Effect of sintering atmosphere on the weak-link behaviour of YBCO superconductors

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Abstract

Weak-link behaviour of YBa2Cu3O7 (123) superconductors sintered in different atmospheres are studied by measuring the variation of critical current densities (Jc) near the superconducting transition temperatures (Tc). The weak links are found to change from superconductor–insulator–superconductor to superconductor–insulator–metal–superconductor and superconductor–metal–superconductor type of junctions as the sintering atmosphere is varied from argon to air and oxygen respectively. The scanning electron microscopy in conjunction with energy dispersive spectroscopy studies indicate that the composition fluctuation at the grain boundaries is the reason for such variation.

Keywords: YBCO; Superconductors; Sintering; Weak link; Composition analysis

1. Introduction

Weak links associated with the grain boundaries are known to limit the Jc values of superconductors [1] and the possible reasons for the formation of these weak links are misorientation of grain boundaries and composition variations at the grain boundaries [2–5]. In the last decade extensive research activities have been carried out on the weak-link characteristics of Y–Ba–Cu–Oxide (YBCO) superconductors, and it has been found that the grain boundaries are the source of weak links in the sintered samples [6–8]. However, significant research has not been carried out towards the effect of sintering atmosphere on the weak-link characteristics of these materials. In our earlier investigation [9], it was observed that the weak-link behaviour of YBCO superconductors could be modified from superconductor–insulator–superconductor (S–I–S) to superconductor–insulator–metal–superconductor (S–I–N–S) and superconductor–metal–superconductor (S–N–S) type by varying the partial pressure of oxygen p(O2) in the sintering atmosphere. The cause for such variation is not understood and in this paper the role of sintering atmosphere on the formation of weak links in YBCO superconductors is reported.
2. Experimental

In the present investigation, YBCO-123 powder was prepared by a chemical pyrophoric reaction process. In this process, required amount of citric acid was added to the stoichiometric mixture of metal nitrate solutions and then the pH of the solution was neutralized to ~7.0 by adding liquor ammonia. Subsequently the solution is heated in a pit furnace preheated at 523 K and simultaneously heated from the top by an IR lamp. Since the pit furnace can provide heat at the bottom and sides of the beaker, an IR lamp was used from the top to ensure uniform drying of the solution. During heating the solution swells and ignites leaving a finely dispersed homogeneous powder mixture of the respective metal oxides. Detailed process is discussed elsewhere [10]. Freshly prepared powders being very fine are highly reactive. Therefore, to prevent the formation of hydroxide and carbonate, the as-prepared powder was calcined at 1173 K for 1 h in air and furnace cooled down to room temperature and subsequently compacted in the form of 2.54 cm diameter pellets by applying a load of 12.4 MPa. The pellets were cut into the form of rectangular bars and sintered at 1233 K for 1 h, either in argon, air, or oxygen atmospheres. After the isothermal sintering, the samples were furnace cooled down to 773 K in oxygen atmosphere (50 ml min⁻¹) and soaked for 20 h at 773 K. The samples were cooled down slowly to room temperature at the rate of 60 K h⁻¹. Hereafter, the oxygenated samples that were sintered in oxygen, air and argon atmospheres will be referred as A, B and C respectively. The superconducting properties of the samples were investigated using a close cycle He cryo-refrigerator (APD Cryogenics, USA). Linear four probe method was used for the $J_c$ measurement near the superconducting transition temperatures and at 77 K. The criterion of 1 μV voltage drop per cm was adopted for the $J_c$ measurement. The densities of the samples were measured by the Archimedes principle of liquid immersion technique. The tested samples were polished and etched by 0.001% hydrochloric acid solution in ethanol for 2 min and washed with ethanol. Short period of etching was adopted here to minimize the preferential etching of the constituents. The etched samples were studied by scanning electron microscope (SEM) (JEOL-JSM 840A, Japan). Energy dispersive spectroscopy (EDS) (KEVEX, USA) system attached with the SEM was used for the composition analysis of the grains and grain boundaries. X-ray diffraction (XRD) analyses of the oxygenated samples were also carried out using nickel filtered CuKα radiation with $\lambda = 0.15406$ nm. Philips PW-1540 X-ray diffractometer (Netherlands) was used in the present investigation.

