Effects of SnO₂ Additives on the Bondability and Superconductivity of YBCO Superconductors

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The influence of tin oxide additives on the diffusion bondability and superconductivity of YBa₂Cu₃Oₓ₋ₓ ceramic was studied. The critical current density Jc and the critical temperature Tc were tested by the standard four-probe technique. In order to study the behavior and thermal properties of SnO₂ additives in the YBa₂Cu₃Oₓ₋ₓ superconductors in sintering processes, the phase structure of YBa₂Cu₃Oₓ₋ₓ powder with different amount of SnO₂ additives were investigated both by X-ray diffraction after sintering and by thermal analysis. The bonding strength of joints were measured by shearing test. The critical current density increased with the SnO₂ additives properly added. This improvement was considered as the results of such phenomena as follows: (1) The density of specimen increased with the SnO₂ additives increasing. (2) The pinning force to magnetic flux was became larger due to the existence of the additives. The shear strength of specimens increased with the SnO₂ additives increasing. It was feasible to bond the YBCO superconductors using the SnO₂ as the additive. The diffusion bonding thermal cycle would not affect the crystal structure of the YBCO.

Keywords: superconductivity, YBa₂Cu₃Oₓ₋ₓ ceramics, SnO₂ bondability, additive, X-ray diffraction, critical temperature, critical current density, thermal analysis

I. Introduction

There are a number of materials problems which must be solved before widespread technological applications of the ceramic superconductors can be realized. The inherent problem of brittleness limits the ability to fabricate these materials in desired shapes required by specific applications. Also, the anisotropic nature of conduction and flux creep with relative ease in these materials demands special processing techniques to achieve high critical current density (Jc). Moreover, in most applications, it will be necessary to devise ways for joining them with the same or other materials so that they can be integrated into microelectronic devices. Most of the past efforts has been devoted to the brittleness and low current carrying capacity problems, which has led to innovative processing and fabrication techniques producing materials with substantial improvement in these properties. Only limited effort has been directed toward joining issues, which are now beginning to attract attention.

Considerable efforts are made to improve the current density of YBCO by deliberate addition of selected impurities in it. These additives can get doped into the system or remain as impurities or react with major phase to form a second phase. Recently there have been reports on the enhancement of current density in YBCO due to the SnO₂ addition. The authors have attributed that the enhanced current density in SnO₂ doped YBCO is due to the fine grain size as well as the increased flux pinning because of the formation of fine precipitation throughout the grains and grain boundaries. It was found that SnO₂ added YBCO absorbs oxygen at a faster rate than of pure YBCO without affecting the Tc of the material. But there are few reports about the bondability of YBCO as well as the influence of additives on bondability. In the present paper, we report the bondability and superconductivity of YBCO by means of SnO₂ doped specimen.

II. Experimental
The YBa$_2$Cu$_3$O$_{7-x}$(123) specimens were prepared by the standard solid-state sintering route. Powders of Y$_2$O$_3$(99.9%), BaCO$_3$(98%) and CuO(99.9%) in the molar ratio of 1:4:6 were thoroughly mixed in a mortar and pestle using ethanol. The mixture was then calcined in air for 12 hours at 1173K and then reground, X-ray diffraction test was used to check its composition and then SnO$_2$ powder was added with 0 to 10mass%. This powder was compacted using a pressure of 200MPa into pellets of 10mm and 12mm in diameter, 2mm thick. These pellets were sintered at 1193K for 12 hours and then cooled about in 1.7K/min. To measure the critical transition temperature Tc and critical current density Jc of YBCO specimen, samples of $12 \times 2 \times 2$mm were cut from the pellets, both Tc and Jc were measured by DC standard 4-probe technique with a criterion of 1 $\mu$V/mm at 0T, the measurements of Jc were carried out at 50K to 90K with the step of 10K. X-ray powder diffraction was conducted both after the sintering and bonding. The diameter 10 and 12mm specimen were diffusion-bonded with the parameters of 1223K for 1 hour under the pressure of 2.4kPa. Shear test was used to investigate the strength of bonded joints. The joint structures and fractured surfaces were observed and analyzed by SEM/EDAX. Also by means of differential thermal analysis, thermal properties of the specimens during the sintering and bonding processes were studied.

III. Results and discussion

1. Effects of SnO$_2$ content on the density of sintered specimens

In general, when the specimen is sintered at higher temperature, the density becomes greater. As shown in Fig.1 the density became 4.17g/cm$^2$ for the non-added samples. By addition of SnO$_2$, the density became greater and reached 4.5 g/cm$^2$ for the 10mass% SnO$_2$ added samples. According to the reference 3, the average grain size was small for the specimen with the higher SnO$_2$ content and became extremely small for the specimen with more than 0.7mass% SnO$_2$.

