Thermal and electrical properties of Ag-Au and Ag-Cu alloy tapes for metal stabilizers of oxide superconductors

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In order to develop new metal stabilizers with a low heat transport capacity for Bi-based oxide superconducting power current leads, the thermal conductivity and electrical resistivity of Ag-Au and Ag-Cu alloy tapes heat treated in air were investigated from 15 to 260 K. The thermal conductivity of Ag-Au alloy tapes decreased drastically at low temperatures with increasing Au content after the heat treatment necessary to realize the superconducting wire. By contrast, the thermal conductivity of Ag-Cu alloy tapes hardly decreased because of oxidation of Cu during the heat treatment.

Keywords: metal stabilizers; current leads; physical properties

In the various wiring processes for oxide superconductors, the choice of metal stabilizer seriously influences superconducting characteristics such as critical current density J_c and critical temperature T_c. Silver (Ag) is widely used as the metal stabilizer in order to realize a high crystal orientation of the oxide compounds and excellent superconducting characteristics[1,2]. The J_c of a $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) oxide superconductor fabricated by the doctor blade method on an Ag substrate was reported to reach $\approx 10^5$ A cm^{-2} at 4.2 K under a magnetic field of 23 T[3]. In cases where Ag-sheathed oxide superconductor tapes are applied to power current leads for cryogenic apparatus such as a high field superconducting magnet (SCM), the Ag sheath acts as a heat conduction medium, and hence the large input of heat becomes a serious problem. For this reason, it is necessary to search for a material with low thermal conductivity as the metal stabilizer instead of pure Ag. A popular method of reducing the thermal conductivity of metals is alloying. For application in power current leads, we have fabricated Bi-2212 oxide thick films on Ag-gold (Au) and Ag-copper (Cu) alloy tapes using the doctor blade method, and have investigated the resulting superconducting characteristics[4]. Ag-Cu alloys were found to seriously damage the Bi-2212 superconductivity. On the other hand, the superconducting characteristics of the Bi-2212 films on Ag-Au alloy tapes remained excellent, as well as on the pure Ag tape.

The thermal conductivity data of the alloy tapes are necessary to calculate the heat flow through the power current leads, and both thermal conductivity and electrical resistivity are important in determining the dynamic stability or the eddy current loss of the superconducting power current lead system. In this paper, we investigated the thermal conductivities, electrical resistivities and metallography of Ag-Au and Ag-Cu alloy tapes with various levels of Au and Cu. The tapes were heat treated in air and in nitrogen. The chemically active nature of Cu in Ag-Cu alloys is suggested to be the main cause of the damage to the Bi-2212 superconducting characteristics for Ag-Cu alloy tapes.

Experimental details

Ag-Au and Ag-Cu alloys, containing Au and Cu from 0 to 11 at% and from 0 to 2.6 at%, respectively, were prepared in a RF induction furnace and cold-rolled into tapes 50 μm in thickness. The composition was measured by inductively coupled plasma (ICP) spectroscopy. Ag, Au and Cu of 4N (99.99%) grade were used as raw materials. The cold-rolled tapes were heat treated in air following the same process as when $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) is heat treated on a pure Ag substrate. The highest temperature of this heat treatment was 840°C, which was applied for 150 h. For the Ag-Cu alloy tapes, heat treatment in a nitrogen atmosphere was also performed, following the same heat treatment pattern, to investigate the influence of oxygen on the alloy tapes. The thermal conductivity was measured using a steady state heat flow method from 15 to 260 K with an automated measuring system of our own making. The system used a closed cycle helium refrigerator as the cryostat. One end of the sample was soldered to the cold head of the cryostat and a small metallic thin

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film chip resistance heater (10 kΩ; 2.2 × 1.6 × 0.4 mm^3) was attached to the other end of the sample using GE7031 varnish. Au + 0.07 at% Fe-chromel thermocouples, 73 μm in diameter, were used differentially in order to measure the difference in temperatures. Two junctions of the thermocouple, ≈ 1 cm apart, were attached to the sample surface using varnish. The electrical resistivity was measured by a conventional four-probe method with a closed cycle helium refrigerator from 15 to 300 K, and in liquid helium at 4.2 K. Metallographic observations and composition analysis of the alloy tapes were performed using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Results and discussion

