Zone-melting Process of NdBaCuO Superconductor under Low Oxygen Pressure

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Abstract— **The NdBaCuO superconductor samples were zone-melted in low oxygen partial pressure (1%O_2 + 99%Ar). The zone-melting temperature was decreased about 120°C from 1,060°C, the zone-melting temperature in air. Thus the loss of liquid phase ($BaCuO_2$ and CuO) was reduced during the zone-melting process. The content of non-superconducting phase Nd422 in zone-melted NdBaCuO samples was clearly decreased and, therefore, the substitution of Nd for Ba was occurred. The superconductivity of zone-melted $Nd_{1+x}Ba_{2-x}Cu_3O_y$ prepared under low oxygen partial pressure was distinctively improved.**

I. INTRODUCTION

As the radius of Nd atom is approximate to that of Ba atom, there tends to exist the substitution of Nd for Ba during the processing of NdBaCuO, i.e. the producing of solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_y$[1]. The superconductive transition temperature (T_c) decreased with the increasing value of x. When x>0.4, $Nd_{1+x}Ba_{2-x}Cu_3O_y$ will transfer into the non-superconducting tetragonal phase[2]. In order to decrease the substitution of Nd for Ba, many authors have prepared $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductors with the method of melt-texture growth under low oxygen partial pressure (1,000 or 100 Pa), which has greatly improved the superconductivity [3]. Later some authors prepared $NdBa_2Cu_3O_y$ in air and heat-treated the samples at 950°C in Ar flow to suppress the substitution of Nd for Ba[4-5].

We have prepared well-oriented Nd123 superconductor by zone-melting in air. After high temperature heat treatment in Ar and following oxygenation, the average critical current density in liquid nitrogen and at zero magnetic field was from 1,000 to 5,000 A/cm^2, but rarely up to 10^4 A/cm^2. The lower J_c might be due to the high zone-melting temperature of 1,050 - 1,060°C. When samples moved at high temperature in the zone-melting process, some liquid phase ($BaCuO_2$ and CuO) which was decomposed from Nd123 would be lost undesirably. This made the content of Nd422 in solidified NdBaCuO crystal up to 40 - 60%, with the maximum of 70%, which might enhance the substitution of Nd for Ba with increasing the value of x in $Nd_{1+x}Ba_{2-x}Cu_3O_y$[6-10]. Though the samples were heat-treated at high temperature in Ar atmosphere, the value of x decreased indistinctively. In this article, the zone-melting method under low oxygen partial pressure (1%O_2+ 99%Ar) was used to prepare NdBaCuO superconductor. The zone-melting method in NdBaCuO superconductor has an advantage to decrease the melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$, and it results to decrease the loss of liquid phase decomposed from $Nd_{1+x}Ba_{2-x}Cu_3O_y$ and the content of Nd422. Another advantage was that the value of x would be greatly reduced under low oxygen partial pressure according to the reference[3]. With such improvement for the zone-melting the critical current density (J_c) of NdBaCuO superconductor was approximated up to 10^4 A/cm^2. In this article the contents of Nd422 phase in NdBaCuO superconductors and correspondent J_c values were measured respectively.

II. EXPERIMENT

2.1 The preparation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor powder

According to the ratio of metal atoms Nd : Ba : Cu = 1 : 2 : 3, Nd_2O_3 (>99.99%), $BaCO_3$(>99.0%), and CuO (>99.0%) were weighed and mixed with alcohol in agate jars. The jars were put in the ball mill running for 12 hours. The milled mixture was put in the oven to evaporate the alcohol. The dried powder in the corundum crucible was sintered at 950°C for 24 hours. After cooling, the powder was ground and pressed into pellets, and then sintered. The above steps were repeated for 2 - 3 times in order to produce the single phase Nd123 powder. Finally the sintered samples were ground into fine particles less than 100 μm.