2. Effects of SnO$_2$ content and sintering temperature on the Meissner effect

A lot of published papers had discussed the Tc and Jc with the relation of additives, but the relation between the Meissner effect and additives was nearly not investigated. By means of the experiments in liquid nitrogen, the Meissner effects of SnO$_2$-added specimens were investigated. Both the specimen pellet and the magnetic-pellet were dipped into the liquid nitrogen, after cooling down to liquid nitrogen temperature, took these out of the liquid nitrogen and put the magnetic-pellet on the specimen's surface. In case that the magnetic-pellet floated above the specimen's surface thoroughly, the Meissner effect of specimen was evaluated strong. In case of partial floatation, it was evaluated weak and without floatation evaluated no Meissner effect. The Meissner effects of SnO$_2$-added specimens are shown in table 1.

<table>
<thead>
<tr>
<th>SnO$_2$ (mass%)</th>
<th>0%</th>
<th>2%</th>
<th>5%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1183K</td>
<td>no</td>
<td>weak</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>1193K</td>
<td>no</td>
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<td>1203K</td>
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</table>

From the table above, we can see that the higher the sintering temperature, the weaker is the Meissner effect. The same tendency can be seen with the SnO$_2$ content increasing. Also in other experiments we carried out in a commercially available stoichiometric 123 high purity(99.9%) powder, the Meissner effect was not observed in the specimen sintered at 1203K, 1193K and 1183K. It was suggested that the Meissner effect was
associated with the purity of YBCO even though the other conditions were the same. From the phenomena above, it seems that the influence of additive on Meissner effect is much similar with the influence on critical current density, i.e. the intensity of Meissner effect of a sample is much associated with the amount of flux pinning centers in the sample. As to the high pure YBCO samples, there is nearly no flux pinning centers in the samples, so the Meissner effect of these is weak. With the increasing amount of additives, the Meissner effect becomes stronger. However if the additives are over added, the fraction of superconducting constitution in the sample is less and not enough to perform the superconductivity, so the Meissner effect becomes weak or zero.

3. Effects of additives and bonding thermal cycle on the YBCO structure

In order to investigate the behavior of SnO$_2$ added YBCO during the sintering and bonding processes, the X-ray diffraction test was carried out. Figure 2 is the X-ray diffraction patterns of specimens with SnO$_2$ added 5mass% and 10mass%. Where (a) is the pure YBCO after sintered in 1173K, (b) is the YBCO+5mass% SnO$_2$ after sintered in 1193K, (c) is the YBCO+5mass% SnO$_2$ after bonded in 1223K, (d) is the YBCO+10mass% SnO$_2$ after sintered in 1193K, (e) is the YBCO+10mass% SnO$_2$ after bonded in 1223K. From the X-ray diffraction patterns it is revealed that YBCO reacts with the added SnO$_2$ to form the BaSnO$_3$ during the sintering process. The relative intensity of BaSnO$_3$ peaks becomes stronger with the increasing SnO$_2$ amount, along with this reaction, the peaks of CuO was appeared. Also the relative intensity of CuO peaks becomes stronger as the SnO$_2$ increasing. The coexistence of the four phases of 123, CuO, Y$_2$BaCuO$_5$ and BaSnO$_3$ was determined, so it can be concluded that the following chemical reaction was taken place during the sintering process.

\[
2\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{SnO}_x+3\text{CuO} = 5\text{CuO} + \text{Y}_2\text{BaCuO}_5 + 3\text{BaSnO}_3
\]

These experimental results are coincident with that of Osamura et.al., but the new compound YBa$_3$SnO$_{5.5}$ found forming in YBa$_2$Cu$_3$O$_{7-x}$SnO$_x$ system reported by Paulose et.al. was not observed. In fact, the X-ray diffraction patterns of compound YBa$_3$SnO$_{5.5}$ given by Paulose et.al. in that paper was almost the same as that of BaSnO$_3$ so how to recognize the YBa$_3$SnO$_{5.5}$ from the BaSnO$_3$ remains a question. In Figure 2 the existence of CuO and Y$_2$BaCuO$_5$, as well as the relative intensity of these two kinds of compounds increase with the increasing of SnO$_2$ is the evidence that equation (1) has really occurred at the sintering temperature.

Figure 3 shows the effect of temperature (DTA) on the interaction of SnO$_2$ with YBCO powders. Pure SnO$_2$ powders show no transformation during the sintering process(Fig.3a). Pure YBCO powders show the incongruous melting point to be 1283K(Fig.3b). From the X-ray diffraction patterns we know that SnO$_2$ added YBCO had the chemical reaction with SnO$_2$ to form BaSnO$_3$. DTA, however, failed to observe
any such reaction at lower temperature (Fig. 3c). In fact, increasing the additive amount can lower the YBCO melting point. In the case of SnO$_2$ 10mass% addition, sintering at 1203K for 12 hours had made the samples partially molten, but this phenomenon was not seen in the nonadded samples sintered at the same temperature for the same time. This indicated that SnO$_2$ added YBCO had a lower melting point. The similar results were obtained in other oxide-YBCO systems by Fagan et al. (2) It seems that higher density of oxide added YBCO samples may be associated with this behavior.