Figure 1 shows the temperature dependence of the thermal conductivity of Ag-Au alloy tapes with various Au levels heat treated in air. The thermal conductivity drastically decreased with increasing Au content at low temperatures. The thermal conductivity of the alloy tape with 11 at% Au was about three orders of magnitude smaller than that of the pure Ag tape at 20 K. Thermal conductivity data for an Ag-Au alloy system were reported by Crisp *et al.*[5]. They used a wire-shaped sample 1–5 cm in length and 0.5–1.0 mm in diameter, which was heat treated at 900°C for 72 h in a low pressure atmosphere of oxygen to reduce the residual Fe concentration. The thermal conductivity data shown in *Figure 1* are fairly consistent with Crisp's data, notwithstanding the fact that the present alloys were cold-rolled to as thin as 50 μm and heat treated in air. The thermal conductivity of an Ag-Au alloy, fabricated using high grade raw materials, seems to depend only on the Au content.

Figure 2 shows the temperature dependence of the electrical resistivity of the Ag-Au alloy tapes with various levels of Au. The electrical resistivity drastically increased with increasing Au content at low temperatures. As the electronic thermal conductivity and the electrical resistivity are related by the Wiedemann–Franz law, the Au content dependences in *Figures 1* and *2* are reasonable.

Figure 3 shows the temperature dependence of the thermal conductivity of Ag-Cu alloy tapes with various Cu levels heat treated in air. The thermal conductivity of the Ag-Cu system only slightly decreased with increasing Cu content at low temperatures. *Figure 4* shows the

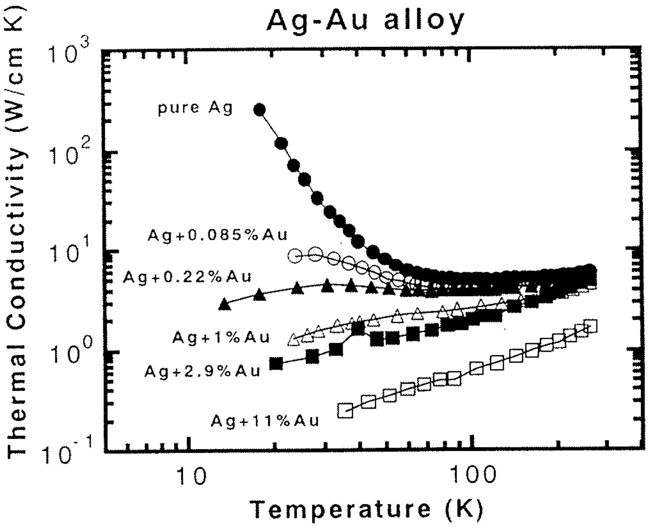

Figure 1 Temperature dependence of thermal conductivity of Ag-Au alloy tapes with various levels of Au

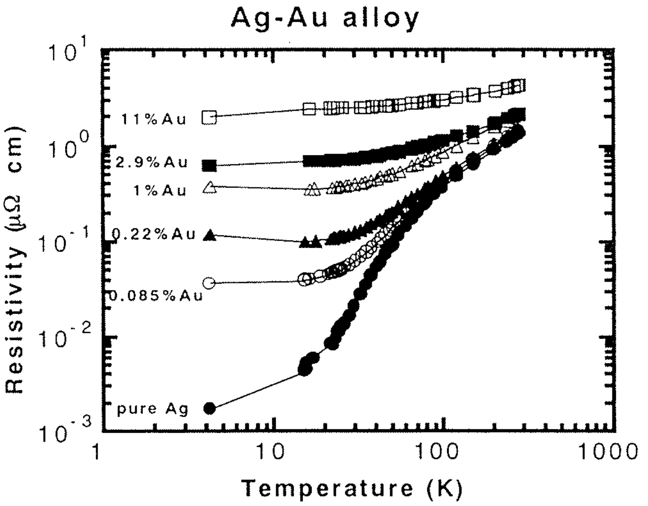

Figure 2 Temperature dependence of electrical resistivity of Ag-Au alloy tapes with various levels of Au

