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# Critical Current Density of Y–Ba–Cu Oxide Wires

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We have prepared Y–Ba–Cu oxide superconducting wires with stainless-steel, Cu–Ni alloy or silver sheath by a powder metallurgy technique, and confirmed superconductivity in stainless-steel or silver-sheathed wires. During the hea-treatment, a dielectric layer was formed at the interface between the sheath and Y–Ba–Cu oxide in stainless-steel-sheathed and Cu–Ni alloy-sheathed wires. The diffusion of the sheath element into Y–Ba–Cu oxide was analyzed using EPMA. The highest critical current density, 560 A/cm$^2$, was obtained for a silver-sheathed wire which was heat-treated in oxygen flow. A multicored wire was produced.

## §1. Introduction

Since the report of possible superconductivity in a La–Ba–Cu–O system by Bednorz and Müller[1] and following investigations by Tanaka and co-workers,[2-3] intense efforts have been made to clarify the properties of the superconducting oxide and to search for materials with higher critical temperatures. Discoveries of 90 K-class superconductivity in Y–Ba–Cu–O[4-7] and Ln–Ba–Cu–O[8-11] systems were breakthroughs. Applications in electric power involving magnets or cables are promising. However, one must first develop wires with good superconducting properties.[12-13]

In this paper, we report the preparation procedure and superconducting properties of Y–Ba–Cu–O wires.

## §2. Experimental

Commercial $Y_2O_3$(purity: 4N), $BaCO_3$(3N) and CuO(3N) powders were mixed in an alumina mortar; the atomic ratio of Y, Ba and Cu was 1:2:3. Then, the mixture was calcined at 900°C for 24 hours in ambient air and cooled in the furnace. The calcined powder was pestled and formed into cylindrical shape (typically 6 mm in diameter and 100 mm in length) using a hydrostatic press. The cylindrical specimens were sintered at 900°C for 24 hours in flowing oxygen gas and then cooled in the furnace.

To prepare wire samples, the sintered cylinder was inserted into a metal tube and cold-drawn to the final diameter without intermediate annealing. Stainless steel (JIS-SUS304), Cu-Ni-alloy or silver were chosen as sheath materials. The dimensions of the wire samples before and after drawing are listed in Table I. To prepare a multicored wire, six cold-drawn wires with silver sheaths and a silver wire were bundled into a tantalum tube and then inserted into a copper tube. The composite was cold-drawn to the final diameter. The wire samples were heat-treated at 900°C in ambient air or oxygen gas flow.

The critical temperatures and critical current densities were measured using a conventional four-probe resistive method. Temperatures were monitored with a germanium thermometer and a Pt–Co alloy thermometer. The discrepancies between the two thermometers was less than 0.2 K. The rate of temperature change over the transition region was less than 0.5 K per minute. Critical current densities were measured in liquid nitrogen, and the magnetic field dependence of the critical current density was measured in liquid helium. The criterion for the critical current was 0.1 $\mu$V/cm.

Table I. Inner and outer diameter of wire samples.

| Sheath material | Before drawing | | After drawing | |
|---|---|---|---|---|
| | Outer(mm) | Inner(mm) | Outer(mm) | Inner(mm) |
| SUS304 | 13.0 | 7.0 | 5.0 | 4.0 |
| Cu–Ni alloy | 15.0 | 10.0 | 1.2 | 1.0 |
| silver | 10.0 | 7.0 | 1.5 | 0.7 |

## §3. Results and Discussion

### 3.1 *Stainless-steel-sheathed wire*

Figure 1 shows a cross-sectional view of a wire sample with a SUS304 sheath. Since a dielectric layer was formed at the interface between the sheath and the superconducting oxide during the final heat treatment, the sheath was partially removed and probes were mechanically attached to the superconducting oxide. It exhibited zero resistance at 89 K. Figure 2 shows the change of the critical current density as a function of the heat-treatment duration. The

