

Improvement of MTG Process for Preparation and its property of YBCO Superconductor

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Abstract

To improve the superconductivity of high temperature YBCO superconductor, it was prepared and examined by MTG (melt-textured growth) process with use of SmBaCuO seed crystal for orientation, additives of Ag and 211 phase for current density and flux pinning, and heat treatment for oxygen absorption. SmBaCuO single crystals were prepared by MTG process with oxygen absorption and analyzed by XRD and Laue technique. It was estimated that optimum value of Y_2BaCuO_5 (211 phase) contents in the textured YBCO superconductor as flux pinning center was about 20wt.%. Ag contents have no influence on the critical temperature but have large influence on the critical current density of the textured YBCO.

In the YBCO matrix in experiment, 10wt.% of Y_2BaCuO_5 was added, the final 211 content of YBCO made by MTG process could reach about 20wt.% which was the optimum value for the critical current density. The Ag contents in textured YBCO and the effects of Ag on the superconductivity were also examined.

A $5 \times 5 \times 2 \text{ mm}^3$ single crystal of SmBaCuO grown by the melted-condensed process was used to be the seed crystal in the preparation of YBCO. It was proved that the orientation of YBCO was the same as the orientation of the SmBaCuO seed. The effect of oxygen absorption of the bulk oriented YBCO was studied and the heat treatment of oxygen absorption would be in flowing oxygen, at 400 °C for about 24 hours. The critical current density of the textured YBCO prepared by the optimum technical conditions was about $7 \times 10^4 \text{ A/cm}^2$ (77K, 0.01T).

Introduction

In recent years, it was investigated on the improvement of critical current density for the high temperature superconductors of YBCO, SmBCO and YbBCO, respectively in the Lab. and presented in the conventional journal, but it would be discussed for the improvement of MTG process limited only for the YBCO superconductor.

There are some extra non-superconducting 211 phase of Y_2BaCuO_5 in the melt-condensed process due to the loss of the liquid phase ($BaCuO_2 + CuO$), which was caused by the slow cooling rate in MTG process. Some works show that the 211 phase of fine particles, as an additive material, are effective in flux pinning center of YBCO superconductor [1,2], and the critical current density J_c could be increased with the increase of 211 phase content [3]. But there are some opposite points of view which say that either J_c has no relation with 211

phase or it declines with increasing 211 phase contents [4,5].

And the research for the effect of Ag in the sintered YBCO shows that the correct amount of Ag can eliminate the micro-cracks in the YBCO and improve the weak link of grain boundaries [6,7]. For the textured YBCO made by MTG, it was found in this study that 10–15wt.% of Ag was useful added in the YBCO matrix [8,9]. It was also estimated that J_c increased with Ag contents in YBCO, but there was a maximum value of Ag contents in which J_c would be start to decrease with increasing Ag contents [10]. The solubility of Ag in the textured YBCO was determined as about 15wt.% in the experiment and it did not have any influence on the critical temperature (T_c) of YBCO, but did on the critical current density (J_c) effectively.

In this paper, it was measured and experienced that the critical current density of textured YBCO with additives in different contents of 211 phase and Ag, tested the regularity of the effects on the

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additives of 211 phase and Ag on the superconductivity. It is very difficult to grow the textured YBCO when the Ag content is more than 4wt.% in the composition [11]. So the small pieces of the bulk SmBaCuO single crystal were prepared to be used as the seeds, which could induce the textured growth of YBCO in the melted process. The oxygen absorption process was also studied in various temperatures and times which is very important for the superconductivity of YBCO.

Experiment

Growth of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ crystals

It was also prepared by melt-condensed method for use of seed crystals SmBaCuO and NdBaCuO for the MTG process of YBCO but it was more difficult to make large pieces of single crystal with NdBaCuO than SmBaCuO [12,13].

The melting point of SmBaCuO is 50 °C higher than that of YBCO. Therefore the single crystal of SmBaCuO can be used enough in temperature as the seed crystal for the growth of the textured YBCO. The $5 \times 5 \times 2 \text{ mm}^3$ single crystal pieces of SmBaCuO can be obtained from the grown bulk crystal by cleaving.