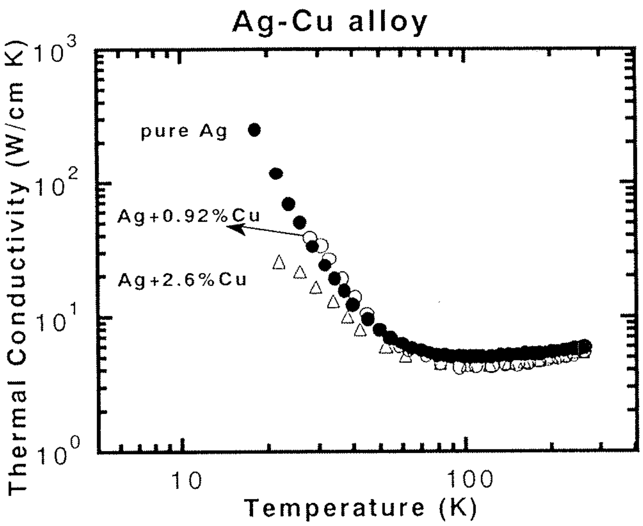

Figure 3 Temperature dependence of thermal conductivity of Ag-Cu alloy tapes with various levels of Cu

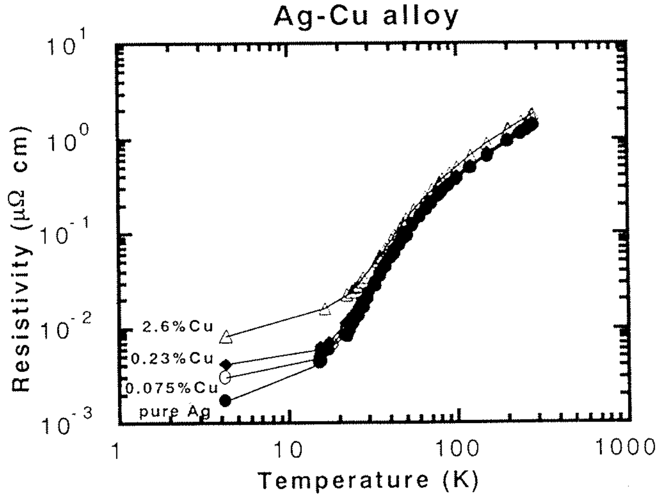

Figure 4 Temperature dependence of electrical resistivity of Ag-Cu alloy tapes with various levels of Cu

temperature dependence of the electrical resistivity of the Ag-Cu alloy tapes with various levels of Cu. In accordance with the thermal conductivity measurements, the change in electrical resistivity with increasing Cu content was very small.

In order to investigate the differences in behaviour between Ag-Au and Ag-Cu alloys, surface observations and a compositional analysis were performed by SEM and EPMA. *Figure 5* shows SEM images of Ag-Au (*Figure 5a*, 1.0 at% Au; *b*, 2.9 at% Au; *c*, 11 at% Au) and