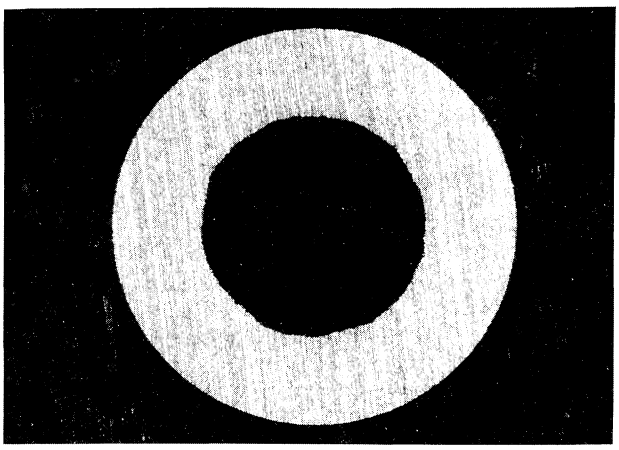


Fig. 1. Cross section of a $Y_1Ba_2Cu_3O_{7-x}$ wire with a stainless-steel sheath. Outer diameter is 5.0 mm.

critical current density increased in the first 12 hours of the heat treatment; however, it began to decrease after 24 hours.

Figure 3 shows the results of a line analysis using an electron probe micro analyzer (EPMA) for a sample heat-treated at 900°C for 24 hours. At the interface between the sheath and core, a layer which is about 20 $\mu$m thick and rich in Fe, Ba, and Ni was observed. This corresponds to the dielectric layer described above. Into the Y–Ba–Cu–O core, the diffusion of Cr to a depth of 20 $\mu$m

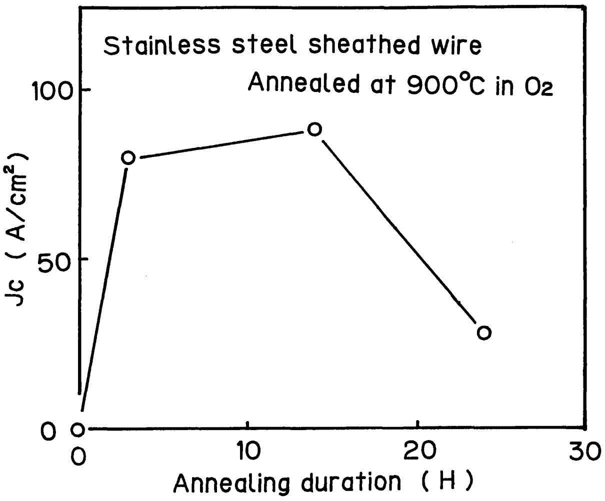



Fig. 2. Change of the critical current density as a function of the heat-treatment duration for a stainless-steel-sheathed wire.

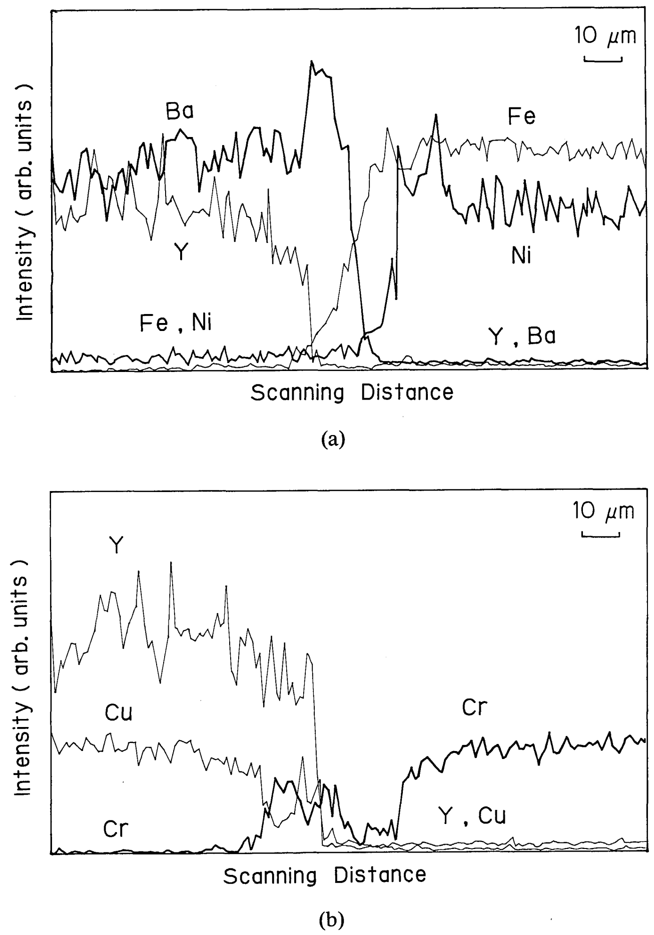



Fig. 3. Result of a line analysis by EPMA for a stainless-steel-sheathed wire heat-treated at 900°C for 24 hours.

and Fe to a depth of 5 $\mu$m was observed. The change in the oxygen distribution was not made clear in the analysis. It is likely that the oxygen content in the Y–Ba–Cu–O compound deviated from stoichiometry, which led to a degradation of the critical current density.

