

N 9 2 - 2 1 6 2 3

## COMPOSITE SUPERCONDUCTING WIRES OBTAINED BY HIGH-RATE TINNING IN MOLTEN Bi-Pb-Sr-Ca-Cu-O SYSTEM

A.D. Grosav, L.A. Konopko, N.I. Leporda  
Institute of Applied Physics, Kishinev, 277028, USSR

### ABSTRACT

Long lengths of metal-superconductor composites have been prepared by passing a copper wire through the bismuth-based molten oxide system at a constant speed. The key to successful composite preparation is the high pulling speed involved, which permits minimization of the severe interaction between the unbuffered metal surface and the oxide melt. Depending on the temperature of the melt and the pulling speed, a coating with different thickness and microstructure appeared. The nonannealed thick coatings contained a  $\text{Bi}_2(\text{Sr,Ca})_2\text{Cu}_1\text{O}_6$  phase as a major component. After relatively short time annealing at  $800^\circ\text{C}$ , both resistivity and initial magnetization-versus-temperature measurements show superconducting transitions beginning in the 110-115 K region. The effects of annealing and composition on obtained results are discussed.

### INTRODUCTION

Bi-Sr-Ca-Cu oxide is one of the most promising high- $T_c$  superconductors currently under investigation. Both stoichiometry and dopant impurities affect the electrical and magnetic properties to the point that Bi-Sr-Ca-Cu-O system can be either a near-insulator or a superconductor, whose transition temperature is well above 77 K. Partial substitution of Pb for Bi has been reported to be effective in obtaining zero-resistance temperatures,  $T_c^{\text{off}}$ , up to 112 K (1). A potential, low-cost alternative to classical Y-Ba-Cu oxide, Bi-Pb-Sr-Ca-Cu-O has many advantages--among them, a lower melting temperature. The latter is very important from a practical point of view.

The introduction of bismuth-oxide-based compounds into the superconducting industry requires the fabrication of the brittle materials into wires and tapes. Several groups have been able to obtain very good quality Pb-free Bi-Sr-Ca-Cu-O fibers with resistive transition comparable to those of  $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$  bulk samples and with high critical current densities. The chosen preparation techniques having included a laser-heated pedestal growth method (2) and a micro-Czochralski method (3). However, it is highly desirable to be able to incorporate these oxides into the existent technology of metal-superconductor composites. The main obstacle to overcome in order to attain this goal is the choice of the proper metal for high- $T_c$  composite fabrication. A number of studies have recently been made on the preparation of Bi-Pb-Sr-Ca-Cu-O superconducting composite wires and tapes by a standard sheathing method (4, 5). This processing technique involves a long annealing step (more than 8 hours) at high temperatures (typically reaching  $850^\circ\text{C}$ ), which makes the sheathing method incompatible with most low-cost metals and alloys, and up until now, required for its utilization only high-cost, noble metals--usually silver.

Our basic aim was to produce long high- $T_c$  superconducting composite wires with low-cost components in as simple a way as possible to facilitate useful applications in the future, which explains our choice of depositing Bi-Pb-Sr-Ca-Cu-O layers directly on copper wires by passing the wires through a bismuth-based molten oxide system. This deposition procedure is similar in a way to a tinning technique employed for the fabrication of metallic superconducting wires such as  $\text{Nb}_3\text{Sn}$  (6). Copper is a relatively inexpensive metal and is commonly used as a ductile matrix in various

composites. We report encouraging results (7) on Pb-free  $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$  wires with unbuffered copper core ( $T_c^{\text{off}}=40\text{-}50\text{ K}$ ). However, copper has proven to be an intractable core material due to the inevitable dissolution and diffusion of Cu into the envelope during the coating and annealing procedures. On the other hand, the communication about superconducting Pb-doped Bi-Sr-Ca-Cu-O glass ceramics ( $T_c^{\text{off}}=100\text{ K}$ ) (8) having Cu content of higher-than-ideal composition (9, see also 10) gave some hope that Cu wires could be used in the case when the source of melt has a stoichiometrical chemical formula of  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ .

