YBa_2Cu_3O_X高温超伝導セラミクスの臨界電流密度の改善に関する実験的研究

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4. IRREVERSIBILITY OF CRITICAL CURRENT AND WEAK INTERGRANULAR COUPLING IN ORIENTED $\text{YBa}_2\text{Cu}_3\text{O}_x$ CERAMIC SAMPLES

4.1. Introduction

In Chapter 2 and Chapter 3, preparation of highly oriented and closely packed $\text{YBa}_2\text{Cu}_3\text{O}_x$ ceramic samples was described. As the result, a considerable improvement in $J_C$ has been made. Nevertheless, this $J_C$ is still rather below the value in single crystals. Besides, the reduction of $J_C$ in external magnetic fields must be also improved. The hindrance to better $J_C$ characteristics is believed to be existing in the intergranular boundaries through which the grains are coupled. We have discovered an unusual irreversibility of $J_C$ in oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ ceramic samples which is considered to be related to the weak coupling. Analyses of this phenomenon may give a better understanding of the intergranular coupling.
4.2. Experimental details

Samples were prepared with the method already described in the previous chapters (large grains aligned by the $f=16$ KHz, $a=1.0 \times 10^{-7}$ m vibration and sintered at 900 °C for 48 hours as described in Chapter 3). $J_c$ was also similarly measured at 77 K with the $1 \, \mu$V/cm criterion. The current flows along the direction of orientation which is vertical to the c-axis in an oriented sample.
4.3. Results and discussions

Fig 4.1 shows the voltage-current characteristics of one representative sample (sample dimensions: 0.29x1.25x8 mm³; current sweeping speed: 0.5 A/s). A $J_C$ enhancement due to current cycling was observed. The critical current density determined from the first sweeping was 1920 A/cm²; it increased to 2110 A/cm² in the following sweepings. It was confirmed that neither zero drift of the X-Y recorder nor any varying of the standard resistance occurred (the V-I curve was drawn by an X-Y recorder and the current signal was obtained from a standard resistance). This 10% increase was also observed in other samples of the same preparation. The results are summarized in Table I.

Table I. $J_C$ values determined from the first current sweeping and the following ones for samples prepared according to Chapter 3 (the vibration intensity G was 2.5 and damaged samples with cracks were also included).

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{c1st}$ (A/cm²)</td>
<td>1920</td>
<td>1510</td>
<td>1320</td>
<td>1360</td>
<td>1540</td>
<td>1140</td>
</tr>
<tr>
<td>$J_{c2nd}$ (A/cm²)</td>
<td>2110</td>
<td>1650</td>
<td>1400</td>
<td>1430</td>
<td>1690</td>
<td>1220</td>
</tr>
<tr>
<td>$J_{c3rd}$ (A/cm²)</td>
<td>2110</td>
<td>1650</td>
<td>1400</td>
<td>1430</td>
<td>1690</td>
<td>1220</td>
</tr>
<tr>
<td>$\Delta J_C$ (%)</td>
<td>9.9</td>
<td>9.3</td>
<td>6.1</td>
<td>5.1</td>
<td>9.7</td>
<td>7.0</td>
</tr>
</tbody>
</table>
Fig. 4.1. Voltage-current characteristics (77 K) of a representative sample ($N=1, 2, 3$ represent the first, second and third sweeping, respectively).
In order to clarify the reason for this phenomenon, same measurement was also conducted on the conventionally prepared samples (powders were mixed and calcined at 750 °C for 1 hour, powdered, pelletized and heated at 950 °C for 5 hours, after repowdering, pressed into approximately the same dimensions as the samples in Table I, then heat-treated at 900 °C for 48 hours.). Increase in critical current as illustrated in Fig. 4.1 was not observed in these ordinarily sintered samples. for comparison, we also summarize the \( J_c \) values in Table II.

**Table II.** \( J_c \) values (77 K) for conventionally sintered samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{c1st} ) (A/cm(^2))</td>
<td>530</td>
<td>780</td>
<td>810</td>
<td>800</td>
<td>790</td>
</tr>
<tr>
<td>( J_{c2nd} ) (A/cm(^2))</td>
<td>530</td>
<td>780</td>
<td>810</td>
<td>800</td>
<td>790</td>
</tr>
<tr>
<td>( J_{c3rd} ) (A/cm(^2))</td>
<td>530</td>
<td>780</td>
<td>810</td>
<td>800</td>
<td>790</td>
</tr>
</tbody>
</table>

