CORRELATION BETWEEN FABRICATION FACTOR AND SUPERCONDUCTING PROPERTIES OF THE TL- AND BI- BASED HIGH-Tc SUPERCONDUCTOR

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ABSTRACT

Large critical current densities (Jc) were obtained in c-axis oriented Tl-1223/Ag composite tapes fabricated by spraying methods without a vacuum. Transport measurements at 77K under a zero field indicated a Jc of $9x10^4$ A/cm^2 and 7×10^3 A/cm^2 at 1T for the tapes fabricated by spray pyrolysis . The novel GPM method was also applied for Bi-2212/Ag PIT composite wire, and found to be very effective for improving the distribution of voids, which caused from the melt-solidifying process. The GPM showed a marked effect for obtaining homogeneous long wire. A 1T class coil was successfully fabricated with monocore wire.

1. INTRODUCTION

It is well known that the Bi-system wires with high critical current density Jc's are much preferable for applications in high magnetic field regions at cryogenic temperature below 20K than Tl-system superconductors from the viewpoint of process easiness realizing good crystal alignment enabling a large current flow, however, the Bi-system superconductors can not be useful in liquid nitrogen temperature applications due to the weak pinning characteristics caused from the two dimensional vortex structure. In the latter case, Tl-1223 with Tc 122K, having strong pinning characteristics (with more three dimensional vortex structure), is thought to be the best candidate. Since, Tl-1223 requires ,however, the three-dimensional crystal alignment for overcoming the grain boundary weak links, the wire fabrication processes are thought to be restricted in a field of the thin film technologies.

In this paper, we show the following two novel processing for both Bi- and Tl- system HTS's,

(1) GPM(gas pressurized melt) process for Bi-2212/Ag solenoid coil using PIT

(2) Spray pyrolysis method for Tl-1223 on silver substrate in ambient pressure conditions.

2. *Bi-2212 GPM Process*

It is well known the Bi-2212/Ag wire with high critical current density Jc can easily be obtained through the partial-melting process.[1] However, the most serious problem of the process is thought to be the oxygen release which causes "*swell*" on the wire. So far, we have already reported that the oxygen release can be reduced using the Bi-2212 powders with Ag,[2] calcined at temperatures around melting point, under a high oxygen partial pressure (100% O_2 - 1 atm). In order to achieve a good superconducting property in a long wire, it is necessary to improve microstructural homogeneity in the longitudinal direction of the wire. In followings, we will discuss the effect of the GPM (Gas Pressurized Melt Process) for Bi-2212/Ag, on microstructure.[3]

2.1 *Experimental*

Commercial powders of 3N pure oxide were mixed in a nominal composition of $Bi_2 Sr_2 Ca_1 Cu_2 Ag_{0.2} O_y$ and calcined twice at 810℃ for 10h. Silver tubes with outer diameter of 6mm, filled with the powder, were processed by drawing to get 0.7mm and 1.2mm outer diameter and 25m length wires. The round wire was cut into 3cm lengths for short sample. As-drawing 25m long wires (1.2mm o.d.) were wound into solenoid type. The fabricated solenoid coil is shown in Fig.1. Both short wires and the coils were partially melted for 10 minutes from 865℃ to 885℃. Short wires were calcined under various conditions of oxygen concentration and total gas pressure. Coils were melted under both atmospheric pressure and a pressurized atmosphere, using GPM. The transport critical current was measured by a four-probe method at 4.2K with a 1 μV / cm criterion for short wires, and with a $10^{-13}\Omega \cdot m$ criterion for coils. The voids distribution inside Ag-sheath was observed using X-ray radiography (Voltage : 180kV, current : 5mA, target : W).

