Peculiarities of ReBaCuO superconductor preparation

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Abstract

From 1994 the cooperation between NEU of China and MJU of South Korea for study of ReBaCuO (Re=Rare earth elements) superconductors has been carried out. The progress has been got in following projects. Critical current density (J_c) of YBaCuO superconductor prepared by Melting Textured Growth (MTG) was improved. In the preparation of textured YBaCuO, 20 wt.% of YBaCuO 211 phase was added, which would be climactic for the microcracks in the textured YBaCuO. The effects of the 211 phase and Ag content on the superconductivity were studied and discussed in detail. The improved J_c value was reached to 8×10^4 A/㎠ (77K, 0T). Single phase $YbBa_2Cu_3O_x$ superconductor was sintered by the traditional powder metallurgical method, and its reaction process was studied. In recent years, NdBaCuO superconductor is being performed. The behavior of $Nd_4Ba_2Cu_2O_{10}$ (Nd422 phase) and the solid solubility, x in the superconductor $Nd_{1+x}Ba_{2-x}Cu_3O_y$ by the heat treatment in the low oxygen partial pressure (1%) or Ar at 950℃ were investigated. The zone-melting process was used to make oriented NdBaCuO superconductor in order to increase the critical current density.

Key words : Melting Textured Growth, ReBaCuO superconductor, Zone-melting process, Melted-Condensed Process,

1. Introduction

Since YBaCuO superconductor with 90K zero resistance[1], many scientists have attempted to improve the critical current density (J_c) by different methods. S. Jin used Melted Texture Growth Method (MTG) to make the oriented YBaCuO superconductor, which had 18,000 A/㎠ critical current density. Salama prepared the textured YBaCuO superconductor with a similar method as like S. Jin and the J_c reached 4×10^4 A/㎠. Murakami innovated the MTG method and discussed the behavior of non-superconducting phase Y_2BaCuO_5 in $YBa_2Cu_3O_x$. A zone melting equipment was designed in our group in order to prepare oriented YBaCuO superconductor. The critical current density in our group reached 37,000 A/㎠(0T, 77K) and 2×10^4 A/㎠(1T, 77K) made by the zone-melting method[2]. In order to improve the superconductivity of the textured YBaCuO, the effects of many factors on the superconductivity were studied, such as the effects of Y_2BaCuO_5 (211 phase) and Ag content. From 1996 to 1997 in Myongji University, Korea, we prepared YbBaCuO superconductor considering the melting point of the system is lower than that of YbaCuO. In resent years the system of Nd(or Sm)BaCuO was studied due to its advantages.

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2. Effect of Y_2BaCuO_5 (211) in the textured YBaCuO superconductor

Six YBCO sintered samples with 5, 10, 15, 20, 30, 40wt.% of 211 phase contents were taken X-ray diffraction under the same test condition. <110> and <013> peaks of 123-phase and <311> peak of 211 phase were selected to be characteristic peaks. The curve of I211/I211+I123 versus 211 phase contents will be used as the reference for the calculation of 211 phase contents in the textured YBCO.

Samples with dimension of about 10×5×1 ㎣ cut from textured YBCO bars were heated at 400 ℃ for 50 hours under oxygen flow to absorb oxygen. After the heat treatment, several 10 milligrams of YBCO powder were taken from each textured YBCO samples to do the X-ray diffraction and the 211 phase contents were calculated. The YBCO samples (10×5×1 ㎣) were used to measure the critical current densities, respectively. The 211 content and critical current density were correspondent with each other for the same sample. It can be seen that the optimum value of its contents in the textured YBCO is about 20 wt.% and before this value, as fig. 1 J_c increases with increasing 211 contents, and after that value J_c decreases with increasing 211 contents.

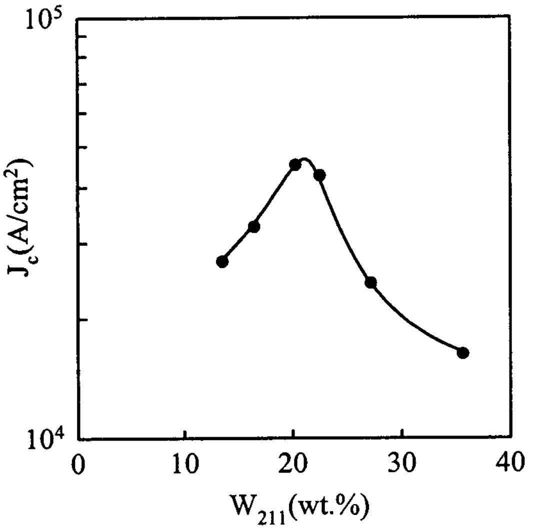

Fig. 1 The relation of J_c and contents of 211 phase under H=0.