The only difference between group I (Table I) and group II samples (Table II) is that in samples of the former group, crystalline grains are closely packed and oriented as the result of the special preparation. In Figs. 4.2 and 4.3, the results of X-ray reflection experiment are shown. X-ray reflection is conducted on
Fig. 4.2. X-ray diffraction intensity patterns of sample I and sample II.
Fig. 4.3. Distribution of X-ray reflection intensity to $\delta$ with $2\delta$ locked at the (006) Bragg peak.
the uniaxially pressed surface of the sample, which is perpendicular to the c axis in an oriented sample. The orientation degree can be estimated quantitatively either by orientation factor $P$ calculated from Fig. 4.2, or more reliably, by the half width $2\gamma$ of the intensity distribution in Fig. 4.3 (for experimental details refer to 2.3.1). For sample I, the intensity peaks of $(00l)$ in Fig. 4.2 are considerably enhanced compared with those of sample II. In Fig. 4.3, the intensity shows a sharp distribution. These facts suggest that in sample I, the crystalline grains are highly oriented in the c-axis direction.

From the figures, $P$ was calculated to be 85% and 24%, $2\gamma$ was measured to be $4^\circ$ and $12^\circ$ respectively for samples I and II. We summarize the orientation factor $P$ and the half width $2\gamma$ of the two samples in Table III.

Table III. Orientation degrees

<table>
<thead>
<tr>
<th>Samples</th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>85%</td>
<td>24%</td>
</tr>
<tr>
<td>$2\gamma$</td>
<td>$4^\circ$</td>
<td>$12^\circ$</td>
</tr>
</tbody>
</table>

These analyses revealed that samples prepared by our method are significantly different from the
conventionally sintered samples in the orientation degree. However, this difference alone does not seem sufficient to explain the irreversibility. In fact, in samples with higher resintering temperatures (950 °C for 5 hours and 1000 °C for 1 hour), the $J_c$ increase observed in sample I was not found. To understand this, the microstructures of these samples were inspected. Fig. 4.4 shows SEM images of the fractured cross sections of a conventional sample and samples prepared by our method at different resintering temperatures. Compared to the conventional sample, grains in the other samples are closely and orderly aligned. It is also noted that in the oriented sample (900 °C), sections of crushed fine powders (circled) can be recognized to be existing between blocks of strongly interconnected grains which are supposed to be highly oriented. These crushed powders were formed during the separation process of large crystalline grains and remained partly after the relatively low temperature (900 °C) resintering. The existence of weak linked sections between locally oriented blocks, we think, is the cause of the deviation in $J_c$ measurement for reasons to be mentioned below.

It is well known that in ceramic samples, irreversibility of $J_c$ occurs in external magnetic fields. For the second or further field cycles starting from the initial remanent state (zero field),
Fig. 4.4. SEM images of the fractured cross sections of (a): a conventional sample, (b), (c) and (d): the mechanically aligned samples resintered at 900 °C, 950 °C and 1000 °C respectively.
$J_c$ in weak field is a little higher than that of the first field cycle. Evetts and Glowack explained this irreversibility by flux trapping and magnetic superposition in grains and intergrain weak junctions in the field cycle.\textsuperscript{28} As shown in their demonstration, at sufficiently large fields, flux will have entered most grains although the overall magnetic moment will still be diamagnetic. When the field is reduced, some of the trapped flux lines in the grains are no longer supported by the external field and the resulting paramagnetic moment will effectively drive a reverse flux component into the sample through the weakest junctions. This reverse flux remains in the second or further increasing field cycles starting from zero field. The average field within the junctions thus becomes less than the applied field in these cycles and $J_c$ will correspondingly increase to a value higher than that of the initial cycle.

The unusual phenomenon reported by us could be explained similarly by applying this model. A schematic illustration of the situation for our oriented samples, in comparison with the conventional sample, is shown in Fig. 4.5. The weakest junctions are considered corresponding to the crushed fine powders in our samples. In our measurement of $J_c'$, since no external field has been applied except the earth field, we attribute the increase of $J_c$ to the self-field which is
produced by the current flowing through the current lead terminals. Reverse fluxes in the weak junctions are induced by decreasing of the first sweeping current, giving rise to the $J_c$ increase in the following current cycles. Such a weak field, which was calculated to be less than 2 mT, would unlikely produce a irreversibility in a conventionally sintered sample. Nevertheless, in our oriented samples of lower temperature resintering, the highly oriented areas behave like single blocks, originating strong paramagnetic moments which drive reverse flux of much higher density into the surrounding weak linked sections.
Fig. 4.5. A schematic illustration of the reverse flux in the weak-linked boundaries (H in (I) is the self field resulting from the current flow).
4.4. Conclusion