3. Results and discussion

From the density and microstructural investigations, it was found that samples sintered in argon have higher densification and larger grain growth compared to samples sintered in air and oxygen. The enhanced densification and grain growth under low partial pressure of oxygen are well established and reported by several groups [9,11]. It is observed that a maximum density of 6.35 g cm⁻³ is achieved in sample C, whereas in the samples B and A, the respective density values are 5.75 and 4.5 g cm⁻³. The cation ratios measured by the EDS analyses show little deviation in the bulk compositions of the samples. The fluctuations are within the accuracy limit of the EDS analyses. The superconducting properties of samples A, B and C also reveal that the transition temperatures are increasing with the decrease of partial pressure of oxygen in the sintering atmosphere. The enhanced densification and grain growth under reduced oxygen partial pressure has resulted in better connectivity between the superconducting grains. The presence of less number grains in samples C also helps in improving the $T_c$ and $J_c$ values. The cation ratios, densities and superconducting data for the samples are given in Table 1.

The critical current densities of the samples were observed to be very low due to the presence of a large number of weak links in the samples. In order to understand the weak-link characteristics the variation of $J_c$ with $T$ (K) near $T_c$ (K) was carried out and is shown in Fig. 1. It is known that the bulk superconductors are array of weak links, which behave like Josephson junctions. The values
Table 1
The cation ratio, densities and the superconducting properties of the samples sintered at 1233 K for 1 h in different atmospheres and oxygenated at 773 K for 20 h.

<table>
<thead>
<tr>
<th>Property</th>
<th>Sintering atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Argon</td>
</tr>
<tr>
<td>Cation ratio (Y:Ba:Cu)</td>
<td>1:1.95:3.04</td>
</tr>
<tr>
<td>Density (g cm$^{-3}$)</td>
<td>6.35</td>
</tr>
<tr>
<td>Superconducting transition temperature ($T_c$(O)) (K)</td>
<td>92.0</td>
</tr>
<tr>
<td>Transition width (K)</td>
<td>3.0</td>
</tr>
<tr>
<td>Critical current density at 77 K (A cm$^{-2}$)</td>
<td>500</td>
</tr>
</tbody>
</table>

Fig. 1. Variation of critical current densities with temperature (near the superconducting transition temperature) for the samples sintered at 1233 K for 1 h in (a) oxygen, (b) air and (c) argon atmosphere.

of the supercurrent that flow through the Josephson junctions was theoretically calculated by de Gennes [12] (for S—N—S) and Ambegaokar and Baratoff [13] (for S—I—S).

The maximum supercurrent ($I_c$) that passes through a tunnel junction S—M—S' (S and S' is superconductor and M is metal or insulator) using phenomenological Landau–Ginsburg equations and can be expressed as [14]

$$I_c = \frac{2e\hbar}{mM_{12}} \phi_0 \phi_x$$  \hspace{1cm} (1)

where $\phi_0$ and $\phi_x$ are the order parameters, $\hbar$ is \hbar/2\pi ($\hbar$ is Planck's constant), $m$ is the mass of electron, $e$ is the charge of the electron and $M_{12}$ is the tunnelling coefficient. If M is an insulator, $M_{12}$ is finite near the transition temperature, $T_c$, the order parameter \phi_x varies with ($T_c - T$)$^{1/2}$, consequently the maximum current varies with ($T_c - T$). In the case of metallic junction the maximum supercurrent can be expressed as,

$$I_c = \frac{2e\hbar}{mM} \left[ \frac{b}{\xi(T)} \right]^{2} \phi_0 \phi_x$$  \hspace{1cm} (2)

where $M$ is the tunnelling coefficient, $\xi(T)$ is the coherence length, and $b$ is the Landau–Ginsburg length. $I_c$ is predicted to vary as ($T_c - T$)$^2$. Combining these two cases of Josephson junctions, the behaviour of $I_c$ at any temperature, $T$ (K), near the superconducting transition temperature can be expressed as

$$I_c(T) = I_c(0)(1 - t)^n$$  \hspace{1cm} (3)

where $t = T/T_c$, and the parameter $n$ indicates the type of weak links that exist between the superconducting grains. As discussed earlier, the value of $n$ is 2 for the S—N—S type of weak links and 1 for the S—I—S type of weak links. The values of $n$ between 1 and 2 indicate the formation of S—I—N—S type of weak links between the superconducting grains.

