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Characteristics of HTS Tube Depending on Chemical Compositions

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***Abstract*-- The Bi2212 based HTS tubes with 4 different compositions, Bi:Sr:Ca:Cu = 2.0:2.0:1.0:2.0, 2.1:2.0:1.0:2.0, 2.2:1.8:1.0:2.0 and 2.2:1.8.1.0.2:2 with 10% of $SrSO_4$ were studied. For tube fabrication the optimum range of melt temperatures and preheating temperature and time for mold were 1050℃ ~ 1100℃ and 550℃ for 30min respectively. The mold rotating speed was 1000rpm. Typical tube dimension was 30/24mm in outside/inside diameter and 60mm in length. A tube was annealed at 840℃ for 40 hours in oxygen atmosphere. The plate like grains more than 20μm were well developed along the rotating direction of mold regardless of initial chemical compositions. The specimen with Bi2212 composition exhibited T_c of 83K while the specimen with other compositions are lower than 60K. The measured I_c and J_c at 77K(B = 0T) in Bi2212 composition were about 80A and 266A/㎠.**

1. INTRODUCTION

$Bi_2Sr_2CaCu_2O_y$(Bi2212) superconductor is one of the most promising materials as a conductor for energy applications. Bi2212 is very attractive materials among the other superconductors because of its easy c-axis alignment, which reduces a weak-link behavior and maintains high critical current density(J_c) of a-b plane orientation. From a practical point of views these features are very important in bulk HTS applications, such as wires, current leads(CL) and fault current limiters(FCL). So far a number of processing techniques, such as the doctor blade method[1], the dip-coating method[2], the organometallic method[3] and the powder-in-tube method[4] have been proposed in order to fabricate conductors with a high critical conductivity. All of these methods employ a slow solidification process from a partially molten state in order to enhance texturing of c-axis grain alignment, which results in a significant improvement of intergrain coupling.

Among them, melt casting process(MCP) is well known as one of novel techniques to manufacture the 3 dimensional compact bodies[5]. MCP Bi2212 rods and the tubes have been successfully tested in a variety of current lead design[6]. The typical advantage of MCP is that any geometry of superconductor with excellent current carrying properties can be easily fabricated. Additionally the temperature and field dependence of the material is superior to sintered HTS bulk parts and is characterized by the absence of weak links. The melt casted Bi2212 tubes fabricated by Aventis & Technologies have reported that they had a critical current density(77K, B = 0T) of 600 4000A/cm2 depending on the tube dimensions[7,8].

The Bi2212 phase is stable in a wide range of compositions and processing temperatures in a form in which T_c is influenced by the composition. It is well known that the highest T_c(93K) can be obtained in Sr rich samples(Sr:Ca = 2.2:0.8) in Bi2212 state[9]. However there are not many reports and results of Bi HTS on the solidification process after complete melting.

In this study, Bi based tubes with 4 different chemical compositions were fabricated by complete melting. Our preliminary results indicate that electrical characteristics and microstructure were quite dependent on the processing parameters and initial compositions after complete melting. This paper will discuss about tube fabrication process and compare the tube characteristics including superconducting properties in terms of different compositions.

2. EXPERIMENTAL

Initially 4 different chemical compositions of the cation ratio of Bi:Sr:Ca:Cu, such as 2.0:2.0:1.0:2.0, 2.1:2.0:1.0:2.0, 2.2:1.8:1.0:2.0 and 2.2:1.8:1.0:2.2 were designed and prepared by routine solid reaction. These powders were well mixed with 10% of $SrSO_4$ and charged into platinum crucible for the complete melting by inductive heating, in which included as one of main parts in Centrifugal Forming Process(CFP). The self-designed equipment for CFP is mainly divided into 3 parts depending on its role and functions, the first part for the meting part by high inductive frequency, the second part for the centrifugal forming part for the tube shape and efficient microstructure control of Bi2212 phase and the third part for the molding part for tube detachment after heat treatment. Fig. 1 shows the schematic diagram of self designed CFP equipment.