Irreversibility of critical current was observed in oriented YBa$_2$Cu$_3$O$_x$ superconducting ceramic samples. In the transport measurement, the apparent $J_c$ determined from V-I characteristics showed an increase of nearly 10% during the current cycling. As the result of a comparison study with conventionally sintered samples, weak intersections existing between oriented blocks were supposed responsible for this phenomenon. In Chapter 1 and 2, we have reported a mechanical aligning method for preparing highly oriented ceramic superconductors of YBa$_2$Cu$_3$O$_x$. Critical current density has been significantly improved by application of this technique. Nevertheless, by analyzing the irreversible phenomenon described here, it is concluded that although a very high c-axis orientation is obtained, weak coupling between grains remains to be an obstacle to higher transport current densities. The necessity for further efforts to improve the weak coupling is suggested. In the next chapter, such efforts will be reported.
5. EFFECT OF INTERGRANULAR ADDITIVES IN YBa$_2$Cu$_3$O$_x$ CERAMIC SAMPLES

5.1. Introduction

The analyses in Chapter 4 suggested that the weak intergranular coupling must be improved in order to obtain higher transport critical current densities. We thought that introducing some kind of additives might strengthen the weak coupling. Accordingly some preliminary experiments have been practiced by us to investigate the effect of the intergrain addition. A "grain coating" method has been also developed for this purpose.29,30,31)

As a matter of fact, since the discovery of the high-$T_C$ ceramic superconductor, a lot of researches have been made in improving the superconducting properties by substitution of the consisting elements with other ones. Nevertheless, enhancement in the critical current density $J_C$ due to this kind of substitution has not yet been reported.

Rather than substituting the composition element, some efforts were made by doping additives such as Ag to lower the melting temperature and produce a much reduced transport resistivity.32) A maximum enhancement in $J_C$ (from 450 to 700 A/cm$^2$) by a 10 wt.% silver doping was reported. The enhancement was attributed to the decrease
of hole numbers and normal-state resistivity, where compactness increased from 75% to 90.5%, resistivity decreased by an order of magnitude.

However, with this large amount of noble metal embodied in the superconductor, its application is limited. Furthermore, higher \( J_c \) is hardly expectable with this method. Although transport \( J_c \) in the ceramics is very low, the intragrain \( J_c \) has a high value sufficient for practical applications, which is suggested by measurement on single crystal.\(^{11} \) Since the intergranular coupling between crystalline grains is the weak neck for transport current, improvement of the weak link should be most effective. We noted that some additives in the grain boundary may strengthen the weak link. In this case, it is also necessary to ensure that the intragrain property is not influenced. For this purpose, we developed a "grain coating" method to introduce a very thin layer of additive into the grain boundaries. The procedures will be described as follows.
5.2. Experimental details

$YBa_2Cu_3O_x$ crystalline grains of even sizes were used for grain coating (preparation process for the grains was described in 2.2).

Grain coating process is illustrated in Fig. 5.1. Grains were coated with the additive by vacuum evaporation in a high vacuum of $10^{-5}-10^{-6}$ Torr. Then the coated grains were pressed and cut into dimensions of $0.3 \times 1.2 \times 9 \text{mm}^3$, resintered at 900 °C for 48 hours. Before coating, grains were heated by a RF lamp for surface cleaning. Vibration of the grains during coating was also introduced to reduce the unevenness of the coating. Thickness of the coated layer was roughly estimated from the evaporated quantity while the grains were assumed to be thin plates. Thickness $t$ of coating is approximated by

$$t = \frac{m}{(4\pi R^2 \rho_d)},$$

(6.1)

where $m$ is the evaporated quantity, $R$ the mean distance between the evaporation source and the grains, and $\rho_d$ the density of the additive. The real value could be greatly influenced by grain form and the relative surface area although uniform-sized grains (20-50 μm) were selected for this experiment. Therefore, it was considered a rough approximation only correct in the
Fig. 5.1. Illustration of the "grain coating" process.
order of the magnitude.

