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Mechanical and Thermal Properties of Ag sheath alloys for Bi-2223 superconductor tape

Tae-Woo Kim[a], Jinho Joo*,[a], Wansoo Nah[b], Jaimoo Yoo[c], Jae-Woong Ko[c],
Hai-Doo Kim[c], Hyungsik Chung[c], and Sang-hyun Lee[d]

[a]*School of Metallurgical and Materials Engineering, Sungkyunkwan University, Suwon, 440-746, Korea*
[b]*School of Electrical and Computer Engineering, Sungkyunkwan University, Suwon, 440-746, Korea*
[c]*Department of Materials Processing, Korea Institute of Machinery and Materials, Changwon, 641-010, Korea*
[d] *Division of Quantum Metrology, Korea Research Institute of Standard and Science, Yusong, Taejon, 305-600, Korea*

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Abstract

We evaluated the effect of alloying element additions to Ag sheath on mechanical, electrical and thermal properties of Bi-2223. Additions of Au, Pd and Mg to Ag sheath increased hardness and strength, while reduced elongation and electrical and thermal conductivity. In addition, microstructural investigation showed that the grain size of Ag significantly decreased with increasing content of alloying elements. The improvements in strength and hardness are believed to be due to the presence of alloying elements that lead to strengthen materials by combined effects of solid-solution, dispersion hardening and grain size hardening. Thermal conductivity of Ag and Ag alloys was evaluated in the temperature range from 77 K to 300 K, and compared to calculated value obtained by Wiedermann-Franz law. It was observed that the thermal conductivity decreased with increasing the content of alloying elements. Specifically, the thermal conductivity of $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ alloy was measured to be 48.2 W/(m · K) at 77 K, which is about 6 times lower than that of Ag (302.6 W/(m · K)).

Keyword: PIT process, superconductor tape; strengthening mechanism; thermal conductivity; thermal diffusivity

I. Introduction

For large scale applications of superconductor such as power systems including power generation (generator and turbine), power distribution (network) and motor, etc., development of long lengths of superconductors with good electrical and mechanical properties is very critical. Among various processing techniques, powder-in- tube (PIT) process is regarded as one of the most promising techniques for fabricating long conductor. The BSCCO tape made by PIT process has been fabricated to 1.2 km long with critical current of 30 A at 77 K [1].

In the PIT process, having a desirable geometry in which brittle superconductor oxide is surrounded by a metal sheath, pure Ag is used as a sheath material due to good chemical stability with superconducting phases, good workability and oxygen transmissivity, etc. [2]. However, low strength and hardness of Ag lead to microstructural damages such as sausage effect, crack and failure by the induced strains during fabrication and in service, resulting in the degradation of critical current and reproducibility. To strengthen the sheath, therefore, it is recommended to develop Ag alloy by addition of alloying elements to Ag.

In addition to fabricating long conductor, PIT-processed tape has recently received considerable attention for different application, i.e. current lead [3].

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*Corresponding author. Fax: +82 331 290 7371
e-mail: jinho@yurim.skku.ac.kr

The current lead for liquid helium cooled superconducting systems is expected to reduce the heat leakage into the coolant. The present superconducting magnets utilize conventional copper current lead requiring four liters of liquid helium per hour for cooling purposes,[4] so the leads cooling requirement was a major load on the liquefaction system. To this end, it was expected that using high T_c superconductor (HT_cS) as a hybrid-type current lead reduce this consumption.

A HT_cS current lead with a stacking structure by assembling Ag-sheathed BSCCO tape has been proposed. This has several advantages of high critical current density (J_c), good strain tolerance and ease in making a long length and various geometries. The only weakness is heat leakage caused by high thermal conductivity of Ag sheath. Thus, sheath materials with lower thermal conductivity are to be developed, and this can be done by developing Ag alloys as suggested earlier.