## EXPERIMENTAL PROCEDURE

Commercial powders of  $\text{Bi}_2\text{O}_3$ , PbO,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and CuO were mixed at the nominal cation ratio Bi:Pb:Sr:Ca:Cu=1.5:0.5:2:2:3, then ground and calcined at  $800^\circ\text{C}$  for 24 hours. The product was reground and then cold-pressed under 8 kBar into a rod (8 mm diameter, 16 mm long). After sintering at  $860^\circ\text{C}$  for 150 hours in air, the rod was held at  $800^\circ\text{C}$  for 24 hours and subsequently air cooled to room temperature. The zero-resistivity transition temperature of the ceramic rod was around 70 K. Available polycrystalline copper wires with diameters from 100 to 400  $\mu\text{m}$  and lengths from 0.5 to 1 m were used for preparing metal-superconductor composites in this study.

The ceramic rod was vertically suspended and was heated above  $900^\circ\text{C}$  in order to form a small molten zone ( $\leq 100\text{ mm}^3$ ) at the bottom part. A copper wire, moving at a constant speed, was passed through the narrow molten zone. The copper wire was not intentionally heated. In a molten state, the Bi-based oxide system is a viscous liquid and it has a strongly pronounced ability to spread on copper wire surfaces. LeBeau et al. (11) reported that the Bi-Sr-Ca-Cu-O melt showed a favourable viscosity-temperature profile for practical shaping during solidification. Although in our case, the melt temperature was not directly measured, it is believed to be above  $900^\circ\text{C}$  and below  $1000^\circ\text{C}$ . Moreover, the real melt temperature was found to vary with the diameter of the copper wire and the speed of its pass. The pass speed of the copper wire has been chosen as a compromise between an adhesion of the melt and a short residence time of the wire in the liquid zone. The residence time was estimated by dividing the measured width of the molten zone by the value of pulling speed ( $\sim 5\text{-}15\text{ cm/s}$ ). Residence times thus calculated were less than 0.1 s. Because of a very short time during which the wire surface and the melt are in direct contact, they seem to contact without disastrous effects in the coating composition due to copper dissolution and diffusion--at least for thick coatings. The realization of the given method of high-rate tinning using a simple laboratory-manufactured technique allowed us to make the long, cylindrical composite wires consisting of the copper in a dense envelope with uniform (to the unaided eye) thickness. Solidified coating thicknesses (h) were typically from 5 to 50  $\mu\text{m}$ .

The microstructures of the coatings were examined by optical and scanning electron microscopes. Most of the electrical and magnetic measurements have been performed with wires having textured coatings (see below). Resistance-versus-temperature curves of the composite wires were measured using a standard DC four-terminal method. Voltage and current probes were attached to the coating surface with silver paste. The sample was 20 mm long and the distance between voltage contacts was about 5 mm. Comparison of 2- and 4-probe resistivities demonstrated  $\sim 10\ \Omega$  contact resistances. Magnetization measurements were performed using a SQUID magnetometer.

## RESULTS AND DISCUSSION

The morphology and electrical properties of the envelopes appear to be highly dependent upon thickness and the parameters of the coating procedure (molten zone temperature, pulling speed, copper wire diameter), perhaps resulting from different solidification rates. The composite wires

with thin cores obtained at the highest possible pulling speeds have a smooth coating surface characteristic for amorphous materials (Figure 1) and good flexibility. For example, composite wire with  $h \approx 10 \mu\text{m}$  ( $h/d \approx 0.05$ ) sustained bending on a 30-mm-diameter bobbin (Figure 2) without breaking. The thicker coatings are composed of densely connected crystallites that are very often overlapping each other. Figure 3 shows a scanning electron micrograph (SEM) of a surface of the coating with a 25- $\mu\text{m}$  thickness and an average crystallite size of several tens of microns. The majority of crystallites are oriented with their basal planes almost parallel to the core axis. It was observed that the size and degree of alignment of the crystallites decreases with pulling speed and distance from the outer coating surface.