It seems that as the flux pinning centers, 211 particles could make critical current density increase with 211 contents, may be the non-superconductive phase 211 particles could make critical current density decrease when the volume ratio of 211 phase was too large.

3. Behavior of Ag in the textured YBCO

The added Ag contents in sintering YBCO and the analyzed Ag contents in condensed YBCO were measured and compared with each other. The analyzed Ag contents in condensed YBCO accord with the added Ag contents, if the added Ag contents are less than 14 wt. %. The analyzed Ag contents are stable at 15 wt.%. When added Ag contents are larger than 16 wt.%, it means that Ag content in YBCO is saturated, or the solubility of Ag in condensed YBCO is 15 wt.%.

However, the Ag contents did not influence on critical temperature of YBCO in the experiment, the same phenomenon was reported in reference for the sintering YBCO sample.

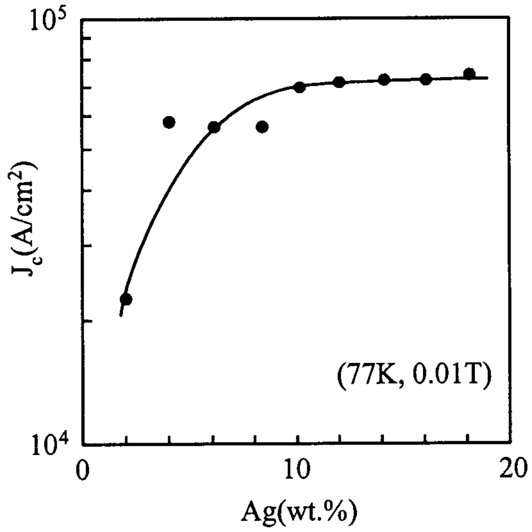

Fig. 2 The relation of J_c and Ag contents.

Whereas Ag contents have large influence on the critical current density, J_c increases with increasing Ag contents when Ag contents are less than 15 wt.%, while J_c tends to a stable value $(7\sim8)\times10^4$ A/㎠ (0.01T, 77K). When Ag contents are over 15 wt.%, the solubility of Ag in condensed YBCO, the extra Ag will escape from the YBCO sample into slag on the substrate. The Ag contents of YBCO were determined by second electron spectrum of SEM, which was shown in table 1.

Table 1. Ag contents in condensed YBCO

Sample No.	A4	A6	A8	A10	A12	A14	A16	A18
Ag contents (wt.%)	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0
measured Ag contents (wt.%)	4.3	6.2	8.1	9.27	12.1	14.2	15.1	15.2

4. The improvement of J_c in textured YBCO

MTG process for YBCO was taken place in a Ni-Cr resistance wire furnace with a constant temperature zone of 60mm, which was controlled by a Pt-Pt·Rh thermocouple. The mixture of YBCO (80 wt.%), Y_2BaCuO_5 (10 wt.%) and Ag (10wt.%) was placed on the high quality alumina substrate. The sample was heated to 1,080℃ in 2 hrs, held at 1,080℃ for 1hr, reduced to 1,030℃ in 20 min. The seed of SmBaCuO was put on the surface of melted YBCO at 1,030~1,050℃ at which YBCO stayed in melted state and the seed stayed in solid state. It was reduced to 980℃ at rate of 1-2℃ per hour, and then reduced to 400℃ at 100℃ per hour. The oxygen absorption was taken place at 400℃ under O_2 environment for about 50 hours. The magnetic hysteresis curve was measured by a vibrating sample magnetometer at 77 K and critical current density (J_c) was calculated by means of Bean's model. The J_c value for the best samples can reach 7×10^4 A/㎠(77K, 0.01T).

5. Textured Growth of YbBCO Superconductor

In this study, based on the research of high temperature YBCO superconductor, using the Yb instead of Y in the YbBCO superconductor powder which was combined by means of conventional solid reaction, the textured directional YbBCO bulk was prepared by MCP(Melted-Condensed Process) method to be analyzed.

