\rho(4.2\text{ K, }0\text{ T})\) is 3.84 nΩ m, giving a \(\text{RRR}\) 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 \(B [\rho(B=0.273\text{ K})/\rho(B=0,4.2\text{ K})]\), 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 \(\kappa\) of Ag and AgMg wires is shown in Figure 2 (D). \(\kappa\) of Ag has a maximum of ~2700 W/Km at ~15 K and is ~500 W/Km at room temperature. \(\kappa\) of AgMg is much lower than Ag and slowly increases with temperature, which is common in silver with low RRR and silver alloys. The thermal conductivity of Ag decreases
significantly with increasing magnetic field, showing a maximum of ~1600 W/Km at 9 T whereas the thermal conductivity of AgMg changes little with increasing magnetic field to 9 T.

**Figure 2.** Resistivity and thermal conductivity of heat-treated Ag and AgMg (0.2 wt.% Mg). (A). \( \rho(T) \) of pure Ag and Ag-0.2 wt.% Mg in zero magnetic field over 4.2 – 300 K. (B): Dependence of \( \rho_{Ag} \) and \( \rho_{Ag-0.2 \text{ wt.} \% \text{ Mg}} \) on magnetic fields at 10 K, 50 K, 100 K and 200 K. (C): Kohler plot generated from all the \( \rho(B, T) \) data obtained with the data reported in Ref [13] shown as two lines. (D): Thermal conductivity of Ag and AgMg as a function of temperature and magnetic field. The inset of (D) shows the low temperature (< 40 K) thermal conductivity data of Ag at 0 T, 1 T, 5 T and 9 T.

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

We 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, CuO 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.
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, did not 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 (hour) | \( \rho_{\text{sheath}}(300 \text{ K}) \) (10\(^{-8}\) Ωm) | \( \rho_{\text{sheath}}(4 \text{ K}) \) (10\(^{-11}\) Ωm) | \( \rho_{\text{Ag}}(4 \text{ K}) \) (10\(^{-11}\) Ωm) | RRR of Ag |
|------|-----------------------|---------------------------------|-----------------|-----------------|-------------|
| “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             |

4. 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-0.2 wt.% Mg to form Cu\(_2\)O particles on their surfaces, providing another strong evidence that Cu-loss is common in reacted Ag/Bi-2212 wires in addition to those presented in [6], [11], [12], [14]. This is consistent with studies of AgCu alloy [15], which shows that Cu tends to segregate and form 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 in Table 1, 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; (ii) Ag and Ag-Mg form a parallel circuit; (iii) the RRR of the Ag-0.2 wt. % Mg is less than 5. The results were also presented in the Table 1. The calculated \( \rho_{\text{Ag}}(4.2 \text{ K}) \) was in the range of 4.02-4.84x10\(^{-11}\) Ωm and 5.85-8.16x10\(^{-11}\) Ωm, close to or smaller than that of the stand-alone Ag sample (7.3x10\(^{-11}\) Ωm), 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\(_2\)O 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. We estimated that the total amount of Cu diffusing from Bi-2212 filaments into Ag is less than 0.1 at.% of Cu in Ag, based on the fact that the number density of Cu\(_2\)O particles is one or two orders lower than that of the MgO particles, shown in Figure 4.

5. Conclusion
We measured the $\rho(B,T)$ and $\kappa(B=0,T)$ of Ag and Ag-0.2 wt.% Mg over the temperature range 4.2 - 300 K for magnetic induction up to 14.8 T. We found strong microstructural evidences that Cu in Bi-2212 filaments dissolves into silver and diffuses through Ag and Ag-0.2 wt.% Mg both when Bi-2212 filaments are in the melt state and when they are in the 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 ºC 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 surprisingly does not degrade with an extended heat treatment of 48 hours at 890 ºC. This is perhaps explained by the fact that Cu diffuses through Ag to form Cu$_2$O precipitates on the surface. The RRR of Ag-0.2 wt.% Mg is determined to be ~5 and the RRR of Ag is determined to be 200-440.

6. References

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