As a rule, the thicker the coating, the smaller its resistivity. However, all of the coatings possessed nonmetallic properties. According to X-ray diffraction (XRD) studies, the nonannealed coatings contained a  $\text{Bi}_2(\text{Sr,Ca})_2\text{Cu}_1\text{O}_8$  phase,\* as a major component, and exhibited 0-1-1 texture. Some of the X-ray peaks belong to  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ . The average composition of the coatings was found to deviate from the starting nominal composition, becoming Cu-rich and (Bi,Pb)-deficient. Nevertheless, sometimes only several minutes in a post-annealing treatment were necessary to obtain a coating with metallic resistivity.

The pieces of composite wire about 50 mm long were annealed in a tube furnace in air at temperatures from 500°C to 800°C. The furnace was heated to the annealing temperature and wires were inserted into the furnace. After the desired annealing time, the wires were quenched to room temperature by removing them from the furnace as fast as possible. Sufficiently high annealing temperature was found to be a decisive factor in obtaining superconductivity; the wires annealed at temperatures below 750°C remained semiconducting.

Figure 4 shows the temperature dependencies of resistance and its derivative,  $dR/dT$ , for the composite wire annealed at 800°C for 40 minutes. The outer wire diameter and the thickness of the coating were about 450 and 30  $\mu\text{m}$ , respectively. The midpoint of the transition is designated as  $T_c^{\text{mid}}$  and in present work, corresponds to the point where the curve  $dR/dT$  versus  $T$  has a maximum. Offset ( $T_c^{\text{off}}$ ) and onset ( $T_c^{\text{on}}$ ) of the transition are defined as the temperatures corresponding to the achievement of zero resistance,  $R(I=10 \mu\text{A})=0$ , and to the deviation from linear of the  $dR/dT - T$  plot. In the case of the sample that was annealed for 40 minutes,  $T_c^{\text{on}}$ ,  $T_c^{\text{mid}}$  and  $T_c^{\text{off}}$  are 110.0, 75.5, and 69.5 K, respectively.

Figure 5 shows changes in  $T_c^{\text{off}}$ ,  $T_c^{\text{mid}}$  and  $T_c^{\text{on}}$  with annealing time,  $t$ , for composite wires annealed at 800°C. One can see that relatively high critical temperatures can be easily attained for short annealing times (less than 40 minutes). The value of  $T_c^{\text{off}}$  ( $t=10$  minutes)=62.5 K, which is higher than we have previously reported (7).  $T_c^{\text{off}} = 45$  K for annealing at 800°C for 10 minutes, using Pb-free Bi-Sr-Ca-Cu-O composite wire with copper core, indicating that Pb doping strongly contributes to increasing the volume fraction of the superconducting phase, even for a relatively rapid thermal annealing. The critical temperatures are observed to gradually increase with time (Figure 5), however, when the duration of annealing is beyond 60 minutes,  $T_c^{\text{off}}$  begins to quickly decrease (not shown here), making the superconducting transitions broader due to the diffusional effects. Besides

\* Sometimes the X-ray peaks of the thick coatings may be assigned as a mixture of two tetragonal crystalline lattices with  $a \approx 5.36 \text{ \AA}$ ,  $c \approx 24.40 \text{ \AA}$ ; and  $a \approx 5.60 \text{ \AA}$ ,  $c \approx 25.86 \text{ \AA}$ , where the former lattice corresponds to the "pure"  $\text{Bi}_2\text{Sr}_2\text{Cu}_1\text{O}_8$  phase. We think that both phases are crystallized together due to a stacking disorder caused by a compositional fluctuation in the melt around the moving copper wire.

that, during long annealing, microcracks are introduced in the coating. These results indicate that there may be a clearly optimum annealing time.

Magnetization-versus-temperature curves of the composite wire annealed at 800°C for 20 minutes are shown in Figure 6. Both the zero-field-cooled (ZFC) and field-cooled (FC) magnetizations were obtained with the magnetic field parallel to the core axis. Because of the small coating volume, a fairly large magnetic field ( $H=65$  G) was required to obtain a good signal-to-noise ratio. The ZFC data revealed diamagnetization below 110 K. This result is consistent with that of resistance measurements (Figure 5).