Preparation of textured YBCO by MTG method

The 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(80wt.%), Y_2BaCuO_5 (10wt.%) and Ag(10wt.%) was placed on the Alumina substrate of high quality. The sample was heated to 1080 °C in 2h, held at 1080 °C for 1h, reduced to 1030 °C in 20 min., and reduced to 980 °C at the rate of 1-2 °C per hour, then reduced to 400 °C at the cooling rate of 100 °C per hour. The oxygen absorption was taken place at 400 °C under O_2 environment for about 24 hours.

Determination of 211 phase contents in the textured YBCO

X-ray diffraction analyses were performed for six samples of the sintered YBCO with 5, 10, 15, 20, 30, 40wt.% of 211 phase contents under the same test condition. $\langle 110 \rangle$ and $\langle 013 \rangle$ peaks of 123 phase, and $\langle 311 \rangle$ peak of 211 phase were selected to be characteristic peaks. The curve of $I_{211} / (I_{211} + I_{123})$ versus 211 phase contents was drawn in Fig.1, in which I_{211} and I_{123} were the integrated peak intensities of above selected peaks, and the relation of J_c and 211 phase of contents was shown in Fig. 2. The relation in Fig. 1 will be used as the reference for the calculation of 211 phase contents in textured YBCO.

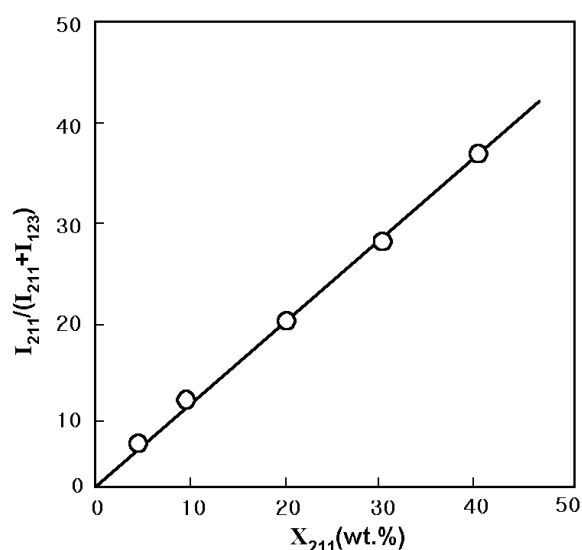


Fig.1 Relation of $I_{211}/(I_{123}+I_{211})$ and 211 contents in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

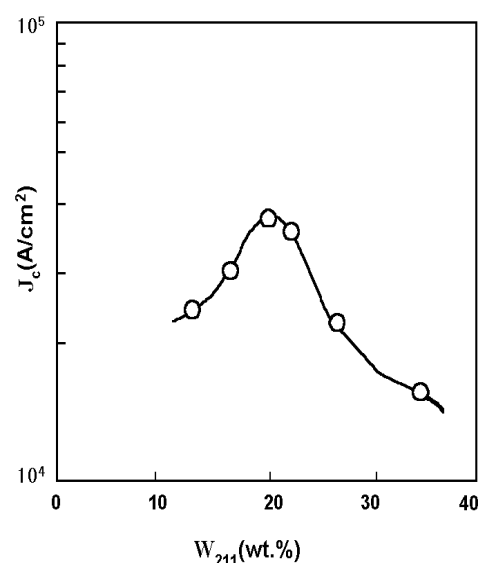


Fig.2 Relation of $J_c(77\text{K}, 0.01\text{T})$ and 211 phase contents

Properties of Ag in YBCO

The black Ag_2O powder, produced from the decomposition of Ag_2CO_3 , was mixed in YBCO powder with several mixing ratio of contents before MTG process. It was observed that the melting point of Ag doped YBCO decreased with increasing Ag contents and the solubility of Ag in YBCO is about 15wt.% which were important references of the MTG program designing for preparation of textured YBCO. The particle size and the distribution in the textured YBCO was observed by SEM and the Ag contents were measured by Electronic Energy Spectroscopy.