Much research has been performed to develop various Ag alloys as sheath materials. Among them, binary systems of Ag-Mg[5],[6], Ag-Au[7],[8], Ag-Cu[9],[10] and Ag-Ni[11] and ternary systems of Ag-Mg-Ni[12],[13], Ag-Pd-Mg[14], Ag-Au-Mg [15] and Ag-Au-Al[16], etc. are reported to alternative sheath alloys without degrading critical current to a large extent. In their studies, however, electrical, mechanical and thermal properties of various sheath alloys were not systematically evaluated. To this end, we fabricated Ag alloys of Ag-Mg, Ag-Au-Mg, Ag-Pd-Mg and systematically characterized strength, hardness, elongation, and electrical and thermal conductivity. Also, the properties of alloys were correlated to microstructural evolution.

II. Experimental Procedure

Ag alloys were fabricated by adding the small amounts of Au, Pd and Mg elements to Ag (99.99% purity) and melting them in a high frequency induction furnace at KIMM (Korea Institute of Machinery and Materials). The compositions of Ag alloys were $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$. These billets were extruded into hollow tubes (OD = 12.7 mm, ID = 9.5 mm) using a specially designed extrusion die and heat treated for 8 h in N_2 atmosphere to release strain hardening during the extrusion. For PIT process, 2223 powder [15] was loaded in extruded tube (OD = 6.5 mm, ID = 4.5 mm), and then the assemblies were compacted by swaging, drawing/groove rolling and rolling. Intermediate annealings were often incorporated between successive swaging and drawing steps. The final thickness and width of the tapes after rolling were 0.2 mm and 2 mm, respectively. These tapes were sintered at the temperature of 840 ℃ in air for 50 h.

Hardness of Ag and Ag alloys was measured by micro hardness tester (MVK-H2, Mytutoyo, 25 g_f) during the working as a function of true strain. Strength was measured in a tension test on a universal testing system (Instron-5655). Electrical conductivity was measured by four-probe method at 77 K and room temperature (300 K). Approximately four to six specimens were tested for both electrical and mechanical property measurements. Microstructure was evaluated by optical and scanning electron microscopy (SEM).

Thermal conductivity of Ag and Ag alloys was evaluated by measuring density, specific heat and thermal diffusivity. Density was measured by Archimdes method. Specific heat was evaluated with enthalpy method [17] by using a differential scanning calorimeter (DSC, Perkin-Elmer, Pyris 1). Thermal diffusivity was measured by a laser flash method [18]-[20]. The specific heat and thermal diffusivity were measured in the temperature range of 77 K - 300 K. For the measurements, Ag and Ag alloys were made in disc shape, i.e., 5 mm of diameter and 2 mm in thickness for specific heat, and 10 mm of diameter and 4.5 mm in thickness for thermal diffusivity. The detailed explanation for thermal diffusivity measurement is mentioned in section 3-2.

III. Results and Discussions

1. Mechanical properties and microstructural investigations

The hardness of extruded Ag, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ was measured to be 35.3, 47.9, 81.9 and 92.5 (Hv(0.025)), respectively. It is to be noted that the values of Ag alloys are higher than those of Ag and increased with increasing the amount of alloying elements. These improvements in the Ag alloys are probably due to the strengthening mechanisms such as solid solution hardening and dispersion hardening resulting from the addition of alloying elements.

To characterize the variation of hardness of Ag and Ag alloys with deformation, hardness was measured during each step of drawing and rolling processes. Fig. 1 shows the hardness dependence of Ag and Ag alloys on the deformation. As shown in the figure, the hardness of Ag and Ag alloys increased with increasing true strain. For pure Ag, hardness increased to 72.4 when specimen was drawn to the diameter of 1.0 mm (true strain = 3.39), and further increased to 79.4 when the specimen was successively rolled to the thickness of 0.20 mm (true strain = 4.86). For Ag alloys, the variation of hardness is similar to that of Ag. However, the values for the specimens of final thickness (thickness = 0.2 mm, true strain = 4.8) are in the range of 110 - 160, which is 39 - 102% higher than that for Ag.