2.2 *Results and discussion*

Since the oxygen partial pressure during melt process affect a release of oxygen gas from Bi-2212 crystals, oxygen partial pressure, pO_2, should be changed to appear the effect on void formation and superconducting properties. It was found that the high Jc values of over 10^5 A/cm^2 were obtained using GPM under a pO_2 of 1.0 to 3.0 atm. And, we investigated the details of the effect of total gas pressure under the condition of pO_2=1.0~1.2atm. Under the total gas pressure over 3.0 atm with a constant pO_2, relatively high Jc values are obtained in a wide temperature range with a little scatterings. According to the X-ray radiography, the distribution of voids in wires melted at P_{total} of 6.0 atm estimated to be smaller than those of melted at the atmospheric pressure (P_{total}=1.0 atm) .Therefore, the GPM method which melted under pO_2 of 1.0 to 3.0 atm and Ptotal over 3.0 atm, are prerequisites for getting wires with the high Jc values and homogeneous distribution of voids. We also fabricated small solenoid coils melted under both ambient and the GPM atmosphere. Fig.2 shows the distribution of voids in both coils. Horizontal axis shows the average length of the voids in the longitudinal direction of the wire, and vertical axis shows the number of the voids. The properties of the coil melted under the atmospheric pressure are markedly depends on the cross-sectional locations. For example, outer-most side, the Jc was lowest, which corresponds to the void concentration of 50 mm long in fig.2. Microstructures and Tc of the coil were homogeneous, however, the distribution of the voids governed the V-I properties. On the other hand, voids of the coil processed through the GPM method were 10mm long at most. Therefore, the GPM method seems to be very effective for improving the distribution of voids, and makes easy for obtaining homogeneous long wire. The coil, using a 5 pieces of 25m long wire, generated a maximum magnetic field of 1.1T at a current of 88A.

3. *Tl-1223/Ag composite tape*

In order to apply high-Tc superconductors to magnets operable in liquid nitrogen, a considerable length of wire must be fabricated with a transport Jc of at least 10^4 A/cm^2 in magnetic fields of 1 T or greater. Key to the fabrication of practical high-Tc superconducting wires is to prepare polycrystalline conductors which have good intergranular connectivity and high flux pinning characteristics. Although YBCO[4] and Tl-1223[5)-7)] has strong pinning force at 77K, the transport capabilities of wires fabricated by the powder-in-tube method are seriously impaired by weak-link behavior resulting from poor intergranular connectivity. In contrast, large transport Jc values have been reported for YBCO thin films epitaxially grown on oxide single crystals[8] and even for those grown on metal with a biaxial aligned buffer layer[9] by physical or chemical vapor deposition. It is important to align the in-plane a- and b-axes of individual grains by using thin film processes in order to inhibit weak-link behavior. Such processes, however, which must be performed under high-vacuum conditions, may not be suitable for wire applications, where long length, high productivity and low cost are required.

The spray pyrolysis method is a film fabrication technique which do not require a vacuum, and which therefore make it possible to produce long lengths of tape shaped wires. In this paper, we report a high Jc value for Tl-based superconductors/Ag composite tapes prepared by spraying methods under ambient pressure, thus verifying the high potential of these methods.

3.1 *Experimental*

The precursor films containing appropriate proportions of all the metals except Tl were deposited under ambient pressure. The deposited films are porous, and so they were pressed or rolled to make them denser and then fired in a controlled thallium oxide vapor.

For the spray pyrolysis, a 0.02 mol/l aqueous solution was prepared from $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2.4H_2O$ and $Cu(NO_3)_2.3H_2O$ with a metal stoichiometric ratio of Ba:Sr:Ca:Cu=1.6:0.4:2:3. The spray solution was converted into a mist with an ultrasonic transducer. The mist was introduced onto the Ag tape which was heated to 700℃. The deposited precursor oxide films were fired at 860℃ for 30 hours in a controlled thallium oxide vapor. The film thickness was approximately 1 μm.

The transport Jc of the films was measured by using the standard four probe method with a criterion of 1 μV/cm. The crystal structure and composition were analyzed by X-ray diffraction (XRD) and energy-dispersive X-ray analysis (EDX). Their microstructure was observed with a scanning electron microscope (SEM) and X-ray pole-figure analysis.