The measurement of superconductivity

The magnetic hysteresis curves of the samples were measured by the Vibrating Sample Magnetometer at 77K and the critical current densities were calculated by means of Bean's model with respect to the preparing conditions. The critical temperatures were also determined by measuring the AC susceptibility of the samples.

Results and Discussions

Growth of SmBaCuO seed crystal

To induce the textured YBCO in MTG process, the pieces of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystals with $5 \times 5 \times 2 \text{ mm}^3$ were also prepared by MTG process and it was proved by X-ray diffraction and X-ray

back reflection Laue technique. The oxygen absorption in $\text{SmBa}_2\text{Cu}_3\text{O}_x$ was studied at several constant temperatures and zero resistance superconductivity at 90K was obtained after heat treated in oxygen flow at 400 °C for 96 hours.

In order to improve the superconductivity of large bulk YBCO superconductor, it should be useful taking a seed in YBCO. As the seed material, it is necessary of particular features: (1) its crystal structure should be same with YBCO, and (2) the melting point must be higher than YBCO. $\text{SmBa}_2\text{Cu}_3\text{O}_x$ and $\text{NdBa}_2\text{Cu}_3\text{O}_x$ crystals have the above particular features of ideal materials as the seed. But for the small grains of $\text{NdBa}_2\text{Cu}_3\text{O}_x$ than $\text{SmBa}_2\text{Cu}_3\text{O}_x$ by MTG process,

$\text{SmBa}_2\text{Cu}_3\text{O}_x$ is more suitable to introduce large bulk YBCO growth in MTG process. The prepared $\text{SmBa}_2\text{Cu}_3\text{O}_x$ samples were well oriented with a-b planes that the all peaks of XRD patterns were 00l planes (quadratic) and confirmed by X-ray back-reflection Laue technique.

It is difficult to make the $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystal with 90K zero resistance by heat treatment in oxygen flow. For the $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystal, the suitable temperature of oxygen absorption was confirmed by thermo-gravimetry at 400 °C. The experimental result is shown in Fig 3. From the figure, it could be seen that the process of oxygen absorption of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystal was accomplished slower than YBCO crystal, and the $\text{SmBa}_2\text{Cu}_3\text{O}_x$ sample was not saturated in oxygen content until it was heat treated for 72 hours.

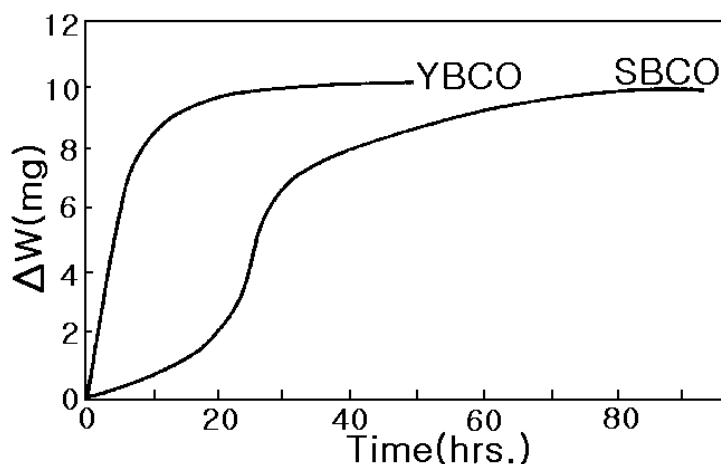


Fig. 3. Weight changes vs heat treatment time of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystal and YBCO crystal in oxygen flow at 400 °C.

To determine the best temperature for oxygen absorption and investigate the effect of heat treatment on the critical temperature, it was heat treated in oxygen flow at 400 °C, 450 °C and 500 °C for 96 hours. The critical temperature of the