Mixing the starting elements(Yb_2O_3, $BaCO_3$, and CuO) and calcining at 890℃, 900℃, 910℃, single phase YbBCO with Yb_2BaCuO_5 and $BaCuO_2$ were certified. And from the powder which was calcined at 900℃ the, sample which became texture-growth by Melted-Condensed Process (MCP) method was well oriented. The result of DTA measurement, the fusing point of YbBCO superconductor and it's critical current was measured to be 979℃, 87K respectively. The critical current density was obtained at the value of 700 A/㎠ (77K, 0T) calculated by Bean's Model using the measured hysteresis curve of VSM. In the preparation of YbBCO superconductor, it comparatively has a little critical current density because of coexisting of superconducting phase YbBCO and non-superconducting combining materials such as Yb_2BaCuO (211 phase) and $BaCuO_2$. in the YbBCO system. Therefore, the research of combining the phase control technique for acceleration of reaction was required.

6. Preparation of NdBaCuO by zone-melting

The $NdBa_2Cu_3O_x$ is one of the most promising high temperature superconductor for its enhanced vortex-pinning, which results in the high critical current density and high irreversibility field of the bulk materials [3]. The higher speed of NdBaCuO crystal formation is interested for the technicians to produce textured bulk superconductors. The Nd atoms to form a solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_y$ may substitute at some Ba sites in the $NdBa_2Cu_3O_x$ crystal lattice. The critical transition temperature (T_c) declines with the increasing x value. In order to overcome the substitution, in some papers, they prepared the NdBaCuO superconductor under 0.1-1 % oxygen atmosphere [4,5]. In the experiment, the NdBaCuO materials were at zone-melted process in air. After zone-melted process, the textured NdBaCuO bulk was heat treated at 900-950℃ under argon atmosphere. That process can suppress the substitution of Nd in Ba site, the effect of which was proved by the comparing both the XRD and the J_c value of the samples before and after heat treatment. The effect of $Nd_4Ba_2Cu_2O_{10}$ (Nd422) phase on the superconductivity of NdBaCuO was also studied.

In order to depress the substitution of Nd for Ba, some authors prepared NdBaCuO superconductor under 1 % or 0.1 % oxygen partial pressure [6]. Salama et al. grew NdBaCuO superconductor in air by the directional solidification in a modified Bridgeman furnace; Hu prepared NdBaCuO superconductor in air by the MTG method [7]. After the processing the superconducting material was heat treated in pure argon at 900~950℃ for 20 hours in order to decline the substitution of Nd for Ba. The heat treatment under Ar at high temperature for the NdBaCuO materials made in air is an important processing. For the zone-melting method because of the movement of equipment, it is difficult to control the oxygen partial pressure. In the experiment the zone melting processing of NdBaCuO was taken in air, and then the zone melted NdBaCuO bars was heat treated in Ar at 950℃. The effects of the Ar treatment on decreasing of the replace of Nd for Ba were examined by the XRD and the measurements of superconductivity (T_c, J_c).

7. Conclusion

For the improving the properties and preparing technique of the high-temperature superconducting materials, the ReBaCUO system consisted with Y, Yb and Nd instead of Re was investigated.

In the YBCO system, the critical current density(Jc) could be sufficiently increased by the optimum value of 211 contents (20wt.%) and Ag addition (15wt.%) including with useful method of MTG for the textured growth of crystalline structure and superconductivity.

However, in the preparation of YbBaCuO superconductor, the critical current density was comparatively smaller than that of YBCO system because coexisting of superconducting 123 phase of YbBCO and non-superconducting materials such as Yb_2BaCuO (211 phase) and $BaCuO_2$. Therefore, further investigation of the non-superconducting phase control and reduction of them would be required for the acceleration of reaction on YbBCO superconductor.

For the NdBaCuO preparation, both sintering and zone-melted samples was made in air existing the substitution of Nd for Ba, namely x>o in $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. The substitution could be reduced by the heat treatment in pure Argon at 950℃, and the superconductivity was improved. When x>0.4, the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ could not be transferred from tetragonal phase into orthorhombic phase even after a long time oxygenation. Addition of Nd422 phase in the $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ could also increase the x value after zone-melting.

Acknowledgments

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