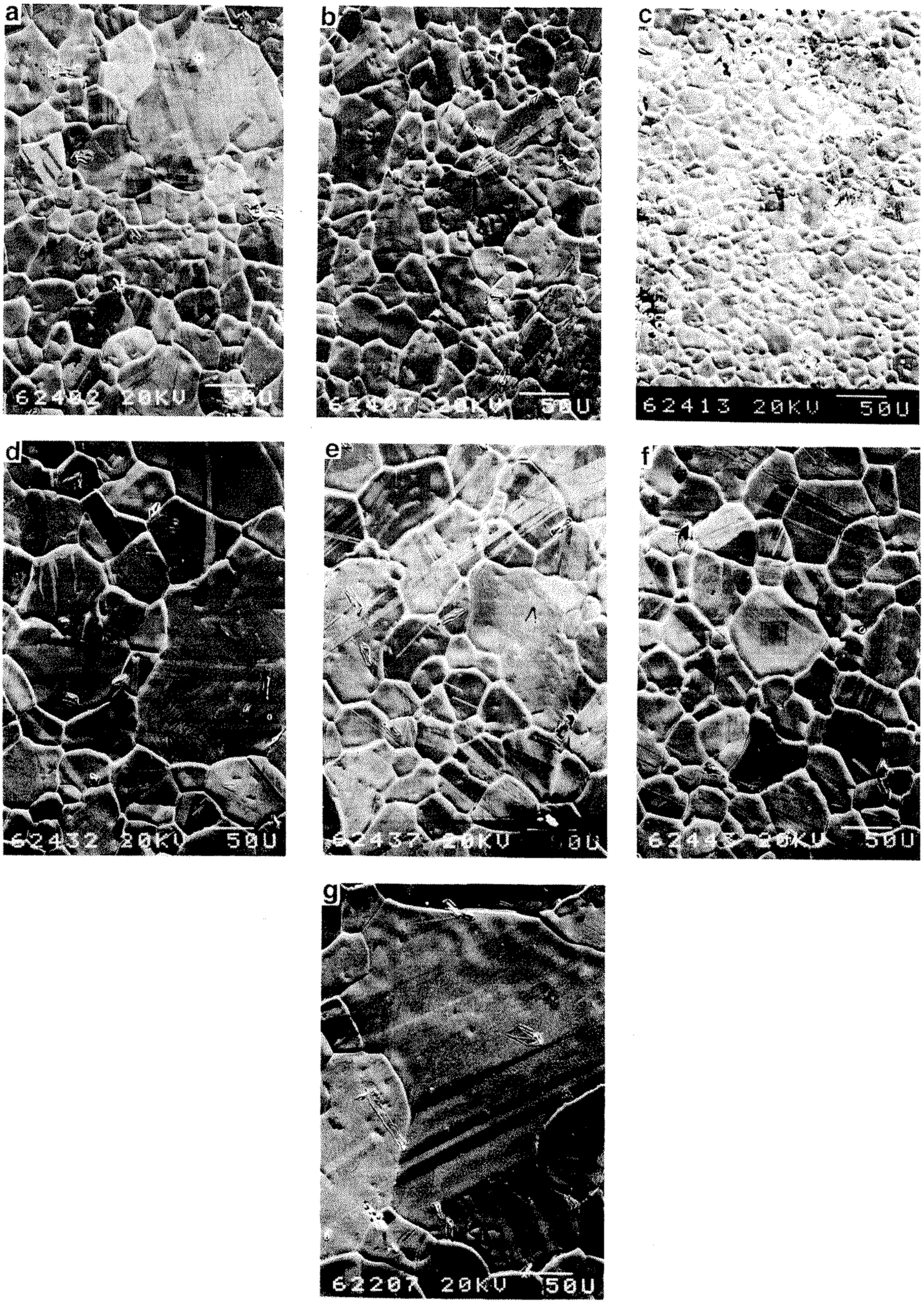

Figure 5 SEM images of Ag-Au alloy tapes [(a) 1.0 at% Au; (b) 2.9 at% Au, (c) 11 at% Au)], Ag-Cu alloy tapes [(d) 0.23 at% Cu; (e) 0.92 at% Cu; (f) 2.6 at% Cu)] and pure Ag tape (g) subjected to heat treatment in air

Ag-Cu (*d*, 0.23 at% Cu; *e*, 0.92 at% Cu; *f*, 2.6 at% Cu) alloy tapes, subjected to heat treatment in air. For comparison, the SEM image of a pure Ag tape subjected to the same heat treatment is also shown (*Figure 5g*). It is found that the recrystallized grain size of the Ag-Au alloy tapes decreases drastically as the amount of Au is increased. On the other hand, the grain size of the Ag-Cu alloy tapes, which is somewhat smaller than for pure Ag, remains almost unchanged even when the amount of Cu added is increased.

Figure 6 shows the relation between the images from the reflection electron microscope and an area analysis of Ag, Au and Cu identified from the characteristic X-ray intensity of each element. *Figure 6a* shows the reflection electron micrograph of a polished Ag + 1.0 at% Au alloy tape. *Figures 6b and c* show the area analysis pattern of Au and Ag elements in the same position. *Figure 6d* shows the reflection electron micrograph of a polished Ag + 0.92 at% Cu alloy tape. *Figures 6e* and *f* show the area analysis pattern of Cu and Ag in the same position. A bright area shows the existence of the element. In the Ag + 1.0 at% Au alloy tape (*Figures 6a–c*), it was found that Au atoms are homogeneously dissolved in an Ag matrix. On the other hand, in the Ag + 0.92 at% Cu alloy tape (*Figures 6d–f*) only a fraction of the Cu atoms are dissolved homogeneously in the Ag matrix, accompanied by local precipitation. The Cu content in the Ag matrix was estimated to be ≈ 0.40 at% from quantitative analysis by EPMA. The equilibrium phase diagrams of these two alloy systems show that the Ag-Au alloy is a solid solution type[6] and the Ag-Cu alloy is a eutectic reaction type[7]. Accordingly, Au atoms can be homogeneously dissolved in the Ag matrix at any concentration, whereas Cu atoms can be dissolved up to 0.35 at% and then the rest of the Cu atoms are precipitated. The results for the Ag-Au alloys shown in *Figures 1, 2* and *6b* are consistent with the phase diagram. For the Ag-Cu alloy system, the results of the EPMA measurements seem to be consistent

