Improved superconducting properties of melt-textured Nd123 by additional heat treatment

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Abstract

We have investigated the effect of additional heat-treatment on the superconducting transition and the flux pinning properties of Nd–Ba–Cu–O melt-textured in air. After the heat-treatment at high temperatures, > 900°C, under low oxygen partial pressure, \( P(O_2) = 0.001 \) atm, the superconducting transition became sharper accompanied by an increase of \( J_c \). However, the increase of \( J_c \) was very small and the secondary peak effect commonly observed in Nd–Ba–Cu–O melt textured in low \( P(O_2) \) could not be observed. Transmission electron microscopic observations and energy dispersive X-ray analyses show that the spatial variation of the Nd/Ba ratio is reduced after high-temperature heat-treatment, which indicates that an improvement in \( T_c \) and \( J_c \) is attributed to a suppression of Nd substitution on the Ba site. © 1997 Elsevier Science B.V.

Keywords: Nd–Ba–Cu–O; Melt process; Heat-treatment; Critical current density; Critical temperature

1. Introduction

For the realization of bulk application, it is necessary to obtain high critical current density (\( J_c \)) by overcoming the weak link problem and introducing effective pinning centers. Melt texturing is one of the most successful methods to fabricate bulk high-\( T_c \) superconductors with large \( J_c \). In YBa\(_2\)Cu\(_3\)O\(_y\) (Y123), strong pinning center was successfully introduced by utilizing the second phase, Y\(_2\)BaCuO\(_4\) (Y211). By optimizing the size of the Y211 by means of melt powder-melt growth (MPMG) process [1,2], \( J_c \) reached 20,000 A/cm\(^2\) at 77 K and 1 T.

It is well-known that a family of REBa\(_2\)Cu\(_3\)O\(_y\) (RE: rare earth element, except Ce, Pr, Pm, Tb) also exhibits superconductivity with transition temperature \( T_c \) > 90 K. Unlike Y123, however, light rare earth elements (LRE: Nd, Sm, Eu, and Gd) with large ionic radii form a LRE Ba Cu O\(_x\) type 1 \( x \)-2 \( y \)-3 solid solution. The presence of such a solid solution causes a depression of \( T_c \) when they are melt-processed in air [3]. Yoo et al. [3] showed that the high-\( T_c \) phase with \( x < 0.1 \) could be preferentially formed by lowering the oxygen partial pressure during the melt-processing.

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Recently, Hu et al. [5] reported that the sample with $T_c > 93$ K could be obtained by employing additional Ar treatment after melt processing in air, although the detailed mechanism for the formation of high-$T_c$ phase is unclear. If high quality Nd–Ba–Cu–O can be fabricated by melt processing in air, the cost of mass production will greatly be reduced, which is highly attractive for the viewpoints of practical application. Hence, we have performed a systematic study on the effect of heat-treatment on the superconducting transition, pinning characteristic, and microstructure.

2. Experimental

Melt-textured Nd–Ba–Cu–O samples were prepared by the MPMG technique in air. The nominal composition of starting material was Nd$_{1.3}$Ba$_2$Cu$_{3.4}$O$_y$, corresponding to Nd$_{0.2}$Ba$_{2.4}$Cu$_3$O$_{10}$ (Nd422). The details of the growth conditions can be found elsewhere [6]. In this study, we used several samples with dimensions of approximately $1.5 \times 1.5 \times 0.7$ mm$^3$. Prior to the experiment, the samples were oxygen-annealed by the following schedule: ramped up to 500°C and held for 1 h, cooled to 400°C for 24 h, then to 250°C for 48 h and finally furnace cooled.

High-temperature heat-treatment was performed at various temperatures in the reduced atmosphere (0.1% O$_2$–Ar ($P(O_2) = 0.001$ atm)). After the high-temperature annealing, the oxygen annealing treatment was carried out in the same manner to recover the oxygen loss.

The measurements of $T_c$ and the magnetic hysteresis loops were performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS), with applied field parallel to the c-axis. The $J_c$ values were evaluated from the hysteresis data using the equation, $J_c = \frac{20 \times \Delta M}{[a(1 - a/b)]}$, based on the extended Bean model [5], where $\Delta M$ (emu/cm$^3$) is the hysteresis width and $a$ and $b$ (cm$^{-2}$, $a < b$) are the dimensions of the sample perpendicular to the applied field.

The microstructural observation was made with a transmission electron microscope (TEM) equipped with a field emission gun (Hitachi HF-2000). The local composition of Nd and Ba was evaluated by energy-dispersive X-ray analysis (Kevex Sigma). Thin samples for TEM observations were prepared by crushing melt-textured blocks. The TEM image was taken from a direction parallel to the [001] axis of the sample.

3. Results and discussion

Fig. 1 shows temperature dependence of normalized magnetic susceptibility before and after the heat-treatment at 800, 900, 980°C for 24 h under $P(O_2) = 0.001$ atm. Before the heat treatment, the sample exhibited very broad superconducting transition around 88 K. The heat treatment at 800°C did...
not affect the superconducting transition. In contrast, after the heat-treatments at 900 and 980°C $T_c$ was increased. It is worth to note that after the heat-treatment at 980°C, $T_c$ (onset) was increased to about 94 K and the superconducting transition became sharper.