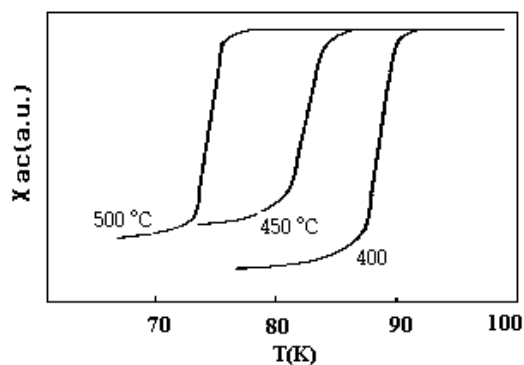


Fig. 4. The χ_{ac} -T curves of the $\text{SmBa}_2\text{Cu}_3\text{O}_x$

In Fig.5, it can be seen that the critical temperatures of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ single crystals which were heat treated at 400 °C, 450 °C and 500 °C for 96 hours were 91K, 86K and 77K, and it was decreased with increasing the heat treatment temperature. When the heat treatment temperature was increased more than 550 °C and 600 °C, the critical temperature could not be measured in liquid nitrogen.

The Orientation of YBCO

In the test, the oriented YBCO was induced by SmBaCuO seed from the molten YBCO. Therefore the position of SmBaCuO seed is quite important for the orientation of YBCO. The a-b plane (001) of the SmBaCuO seed which was carefully cloven from the bulk crystal should be paralleled with the surface of the melted YBCO. Fig.6(a) is the X-ray diffraction pattern of SmBaCuO seed, it is perfectly C-axis orientation.

The seed of SmBaCuO was put on the surface of melted YBCO at 1030-1050 °C, at which YBCO was stayed in melted state and SmBaCuO seed was still stayed in solid state. When the temperature of the system reached about 1010 °C, the melting point of YBCO, it would be started to crystallize around the SmBaCuO seed with the same orientation. The orientation of YBCO was tremendously in agreement with that of SmBaCuO seed, which was proved by the comparison of XRD patterns of oriented YBCO made by MTG in Fig.6(b), and of SmBaCuO seed in Fig.6(a).

samples was measured by the way of magnetic susceptibility, the results are shown in Fig. 4 and 5. Samples which were heat treated in oxygen and the heat treatment temperature of $\text{SmBa}_2\text{Cu}_3\text{O}_x$ flow at 400 °C, 450 °C and 500 °C for 96 hours samples.

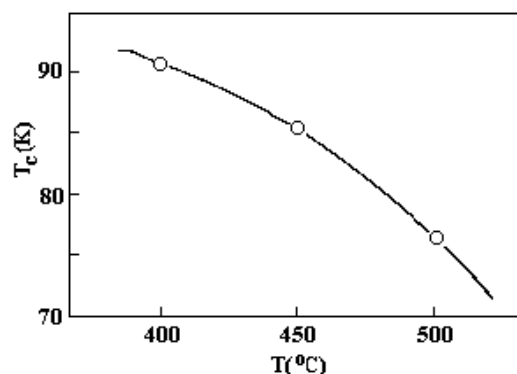


Fig. 5. Relationship between the critical temperatures

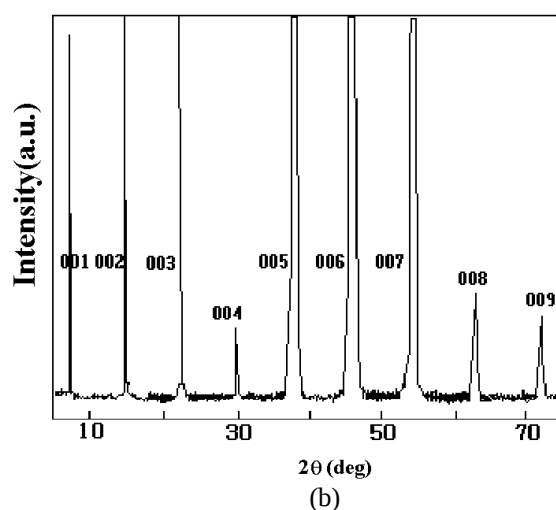
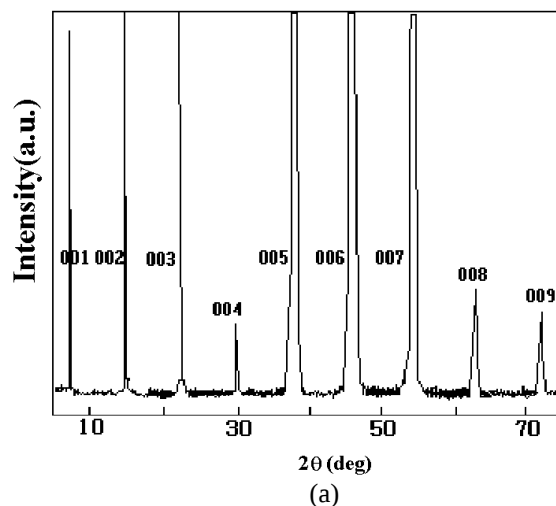


Fig.6 X-ray diffraction patterns of (a) SmBaCuO seed and (b) oriented YBCO.

