Low Temperature Thermal Conductivity of Sheath Alloys for High T_c Superconductor Tape

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Effect of alloying element additions to Ag on thermal conductivity and electrical conductivity of sheath materials for Bi-Pb-Sr-Ca-Cu-O(BSCCO) tapes has been characterized. The thermal conductivity at low temperature range (10~300 K) of Ag and Ag alloys were evaluated by both direct and indirect measurement techniques and compared with each other. It was observed that the thermal conductivity decreases with increasing the content of alloying elements such as Au, Pd, and Mg. Thermal conductivity of pure Ag at 30 K was measured to be 994.0 W/(m·K), on the other hand, the corresponding values of $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$, and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 342.6, 62.1, 59.2, and 28.9 W/(m·K), respectively, indicating 3 to 30 times lower than that of pure Ag. In addition, the thermal conductivity of pure Ag measured by direct and indirect measurement techniques was 303.2 and 363.8 W/(m·K). The difference in this study is considered to be within an acceptable error range compared to the reference data.

Keywords : current leads, PIT process, alloy, superconductor tape, specific heat, thermal conductivity and thermal diffusivity

1. INTRODUCTION

Superconductors can be applied to various power systems such as power generation (motor and generator), transformer, current limiter, and power distribution (network), etc., owing to the zero resistance and Meissner effect. For these systems, it is necessary to use current leads with good properties in order to deliver power at liquid helium. The present superconducting magnets utilize conventional copper current leads requiring four liters of liquid helium per hour for cooling purposes, so the leads cooling requirement was a major load on the liquefication system[1]. Whereas, high-T_c superconductor(HT_cS) current leads are expected to lead enhancement of carrying capacity and reduction of heat leakage into the coolant: the former extends the application range for large scale superconducting systems, while the latter improves total performance due to decreasing the consumption of expensive cryogen[2]. To this end, it was expected that using high T_c superconductor as a hybrid-type current leads reduce this consumption.

Recently, the powder-in-tube(PIT)-processed tape has received considerable attention for the application of current leads[3], since HT_cS current leads with a stacking Ag-sheathed BSCCO tape have been proposed. The BSCCO tape made by the PIT process has a desirable geometry in which brittle superconductor oxide is surrounded by an Ag sheath. The current leads made of stacking Ag-sheathed BSCCO tape 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 significant helium consumption caused by heat leakage due to high thermal conductivity of the Ag sheath so that the electrical and thermal properties of sheath materials need to be modified for the application of current leads. To this end, sheath materials with lower thermal and electrical conductivity need to be developed, and this can be done by developing Ag alloys by the addition of alloying elements to Ag.

Much research has been performed to develop various Ag alloys as sheath materials. Among them, binary systems of Ag-Mg [4,5], Ag-Au [6,7], Ag-Cu [8,9], and Ag-Ni [10] and ternary systems of Ag-Mg-Ni [11,12], Ag-Pd-Mg [13], Ag-Au-Mg [14], and Ag-Au-Al [15] were reported to alternative sheath alloys without degrading critical current to a large extent. In their studies, however, the electrical and thermal properties of various sheath alloys did not systematically evaluated. To this end, we fabricated Ag alloys of Ag-Mg, Ag-Au-Mg, and Ag-Pd-Mg, and characterized the thermal and electrical conductivity at the temperature range of 10~300 K.

2. EXPERIMENTAL PROCEDURE

Ag alloys were fabricated by adding small amounts of Mg, Au, and Pd elements to Ag (99.99% purity) and melting them in a high frequency induction. In order to make a solid solution, the contents of alloying elements were selected to be less than their solubility limits for Ag [16]. The compositions of Ag alloys were Ag-Mg(0.0005 at.%), Ag-Au(0.025 at.%)-Mg(0.001~0.002 at.%), and Ag-Pd(0.06 at.%)-Mg(0.02 at.%).