Ag, SnO2 and Bi2O3 were coated respectively as the additive. Variety in conductivity was valued since we thought a poor conducting layer might behave as pinning forces, while Ag, SnO2 and Bi2O3 represent conducting, semiconducting and insulating material respectively. In fact, preliminary experiments of powder mixing were also conducted to choose the suitable coating material. As the result, superconducting property in YBa2Cu3Ox did not deteriorated with a large amount doping of Ag, SnO2 or Bi2O3. Oxide of Mn was chosen for its antiferromagnetic property. The experimental results will be reported in detail.
5.3. Results of Ag coating

5.3.1. The optimum coating thickness

As proved by the reported experiment of powder mixing, superconductivity was not destroyed even with a huge amount of silver doping. We think that if Ag has any positive effect on the ceramics, then it may help to strengthen the weak intergrain junctions by introducing Ag into the junctions. First to see the effect of Ag coating and to determine the proper coating thickness, samples were prepared by grain coatings of 0.01 - 1 μm (~0.1-10 wt.%). J_c measurement was performed with steady DC current in liquid nitrogen bath. Electrical contacts were made by ultrasonic indium soldering. To enhance the connection, silver was deposited onto the contact areas beforehand. J_c was determined with the criterion of 1 μV/cm.

J_c values from this measurement are shown in Fig. 5.2. There is a tendency of J_c enhancement in the 0.01 μm sample. On the contrary, J_c decrease was clearly recognized in the 0.2 and 1 μm coated samples. This means that too much coating is not desirable although it is less than the quantity of 10 wt.% which brought a maximum J_c increase in the powder mixing.

Microstructure of Ag coated samples shows no obvious difference as seen from SEM images of the
Fig. 5.2. Dependence of the critical current density $J_c$ (77K) on the coating thickness $t$. 
fractured cross sections (Fig. 5.3). No obvious traces of progressed melting or changes in the compactness as reported in Ag powder mixing\textsuperscript{32}) are recognized. Nevertheless, X-ray reflection distribution, which was utilized to evaluate the grain alignment (see 2.3.1) clearly shows a negative result for the thickly coated samples. As shown in Fig. 5.4, compared with samples of noncoating or thin coating, X-ray reflections in 0.2 μm and the 1 μm coated samples split into many minipeaks, which is considered to be a result of Ag aggregation in these samples.
Fig. 5.3. SEM images of the fractured cross sections of Ag-coated samples with coating thickness of 0, 0.01, 0.05, 0.2 and 1 μm respectively ($J_C$ was measured with the current direction from the left to the right).
Fig. 5.4. Distributions of X-ray reflection to $\delta$ with $2\delta$ locked at (006) peak (top to bottom: 0, 0.01, 0.05, 0.2 and 1\,\mu m$ coated samples).
5.3.2. Effect of Ag coating on intergranular coupling

From the above experimental results, it is concluded that $J_C$ improvement can be expected in thin coatings below 0.01 µm (10 nm). Therefore, thinner coatings of 1 nm, 3 nm and 10 nm were conducted in particular. The result of $J_C$ measurement is shown in Fig. 5.5. The tendency of $J_C$ enhancement can be clearly recognized from this graph. Normal-state resistivities of these samples showed little variance (all were in the range of 0.55 mohm·cm to 0.70 mohm·cm at room temperature). Therefore, the $J_C$ increase could be only attributed to the improvement of the intergrain boundary. While in the case of Ag powder mixing, the reported increase of $J_C$ is doubted because the much decreased resistivity (resistivity decreased 90 %) is suspected to have influenced the measurement.

In Fig. 5.6, $J_C$ characteristics of the optimum sample and the uncoated sample in external magnetic field are shown. To see the effect on the weak link, $J_C$ is unified by the zero-field value. The quick deterioration of $J_C$, reportedly resulting from the intergrain weak links, has been also slightly improved by the silver coating. Further experiments are necessary to clarify the origin of the $J_C$ enhancement.

In summary, $J_C$ has been improved by a very small quantity (<0.01 wt.%) of Ag coating around crystalline
Fig. 5.5. Relation of $J_c$ (unified by the noncoating value) to coating thickness $t$. 
Fig. 5.6. $J_c$ (77K) characteristics (unified by the zero-field value) in external magnetic field (parallel to the current flow).
grains. The most effective coating thickness appears to be around 1 nm, which falls in the vicinity of the coherence length. This probably suggests a promising way of improving the weak intergrain links. With evenly distributed coatings, better results should be possible. The possibility also exists that there are better metals or oxides to be utilized as the coating material.
5.4. Effect of intergranular Bi$_2$O$_3$

5.4.1. Preliminary experimental results

On choosing Bi$_2$O$_3$, we also referred to the reported fact that oxygen composition varied across the grain boundary, resulting a deficient oxygen concentration near the boundaries. This consideration is satisfied by Bi$_2$O$_3$ which is able to absorb oxygen at high temperatures and feed the over-contented oxygen to the grain boundary when the temperature is lowered (e.g. the solubility of oxygen in bismuth changes from 0.20 at.% at 750 °C to 0.0044 at.% at 400 °C).)