The melting was done by inductive heating at 1050℃ ~ 1100℃ within 5min in platinum crucible in order to maintain initial composition from excessive Bi evaporation and contamination. Following that, the solution of the melted powder was pour into the steel mold rotating at 1000rpm, which was preheated at 550℃ for 30min. The

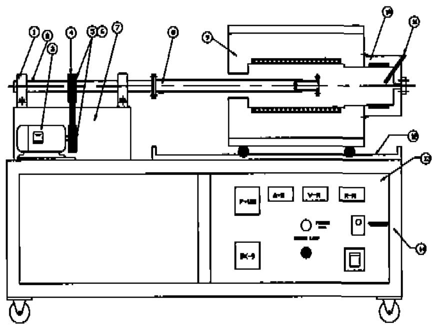

Fig. 1. The schematic diagram of self designed CFP equipment

purpose of preheating is to prevent mechanical damage during transportation of melt from the crucible to the mold. Typical steel mold dimension was 30㎜ in diameter and 70 ㎜ in length. For the electrical contact 0.5mm thickness of silver tape was inserted into the top and bottom of mold. Normally the specimen was mechanically stable when the melting temperature was over 1035℃ and steel mold was preheated over 400℃ for 30min. The tube was heated at 740℃ and kept for 5hrs in order to release the residual stress caused by rapid solidification from melt. After that, the tube was again annealed at 840℃ for 40hrs in oxygen atmosphere. Finally the temperature was slowly cooled down to 740℃ at a rate of 1.5℃/min. The detailed heat treatment schedule and overall processing chart for CFP are shown in Figs. 2. and 3. After heat treatment tube was easily removed from the steel mold.

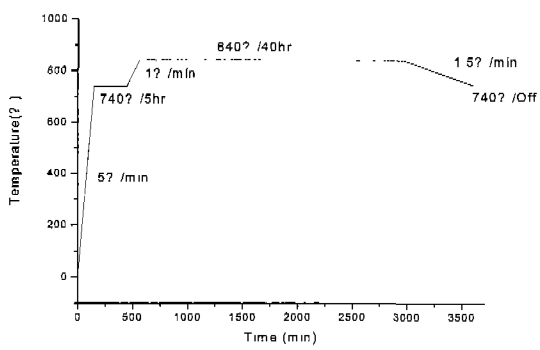

Fig. 2. The detailed heat treatment schedule for tube fabrication

For the structural analysis and phase identification X-ray diffraction method was employed. Microstructure observation was performed with scanning electron microscopy(SEM) on both the surface and inner side of tube. The critical temperature(T_c) and the critical current(I_c) were measured by four-probe resistive method and the transport current density were determined from the current/voltage curve using a 1μV/cm criterion.

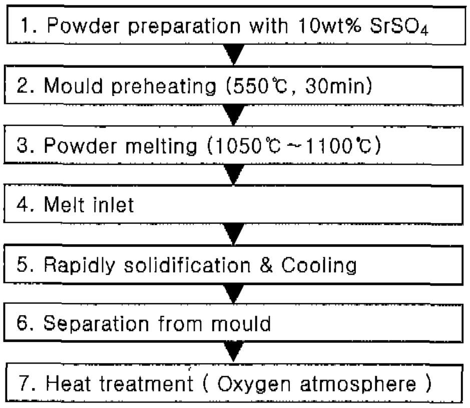

Fig. 3. Overall processing chart for CFP

3. Results and Discussions

The Bi2212 based tubes with 4 different compositions were successfully fabricated with silver electrode by CFP. Typical dimension of tube was 30/27mm in outside/inside diameter and 60mm in length. For the process, the optimum range of melt temperatures and preheating temperature and time for mold were 1050℃~1100℃, 550℃ for 30min respectively. The mold rotating speed was 1000 rpm.