### 3.2 *Cu-Ni-alloy-sheathed wire*

When a wire sample with a Cu–Ni alloy sheath was heat-treated at 900°C for 30 minutes, a thick dielectric layer (0.1 mm thick, green in color) was formed at the interface between the sheath and the Y–Ba–Cu–O compound. The thickness of the dielectric layer increased with longer heat treatment. Superconductivity was not observed, even at 4.2 K in this sample, while a sample heat-treated after removing the sheath exhibited zero resistance at 89 K. This degradation was caused mainly by a reaction between the sheath material and the Y–Ba–Cu oxide.

### 3.3 *Silver-sheathed wire*

Figure 4 shows a cross-sectional view of a wire sample with a silver sheath. The formation of dielectric oxide at the interface was not observed. Figure 5 shows the critical current densities of samples heat-treated in air.

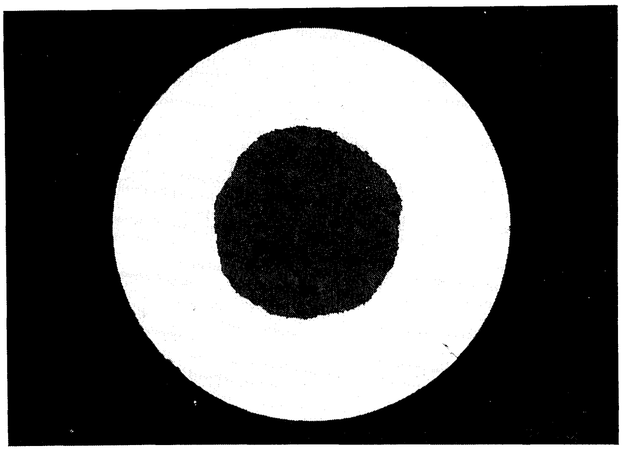


Fig. 4. Cross-section of a $Y_1Ba_2Cu_3O_{7-x}$ wire with silver sheath. Outer diameter is 1.5 mm.