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 for N_2 atmosphere in order to release strain hardening during the extrusion. The extruded tubes were compacted by swaging and rolling. Intermediate annealings were often incorporated between successive swaging and drawing steps. The final thickness and width of the tapes after rolling were 2 mm and 6 mm, respectively. These tapes were sintered in a temperature of 840°C in air for 50 h.

Thermal conductivity of Ag and Ag-alloys was evaluated by using two different methods : (1) direct measurement of thermal integral technique and (2) indirect measurement technique by measuring density, specific heat, and thermal diffusivity. In the direct measurement, cryocooler (CTI model 350) was used to vary temperature from 10 to 100 K. Ag and Ag alloys (80 mm x 6 mm x 0.2 mm) were loaded in the cryocooler chamber and then thermal conductivity was measured by thermal integral method under steady state condition.

In the indirect measurement, density was measured by Archimdes method. Specific heat was evaluated using the 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 evaluated in the temperature range of 70~300 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 both thermal conductivity measurements is mentioned in section 3-1.

3. RESULTS AND DISCUSSION

3-1. Direct and indirect measurement techniques

Thermal conductivity was directly evaluated for Ag and Ag alloys by thermal integral method as following equation:

$$Q = \frac{A}{L}\int_{T_1}^{T_2} k dT \qquad (1)$$

where Q is the heat flux(W), A is the cross section area(m^2), and L is the length of the specimen(m), and k is the thermal conductivity(W/(m·K)). In the measurement, specimen was loaded on the copper block(oxygen free high copper(OFHC) holder) in the cryocooler chamber as shown in Figure 1. One end of specimen was connected to the OFHC holder and the other end contacted to heater (LakeShore, Nichrome heater wire-NC-32) in order to induce temperature gradient (ΔT) on the specimen. To reduce the heat flow through the air and assemblage, atmosphere was set to 10^{-6} torr and epoxy glass was inserted between heater and OFHC holder. Once the chamber was cooled down to 10 K, predetermined current was applied to the heater and hold until steady state condition was obtained. The input heat flux was measured by nanovoltmeter and multimeter (Keithley model 2182 and 2000) resultant