The optimum value of 211 phase contents in the textured YBCO

Samples with dimension of about $10 \times 5 \times 1 \text{ mm}^3$ which were cut from textured YBCO bars were heated at 450°C for 50 hours under flowing oxygen to absorb it. After the heat treatment, several 10 milligrams of YBCO powder were taken from each textured YBCO sample for the X-ray diffraction analysis and the 211 phase contents were calculated using the curve in Fig.1. Also YBCO samples ($10 \times 5 \times 1 \text{ mm}^2$) were used to measure the critical current densities. The 211 content and critical current density were inter-related with each other as shown in Fig.2. It can be seen that the optimum value of its contents in the textured YBCO is about 20wt.%, and before this value J_c increases with increasing 211 contents, but after that value J_c decreases with increasing 211 contents. It seems that as the flux pinning centers, 211 particles could make critical current density increase with 211 contents, but as the non-superconductive phase of 211 particles could make critical current density decrease when the volume

ratio of 211 phase was too large.

Ag behavior in the textured YBCO

The solubility of Ag in condensed YBCO

The added Ag contents in the sintered YBCO and the analyzed Ag contents in the condensed YBCO were shown in table 1. The analyzed values of Ag contents in condensed YBCO were in accord with the added Ag contents, if the values of added Ag contents were less than 14wt.%. But the analyzed values of Ag contents did not increase and remain as constant value of 15wt.% when the added values of Ag contents were larger than 16wt.%. This suggests that Ag contents in YBCO would be saturated, or the solubility of Ag in condensed YBCO would be 15wt.%. When Ag additions were over the solubility (15wt.%) of Ag in condensed YBCO, the extra Ag would migrate or escape from the YBCO sample into slag on the substrate. The relation between Ag contents analyzed in textured YBCO and added in sintered YBCO before melting process was shown in Fig.7.

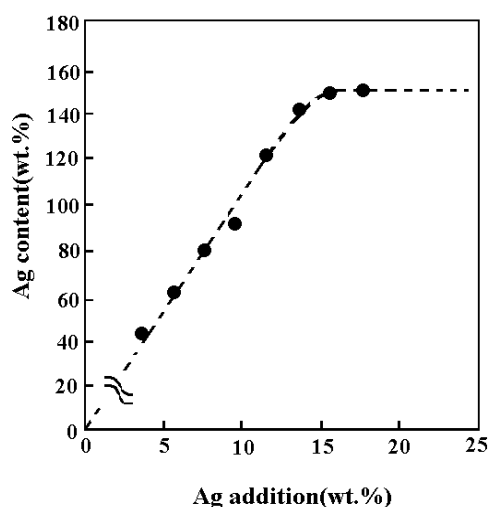


Fig.7 The relation between Ag contents analyzed in textured YBCO and Ag addition

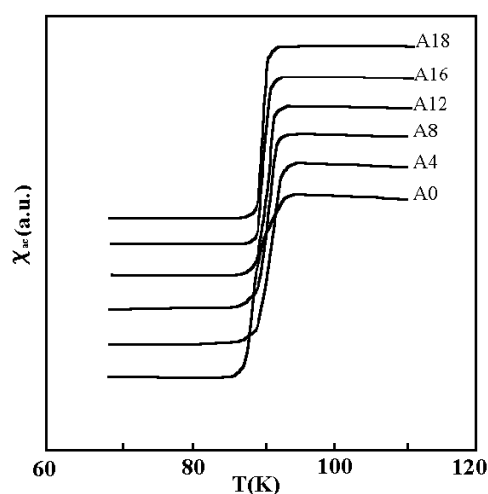


Fig.8 AC susceptibility of textured YBCO

Table 1
Ag contents in the condensed YBCO

No. Sample	A4	A6	A8	A10	A12	A14	A16	A18
Added Ag contents	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0
Analyzed Ag contents	4.3	6.2	8.1	9.2	12.1	14.2	15.1	15.2