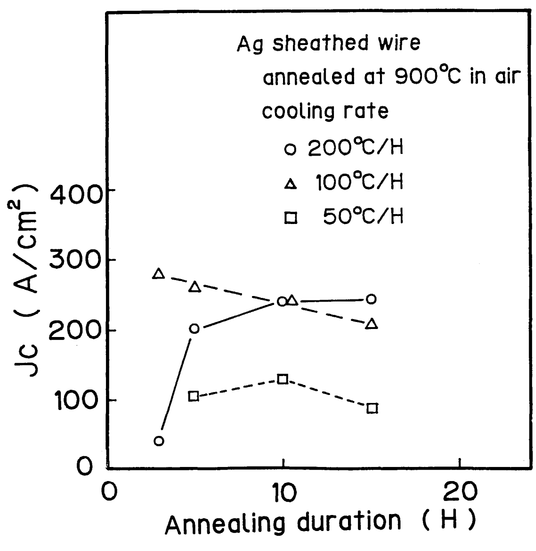
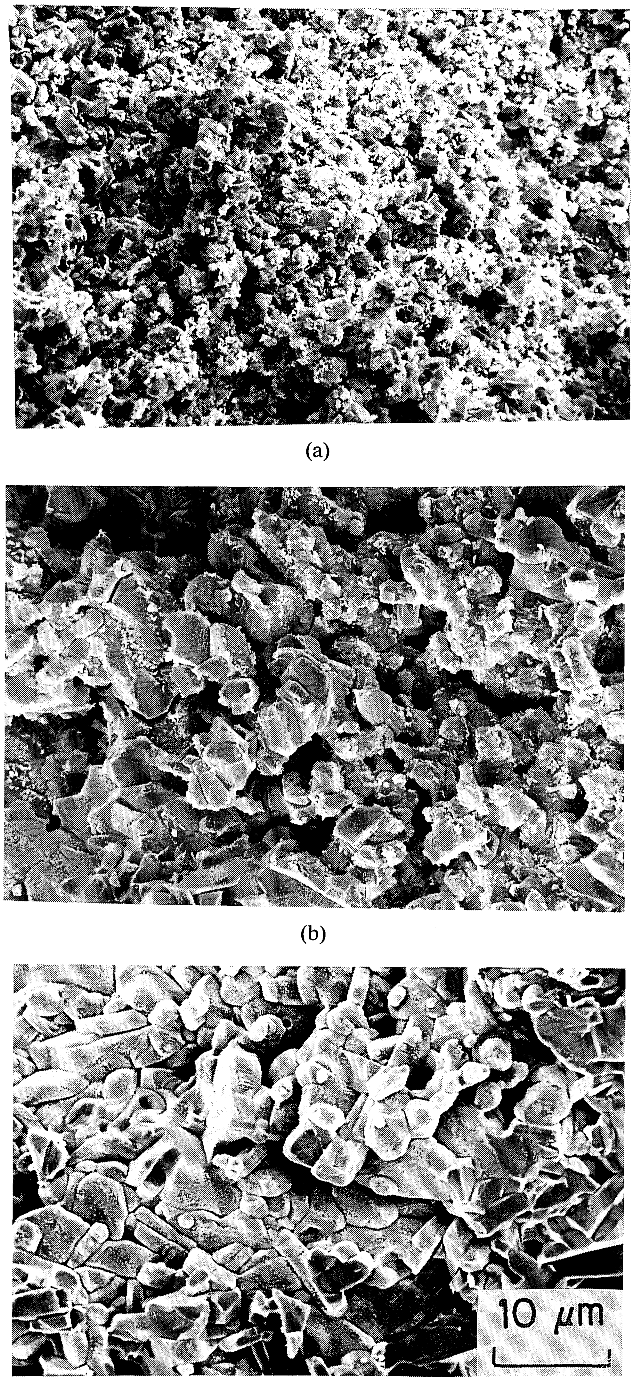



Fig. 5. Critical current density and heat-treatment condition for silver-sheathed wires.

Except for a sample heat-treated for 2 hours and cooled at 200°C per hour, the critical current density was not strongly dependent on the heat-treatment duration. In contrast, the cooling rate had a large effect on the critical current density. It was observed that a slower cooling rate drastically decreased the critical current density. Figure 6 shows fractured cross-sectional views of the Y-Ba-Cu-O core in a silver-sheathed wire before and after heat treatment. The morphology of the grains of the sample, cooled at 200°C per hour, was found to be a mixture of relatively large grains (1 to 10 $\mu$m) and original grains (0.3 to 1 $\mu$m), while only large grains are observed in the sample cooled at 50°C per hour. The difference of grain size is due to the change in the duration of grain growth. The grain growth was interrupted when cooled at 200°C per hour. The relation between the critical current density and the grain size observed here is well recognized in such conventional superconducting materials as $Nb_3Sn$. The magnetic field dependence of the critical current density at 4.2 K of a sample heat-treated for 15 hours and cooled at 200°C per hour is shown in Fig. 7.




(a) (b) (c)

Fig. 6. SEM micrograph of fractured $Y_1Ba_2Cu_3O_{7-x}$ oxide core in the silver-sheathed wire a) before heat treatment; b) cooled at 200°C/h; and c) cooled at 50°C/h.

A sample was heat-treated for 15 hours and furnace-cooled in flowing oxygen gas. Here, the cooling rate of "furnace-cooling" down to 200°C was between 200 and 100°C per hour. A maximum critical current density in liquid nitrogen of 560 A/cm$^2$ was obtained. The transition curve is shown in Fig. 8. Since the diffusion coefficient of oxygen in silver is sufficiently large[14] at high temperatures, the penetration of some amount of oxygen through the silver sheath is possible during both heat-treatment and cooling processes. It seems that the Y-Ba-Cu oxide core absorbed oxygen through the silver sheath, and that a higher oxygen partial pressure may enhance the diffusion of oxygen through the sheath.