Magnetization measurements and studies on the annealing process by X-ray diffraction analyses indicate that the  $\text{Bi}_2(\text{Sr,Ca})_2\text{Cu}_1\text{O}_6$  phase formed during coating solidification is converted to the  $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$  phase ( $a \cong 5.4 \text{ \AA}$ ,  $c \cong 30.6 \text{ \AA}$ ) during the annealing at 800°C. After 40 minutes, no peaks corresponding to the  $\text{Bi}_2(\text{Sr,Ca})_2\text{Cu}_1\text{O}_6$  phase were observed in the X-ray diffraction scans, although the coating did contain large amounts of CuO and (Bi,Pb)-free (Sr,Ca)-Cu-O compounds. At the same time, the broad tail in ZFC magnetization above 85 K suggests the presence of the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  phase as well. Note that since the annealing was carried out at 800°C, only a very small amount of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  phase can be formed (12).

The surface of 800°C-annealed coatings (Figure 7) is covered with granular particles of several microns of average diameter, and the original crystallite surfaces became roughened. It seems that after rapid cooling from the melt, (Sr-Ca)-Cu-O was in the glassy state, and that it became crystalline when the sample was annealed. The SEM observations, however, clarified within their degree of resolution that no apparent change occurred in the bulk part of the coatings by annealing at 800°C. Further details are under investigation.

## CONCLUSION

In summary, we have shown that composite wires with ductile cores can be obtained by passing a copper wire through the molten Bi-Pb-Sr-Ca-Cu-O system at a high speed. Depending on the pulling speed and the viscosity of the melt, a different coating microstructure with different crystallite sizes appeared. After isothermal annealing at 800°C in air for 20-40 minutes, composite wires with textured coatings exhibited superconductivity onsets above 100 K and zero resistance in the range of 65-70 K. We expect that some improvements in superconductivity properties may be possible by optimizing the annealing conditions in air, or by conducting the heat treatment in a vacuum-sealed system or under low oxygen pressures, where the melting temperature is lowered and, respectively, superconducting phase formation is enhanced (13, 14). This appears to be especially important for the composites.

According to preliminary energy-dispersive X-ray analyses, the coating composition shifts from the starting nominal composition, becoming Cu-rich and (Bi,Pb)-deficient. Considering the origin of core materials and the high evaporation rates of Bi and Pb from the molten zone during coating procedures, these results are reasonable. Taking the latter into account (i.e., the reduction of the Bi and Pb contents in the solid-state coating), the pieces of as-prepared composite were coated thickly with molten binary alloy (Bi:Pb=1.5:0.5), and later annealed with the same heat treatment used for the wires as described above. For composite wires coated with Bi-Pb alloy, the values of  $T_c^{\text{on}}$  were gathered in the region of 77 K (Figure 8 presents one of the resistance measurements), which is almost 10 K higher than the maximum  $T_c^{\text{on}}$  for the (Bi,Pb)-poor coatings (Figure 4). Therefore, though the conditions for the coating and annealing processes have not been optimized yet, one may assume that