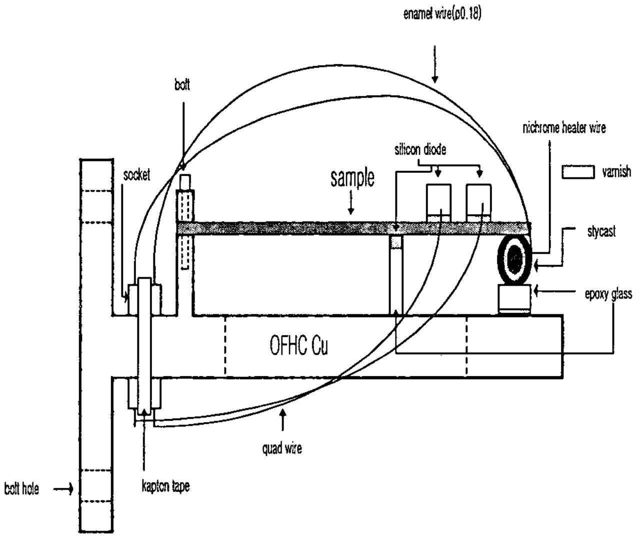


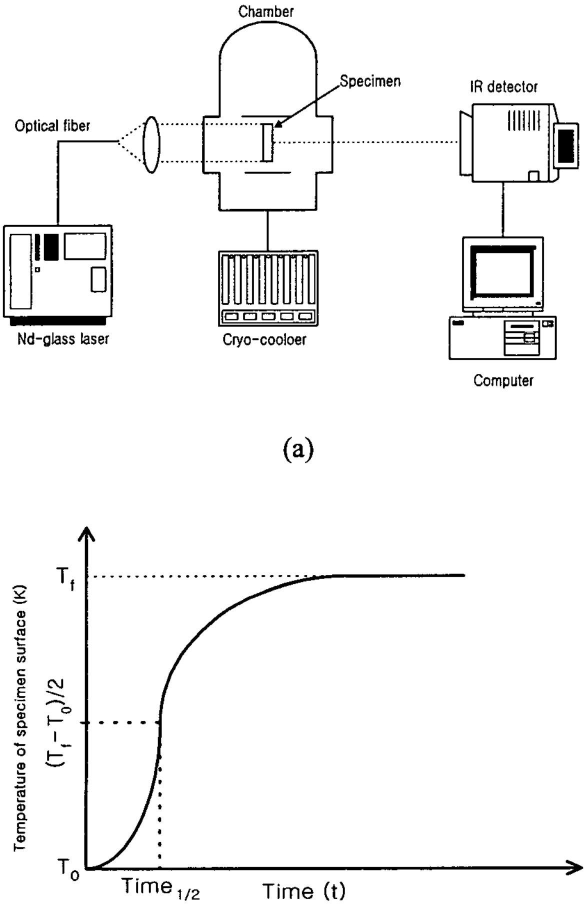
Fig. 1. Schematic diagram of OFHC holder, sample, diodes, heater, and their connections.

was measured with Si-diode temperature sensors (LakeShore, DT-470, 471), which were calibrated to an accuracy of 0.05 K. The measurement was done at approximately 20 different temperature ranges between 10~100 K and temperature difference at each range was controlled to be less than 0.5~2 K by using temperature controller(LakeShore, model 330).

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

$$k = \varrho \cdot C_p \cdot \alpha \qquad (2)$$

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. 2. In the measurements, a disc shaped specimen was loaded into tungsten-meshed sample holder in a vacuum chamber. Once the chamber cooled down to 77 K, the temperature of the specimen was controlled by applying current to the sample holder. At the desired temperature, a pulse laser was applied perpendicular to the surface of disc specimens and the resultant temperature rise was measured from the back side of the specimen. The wavelength and intensity of Nd-glass laser are 1.06 μm and 2 J/pulse, respectively. The temperature rise was continuously detected by an InSb infra-red detector and the resultant temperature variation with time is schematically shown in Fig. 2(b). From the curve, the thermal diffusivity was determined by the following equation:



(a)

(b)

Fig. 2. Schematics of (a) laser-flash measurement system and (b) defining the half time for thermal diffusivity.

$$k = 0.1388 \cdot t^2/\text{time}_{1/2} \qquad (3)$$

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_f and T_0 is the temperature before and after laser irradiation, respectively, as indicated in the figure.

3-2. Thermal conductivity of Ag and Ag alloys

The measured thermal conductivity of Ag and $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$, and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ alloys in the temperature range of 10~100 K was shown in Figure 3. As shown in the figure, thermal conductivity of Ag at 77 K was measured to be 368.8 W/(m·K). Compared to the value of Ag at room temperature (427.0 W/(m·K), thermophysical research conference(TPRC) standard value [21]), it is likely that the thermal conductivity is reduced with decreasing temperature. On the other hand, the value increased as the temperature decreased further and reached to the peak value of 2037.0 W/(m·K) approximately at 15 K, and then slightly decreased with decreasing temperature to ~10 K. This variation of thermal conductivity at low temperature is similar to the typical trend of those for pure materials. It is believed that the increase in thermal conductivity at low temperature is related to the phonon effect[22].