Figure 9 shows the result of a line analysis by EPMA for a silver-sheathed wire. The diffusion of Ag into Y-Ba-Cu oxide was not observed. The diffusion of Y, Ba or Cu into the silver sheath was very slight or negligible, as can be seen from the figure. One of the reasons for the high superconducting properties of the silver-sheathed wire is the low diffusibility of elements other than oxygen. Also, it should be noted that silver showed low reactivity with those elements.

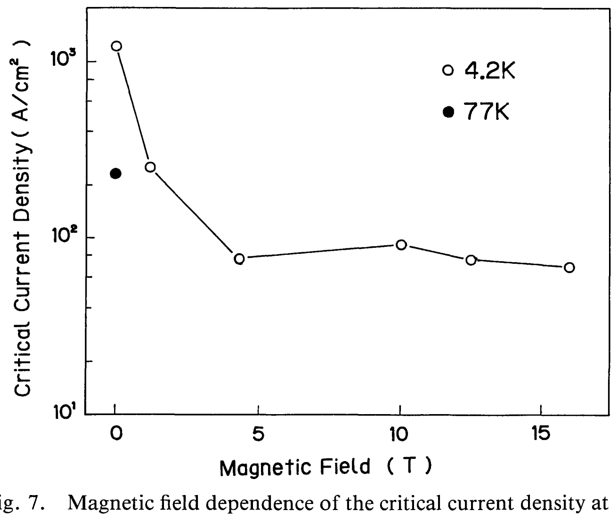



Fig. 7. Magnetic field dependence of the critical current density at 4.2 K for a silver-sheathed wire heat-treated at 900°C for 15 hours and cooled at 200°C/h in ambient air.

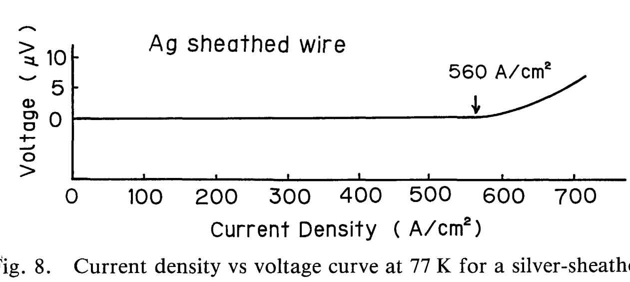



Fig. 8. Current density vs voltage curve at 77 K for a silver-sheathed wire heat-treated at 900°C for 15 hours and furnace-cooled in oxygen gas flow.

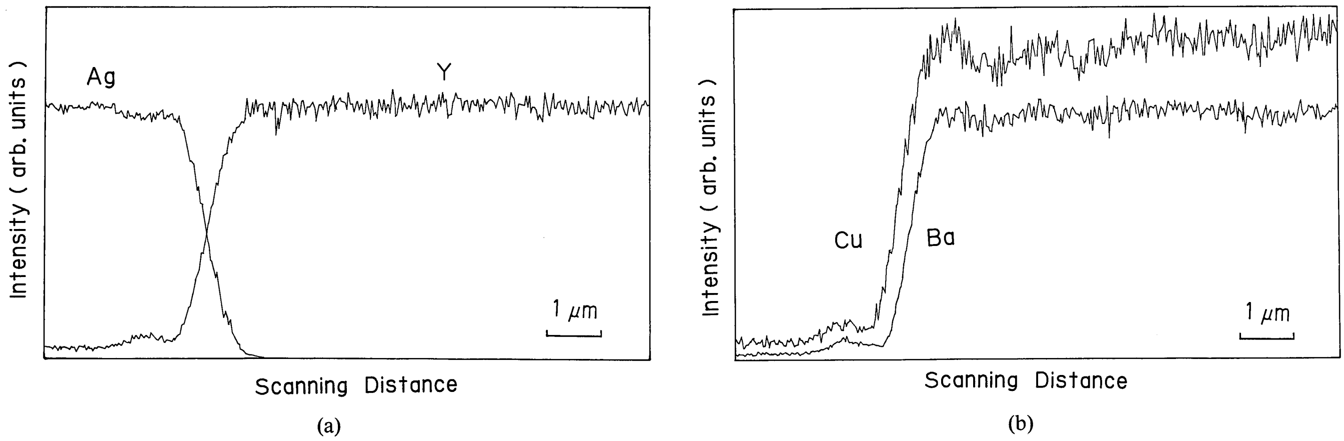



Fig. 9. Result of a line analysis by EPMA for a silver-sheathed wire heat-treated at 900°C for 15 hours and furnace-cooled in an oxygen flow.

