研究

Study of Silverclad High Tc Superconducting Film—Critical Current—

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Critical current value of $\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.0}\text{O}_y$ film was studied at liq. N_2 temperature. It was found that silver-clad was useful for enhancement of the critical current and the obtained maximum value (I_c) reached around 4A (an equivalent J_c value of around $2000\text{A}/\text{cm}^2$).

Introduction

After the discovery of the high Tc superconducting oxide materials at 1989, the research and development of feasibility of these materials as current wire had began. A huge number of works picked two potentially feasible compounds : YBC and Bi-2223 in their abbreviated representation. Especially Bi-2223 and its Pb-substituted one had been attracting researchers to their hopeful properties, such as high Tc, non-poisonous and cheap cost of raw materials.

At present time, reduced critical current density (J_c), which is one of the most important characters of current wire, reached more than 100 million A/cm^2 . The value was obtained in the thin film sample as current carrier. But thin film is not the best form for current wire. Being usually deposited on substrate material, actual critical current value (I_c) is far below the critical current (J_c).

The other required character, easiness for wire manufacture, is

also hard to be fulfilled. Though having less J_c value, more powerful contender is the silver sheathed, uniaxially pressed and sintered form of the samples. The sample form is often called "metal sheathed material" in abbreviated expression. The J_c data of $5.4 \times 10^4 \text{A}/\text{cm}$ for "silver sheathed material" in short-length size (about a few mm in length) has been reported¹⁾. The manufacturing technique of the sheathed material was originated from the conventional production of metal superconducting wires. Today an up-to-100m length current wire has been manufactured. Some trial manufactures of the equipments using "metal sheathed material" wire of the high Tc superconductor have started bright future, yet it has some disadvantages stemming from the manufacturing method. To develop another wire manufacturing method, therefore, is very valuable to us. In this paper we'll report a model experiment of manufacturing wire in which usage of thick film as a current carrier will be discussed.

Fig.1 Sintering temperature dependence of I_c for $\text{Pb}_x\text{Bi}_{1-x}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$. $x=0.20, 0.25, 0.35$, and 0.40 .

Experimental

Appropriate selection of the starting material and heat treatment conditions are important for the experiment. We picked up Bi-2223 of partially Pb substituted phase as a raw material phase. The explicit nominal composition is given as $\text{Pb}_x\text{Bi}_{1-x}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$. In the range of x value from 0.05 to 0.3, critical transition temperature (T_c) was around 105K.

The appropriate nominal composition for I_c experiment is determined through the following preliminarily experiments. After weighed one gram of powder sample, each sample of different compositions was pressed to a rod (molding pressure; 0.8 ton/cm^2 , size; $7\text{ mm} \times 30\text{ mm} \times 1\text{ mm}$, green density; $4.5\sim 4.6\text{ g/cm}^3$). These rods were sintered to the test pieces for I_c measurement (sintering conditions: atmosphere; air, time; 90h, temperature; 820 to 850°C). The test pieces kept nearly the same size before and after the heat treatment, and no remarkable shrinkage or dilatation was

Fig.2 Time dependence of I_c for $\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$ at $T=835$ and 850°C

observed. The I_c was measured by conventional four probe method (measurement conditions: inner probe gap; 5mm, threshold voltage; 1uv, temperature; liq. N_2 temp.).

Results and Discussion

A part of results are given in Fig. 1. Observed I_c values exhibit a maximum when the sintering temperature is between 830 to 845°C in all samples of different compositions. At sintering temperatures out side of ones mentioned above the observed I_c value is steeply decreased to zero. Composition dependence of the maximum I_c value is small. We concluded, therefore, the composition of $\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$ and the heat treatment temperature of 835°C is one of preferable options for I_c experiment.

More detailed experiment of $\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$ was most suitable for following experiment. The conclusion was also supported subsidiarily by the results shown in Fig. 2. The prolonged sintering of the sample ($\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_y$) is

Fig.3 I_c dependence of bare films on the number of repeats of uniaxial loading and sintering.

Fig.4 Film thickness dependence on the number of times of uniaxial loading and sintering.

profitable for I_c at 835°C , whereas, unprofitable above 845°C . Prolonged sintering below 830°C , as well known, is also unprofitable because of the disproportionation reaction of the sample. The results also tells us that if the cyclic process of uniaxial loading and sintering is adopted in a sample of $\text{Pb}_{0.2}\text{Bi}_{0.8}\text{Sr}_{1.0}\text{Ca}_{1.0}\text{Cu}_{1.6}\text{O}_x$, it should done in the narrow temperature range of around 835°C .

Film sample was prepared by conventional thick film making technique. These thick film are cutted to test pieces of rectangular shape (size: $30\text{mm} \times 7\text{mm} \times \text{tens } \mu\text{m}$). After eliminating binding reagent by calcination, the test pieces were subjected to two kinds of I_c enhancement seeking trials. The first trial is for the evaluation of the repeated process of uniaxial loading and sintering of the bare test pieces. The second is the evaluation of " metal clad " on thick-film type test pieces (hereafter the sample is described as " metalclad material "). Silver metal of $100\mu\text{m}$ thickness is used for metalclad. Repeated process of

uniaxial loading and sintering is also adopted on the silverclad sample. After uniaxial load of $1\text{ton}/\text{cm}^2$ was added on a sample, the sample was heat treated at 835°C for about 90h in air. Then sample was slowly cooled to room temperature and subjected to conventional I_c measurement which was the same as in the preliminary experiment. In some cases of I_c experiment, gap distance between inner probes was altered to evaluate the uniformity of the sample. It was thus affirmed inner gap of 5mm was sufficient for I_c evaluation.

Fig. 3 shows I_c dependence of bare films on the number of repeats of uniaxial loading and sintering. This experiment showed uniaxial loading was surely effective at the first or second stages of the process, but further repeating was of little or no effect on I_c enhancement. Uniaxial loading brought slight increase of density in the initial stage of the processing. After the period, the thickness and the density of the test piece film kept nearly the same values in experimental error.

Fig.5 I_c dependence of silverclad films on the number of uniaxial loading and sintering.

These results are shown in Fig. 4. In short it may be concluded the adopted uniaxial loading and sintering of a bare sample has little effect on I_c enhancing.

Next we examined the effect of silverclad on I_c of a test piece. Results are given in Fig. 5. Observed I_c value increased with increase of the number of processing times and reached around 4A (J_c value equals to around $2000\text{A}/\text{cm}^2$) when 4 times of uniaxial loading and sintering were repeated. The obtained critical current may not be matched to that of "silversheathed material", but lies in accountable value as for silverclad thick film type wire.

We also tried the model wire connecting six test pieces in parallel form. In the wire was attained I_c value of around 30A in liq. N_2 temp. In Photo. 1 is given the figure of the model wire.

Photo.1 The model wire connecting six test pieces in parallel form.

Regrettably we have yet no chance of evaluating the overall characteristics of the "silverclad film" in terms of current wire. But both relative simplicity of manufacturing and the resultant I_c suggest the silverclad thick film is worth developing as a current wire manufacturing technique. Further works are in progress and will be reported in near future.

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