It was suggested that the interface irregularity between Ag and superconducting core (sausage effect) is caused by the different mechanical properties for Ag and superconductor. In view of the fact that the hardness of metallic sheath (Ag) is lower than that of ceramic core, it is expected that sausage effect reduce when the hardness of sheath material enhance [2],[21],[22]. It is still unknown the hardness of superconducting core during drawing and rolling due to difficulty in measurement for such a small and thin one at this stage. However, it is likely that the improved hardness of Ag alloy help reduce the sausage effect.

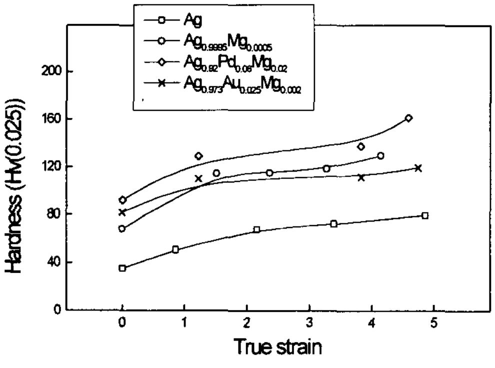


Fig. 1. Dependence of hardness on true strain for Ag and Ag-alloyed sheath materials.

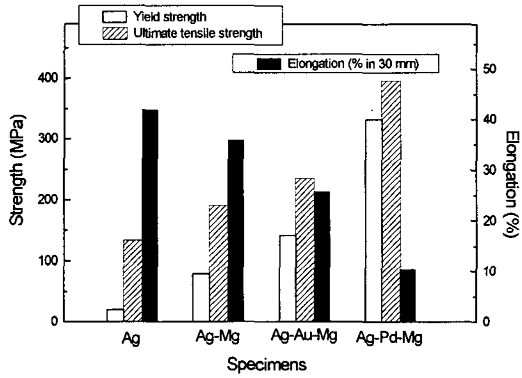
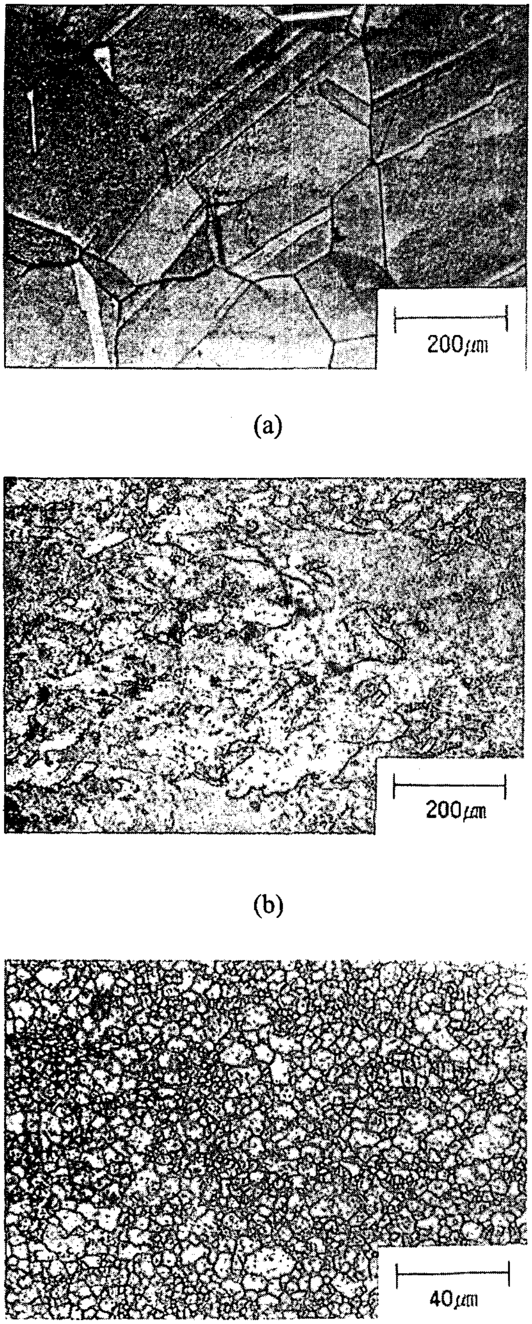


Fig. 2. Variations of yield strength, ultimate tensile strength and elongation of Ag and Ag-alloyed tapes after sintering.