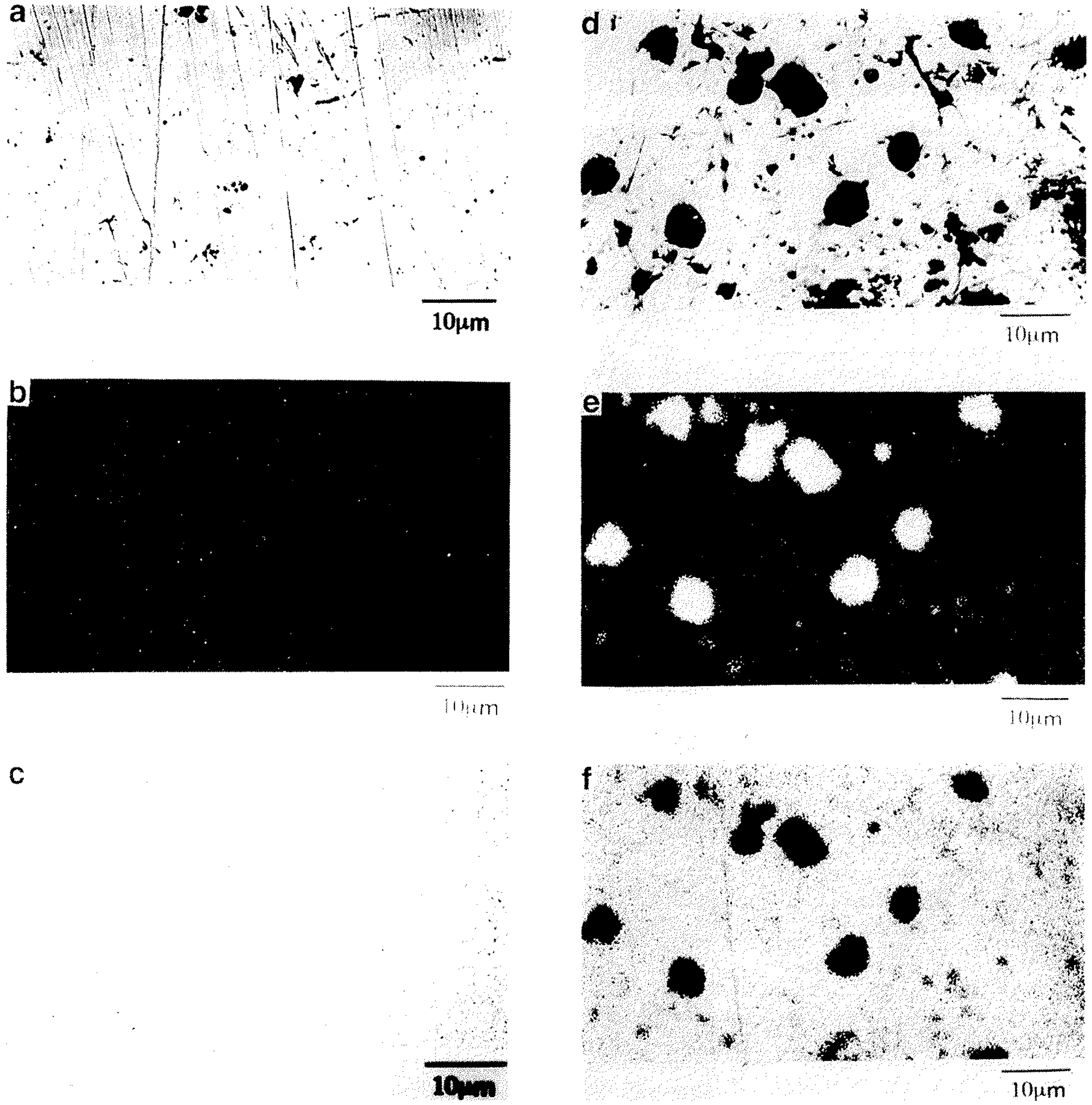

Figure 6 (a) Reflection electron micrograph of polished Ag + 1.0 at% Au alloy tape. (b), (c) Area analysis patterns of Au and Ag elements in same position, respectively. (d) Reflection electron micrograph of polished Ag + 0.92 at% Cu alloy tape. (e), (f) Area analysis patterns of Cu and Ag elements in same position, respectively