2.2 Zone-melting $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor

In this experiment, the heating element in zone-melting furnace was SiC tube. The width of high temperature zone of the furnace (i.e. the melting width of samples) was 7 mm. The solidified samples were put in long quartz tube through which the gas mixture (1% + 99%Ar) flowed. The samples for zone-melting were the mixture of 90% of Nd123 powder and 10wt% of Nd422 powder, which were pressed under 30 MPa into a rectangle of 1 mm × 5 mm × 60 mm. The samples were solidified at 950℃ for 5 - 6 h. During the zone-melting process the moving speed of samples was 6 mm/h. 4 samples (A, B, C, D) were cut from the zone-melted NdBaCuO. Then the four samples were annealed under oxygen at 350°C for 120 hours. For the comparison with above tests, another four samples (E, F, G, H) were cut from the zone-melted NdBaCuO prepared in air, and these samples were heat treated in Ar at 950°C for 24 hrs for suppressing the substitution of Nd for Ba. All of the zone-melted samples were oxygenated at 350°C for 120 hrs. Standard four-probe method was used to measure the transition temperature T_c, and MPMS-SQUID magnetometer was used for magnetization hysteresis (M-H loop). The value of J_c was calculated by Bean's model.

III. . RESULTS AND DISCUSSION

3.1 Oxygenation of zone-melted NdBaCuO under low oxygen partial pressure

The oxygenation of textured $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was reported by various different references [5,6] in temperatures and normally they were 200 - 300°C. The difference might be caused by the different sizes of samples. In order to get rid of the influence of the size factor, oriented zone-melted samples of same size were prepared. The samples with the same size were put at different temperature zones, for example, 200, 250, 300, 350, and 400°C in the same furnace, through which a constant Ar flowed. The relations between weight increase of samples and time at different temperatures were showed in figure 1.

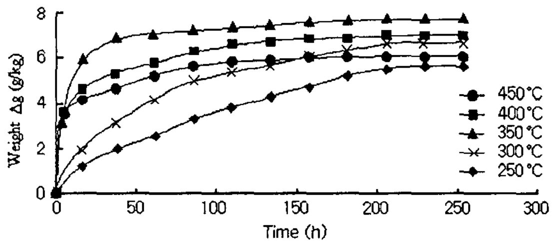

Fig. 1. Weight variation of zone-melted samples with different oxygen absorption time.

It can be seen that the optimum oxygenation temperature for NdBaCuO was 350°C. The same results of optimum oxygenation temperature were obtained which was approximately 100°C higher than that of sintered samples. Also the speed of oxygen flow had large effect on the increase of the oxygen content.

3.2 Melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ under low oxygen partial pressure atmosphere

T.B. Lindemer, et al. have defined the relationship among melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor, oxygen partial pressure and the value of x as:

$$\log(P[O_2][MPa]) = 33.82 - 17.9x + (-48{,}226 + 24{,}983x)/T.$$

Table 1. Melting temperature (K) of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ samples, which have several x values with different oxygen pressures.

	x				
Oxygen Pressure(Pa)	0	0.05	0.10	0.15	0.20
10^5	1,385.0	1,384.7	1,384.4	1,384.1	1,383.8
10^3	1,309.8	1,307.6	1,305.4	1,303.0	1,300.5
10	1,275.1	1,272.2	1,269.2	1,265.9	1,262.5

The melting temperatures of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ with different values of x and oxygen partial pressures were calculated according to the above formula and listed in table 1. As table 1 revealed, with the increasing of the value of x, the melting temperature tends to decrease slightly. For examples when the value of x raised from 0 to 0.2, the melting temperature dropped only 1.2°C in pure oxygen atmosphere, 9.3°C at oxygen partial pressure of 0.01 MPa, and 12.6°C at oxygen partial pressure of 0.001 MPa. However, the oxygen partial pressure affected the melting temperature relatively great. When it decreased from pure oxygen down to 0.01 MPa, the melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ dropped about 75℃. When $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was zone-melted in air, the melting temperature was 1,060°C or so, it was 1,084.7°C based on Lindemer's formula. However, if the oxygen partial pressure was 0.001 MPa, the experimental zone-melting temperature was about 940°C, which is 120°C lowered from 1,060°C of zone-melting temperature in air. The large decreasing of melting temperature caused the decreasing of flow ability of liquid phase in the melting zone, which was decisive to the loss of liquid phase. Therefore, the content of Nd_2BaCuO_5 (Nd422) phase in solidified $Nd_{1+x}Ba_{2-x}Cu_3O_y$ matrix would be decreased. So, it could contribute to the high critical current density of zone-melted NdBaCuO superconductor.