4. Effect of SnO$_2$ content on Tc and Jc

Figure 4 shows the effect of additions on the critical temperature Tc for specimens before and after bonding. The Tc value of 90.8K was obtained for pure YBCO, and 90.4K for SnO$_2$ 5mass% added specimen, tended slightly to decrease with the higher SnO$_2$. After bonding, the Tc value was 90.2K for pure YBCO and 90K for SnO$_2$ 5mass% added specimen. Compared with the value before bonding, there was a little decreasing in Tc. As to SnO$_2$ 10mass% added specimen there was no superconductivity. From the X-ray diffraction patterns, it was clear that due to the SnO$_2$ over added, the superconducting constitution became too small to perform the superconductivity.

The critical current density Jc measured in 0 magnetic field was observed to increase with the addition of SnO$_2$ up to 2mass% (Fig. 5). It was suggested that the critical current density might be related to the pinning of magnetic flux lines against Lorentz force, where the Lorentz force is defined as $F = Jc \times B$. Several kinds of pinning sites inside the grains can be considered. The flux pinning mechanism for the SnO$_2$ added specimens may be attributed to one or a combination of the following: 1) Refinement of grain size and associated increase of surface pinning, 2) direct flux pinning by Sn-rich precipitates and 3) flux pinning by other phases induced by the chemical reaction of equation (1). When the addition of SnO$_2$ increases, the pinning force becomes greater, so the Jc get bigger. On the other hand, along with the addition, the amount of non-superconducting phases induced by equation (1) increases, up to a certain degree, the fraction of
superconducting constitution in specimen becomes less until lose its superconductivity. From the point of view mentioned above, it was sure for the cases of SnO$_2$ added 5mass% and 10mass%, the X-ray diffraction patterns could give the evidence of constitutions of specimens. This was the reason that SnO$_2$ added 5mass% specimen had a lower Jc value and became non-superconductivity for SnO$_2$ added 10mass% specimen.

5. Shear strength and SEM observation of the joint

The influence of SnO$_2$ addition on the bonding strength is illustrated in Fig.6. These data indicate that addition of 2mass% SnO$_2$ increases the average shear strength from 2.16MPa to 8.29MPa. Further improvement to 10.51MPa results from the addition of 5mass%. The influence of SnO$_2$ addition on the strength has the same tendency as that of density (Fig.1). It is believed to result primarily from the increase in the density of 123 due to the SnO$_2$ addition. Furthermore, the second phase inclusions may relax residual stresses resulting from the expansion anisotropy of grains and provide increased resistance to crack propagation by pinning the propagating crack, and thus increase the strength.

Fig.6 Relation between SnO$_2$ content and shear strengths of joints

![Graph showing shear strength versus SnO$_2$ content](image)

- Bonding Conditions: Temp.: 1223K in air
- Time: 1 hour
- Load: 2.4kPa

Fig.7(a) SEM photo (secondary electron image) of bonded zone (2mass% SnO$_2$)

![SEM photo with 25 μm scale](image)

Fig.7(b) Cu distribution of area as in Fig.7(a)

![Cu distribution with 25 μm scale](image)

Arrows show the joint area

Fig.8(a) SEM photo (backscattered electron image) of bonded zone (10mass% SnO$_2$)

![SEM photo with 25 μm scale](image)

Fig.8(b) Cu distribution of area as in Fig.8(a)

![Cu distribution with 25 μm scale](image)

Arrows show the joint area
Fig. 7(a) is the SEM photo (secondary electron image) of bonded zone of 2 mass% SnO₂ added specimen and Fig. 7(b) is the Cu distribution in the same area in Fig. 7(a). No defect is observed at the joint area, but the Cu content is slightly increased there. Fig. 8(a) is the SEM photo (backscattered electron image) of bonded zone of 10 mass% SnO₂ added specimen and Fig. 8(b) is the Cu distribution in the same area in Fig. 8(a). Backscattered electron image shows the difference in composition, and the joint area is distinguished. X-ray mapping shows the increase in Cu content at the area. But, in these area, observation in secondary electron image showed almost no defects without the edge area of joint. From the photos above we can see that due to the increasing of SnO₂ content, the Cu-rich phase was appeared and aggregated in the bonded zone, it was known by EDAX that the Cu content in the bonded zone was as 2 times as the content in other area. As a whole, the bonding appearance along the bonded interface was good, but there was still lack of close contact between the surfaces of specimens in the edge area of joints, this was the reason that the strength of joint was still lower than that of basic materials, though the strength of the base specimens are increased by SnO₂ additives.

IV. Conclusions

The effect of SnO₂ additions up to 10 mass% has been investigated in YBCO superconductors. The results from the studies can be summarized as follows:

1. The SnO₂ impurity added to the 123 system reacts with it to form BaSnO₃.
2. Both the density and shear strength of SnO₂ added specimens increase with increasing SnO₂ content.
3. To obtain a positive effect with SnO₂ addition in 123, the processes and the doping level should be properly controlled. Over addition would result in detriment of the superconductivity, although the density and strength could be improved.
4. Within the added amount up to 5 mass% SnO₂, the Tc is nearly constant regardless of the change of SnO₂ content, but the Jc has the optimum value under SnO₂ proper addition of about 2 mass%.
5. It is feasible to bond the YBCO superconductor using the SnO₂ as the additive. The thermal cycle subjected in bonding processes would not affect the superconductivity of the YBCO.

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