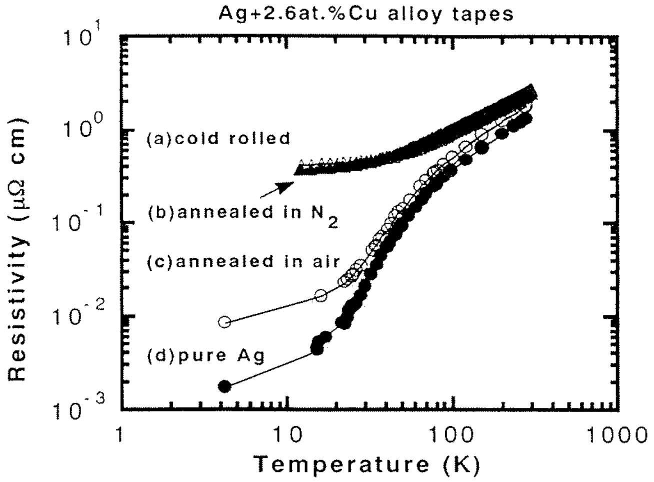

Figure 7 Temperature dependence of electrical resistivity of Ag + 2.6 at% Cu alloy tapes for various heat treatment conditions: (a) cold-rolled tape; (b) tape annealed in nitrogen; (c) tape annealed in air; (d) annealed pure Ag tape (shown for comparison)

with the phase diagram. The thermal conductivity and electrical resistivity results shown in *Figures 3* and *4*, however, are inconsistent with the phase diagram. If Cu atoms are soluble up to 0.35 at% in the Ag matrix, a remarkable decrease in the thermal and the electrical conductivity of Ag-Cu alloys should be observable, as in the Ag-Au alloy system, with an increase in Cu content up to 0.35 at%.

In order to investigate this discrepancy, the electrical resistivity was measured for Ag-Cu alloy tapes heat treated following the same heat treatment pattern but in a nitrogen atmosphere. *Figure 7* shows the temperature dependence of the electrical resistivity of Ag + 2.6 at% Cu alloy tapes, where (a) stands for the cold-rolled tape, (b) the tape heat treated in nitrogen gas and (c) the tape heat treated in air. The electrical resistivity of a pure Ag tape which was heat treated in air is also shown [curve (d)] for comparison. The electrical resistivity shown in curves (a) and (b) is almost the same. On the other hand, the electrical resistivity of the tape heat treated in the oxidizing atmosphere, shown in (c), drastically decreased, to give values as low as those for the pure Ag tape [curve (d)]. These results indicate that Cu atoms react with oxygen during heat treatment in air to produce copper oxide. The oxidized copper does not seem to seriously affect the thermal conductivity and electrical resistivity. From the area analysis of oxygen by EPMA, oxygen signals were confirmed in the positions of Cu precipitates in tapes heat treated in air, although they were very weak due to the poor sensitivity of EPMA to oxygen. We conclude that the thermal conductivity and electrical resistivity of Ag-Cu alloy tapes are virtually unchanged by addition of Cu because copper atoms react with oxygen during the heat treatment in air. We also infer that the very reactive nature of Cu in Ag-Cu alloys is the main cause of the damage to the Bi-2212 superconducting characteristics observed in Au-Cu based tapes.

Summary

The thermal conductivity and electrical resistivity of Ag-Au and Ag-Cu alloy tapes were investigated from 15 to 260 K for the purpose of developing a metal stabilizer to replace pure Ag in superconducting Bi-based oxide power current leads. The results are summarized as follows.

1. The thermal conductivity of Ag-Au alloy tapes can decrease drastically at low temperatures with increasing Au content. When Au is dissolved in an Ag matrix at 2.9 and 11 at%, the Ag-Au alloy has a thermal conductivity as low as that of deoxidized copper and Cu-Zn alloy, respectively.
2. The thermal conductivity of Ag-Cu alloy tapes which have been heat treated in air does not decrease notably at low temperatures with increasing Cu content. It seems that Cu atoms react with oxygen during the heat treatment, producing copper oxide.
3. The Ag-Au alloy is the most promising as a metal stabilizer of Bi-based oxide superconductors for application in low thermal conductivity power current leads.

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