The critical current density values near the transition temperatures are fitted as a function of ($1 - t$)$^n$ by varying the values of $n$. From the fitting data it has been observed that the best fitting for sample A is obtained when $n$ is 2, which suggests the presence of S—N—S type of weak links between the superconducting grains. Similarly in the case of samples B and C, the best fitting is achieved when the respective values of $n$ is 1.5 and 1.0. This indicates the presence of S—I—N—S type of weak links in sample B and S—I—S type of weak links in sample C. Best fitted curves for the samples A, B and C are given in Fig. 2. The observed variations
of weak links in the samples are due to increase of $p(O_2)$ in the sintering atmosphere, as the other processing parameters are identical. It can also be noted from Table 1 that at 77 K the $J_c$ value for sample C having S—I—S type of weak link is higher than for sample A which has S—N—S type of weak link. This is due to the improved densification and presence of less number of grains in the sample C.

In order to understand the possible reasons for such variation of the weak-link characteristics, systematic composition analyses across the grain boundaries have been performed by SEM/EDS using spot mode. After each interval of 0.5 μm, the composition was measured on both the sides on the grain boundaries. It is assumed that the interval of 0.5 μm is larger than the spatial resolution of the EDS analysis in the present study. The concentrations of the Ba and Cu are normalized to Y as 1.0 and the variations of the composition are shown in Fig. 3. The centre of the grain boundary has been assumed to be the origin of the axis in the plot. From the composition variations, it was found that there is an excess amount of Ba and Cu at the interface of samples B and C. The presence of Ba—Cu rich phases at the interface is probably the source of S—I—N—S and S—I—S type of weak links in the samples sintered in air and argon. The absence of any composition fluctuation in the oxygen sintered specimen, i.e. in sample A, resulted in the formation of S—N—S type of weak links. From the above observations, it appears that composition fluctuations at the grain boundaries are the cause of weak-link formation in the present case. The excess amount of Ba and Cu at the interfaces of the samples sintered in air and argon is possibly due to the formation of liquid phase that wets the grain boundary and solidifies therein during cooling. The lowering of melting point of YBCO superconductors with decrease of partial pressure of oxygen is well known and reported by Lay and Renlund [15], Gallagher [16] and Greuter et al. [17]. However, the liquid phase was not found during our SEM and XRD studies. Typical SEM images showing the grains and grain boundaries of the samples sintered at 1233 K for 1 h in argon, air and oxygen atmosphere are shown in Fig. 4. The XRD analyses of the samples sintered in different atmospheres show that the oxy-

Fig. 2. The fitting plots showing the variation of $J_c$ with $(1-T/TC)^n$ for the samples sintered at 1233 K for 1 h in (a) oxygen ($n = 2$), (b) air ($n = 1.5$) and (c) argon ($n = 1$) atmosphere.
Fig. 3. The variation of composition across the grain boundaries for the samples sintered at 1233 K for 1 h in (a) oxygen, (b) air and (c) argon atmosphere.

degenerated samples are orthorhombic and only YBCO-123 phase is present in all the samples (Fig. 5). Except for the 123 phase, no other phase could be detected in the diffractograms.

It is well known that the pure YBa$_2$Cu$_3$O$_x$ does not have any eutectic point, it decomposes peritectically to yield

\[ \text{YBa}_2\text{Cu}_3\text{O}_x \rightarrow 211 + L \]  \hspace{1cm} (4)

and the peritectic decomposition occurs at various temperatures depending upon the $p$(O)$_2$ in the atmosphere. The variation of the peritectic decomposition temperatures with $p$(O)$_2$ was studied by several groups [15–17] and is given in Table 2. From Table 2 it is evident that the formation of liquid phase may take place as low as 1211 K at 0.002 bar of $p$(O)$_2$. In the present investigation ILOR-1 argon gas with 4 ppm of oxygen was used, which may have increased the liquidus temperature. Moreover, the liquid phase even if formed.
that includes misorientation and oxygen deficiency at the grain boundaries cannot be ruled out.

4. Conclusion

The weak-link behaviour of YBCO superconductor was found to be dependent upon the sintering atmosphere and can be altered from S-N-S (in oxygen) to S-I-S type (in argon). The composition deviation at the grain boundaries was found to be the reason for the formation of these weak links. The width of the Ba-Cu rich interface was also found to increase with the decrease of partial pressure of oxygen in the sintering atmosphere.

References