3.2 Results and discussion

Figure 3 shows the XRD pattern of Tl-1223/Ag composite tape prepared by the spray pyrolysis method. All the peaks can be assigned to the (00l) diffraction of the Tl-1223 phase, except for the (hkl) diffraction of Ag metal. The film was confirmed to consist of single phase Tl-1223 with c-axis crystal orientation. The specimen for Jc measurements was cut from the 1 m long composite tape. The Jc variation was within 5 % for all the pieces. The highest Ic value of any sample was 6.0 A and its Jc was $9x10^4$ A/cm^2 at 77 K without a magnetic field. Figure 4 shows the magnetic field dependence of the Tl-1223/Ag composite tape with the field applied parallel to the c-axis. The Jc at 1T was $7x10^3$ A/cm^2 which is 10 times the value of our silver sheathed Tl-1223 wire. To improve the Jc for practical high-Tc superconducting wire, it is important to achieve three dimensional alignment of the in-plane a-axes (biaxial orientation) of individual Tl-1223 grains.

Recently we have found that biaxially oriented Tl-1223 films can be successfully formed on a $SrTiO_3$(100) single crystal substrate by spray pyrolysis. Figure 5 shows the magnetic field dependence of Jc for Tl-1223 film with the field applied parallel and perpendicular to the c-axis up to 8T at 77K. The curves reveal a relatively weak dependence under low fields. When the fields were applied parallel to the c-axis, Jc reached $5x10^4$ A/cm^2 at 1T. The gentle magnetic field dependence of Jc below 1T for the biaxial oriented Tl-1223 film suggests that the weak-link problem is almost eliminated in the film.

To achieve biaxial orientation in Tl-1223/Ag composite tapes, the "buffer layer" or "metal substrate" itself have to be aligned biaxially. Iijima et al.[9)] reported the successful growth of a biaxially aligned YSZ buffer layer on a hastelloy substrate by the ion-beam assisted deposition process, and biaxially aligned YBCO films with high transport Jc values were formed on it.

YBCO films grown by the laser ablation method on Ag(001), Ag(110) and Ag(111) single crystal substrates show specific in-plane epitaxial orientation with respect to the crystallographic axes of the substrate[10)]. This result has important consequences in terms of in-plane alignment on metal substrates. It is well known that a (100)[001] texture can be easily formed by rolling and annealing with fcc metals such as Cu where the metal surface consists of a square arrangement of atoms. In the case of Ag, the annealed texture is different from that of Cu, which is mainly (110)[112] and which is described as a rectangular lattice. Yoshino et al.[11)] showed that YBCO films grown on a (110) textured Ag substrate by ionized-cluster-beam-deposition, were aligned with in-plane orientation. However, this textured substrate was not suitable for use with our spraying method because of its instability of texture and surface irregularity at higher temperature. We examined the optimum rolling and annealing conditions with which to obtain the (100) texture. Figure 6 shows the XRD (θ-2θ) pattern and surface morphorogy of the nearly (100) textured Ag substrate. The texture and surface flatness of the Ag substrate remained even at 850℃ which corresponds to the heating temperature for the precursor films.

The results of this study demonstrate the considerable potential of the spray pyrolysis method, which does not require a vacuum, for the fabrication of practical superconducting wires and tapes.

4. *Acknowledgments*

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5. *References*

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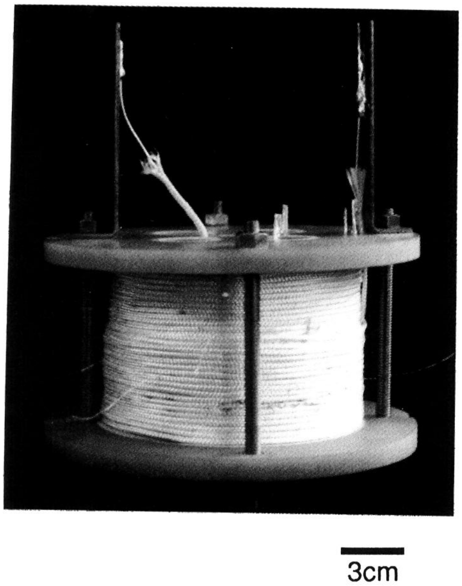