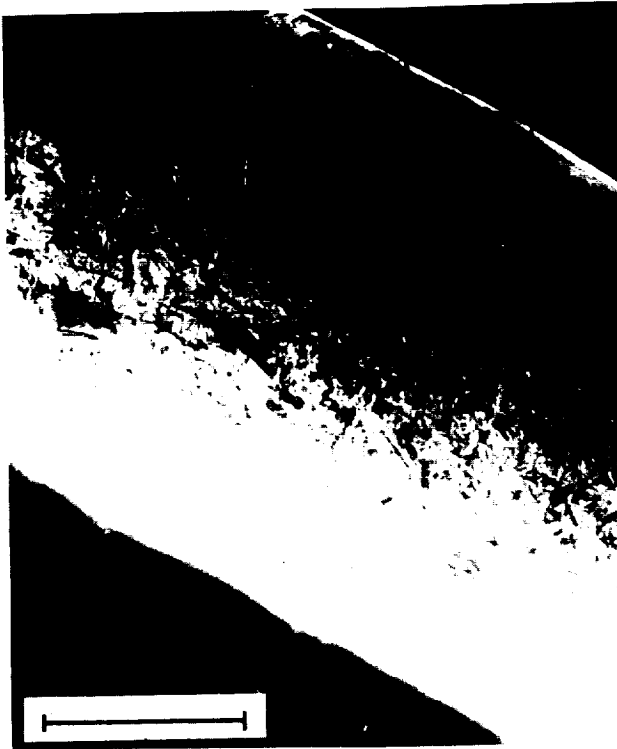


Figure 1. Scanning electron micrograph of the 200- $\mu\text{m}$ -diameter metal wire after it had been rapidly coated with the molten Bi-Pb-Sr-Ca-Cu-O oxide. It can be seen that the thin coating is dense and has a fairly smooth surface. The bar represents 100  $\mu\text{m}$ .

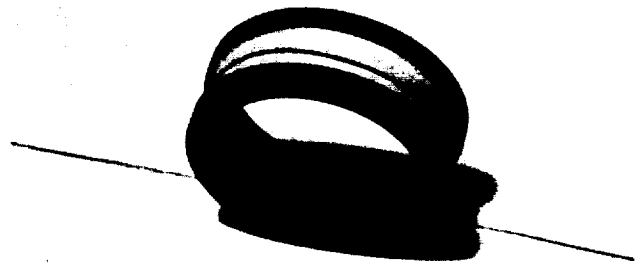


Figure 2. Bi-Pb-Sr-Ca-Cu-O composite wire of the type illustrated in Figure 1 bent on a 30-mm-diameter bobbin.



Figure 3. Scanning electron micrograph showing surface of as-prepared Bi-Pb-Sr-Ca-Cu-O composite wire with 25- $\mu\text{m}$  coating thickness and 400- $\mu\text{m}$  core diameter. The bar represents 200  $\mu\text{m}$ .

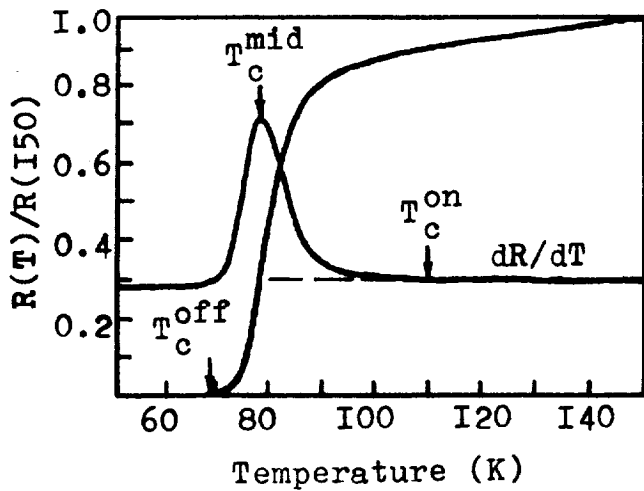


Figure 4. Temperature dependences of the relative resistivity,  $R(T)/R(150)$ , and derivative of the resistance,  $dR/dT$ , for composite wire annealed at  $800^\circ\text{C}$  for 40 minutes.

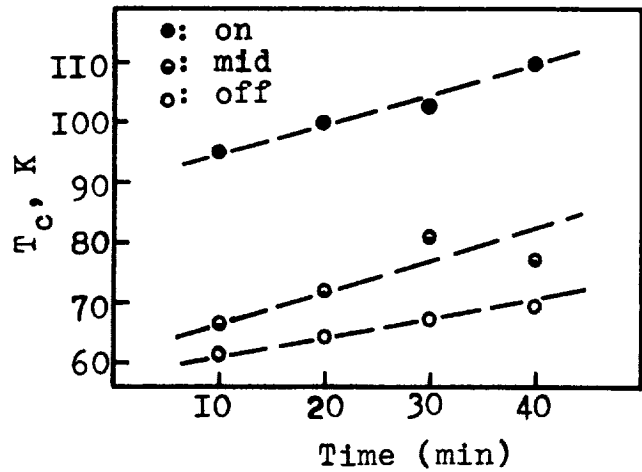


Figure 5. Changes in  $T_c^{\text{off}}$ ,  $T_c^{\text{mid}}$ , and  $T_c^{\text{on}}$  with annealing time for composite wires annealed at  $800^\circ\text{C}$ .