The strength and elongation of Ag and Ag alloy tapes after sintering were measured in a tension test and shown in Fig. 2. The yield strength and ultimate tensile strength of Ag were 20 and 135 MPa, respectively. Corresponding values of Ag alloys were higher than those of Ag. The yield strength for $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ was 80, 143 and 333 MPa, respectively, and the ultimate tensile strength for these was 192, 236 and 397 MPa, respectively. On the other hand, elongation of Ag, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ was measured to be 42, 36, 26 and 11%, respectively, indicating that the elongation of Ag alloys is smaller than that of Ag. It is to be noted that mechanical integrity increased but workability decreased with increasing alloying elements in Ag.

Fig. 3 shows the microstructure of polished surface for Ag, $Ag_{0.9995}Mg_{0.0005}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$. As shown in the figures, the grains in both Ag and Ag alloys are almost in the form of equiaxial even these specimens were undergone a substantial amount of deformation. It is also to be noted that the grain size decreased with increasing content of alloying elements. For Ag, grain size was measured to be 240㎛ and annealing twin is seen in the grain, which is usually observed for annealed specimen that had undertaken severe deformation.



(a)

(b)

(c)

Fig. 3. Optical photographs showing the microstructure of (a) Ag, (b) $Ag_{0.9995}Mg_{0.0005}$ and (c) $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ tapes after heat treatment

For Ag alloys, the grain size was measured to be 100 μm for $Ag_{0.9995}Mg_{0.0005}$ and 10 μm for $Ag_{0.92}Pd_{0.06}Mg_{0.02}$. This decrease in the grain size may be related to the existence of alloying elements in the form of either solute or segregated one. As indicated by Yoo et al. [15], the dissolved Mg is transformed to MgO phase by internal diffusion during heat treatment. The presence of MgO may restrict grain believed that the smaller grain size in Ag alloys is partly attributed to the higher hardness and strength as shown in Figs. 1 and 2.

2. Thermal and electrical properties

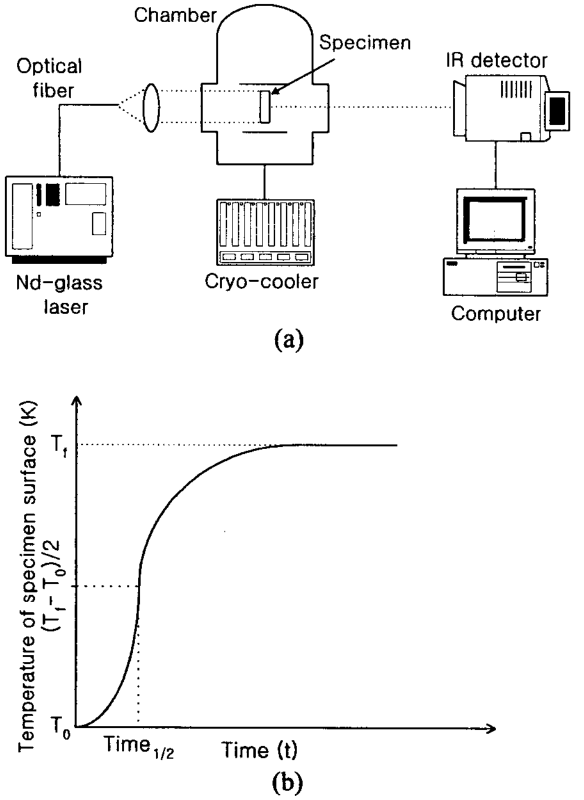
Thermal conductivity was evaluated for Ag and Ag alloys by the following equations:

$$k = \rho C_p \alpha \qquad (1)$$

, where k is thermal conductivity, ρ is density, C_p is specific heat and α is thermal diffusivity. The thermal diffusivity was measured by laser flash method as illustrated in Fig. 4. In the measurements, disc shaped specimen is loaded at tungsten-meshed sample holder in vacuum chamber. Once the chamber become cool down to 77 K, the temperature of specimen is controlled by applying current to sample holder. At the desired temperature, laser pulse is applied perpendicular to the surface of disc specimens and resultant temperature rise is measured from the back side of specimen. The wavelength and intensity of Nd-glass laser are 1.06 μm and 2 J/pulse, respectively. The temperature rise is continuously detected by InSb infra-red detector and the resultant temperature variation with time is schematically shown in Fig. 4(b). From the curve, the thermal diffusivity was determined by the following equation:

$$\alpha = 0.1388t^2/\text{time}_{1/2} \qquad (2)$$

, where t is thickness of specimen and $\text{time}_{1/2}$ is half time which is elapsed time to the temperature of $(T_f - T_0)/2$: T_0 and T_f is the temperature before and after laser irradiation, respectively, as indicated in the figure. The measured values of specific heat, thermal diffusivity and resultant thermal conductivity were shown in Fig. 5. As shown in Fig. 5(c), the thermal



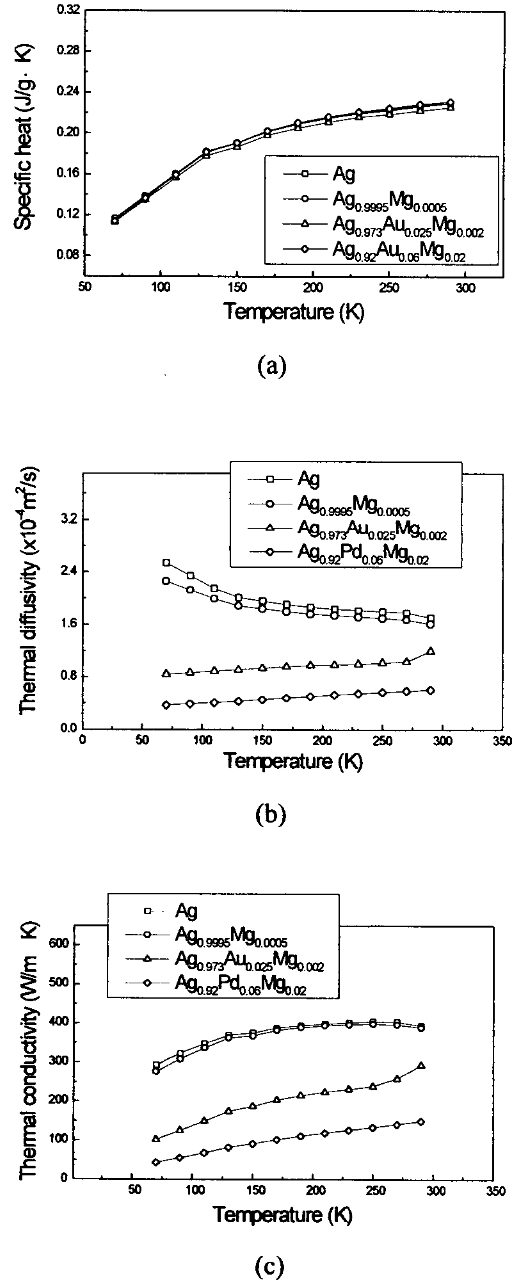
(a)

(b)

Fig. 4. Schematics of (a) laser-flash measurement system and (b) defining the half time for thermal diffusivity

conductivity of Ag was evaluated to be 392.5 W/(m . K) at 300 K. In comparison with the standard reference value of 427 W/(m. K) for Ag at the temperature in TPRC[23], our result is 8% smaller than the standard value. This difference is considered to be within an acceptable error range and probably due to the indirect measurement of thermal conductivity in this study.