To investigate the effect of introducing Bi$_2$O$_3$ into YBa$_2$Cu$_3$O$_x$, first we conducted the addition in a conventional way by mixing Bi$_2$O$_3$ (98% pure) fine powders into the YBa$_2$Cu$_3$O$_x$ grains. Samples with Bi$_2$O$_3$ proportions of 0%, 5%, 10% and 20% were prepared. The mixed powders were then pressed and cut into dimensions of -0.3mmx1.2mmx9mm. The resintering heat-treatment was carried out at 900 °C for 48 hours, followed by a slow cooling in oxygen flow. The superconducting properties of transition temperature $T_c$, critical current density $J_c$ are summarized in Table I.

$T_c$ is not reduced by the addition. Although the normal-state (room temperature) resistivity increases exponentially with the increase of Bi$_2$O$_3$, the
Table I. Transition temperature $T_c$, critical current density $J_c$ (77 K) and resistivity $\rho$ of the $\text{Bi}_2\text{O}_3$ doped samples.

<table>
<thead>
<tr>
<th></th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>89.3</td>
<td>90.4</td>
<td>89.3</td>
<td>89.3</td>
</tr>
<tr>
<td>$J_c$ (A/cm$^2$)</td>
<td>920</td>
<td>800</td>
<td>560</td>
<td>120</td>
</tr>
<tr>
<td>$\rho$ (mohm·cm)</td>
<td>0.82</td>
<td>1.44</td>
<td>2.73</td>
<td>11.2</td>
</tr>
</tbody>
</table>

The superconducting state is not destroyed by doping of even 20%. As to the $J_c$ deterioration, uneven distribution of $\text{Bi}_2\text{O}_3$ in the ceramic sample was suspected the reason. To prove this, the 10% doped sample was investigated by SEM. Evidence of uneven distribution of the additive can be found in the SEM image (see the circled areas in Fig. 5.7.). This proves the merit of the grain coating method.
Fig. 5.7. SEM image of the surface of 10% Bi$_2$O$_3$-doped sample (the circled areas are supposed to be accumulated Bi$_2$O$_3$ and the black bar represents 0.1 mm).
5.4.2. Effect of Bi$_2$O$_3$ coating

Experimental procedure for Bi$_2$O$_3$ coating is similar to that for Ag. The results of $J_C$ and electrical resistivity $\rho$ are shown in Fig. 5.8 and Fig. 5.9 respectively. Tendency of $J_C$ enhancement accompanied by resistivity decrease can be clearly recognized. The maximum $J_C$ value appears in the vicinity of 1 nm, which is similar to that of Ag coating. An over-coating of Bi$_2$O$_3$ reduces the $J_C$ value and increases the normal-state resistivity.
Fig. 5.8. Critical current density $J_c$ (77K) of Bi$_2$O$_3$-coated samples resintered at 900 °C for 48 h.
Fig. 5.9. Electrical resistivity $\rho$ (300 K) of $\text{Bi}_2\text{O}_3$-coated samples resintered at 900°C for 48 h.
5.4.3. Influence of post-coating sintering

Grains coated with Bi$_2$O$_3$ were also sintered at 900 °C for 10 h and 5 h in order to investigate the influence of the post-coating heat treatment.

$J_C$ and room temperature (300 K) resistivity were measured for these samples. The results, together with data of the 48 h sintering, are summarized in Fig. 5.10 and Fig. 5.11. A strong correlation between $J_C$ and the coating thickness is exhibited. Especially in the 900 °C-5h samples, $J_C$ deteriorated to a large extent with a thin coating of 7 nm, which is fewer than 0.1% in weight proportion. The difference in the cases of long and short time resintering is probably caused by the dispersion of Bi$_2$O$_3$ at the grain surfaces. In the 48 h treatment, the over-coated Bi$_2$O$_3$ may disperse or diffuse along the boundaries, enhancing the uniformity of the post-heat-treatment distribution of the coated Bi$_2$O$_3$ (note the fact that the grain surfaces are not uniformly deposited due to the limitation of the coating process).