Effect of Ag on the superconductivity of textured YBCO

The critical temperatures were determined by AC susceptibility of textured YBCO samples with different Ag contents (0, 4, 8, 12, 16, 18wt.%) as shown in Fig.8. The Ag contents did not influence on critical temperature of YBCO in the experiment, which was showed in good agreement with the reported results [14] for the sintered

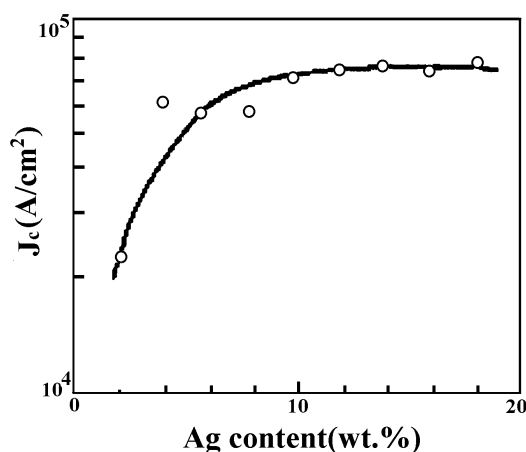


Fig.9 Relation of J_c and Ag contents with different Ag contents of textured YBCO

Ag inclusions in YBCO superconductors

When Ag contents in YBCO was larger than 6wt.%, the diffraction peaks of Ag contents could be found in the X-ray diffraction patterns. Fig.6 shows the X-ray diffraction pattern of textured YBCO with 18wt.% of Ag contents. The intensity of Ag pattern increased with increasing Ag

YBCO sample. But Ag contents had large influence on the critical current density as shown in Fig.9, in which J_c was increased with increasing Ag contents up to 15wt.%, at which J_c showed a constant value of $(7-8) \times 10^4 \text{ A/cm}^2$ (0.01T, 77K). The result was corresponded with the Ag solubility (15wt.%) in condensed YBCO.

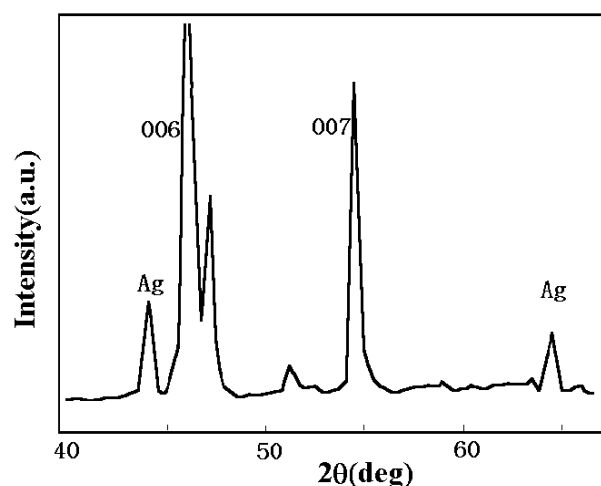
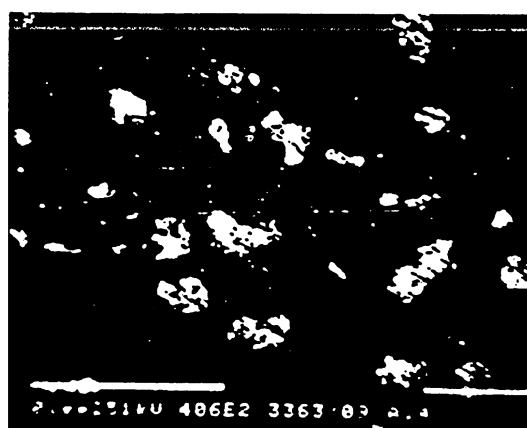


Fig.10 X-ray diffraction pattern of 123 + 18wt.% Ag sample

contents in YBCO. It means the doped Ag did not react with YBCO, but existed in the form of the inclusions in the YBCO matrix. SEM photographs [Fig.11.(a) and (b)] of textured YBCO were observed with Ag contents of 14wt.% and 18wt.% respectively. In the pictures the Ag inclusions were distributed in YBCO matrix as particles in the range of 10-50 μm in diameters.