ORIGINAL PAGE  
BLACK AND WHITE PHOTOGRAPH

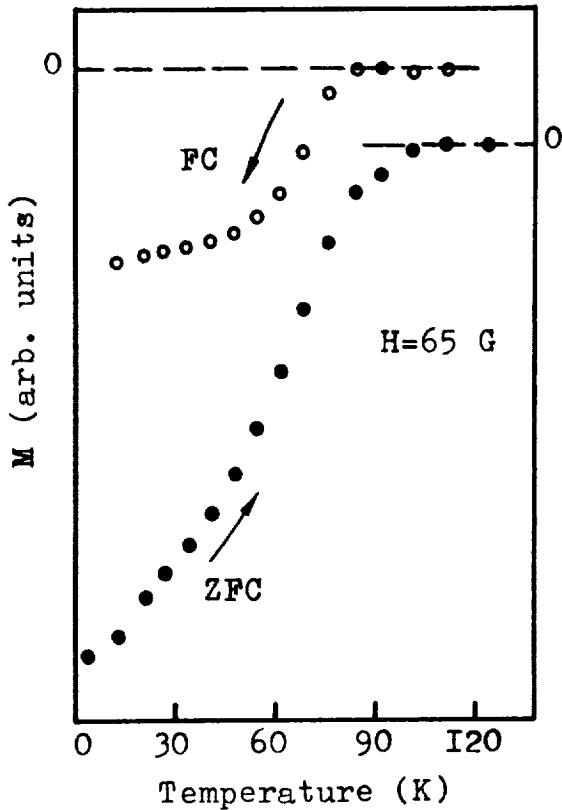


Figure 6. The dc magnetization as a function of the temperature for the composite wire annealed at  $800^\circ\text{C}$  for 20 minutes in air.



Figure 7. Scanning electron micrograph of the composite wire annealed at  $800^\circ\text{C}$  for 30 minutes. The bar represents  $200\ \mu\text{m}$ .

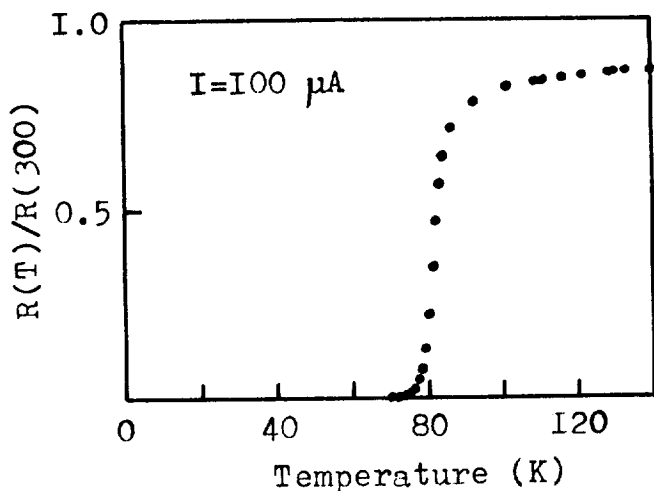


Figure 8. Superconducting transition curve of a Bi-Pb-Sr-Ca-Cu-O composite wire heat-treated with coated Bi-Pb alloy.

for the fabrication of composite wires with improved superconducting properties (especially to obtain the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  phase in appreciable proportion), it is necessary to use starting material with a nonstoichiometric composition having an excess of Bi and Pb, a lack of Cu, and probably, the addition of Ca.

#### ACKNOWLEDGMENTS

The authors would like to acknowledge D. V. Gitsu, F.M. Muntianu and V.G. Kantser for continuous encouragement and helpful discussions. We also wish to thank G.I. Panaitov for taking the magnetization measurements, and A.I. Socolovsky, Y.G. Soltanovsky, G.F. Volodina and M.I. Onu for technical assistance.