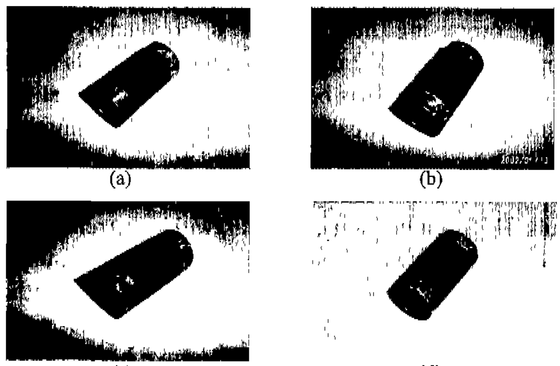

Fig. 4. Various Bi Tubes with silver electrode fabricated by Centrifugal Forming Process in terms of compositions
(a) $Bi_2Sr_2Ca_1Cu_2O_x$ (b) $Bi_{2.1}Sr_2Ca_1Cu_2O_x$ (C) $Bi_{2.2}Sr_{1.8}Ca_1Cu_2O_x$ and (d) $Bi_{2.2}Sr_{1.8}Ca_{1.2}Cu_2O_x$

Fig. 4 shows various Bi Tubes with silver electrode fabricated by Centrifugal Forming Process in terms of compositions. Final tube density and shape were quite dependent on many processing parameters such as melting temperature, melting time, mold rotation speed and heat treatment schedule. Especially proper adjustment in viscosity of melted powder is important to control the uniform thickness. It was confirmed powder solution was solidified within 5sec when it poured and contacted with a mold, preheated at 550℃. Therefore it seems mold rotation speed more than 500rpm does not much affect texture formation.

Fig. 5 represents XRD diffraction patterns taken from the surface of tube with 4 different chemical compositions. XRD data suggests that the phase formed after direct solidification from melt identified as amorphous phase.

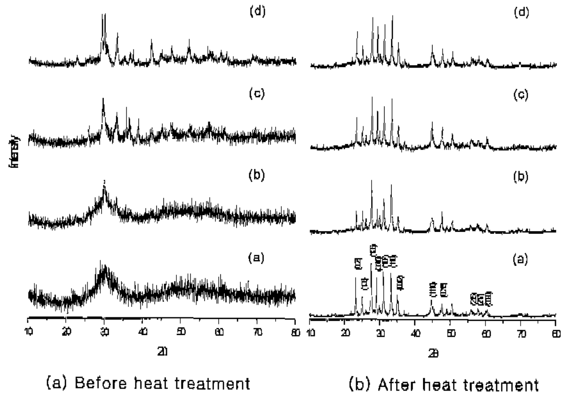

Fig. 5. XRD diffraction patterns taken from the surface of tube with 4 different chemical compositions before and after heat treatment

After heat treatment the diffraction patterns observed from Fig. 5 indicate the existence of multiphase mixture consisting of prominent 2212 with some additional peaks from some other phases of 2201, Cu-free and (SrCa)-Cu-O phases. However generally Bi2212 phase is predominant regardless compositions while the intensity was varied in terms of initial chemical composition. This kind of feature was noticeable except XRD pattern of tube with Bi2212 composition. This can be explained that the excess Bi and Ca might form the non-superconducting phases. Also it was known that Bi2212 phase decomposes into a liquid phase plus the solid phase of Bi-(SrCa)-O(Cu free phase) and (SrCa)-Cu-O at the partial melting temperature, about 870℃ in the heating process[10]. Therefore these XRD results suggest that the electrical properties will be hindered or influenced by the existence of some other non-superconducting phases.

Fig. 6 shows SEM micrographs of fractured tube surface with different compositions. The plate like grains was well developed and densified along the rotating direction of mold regardless of initial chemical compositions. Theses kinds of orientations were significant for the fractured surface close to mold as compared with one near the inner part of the tube. Typical plate like grain size was about 20μm.

Fig. 7 shows temperature-resistance of the tube fabricated with 4 different compositions. The specimen with 2212 composition exhibited T_c of 83K while the specimen with other compositions are lower than 60K with a broad transition width and tail, which is lower than we