The thermal conductivity of $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$, and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ alloys at 77 K was measured to be 266.5, 118.1, 112.6, and 82.5 W/(m·K), respectively. It is to be noted that the thermal conductivity decreases 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. In addition, it is observed that the phonon effect was significantly reduced as the content of alloying element increased. This reduction of thermal conductivity of the alloys at low temperature is similar to the observation by Fujishiro et al., for Ag-Au alloys [23]. Specifically, the thermal conductivity of Ag at 30 K was measured to be 994.0 W/(m·K) K, the corresponding values for $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$ and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ alloys were 342.6, 62.1, 59.2, and 28.9 W/(m·K), respectively, which is 3~30 times lower t-

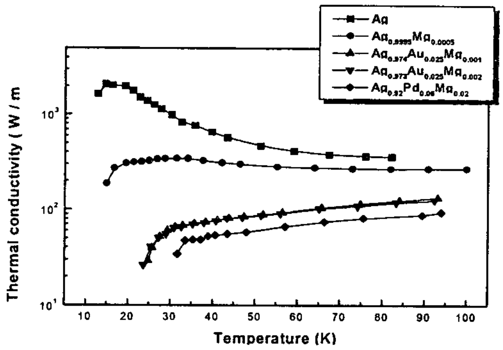


Fig. 3. Thermal conductivity of Ag and Ag alloys from 10 to 100 K measured by direct method.

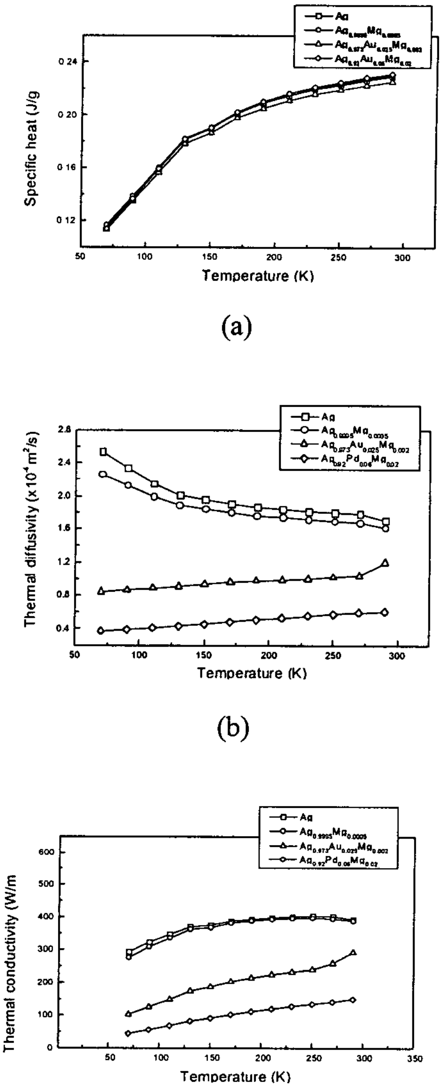
han that of Ag.

In view of the fact that the hybrid-type current leads are used in the temperature range of 4.2~77 K, it is necessary that the current leads have low thermal conductivity at the temperature range to reduce helium loss. Based on our data, it is expected that current leads made by Ag-alloy sheathed superconductor tape effectively reduce the helium loss due to the lower thermal conductivity.

In the indirect measurement, the measured values of specific heat, thermal diffusivity, and resultant thermal conductivity are shown in Fig. 4. As shown in Fig. 4(c), the thermal 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 [24], our result is 8% smaller.

As shown in the figure, thermal conductivity of both Ag and Ag alloys monotonically decreases 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 48.2 W/(m·K) at 77 K. In addition, the thermal conductivity decreases with increasing content of alloying elements of Mg, Au, and Pd, as observed earlier at lower temperature.

In order to evaluate the accuracy of the obtained data, the values of thermal conductivity measured by both direct and indirect techniques were compared with each other. As shown in Table 1, the thermal conductivity of Ag measured by direct and indirect techniques was 303.2 and 363.8 W/(m·K) at 77 K, respectively, indicating that the difference is about 16.6%. Compared to the differences of reference data, which were reported to be at most 1,500% [21], the difference in the study is considered to be within an acceptable error range. It is likely that the difference is due to (1) the larger tempera-



(a)

(b)

(c)

Fig. 4. Dependence of (a) specific heat, (b) thermal diffusivity, and (c) thermal conductivity of Ag and Ag alloys on the temperature.