Traces of improvement of the inter-granular weak links were also observed from the $J_C$ behavior in magnetic fields since the weak links were quickly penetrated by the magnetic flux. In Fig. 5.12, $J_C$ characteristics of the samples of optimum coating and non-coating are illustrated. $J_C$ is unified by the zero-field value for assessment of the decreasing slope. In
Fig. 5.10. Critical current densities (77K) of Bi$_2$O$_3$-coated samples with various sintering periods.
Fig. 5.11. Electrical resistivities (300K) of Bi$_2$O$_3$-coated samples.
the two groups of samples (900 °C, 48h and 900 °C, 5h), the quick $J_c$-decrease caused by the magnetic field is improved slightly by the optimum coating. A similar improvement is also observed in the 10 h samples. Improvement of the weak links may be understood more clearly by noting the well known fact that a longer sintering strengthens the weak links.\cite{28} Compared with the uncoated sample, behavior of the coated sample sintered at 900 °C for 5h is closer to that of the uncoated sample sintered at 900 °C for 48 h.
Fig. 5.12. $J_c$ (77K) characteristics (unified by the zero-field value) in external magnetic fields.
5.5. Results and summary of grain coating with other additives

Results on Ag and Bi$_2$O$_3$ show the possibility of improving the transport $J_C$ by application of the grain coating method. A contrasting result was also obtained for SnO$_2$ and MnO$_2$. For understanding of the phenomenon, the results of $J_C$ and $\rho$ are summarized in Fig. 5.13 and Fig. 5.14 respectively.

Tendency of $J_C$ enhancement accompanied by resistivity decrease can be clearly recognized for either of Ag, SnO$_2$ or Bi$_2$O$_3$. The optimum coating thickness is slightly influenced by the sintering time, which is probably caused by diffusion of the additive along grain boundaries as explained in 5.4.3. Therefore, post-heat-treatment thickness of the additive layer in the optimum samples is considered to be in the vicinity of 2 nm (location of the maximum peak in Bi$_2$O$_3$5h curve). It is of interest to note that this value is approximately the magnitude of the coherence length in YBa$_2$Cu$_3$O$_x$.\textsuperscript{15) A thin layer of Ag, SnO$_2$ or Bi$_2$O$_3$ in the magnitude of the coherence length seems to have improved the weak intergranular coupling. While in MnO$_2$ coated samples, the property of $J_C$ and conductance deteriorates quickly for coating beyond 2 nm (the 5 h sintering was chosen since shorter sintering showed a distinct correlation between $J_C$ and coating thickness, as suggested by
Fig. 5.13. Relation of $J_c$ (unified by a $J_c(0)$ of $\sim 10^3$ A/cm²) to coating thickness $t$ (Ag48h, SnO₂48h and Bi₂O₃48h: Ag, SnO₂ and Bi₂O₃ coated samples sintered at 900 °C for 48 hours, Bi₂O₃5h and MnO₂5h: Bi₂O₃ and MnO₂ coated samples sintered at 900 °C for 5 hours).
Fig. 5.14. Relation of resistivity $\rho$ (unified by a $\rho(0)$ of ~1 m$\Omega$·cm) to coating thickness $t$. 
It is reasonable to suppose that when a layer of non-superconducting material in the order of the coherence length is existing between the adjacent superconducting crystalline grains, the transport current is not obstructed. While a layer thicker than the coherence length will block the superconducting carrier effectively. Result of MnO₂ coating shows the propriety of this hypothesis, where the decreasing curve of \( J_C \) or increasing curve of \( \rho \) can be divided into two sections each with a different slope. Meanwhile, Ag, SnO₂ and Bi₂O₃ are positive to the transport superconductivity. Two probable reasons are considered. One is that some changes occur in the microstructure of the superficial surfaces of the crystalline grains. For example, oxygen content, which is deficient across the boundaries,³³ may be increased by forming of Ag, SnO₂ or Bi₂O₃ layer. The other one is that pinning forces are strengthened by the non-superconducting layer. Improvement of the rapid \( J_C \) deterioration in magnetic fields (already seen in Fig. 5.6 and Fig. 5.12) seems to approve the latter explanation (the relative \( J_C \)'s normalized by the zero-field value have been enhanced).