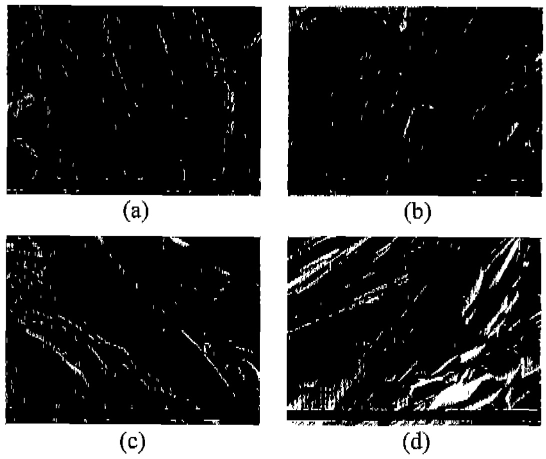

Fig. 6. SEM micrographs of fractures tube surface with different composition
(a) $Bi_2Sr_2Ca_1Cu_2O_x$ (b) $Bi_{2.1}Sr_2Ca_1Cu_2O_x$ (C) $Bi_{2.2}Sr_{1.8}Ca_1Cu_2O_x$ and (d) $Bi_{2.2}Sr_{1.8}Ca_{1.2}Cu_2O_x$

expected. This can be explained by the poor grain boundary connectivity related with the random grain orientation, the phase decomposition of Bi2212, porosity and other impurities near the grain boundary area.

The I_c and J_c were measured at 77K(B = 0T) on the specimen with sectional area of 0.3cm^2. Fig. 8 shows the I-V characteristics of tube with Bi2212 composition. The measured I_c and J_c at 77K(B = 0T) were about 80A and 266A/㎠. This obtained value is still somewhat lower than the data by Hobl group[8]. Now further detailed work to optimize the process and chemical composition is still undergoing.

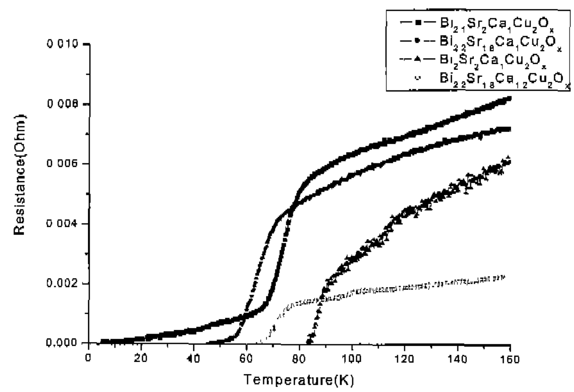

Fig. 7. Temperature-resistance of the tube fabricated with 4 different compositions
(a)$Bi_2Sr_2Ca_1Cu_2O_x$ (b) $Bi_{2.1}Sr_2Ca_1Cu_2O_x$ (C) $Bi_{2.2}Sr_{1.8}Ca_1Cu_2O_x$ and (d) $Bi_{2.2}Sr_{1.8}Ca_{1.2}Cu_2O_x$

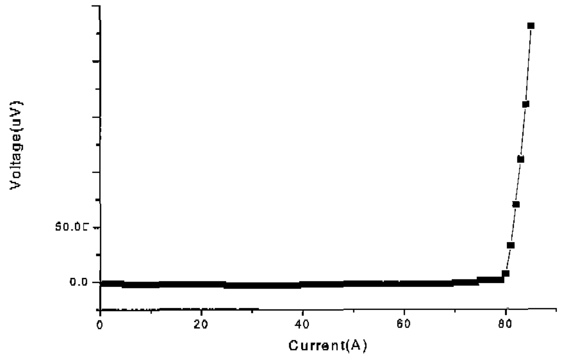

Fig. 8. I-V characteristics of the tube with Bi2212 composition

4. CONCLUSIONS

The tubes with 4 different chemical compositions were successfully fabricated by CFP. For tube fabrication the optimum range of melt temperatures and preheating temperature and time for mold were 1050 1100 and 550 for 30min respectively. The applied mold rotating speed was 1000rpm. Normally the specimen was mechanically stable when the melting temperature was over 1035 and steel mold was preheated over 400 for 30min. Typical tube dimension for this study was 30/27mm in outside/inside diameter and 60mm in length. A tube was annealed at 840 in oxygen atmosphere for 40 hours. XRD data suggests that the phase formed after direct solidification from melt identified as amorphous phase and this phase was transformed into Bi based structure after heat treatment. The plate like highly oriented grains were well developed along the rotating direction of mold regardless of initial chemical composition. Typical grain size was about 20㎛. The specimen of Bi2212 composition exhibited T_c of 83K while the specimen with other compositions are lower than 60K with a broad transition width and tail. The measured I_c and J_c at 77K(B = 0T) in Bi2212 composition were about 80A and 266A/㎠.

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