### 3.4 *Multicored wire*

Figure 10 shows a cross-sectional view of a multicored wire. The critical current density of the wire, which was heat-treated at 900°C for 15 hours and furnace-cooled in oxygen flow, was 70 A/cm$^2$.

## §4. Conclusions

We have produced Y–Ba–Cu oxide wires with stainless-steel, Cu–Ni-alloy and silver sheathes by a powder metallurgy technique. Superconductivity was confirmed in the stainless-steel-sheathed and silver-sheathed wires, while a Cu–Ni-alloy-sheathed wire did not exhibit superconductivity, even at 4.2 K. The maximum critical current density was 88 and 560 A/cm$^2$ for the stainless-steel-sheathed wire and the silver-sheathed wire, respectively. The diffusion of elements from both the sheath and superconducting core was found to degrade the superconducting properties. Heat treatment in oxygen gas flow was effective in enhancing the critical current density for the silver-sheathed wire. A multicored wire was produced.

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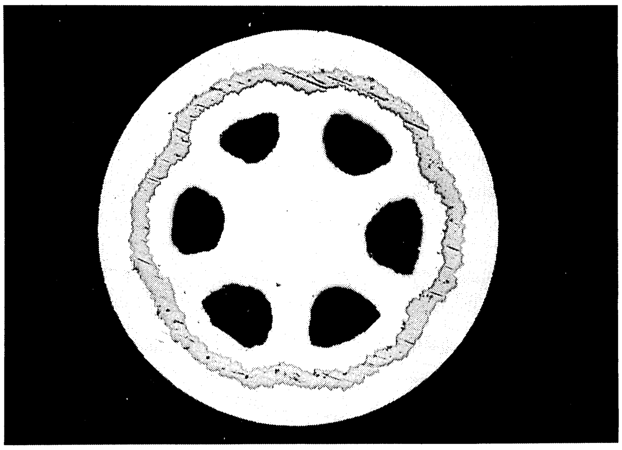

Fig. 10. Cross-sectional view of a multicored wire. The outer diameter is 2.0 mm.

### References

1) J. G. Bednorz and K. A. Müller: Z. Phys. **B64** (1986) 189.
2) S. Uchida, H. Takagi, K. Kitazawa and S. Tanaka: Jpn. J. Appl. Phys. **26** (1987) L1.
3) K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki and S. Tanaka: Chem. Lett. (1987) 429.
4) C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Haung and Y. Q. Wang: Phys. Rev. Lett. **58** (1987) 405.
5) K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fueki and S. Tanaka: Chem. Lett. (1987) 429.
6) D. W. Capone II, D. G. Hinks, J. D. Jorgensen and K. Zahng: Appl. Phys. Lett. **50** (1987) 543.
7) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Haung, Y. Q. Wang and C. W. Chu: Phys. Rev. Lett. **58** (1987) 908.
8) S. Hikami, S. Kagoshima, S. Komiyama, T. Hirai, H. Minami and T. Masumi: Jpn. J. Appl. Phys. **26** (1987) L347.
9) K. Kitazawa, K. Kishio, H. Takagi, T. Hasegawa, S. Kanbe, S. Uchida and K. Fueki: Jpn. J. Appl. Phys. **26** (1987) L339.
10) S. Oshima and T. Wakiyama: Jpn. J. Appl. Phys. **26** (1987) L815.
11) H. Minami, T. Masumi and S. Hikami: Jpn. J. Appl. Phys. **26** (1987) L783.
12) O. Kohno, Y. Ikeno, N. Sadakata, M. Sugimoto and M. Nakagawa: Jpn. J. Apl. Phys. **26** (1987) L759.
13) Y. Yamada, N. Fukushima, S. Nakayama, H. Yoshino and S. Murase: Jpn. J. Appl. Phys. **26** (1987) L865.
14) Japan Institute of Metals: *Kinzoku Databook* (Metals Databook) (Maruzen, Tokyo, 1974) 2nd ed., Chap. 1, p. 24 [in Japanese].