(a)



(b)

Fig.11.SEM Photograph of textured YBCO with 14wt.% Ag(a) and with 18wt.% Ag(b)

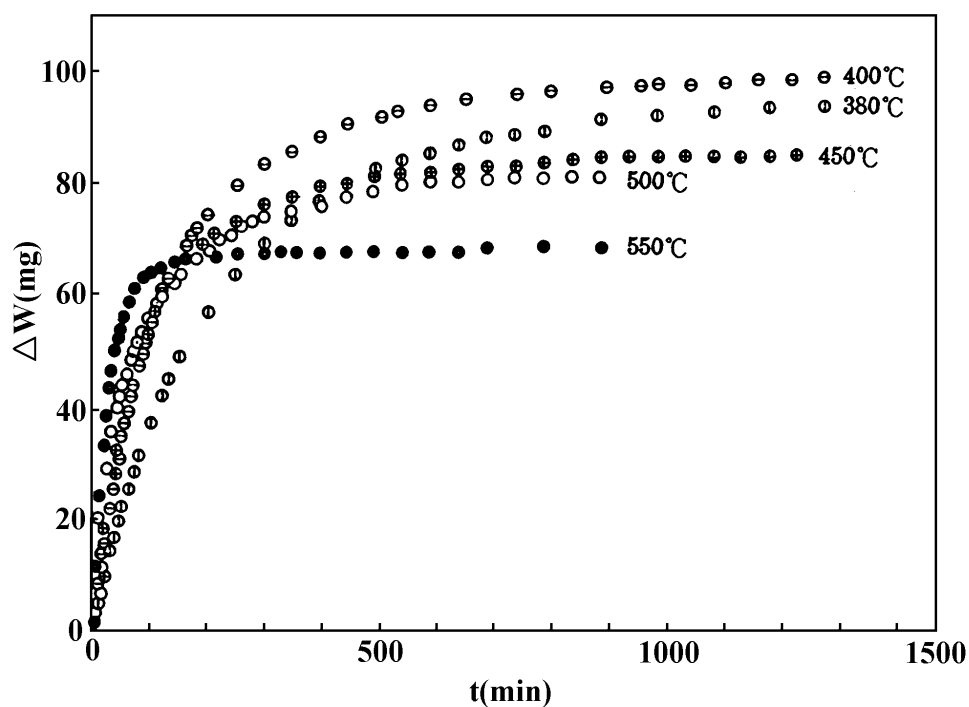


Fig.12 Weight changes in oxygen absorption of oriented YBCO at various temperatures.