As shown in the figure, thermal conductivity of both Ag and Ag alloys monotonically decreased with decreasing temperature. The thermal conductivity of Ag reduced from 392.5 W/(m. K) to 302.6 W/(m. K) as temperature decreased from 300 K to 77 K. Similarly, the values for $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 387.6,292.1 and 149.2 W/(m. K), respectively, at 300 K, and decreased steadily to 288.2, 108.9 and



(a)

(b)

(c)

Fig. 5. Dependence of (a) specific heat, (b) thermal diffusivity and (c) thermal conductivity of Ag and Ag-alloyed materials on the temperature

48.2 W/(m· K) at 77 K. It is also to be noted that the thermal conductivity decreased with increasing the content of alloying elements of Au, Pd and Mg, suggesting that the alloying elements play an important role for determining the value. Specifically the thermal conductivity of $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ is six times lower than that of Ag.

Thermal conductivity of metals, in general, slowly decreases as temperature decreases to about 70 K, and then increases sharply in the temperature to 10 K. Since HT$_c$S current lead for hybrid type should be operated at 4.2 - 77 K, the thermal conductivity would be evaluated at the temperature range. The measurement of thermal conductivity for Ag alloys at the temperature range is in progress.

Electrical conductivity of Ag and Ag alloys was measured at 77 and 300 K as shown in Table I. For Ag, electrical conductivity was measured to be 0.61 $\mu\Omega^{-1}cm^{-1}$ at 300 K which is consistent to literature value (0.63 $\mu\Omega^{-1}cm^{-1}$) [24]. From the table, it is to be noted that electrical conductivity for both Ag and Ag alloys increased as temperature decreased. In addition, electrical conductivity for Ag alloys is lower than that of Ag, and the value decreased with increasing alloying elements. The electrical conductivity for Ag, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 3.34, 1.87, 0.41 and 0.38 $\mu\Omega^{-1}cm^{-1}$, respectively, at 77 K. This result is consistent with Nordheim rule.

Table Ⅰ. Electrical conductivity and measured and calculated thermal conductivity of Ag and Ag-alloyed specimens at 300 K and 77 K

Specimens	Electrical conductivity ($\mu\Omega^{-1}cm^{-1}$)		Calculated thermal conductivity (W/m· K)		Measured thermal conductivity (W/m· K)	
	300 K	77 K	300 K	77 K	300 K	77 K
Ag	0.61	3.34	392.5	596.7	410.4	596.7
$Ag_{0.9995}Mg_{0.0005}$	0.46	1.87	387.6	334.0	309.5	334.0
$Ag_{0.973}Au_{0.025}Mg_{0.002}$	0.28	0.41	256.7	73.2	188.4	73.2
$Ag_{0.92}Pd_{0.06}Mg_{0.02}$	0.26	0.38	149.2	67.9	174.9	67.9

From the measured value of electrical conductivity, thermal conductivity was calculated by using Wiedermann-Franz law and compared to measured values in Fig. 5. From the table, calculated values for Ag, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 596.7, 334.1, 73.2 and 67.9 W/(m· K), respectively, at 77 K. By comparison to the measured values, calculated values are about 5 - 97% different from the measured ones, indicating that Wiedermann-Franz law shows a certain error range for Ag and Ag alloys.

Ⅳ. Conclusions

Additions of Au, Pd and Mg to Ag sheath increased hardness and strength, while reduced workability and electrical and thermal conductivity. Hardness and tensile strength of $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ sheath alloy tapes were improved to 81.9(Hv), 236 MPa and 92.5(Hv), 397 MPa, respectively, on the other hand, the corresponding values of Ag were 55.4(Hv) and 135 MPa. It was also observed that the grain size of Ag in $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ sheath alloy was 10 ㎛, which is significantly smaller than that of Ag sheath (240 ㎛). The improvements in hardness and strength are believed to be due to the presence of alloying elements that lead to strengthen materials by combined effects of solid-solution, dispersion and grain size hardening.

Electrical and thermal conductivity of Ag and Ag alloys decreased with increasing alloying elements. Specifically, the thermal conductivity of $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ alloy was measured to be 48.2 W/(m· K) at 77 K, which is about 6 times lower than that of Ag (302.6 W/(m· K))

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