3.3 Orientation of zone-melted NdBaCuO

The XRD of sample was showed as figure 2. It was obvious that the maximum diffraction of grain face was (011), along which direction the sample grew. But in the anisotropy $Nd_{1+x}Ba_{2-x}Cu_3O_y$ superconductor, the superconductivity along a-b plane was better than that along other faces.

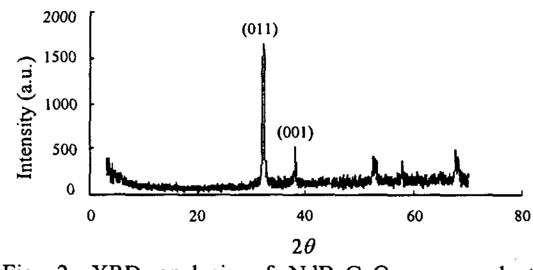

Fig. 2. XRD analysis of NdBaCuO superconductor prepared by zone-melting method.

Therefore, it was disadvantage to improve J_c if grains grew along (011) compared with (001) expected.

There barely existed (001) diffraction peak in figure 2. The grain orientation of sample during zone-melting attached much to the distribution of temperature field, while the temperature field of SiC tube generating heat could hardly be changed at once, and it was processed and fixed.

3.4 Superconductivity

The superconductivity of NdBaCuO zone-melted in low oxygen partial pressure atmosphere, the content of Nd422 and melting temperature correspondent were listed in table 2, and those of NdBaCuO zone-melted in air were listed in table 3.

Table 2. Experimental results of NdBaCuO superconductor prepared by zone-melting method in air.

Samples	Melting temp. (°C)	Nd422 content (%)	T_{c0}	ΔT(K)	$J_c(A/cm^2)$
E	1,050	37.9	94	2	5,100
F	1,060	42.8	87.5	5	400
G	1,070	49.5	90	3	510
H	1,090	63.2	85	5	80

When comparing the data in the two tables, it was clear that the melting temperatures under low oxygen partial pressure were lower about 120°C than those of NdBaCuO zone-melted in air, either were the contents of Nd422 phase of samples.

Table 3. Experimental results of NdBaCuO superconductor prepared by zone-melting method in low oxygen pressure.

Samples	Melting temp.(°C)	Nd422 content(%)	$T_{c0}(K)$	ΔT(K)	$J_c(A/cm^2)$
A	933	33.7	94	1.9	28,468.6
B	940	<5	90.2	2	9,461.7
C	955	<5	91.2	2	12,910.7
D	990	58.8	90.2	2	6,506.8

But we could not figure out the optimum content of Nd422 responsible for good superconductivity. Zero resistance temperature T_{c0} and transition width of NdBaCuO superconductor zone-melted in low oxygen partial pressure atmosphere were somewhat improved, especially the critical current density J_c (A/cm^2) were raised up to 28,468.6 A/cm^2 (sample A). It could be believed that the decreasing of the amount of Nd422 directly meant the increasing of superconducting phase. On the other hand, the contents of Nd422 affect the substitution of Nd for Ba. When there was a lower content of Nd422, lower Ba atoms were replaced by Nd atoms, i.e. the value of x in $Nd_{1+x}Ba_{2-x}Cu_3O_y$ was smaller, thus improving the superconductivity of samples.

IV. CONCLUSION

The low oxygen partial pressure lowered the melting temperature of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ about 120°C during zone-melting process. It led to less loss of liquid phase ($BaCuO_2$+CuO) and less content of non-superconducting phase Nd422, which gave less opportunity of the substitution of Nd for Ba or lowered down the value of x. The above factors improved the superconductivity of zone-melted NdBaCuO remarkably. NdBaCuO zone-melted in low oxygen partial pressure atmosphere could be directly put to oxygen annealing without Ar annealing procedure. The optimum oxygen annealing temperature was 350°C. As the distribution of temperature field was not ideal enough in furnace, the growing orientation of samples was paralleled to (011), as was expectedly.

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