Fig.1 Photograph of the Bi-2212/Ag coil

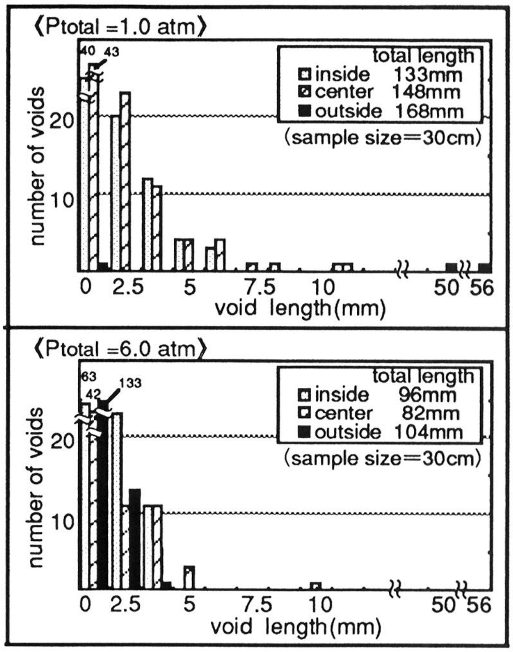

Fig.2 Void distribution of coils

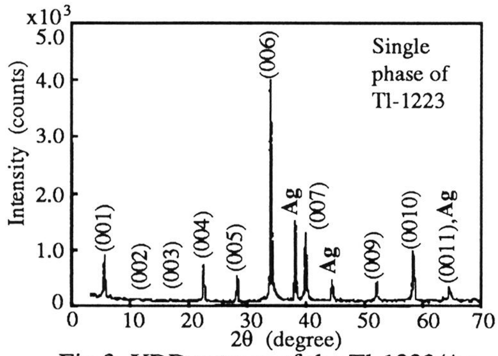

Fig.3 XRD pattern of the Tl-1223/Ag prepared by spray pyrolysis method

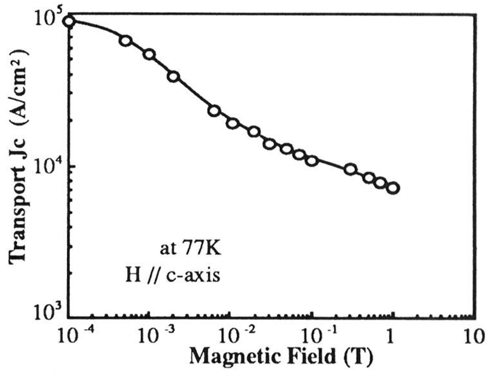

Fig.4 Jc versus field for the Tl-1223/Ag prepared by spray pyrolysis method

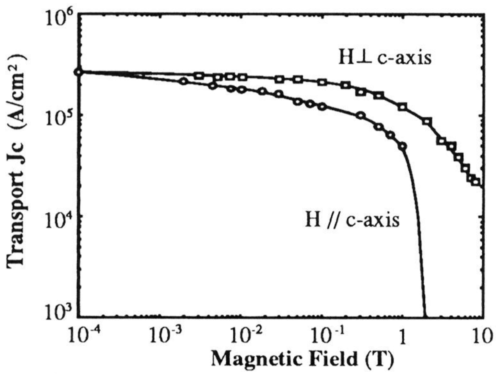

Fig.5 Jc versus field for the Tl-1223 on STO(100) prepared by spray pyrolysis method

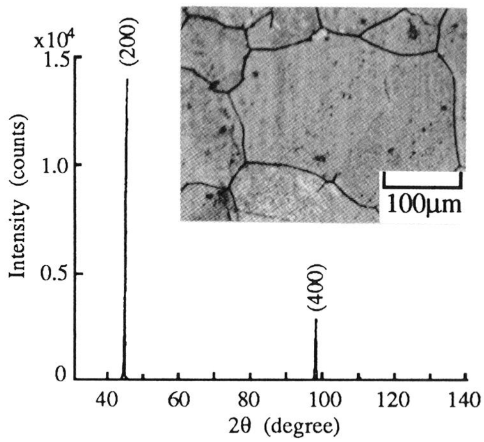

Fig.6 XRD pattern and surface morphorgy of the nearly (100) textured Ag substrate