#### REFERENCES

1. Togano, K. H. Kumakura, and D.R. Dieterich, 1989, "Critical currents and magnetic properties of Bi- and Tl-based new high  $T_c$  superconductors," *Cryogenics*, **29**, 3A, pp. 286-290.
2. Feigelson, R.S., D. Gazit, D.K. Fork, and T.N. Geballe, 1988, "Superconducting Bi-Ca-Sr-Cu-O fibers grown by the laser-heated pedestal growth method," *Science*, **240**, pp. 1642-1645.
3. Kurosaka, A., M. Aoyagi, H. Tominaga, O. Fukuda, and H. Osanai, 1989, "Superconducting Bi-Sr-Ca-Cu-O crystalline fibers prepared by the micro-Czochralski method," *Applied Phys. Lett.*, **55**, 4, pp. 390-392.
4. Sekine, H., K. Ogawa, K. Inoue, H. Maeda, and K. Numata, 1989, "Metallurgical studies and optimization of critical current density in Bi-(Pb)-Sr-Ca-Cu-O superconductors," *Jap. J. Appl. Phys.*, **28**, 7, pp. 1185-1188.
5. Hikata, T., T. Nishikawa, H. Mukai, K. Sato, and H. Hitotsuyanogi, 1989, "Electromagnetic properties and morphology of Ag-sheathed Bi-Pb-Sr-Ca-Cu-O superconducting wires," *Jap. J. Appl. Phys.*, **28**, 7, pp. L1204-L1206.
6. Savitsky, E.M., 1981, "Phisico-himicheskie osnovy polucheniya sverhprovodyaschih materialov," *Metallurgia*, Moscow, pp. 193-218 (in Russian).
7. Grozav, A.D., L.A. Konopko, and N.I. Leporda, 1989, "Superconducting composite wires prepared by high-rate tinning in molten Bi-Sr-Ca-Ca-Cu-O system," *Pis ma Zh. Techn. Fiz. (Sov. Techn. Phys. Lett.)* **15**, 19, pp. 1-5.

8. Komatsu, T., R. Sato, K. Imai, K. Matusita, and T. Ymashita, 1989, "High- $T_c$  superconducting glass ceramics based on the Bi-Ca-Sr-Cu-O system," IEEE Trans. Magn., **25**, 2, pp. 2150-2153.
9. Statt, B.W., Z. Wang, M.J.G. Lee, J.V. Yakhmi, P.C. deCamargo, J.F. Major, and J.W. Rutter, 1988, "Stabilizing the high- $T_c$  superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$  by Pb substitution," Physica C, **156**, 2, pp. 251-253.
10. Zhu, W., M.M. Miller, P.A. Metcalf, and H. Sato, 1989, "Preparation of superconducting films of Bi-Sr-Ca-Cu oxides by in-situ melting," II. Materials Letters, **8**, 9, pp. 340-342.
11. LeBeau, S.E., J. Righi, J.E. Ostenson, S.C. Sanders, and D.K. Finnemore, 1989, "Preparation of superconducting Bi-Sr-Ca-Cu-O fibers," Appl. Phys. Lett., **55**, 3, pp. 292-294.
12. Nishi, Y., S. Moriya, and T. Manabe, 1989, "Effect of annealing on  $T_c$  of liquid-quenched  $\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_{1.8}\text{O}$ ," J. Appl. Phys., **65**, 6, pp. 2389-2391.
13. Oka, Y., N. Yamamoto, A. Yuba, H. Kitaguchi, and J. Takada, 1988, "Crystal phases of  $\text{BiSrCaCu}_2\text{O}_x$  heat treated in a vacuum-sealed system," Jap. J. Appl. Phys., **27**, 8, pp. L1429-L1431.
14. Endo, U., S. Koyama, and T. Kawai, "Preparation of the high- $T_c$  phase of Bi-Sr-Ca-Cu-O superconductor," Jap. J. Appl. Phys., **27**, 8, pp. L1476-L1479.