Table 1. Thermal conductivity of Ag and Ag alloys by direct and indirect measurement techniques at 77 K.

Specimens	Thermal conductivity at 77 K(W/m·K)		
	Direct measurement	Indirect measurement	% difference
Ag	303.2	363.8	-16.6
$Ag_{0.9995}Mg_{0.0005}$	287.1	266.5	7.7
$Ag_{0.974}Au_{0.025}Mg_{0.001}$	109.5	118.1	-7.3
$Ag_{0.973}Au_{0.025}Mg_{0.002}$	99.7	112.6	-11.5
$Ag_{0.92}Pd_{0.06}Mg_{0.02}$	47.9	82.5	-41.9

Table 2. Electrical conductivity and measured and calculated thermal conductivity of Ag and Ag alloys at 300 and 77 K.

Specimens	Electrical conductivity ($\mu\Omega^{-1}cm^{-1}$)		Measured thermal conductivity (W/m ·K)		Calculated thermal conductivity (W/m ·K)	
	300 K	77 K	300 K	77 K	300 K	77 K
Ag	0.66	3.40	392.5	363.8	444.0	607.4
$Ag_{0.9995}Mg_{0.0005}$	0.47	1.85	387.6	266.5	316.2	330.5
$Ag_{0.974}Au_{0.025}Mg_{0.001}$	0.28	0.43	292.1	118.1	188.4	76.8
$Ag_{0.973}Au_{0.025}Mg_{0.002}$	0.27	0.41	256.7	112.6	181.7	73.2
$Ag_{0.92}Pd_{0.06}Mg_{0.02}$	0.25	0.35	149.2	82.5	168.2	62.5

ture gradient (ΔT) at the higher temperature range, (2) the slight heat flow across insert materials such as stycast, epoxy glass, and varnish in direct measurement, and (3) the indirect measurement of thermal conductivity in this study.

Electrical conductivity of Ag and Ag alloys was measured at 77 and 300 K as shown in Table 2. For Ag, electrical conductivity was measured to be 0.66 $\mu\Omega^{-1}cm^{-1}$ 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, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}Mg_{0.002}$, and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 3.40, 1.85, 0.43, 0.41, and 0.35 $\mu\Omega^{-1}cm^{-1}$, respectively, at 77 K. This result seems to be consistent with Nordheim rule.

From the measured value of electrical conductivity, thermal conductivity was calculated by using Wiedermann-Franz law and compared to measured values in Fig. 4. From the table, calculated values for Ag, $Ag_{0.9995}Mg_{0.0005}$, $Ag_{0.974}Au_{0.025}Mg_{0.001}$, $Ag_{0.973}Au_{0.025}$-$Mg_{0.002}$, and $Ag_{0.92}Pd_{0.06}Mg_{0.02}$ were 607.4, 330.5, 76.8, 73.2, and 62.5 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.

4. CONCLUSIONS

The thermal conductivity at low temperature range (10~300 K) of Ag and Ag alloys were evaluated by both direct and indirect measurement techniques and compared with each other. It was observed that thermal conductivity decreases with increasing the content of alloying elements such as Au, Pd, and Mg. Thermal conductivity of pure Ag at 30 K was measured to be 994.0 W/(m·K), on the other hand, the corresponding values of Ag alloys were 342.6~28.9 W/(m·K), respectively, indicating 3 to 30 times lower than that of pure Ag. In addition, the thermal conductivity of pure Ag measured by direct and indirect measurement techniques was 303.2 and 363.8 W/(m·K), respectively, indicating that the difference is about 16.6%. The difference in this study is considered to be within an acceptable error range compared to the reference data.