One may note that there was a slight difference in the superconducting transition of pristine samples even though the samples were cut from the same single domain bulk, which indicates a wide range of RE–Ba solid solution in the sample melt processed in air. We have performed the same heat-treatment on several samples and we confirmed that the results shown in the present paper are reproducible in regard to $T_c$ improvement.

We then performed similar heat-treatments under higher $P(\text{O}_2)$: 1% $\text{O}_2$–Ar ($P(\text{O}_2) = 0.01 \text{ atm}$) and air ($P(\text{O}_2) = 0.2 \text{ atm}$), however, no increase in $T_c$ was observed, indicating that such an enhancement of $T_c$ only occurs under very low oxygen partial pressures.

Fig. 2 shows the field dependence of $J_c$ at $T = 77$ K and 40 K for the sample annealed at 980°C for 24 h in 0.1% $\text{O}_2$–Ar, for which an improvement in $T_c$ was observed. As can be seen from the figure, $J_c$ values were also increased by additional annealing in low $P(\text{O}_2)$. It should also be noted that secondary peak effect commonly observed in Nd–Ba–Cu–O melt textures in low $P(\text{O}_2)$ is absent at 77 K. There are two possible sources for $J_c$ improvement and those are an increase in $T_c$ and microstructural change.

For further information, we have performed microstructural characterization using TEM equipped with a field-emission gun. In addition, we made EDX analyses to evaluate compositional variation.

Fig. 3(a) shows a dark-field TEM image of the sample before high-temperature annealing viewed from a direction perpendicular to the $ab$-plane. Strong contrasted regions are visible in the TEM image. Similar contrasts have been observed in both Nd123 single crystals and melt-textured Nd123 samples when they are prepared in low oxygen partial pressures, and the origin of such contrast is ascribed to the presence of small local distortion caused by Nd/Ba substitution [7,8]. However, the contrast in the present sample is much stronger than that observed in the samples prepared in low $P(\text{O}_2)$, which suggests that the Ba site is heavily substituted by Nd ions for the sample melt processed in air. Broad superconducting transition and low $T_c$ for the sample melt processed in air also support the fact that a range of Nd/Ba substitution is quite large. Fig. 3(b) displays the variation of Nd/Ba ratio along lines L1 and L2 which are marked in Fig. 3(a). It is clear that there is a large variation of Nd/Ba ratio, well matching the white–black contrast in the TEM image.

Fig. 4(a) shows the dark field TEM image of the sample heat treated at 980°C for 24 h at $P(\text{O}_2) = 0.001 \text{ atm}$. It is interesting to note that the white–black contrast observed in the untreated sample almost completely disappeared after the heat-treatment. This result indicates that variation of Nd/Ba ratio is reduced by this heat treatment, which can be further confirmed by EDX data shown in Fig. 4(b). The EDX data also show that the average value of Nd/Ba is decreased after the heat-treatment, suggesting that Nd substitution on Ba site was reduced. For Nd–Ba–Cu–O, a decrease of $T_c$ occurs when
trivalent Nd ion substitutes on bivalent Ba site, which leads to a decrease in the carrier concentration. Therefore, we can conclude that the observed increase of $T_c$ is due to this reduction of Nd/Ba substitution. It is also true that the improvement of $J_c$ is mainly due to $T_c$ improvement, since contrasted regions disappeared after the heat treatment.

There are two possible mechanisms which cause the reduction of Nd/Ba variation. One is the partial melting of the sample. Broad superconducting transition and large variation in Nd/Ba ratio suggests that Nd–Ba–Cu–O sample melt-processed in air contains a wide range of $x$ in the form of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$. As reported by Yoo et al. [9,10], the peritectic decomposition temperature ($T_m$) of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solution decreases with increasing $x$. For example, in $P(\text{O}_2) = 0.001$ atm, $T_m$ of $x = 0.05$ is 1017°C, while $T_m$ of $x = 0.5$ is as low as 959°C. During the heat-treatment at 980°C in $P(\text{O}_2) = 0.001$ atm, the phase with large $x$, which have
lower $T_{\text{tr}}$, will decompose and the phase with small $x$ values will crystallize when the sample is cooled in low $P(O_2)$. The other possibility is the exchange of Nd/Ba site in the solid state. In low $P(O_2)$, Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ with small $x$ is stable, and therefore when the diffusion rate of cations is large enough, such site change may take place, although it will take a rather long time.

The present results indicate that high temperature annealing in low $P(O_2)$ is effective in increasing $T_c$ through the suppression of Nd/Ba substitution. However, the Nd–Ba chemical variation was also reduced, which leads to the absence of the secondary peak effect and thereby relatively low $J_c$.

4. Conclusion

Nd–Ba–Cu–O samples melt processed in air exhibit broad superconducting transition and low $T_c$. TEM observations show that a wide range of Nd$_{1+x}$Ba$_{2-x}$Cu$_3$O$_y$ with relatively large $x$ values are present in such samples. High temperature annealing in low $P(O_2)$ results in the suppression of
Nd/Ba substitution and thus $T_c$ is improved, however, simultaneously chemical variation of Nd/Ba ratio, which is favorable for $J_c$ improvement in high field also disappeared.

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