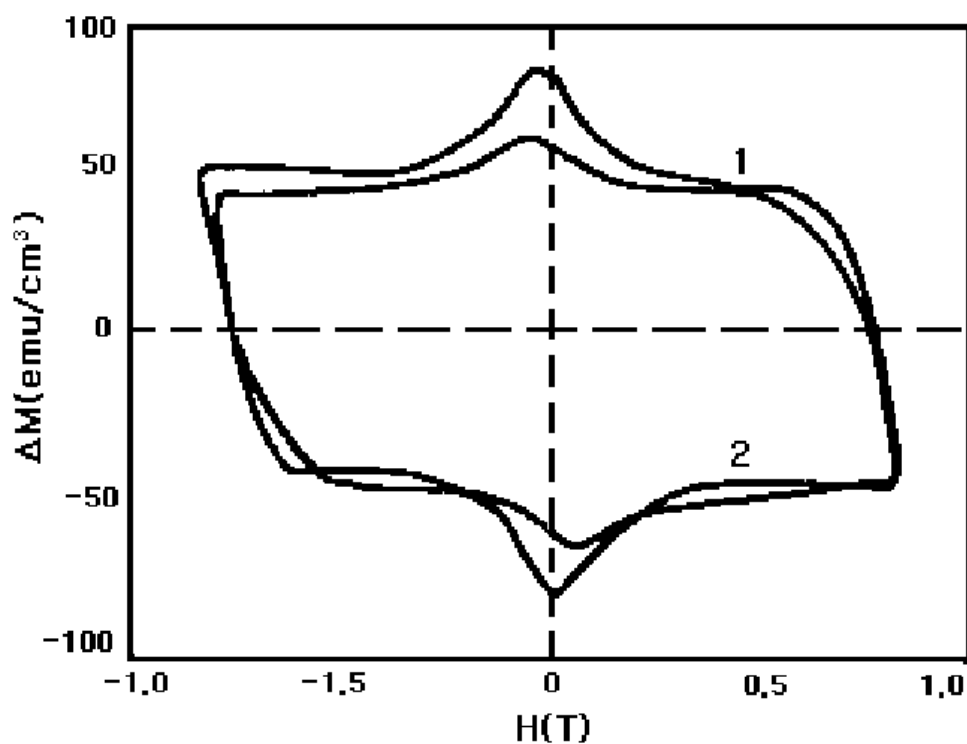


Fig.13 Hysteresis loops of oriented YBCO after heat treatment at 400 °C under O_2 flow for 24 hours.

Oxygen absorption and current density of textured YBCO

The oxygen absorption of the oriented bulk YBCO has some different behavior due to its large volume and high density, in which oxygen diffusion is more difficult than that in small YBCO sample [10]. In the test, oriented YBCO sample of 9.76g was used under flowing O₂. The temperatures for oxygen absorption are 380 °C, 400 °C, 450 °C, 500 °C and 550 °C respectively. An electronic balance with 10⁻⁴g accuracy was used to record the weight change in oxygen absorption process. The best temperature for oxygen absorption was 400 °C among the results of test temperatures as shown in Fig.12. It seems that after 1300 minutes (22 hours), the oxygen absorbed in YBCO was still unsaturated. Recently, more than 100 hours was used for oxygen absorption [15]. If the time of oxygen absorption of the textured YBCO was over 100 hours, the critical current density would be larger than 7×10⁴A/cm² (77K, 0.01T) as shown in Fig.9.

Critical current density of the oriented YBCO

The hysteresis loops of two samples of 8.34×4.00×1.62mm³ and 9.76×4.44×2.16mm³ after heat treatment at 400 °C under O₂ for 24hours were measured by a Vibrating Sample Magnetometer (see Fig13). According to bean's model, $J_c = 20 \cdot \Delta M d^{-1}$ was used to calculate the critical current density (J_c).

From the hysteresis loops of oriented YBCO after heat treatment at 400 °C under O₂ flow for 23hours, J_c of both samples were calculated with 7×10⁴A·cm⁻² (77K, 0.01T). The magnetic levitation force of oriented YBCO sample, 21mm in diameter, 10mm in height, is about 4.6N·cm⁻² in liquid nitrogen.

Conclusions

To improve the superconductivity of the high T_c superconductor, YBaCuO superconductor was prepared by MTG process with use of SmBaCuO seed crystal and additives of Ag, Y₂BaCuO₅ (211 phase) to eliminate the weak links of the grain boundaries and micro-cracks,

to increase the flux pinning effect in the bulk YBCO.

From the investigation and analysis of the experimental results, it was concluded as follows ;

20wt.% of 211 contents in textured YBCO was the optimum value in YBCO for the flux pinning center.

The solubility of Ag in condensed YBCO was about 15wt.% and J_c of textured YBCO was increased with increasing Ag contents. But the Ag contents was more than 15wt.%, the J_c of YBCO was tended to a stable value.

When the SmBaCuO single crystals were used as seeds to induce the growth of YBCO, the orientation of YBCO was the same as SmBaCuO seeds.

The optimum condition of heat treatment for oxygen absorption of bulk condensed YBCO was at 400 °C in O₂ flow for more than 24 hours.

The critical current density of a typical sample of oriented YBCO, which was included 20wt.% of 211 phase and 10wt.% of Ag, was obtained with the value of 7×10⁴A·cm⁻² (77K, 0.01T).

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