REFERENCES

[1] NST – General Product Information (www.nst.com)

[2] T. Masegi, S. Kimura, Y. Yamada, and T. Fujioka, presented in the 7th International Symposium on Superconductivity, Nov. 8-11, Fukuoka, Japan, 1994.

[3] T. Sasaoka, K. Nomura, J. Sato, S. Kuma, H. Fujishiro, M. Ikebe and K. Noto, *Appl. Phys. Lett.*, Vol. 64, p. 10, 1994.

[4] W. Goldacker, J. Kebler, B. Ullmann, E. Mossang and M. Rikel, *IEEE Trans. Appl. Supercond.*, Vol. 5, No. 2, p. 1834, 1995.

[5] Y. Yamada, M. Sato, T. Masegi, S. Murase, T. Koizumi and Y. Kamisada, *Adv. Supercond.*, VI, Vol. 2, p. 609, 1993.

[6] H. Fujishiro, M. Ikebe, K. Noto and M. Matsukawa, *IEEE Trans. Mag.*, Vol. 30, No. 4, p. 1645, 1994.

[7] T. Sasaoka, K. Nomura, J. Sato and S. Kuma, *Appl. Phys. Lett.*, Vol. 64, No. 10, p. 1005, 1994.

[8] J. H. Ahn, K. H. Ha, S. Y. Lee, J. W. Ko, H. D. Kim and H. Chung, *Physica C*, Vol. 235-240, p. 3405, 1994.

[9] Y. Tanaka, T. Asano, T. Yanagyi, M. Fukutomi, K. Komori and H. Maeda, *Jpn. J. Appl. Phys.*, Vol. 31, L235, 1992.

[10] B. N. Hurbert, R. Zhou, T. G. Holesinger, W. L. Hults, A. Lacerda and A. S. Murray, *J. Elec. Mater.*, Vol. No. 24, p. 12, 1995.

[11] H. W. Neumuller, M. Wilhelm, K. Fischer, A. Jenovelis, M. Schubert and Chr. Rodig, *Adv. Cryo. Eng.*, Vol. 40, p. 139, 1994.

[12] J. A. Parrell, S. E. Dorris and D. C Labalestier, *Adv. Cryo. Eng.*, Vol. 40, p. 193, 1994.

[13] Jaimoo Yoo, Hyungik Chung, Jaewoong Ko and Haidoo Kim, *IEEE Trans. Appl. Supercond.*, Vol. 7, p. 2, 1997.

[14] Jaimoo Yoo, Hyungsik Chung, Jaewoong Ko and Haidoo Kim, *Physica C*, Vol. 269, p. 109, 1996.

[15] Ling Hua, Jaimoo Yoo, Jaewoong Ko and Haidoo Kim, Hyungsik Chung and Guiwen Qiao, *Supercond. Sci. Technol.*, Vol. 12, pp. 153-157, 1999.

[16] T. B. Massalski, *Binary Phase Diagram*, Vol. 1, 19-18, ASM, 1986.

[17] British Standard, BS DD-ENV 1159-3, 1995.

[18] W. J. Parker, R. J. Jenkins, C. P. Butler and G. L. Abbot, *J. Appl. Phys.*, Vol. 32, p. 1979, 1961.

[19] W. J. Water et al., *High temp.-High Press.*, Vol. 4, p. 439, 1972.

[20] K. Maglic et al., *Compendium of Thermophysical Property, Measurement Methods*, Vol. 2, Plenum Press , 1992.

[21] Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Klemens, *Thermophysical Properties of Matter*, TPRC Data Series 1, IFI/Plenum, 1970.

[22] C. Kittle, *Introduction to Solid State Physics*, 6th Eds., John Wiley & Sons, Inc., 1986, p. 121.

[23] H. Fujishiro, M. Ikebe, K. Noto, and M. Matsukawa, *IEEE Trans. Magnets*, Vol. 30, p. 4, 1994.

[24] *Metal Handbook*, 8th Ed., American Society for Metals, I, 1972.