Upon estimating the coating thickness, we have assumed that the transition metals or their oxides are coated onto the grain surface in an exact proportion to
the evaporated material. As a matter of fact, these oxides may dissolve before deposition onto the crystals. The optimum coating thickness would hence deviate from the estimated value. Extent of the deviation could be estimated by supposing a complete dissolution of SnO\textsubscript{2} to SnO, MnO\textsubscript{2} to MnO.\textsuperscript{35} Error of the estimated coating thickness due to the dissolution is within 10 %. In the present experiment, grains of nearly same morphology and size are used, therefore, comparison between the additives could be made.
5.6. Conclusion

A "grain coating" method was developed for improving the critical current density $J_C$ in polycrystalline $\text{YBa}_2\text{Cu}_3\text{O}_x$. With this method, thin layers of additives were coated onto the surface of the crystalline grains. Significant enhancement of $J_C$ was observed for coating of Ag, SnO$_2$, and Bi$_2$O$_3$ respectively. The optimum coating thickness is approximately 1 nm, which is believed to be related to the coherence length in $\text{YBa}_2\text{Cu}_3\text{O}_x$. Compared with the well reported Ag or Ag$_2$O doping (where 10 wt.% of Ag powder is mixed into the superconducting ceramics to get a 50% increase of $J_C$),$^{32,36,37}$ only a very small amount (0.01 wt.%) of alien material is added to the superconductor. This is beneficial in many applications. The results show the possibility of improving the weak coupling in polycrystalline superconductors by utilization of the present method.
6. SUMMARY AND DISCUSSION

High critical current density is an important prerequisite for the application of all kinds of superconductors. The discovery of the high Tc superconductors created enormous new hopes for a much broader breakthrough for superconductivity applications. High critical current densities were achieved in single crystals and thin films. But it was not succeeded in the polycrystalline ceramics due to poor orientation and weak coupling between the crystalline grains (the critical current density $J_c$ was generally $\sim 10^2$ A/cm² at 77 K).

In order to improve the low $J_c$ we have developed original methods for sample preparation. An experimental study of the critical current density has been done with YBa$_2$Cu$_3$O$_x$ ceramic samples. Here we review the main results described in the divided chapters and give a short summary.

Highly oriented YBa$_2$Cu$_3$O$_x$ ceramics were prepared by a "mechanical aligning" method which involved large crystallite growth and an intermediate vibrational treatment. In these samples, crystalline grains were highly oriented and densely aligned. As the result, a maximum $J_c$ of 4200 A/cm² was obtained at 77 K.

The large crystallites excelled the small ones ($< 10 \mu$m in diameter) for their anisotropic morphology on
cleavage, hence the tendency of inclined c-axis oriented alignment was strong in the large-grain samples. $J_C$-improving effect of the intermediate vibration was clarified by a theoretical analysis of the grain alignment in the vibration field.

However, the remarkable $J_C$ reduction in external magnetic field still existed in the mechanically aligned ceramic samples. Weak coupling between oriented grain blocks, which was the origin of an unusual irreversibility in the critical current, was proved to be responsible for the $J_C$ reduction.

To improve the weak coupling, we also developed a "grain coating" process in which thin layers of additives were created in the grain boundaries. In the preliminary experiments, $J_C$ at zero-field was nearly doubled and the rapid reduction in magnetic field was also improved, giving substantial hope for improving the weak intergranular coupling in polycrystalline high-$T_C$ superconductors.

It should be pointed that in these processing techniques, the universal properties of the high-$T_C$ superconductors were utilized and the processes did not involve sophisticated treatment or demand critical conditions. Therefore, it could be applied to the other high-$T_C$ superconductor systems. As a matter of fact, better results may be obtained in other systems. For example, the anisotropic morphology is even stronger in
the Bi-Sr-Ca-Cu-O system, thus the mechanical aligning may be more effective. We have tried the method in preparation of Bi1.85Pb0.35Sr2Ca2Cu3Oy, and obtained a \( J_C \) enhancement from 210 A/cm² to 1200 A/cm² (in this sample low-\( T_C \) phases were present which reduced the critical current density).

The ultimate purpose of the \( J_C \) improvement in \( YBa_2Cu_3O_x \) ceramics is the utilization in wires or tapes. Because of the merits as described, the present technique can be applied directly to wires or tapes. For practical applications of high-\( T_C \) superconducting tapes, it is necessary to guarantee \( J_C \) values of \( 10^4-10^6 \) A/cm² with a minimum \( J_C \) of \( 10^4 \) A/cm². At the present time, tapes of \( YBa_2Cu_3O_x \) as well as other high-\( T_C \) superconducting materials have been manufactured by other researchers. In \( YBa_2Cu_3O_x \) tape of 0.06 mm, \( J_C \) of 3300 A/cm² was obtained. High values over \( 10^4 \) A/cm² have been also reported to be achieved in Tl and Bi systems, probably as the result of stronger anisotropic morphology as well as larger margins between the liquid nitrogen temperature and \( T_C \) (see Fig. 1.4).

In superconducting tapes or thin bulk samples, the obtainable maximum \( J_C \) is relevant to the thickness of the samples. For thickness below 0.5 mm \( J_C \) increases proportionally with decrease in the thickness. The correlation is expressed by the curves in Fig. 6.1. In Fig. 6.1, critical current densities representing the
Fig. 6.1. Critical current density in superconducting tapes (the broken line shows the should-be $J_c$s of the mechanically aligned YBa$_2$Cu$_3$O$_x$."

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state-of-the-art in superconducting tapes are also shown. Being manufactured into a thin tape of 0.06 mm, a high \( J_C \) value of 26000 A/cm\(^2\) could be expected in our mechanically aligned \( \text{YBa}_2\text{Cu}_3\text{O}_x \). Combining the mechanical aligning and the grain coating methods, higher values are also possible. Thus the minimum \( J_C \) of \( 10^4 \) A/cm\(^2\) for practical uses seems to be obtainable with these techniques.

The greatest obstacle to practical applications is the remarkable decrease of \( J_C \) in magnetic fields. In order to improve the behaviour of the \( J_C \) in a magnetic field, the grain boundary must be improved. Creating thin layers (close to the coheren length length) of additives, as suggested by the results on grain coating, seems to a solution. For this purpose, improvement of the grain coating process must be made and some other additives acting as strong pinning centres should be also found. Furthermore, it is desirable to combine the present techniques with other techniques such as directional heat treatment in the fabrication process.
We have found that the profile shapes of the X-ray reflection for YBa$_2$Cu$_3$O$_x$ ceramic samples can be fitted by a 'pseudo-Voigt' function (convolution of Gaussian and Lorentzian functions). Here a summary of the experimental results is presented.

The 'pseudo-Voigt' function has previously been used as profile shape function in Rietveld refinement of synchrotron X-ray data. Applying this function to the reflectivity distributions obtained in our experiment (refer to 2.3.1), the function can be given by the expression

\[
I(\Delta \theta) = I_0 \left\{ \left( \frac{\delta}{\pi Y} \right) \left[ 1 + 4(\Delta \theta/2Y)^2 \right]^{-1} \right. \\
+ \left. (1-\delta)(1/Y)(\ln 2/\pi)^{1/2} \right. \\
\left. \times \exp\left[-4\ln 2(\Delta \theta/2Y)^2\right] \right\},
\]

where $I_0$ is the integrated intensity, $I(\Delta \theta)$ the intensity of a point displaced by $\Delta \theta$ from the Bragg angle of 006 peak, $2Y$ the full width at half-maximum (half width) and $\delta$ a parameter which mixes the two functions. For $\delta=0$ it is a Gaussian function, and for $\delta=1$ a Lorentzian one.

In our experiments to investigate the extent of the c-axis orientation, we found that along with the half width which is usually used to assess the orientation,
the coefficient $\delta$ may also be used as an indicator. High $\delta$s near 1 have been obtained for well oriented ceramic samples, and low $\delta$s for poorly oriented samples.

In Fig. A, data of three representative samples (fine powders, a conventional sample and a mechanically aligned sample) are shown. The rightness of the fitting is supported.

Furthermore, we summarize the data obtained from YBa$_2$Cu$_3$O$_x$ ceramic samples of varied orientation degrees in Fig. B. A correlation of $\delta$ and the half-width $2\gamma$ can be found, which suggests that it is possible to utilize the parameter $\delta$ to assess the extent of the oriented alignment in c-axis direction. Especially for the fine powders in which the small grains are considered to be randomly oriented, $\delta$ is 0 while a definite $2\gamma$ is obtained. Theoretically, the half-width for the fine powders should be indefinite since the reflection is not influenced by the variance in the incident angle in such a situation. The difference between experimental results and the theoretical prediction probably results from the measuring conditions and instruments. In this respect, the parameter $\delta$ proposed by us serves as an objective indicator.
Fig. A. Dot: Distribution of the X-ray reflection as described in 2.3.1 (top: fine powders, middle: a conventional sample, bottom: a mechanically aligned sample), Line: The 'pseudo-Voigt' functions calculated from (2.4).
Fig. B. Correlation of parameter $\delta$ and the half-width $2\theta$ for YBa$_2$Cu$_3$O$_x$ ceramic samples.
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