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Important factors affecting J_c in bulk $YBa_2Cu_3O_{7-\delta}$

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The relationship between the transport J_c and the microstructure of the bulk $YBa_2Cu_3O_{7-\delta}$ samples prepared in various sintering conditions has been studied. The results show that the oxygen atmosphere during sintering and cooling not only influence the crystal structure of the grains but also the grain sizes and the nature of the grain boundaries. The pellet forming pressure affects the orientation of the grains. The width of the grain boundaries is the most important factor in determining the values of transport J_c.

1. Introduction

Since the discovery of the high T_c (*transition temperature*) superconductor $YBa_2Cu_3O_{7-\delta}$ [1, 2], much work has been devoted to raise the critical current densities for the purpose of practical applications. For thin films, a critical current value (J_c) as high as 1.8×10^6 A cm^{-2} at 77 K has been reported [3]. For sintered bulk samples, however, the highest J_c value published up to date is 1.8×10^3 A cm^{-2} [4] which is much lower than that of the theoretical predictions [5] and far from the requirements for practical usage. Although many papers have been published [6, 7] about the microstructure of the bulk samples related to the values of J_c, their relationship are still not clear. We have recently presented a paper on sputter-deposited $YBa_2Cu_3O_{7-\delta}$ thin films [8]. In this report, we present the results of the scanning electron microscope (SEM), X-ray diffraction and electric measurement studies of the bulk $YBa_2Cu_3O_{7-\delta}$ samples prepared under different sintering conditions. The experimental results show that the width of the grain boundaries, is the most important factor in determining the values of transport J_c.

2. Experimental details

The samples were prepared by the solid state reaction of the powder mixture of Y_2O_3, $BaCO_3$ and CuO with the conditions stated in Table I. The well reacted superconducting powder was pressed to form pellets of 16 mm diameter under different pressures.

The transport critical current I_c (at 77 K and zero magnetic field) and the normal state resistance were measured by the standard four-terminal method. The criterion to determine I_c was chosen to be 1 μV cm^{-1}. The samples for I_c measurements were made into narrow strips with cross-sectional areas of 0.25–0.5 mm^2. To avoid the possible influence of the difference of orientation, all strips were cut along the direction of the surface of the pellet. The error in determining J_c comes mainly from the inaccuracy of the measurement of the cross-sectional area and is estimated to be less than 10%. The accuracy of J_c determination is better than 90%.

SEM observations were performed on Hitachi-S580 scanning electron microscope with a resolution of 3.5 nm with an accelerating voltage of 25 kV. The crystal structures of the samples were determined by X-ray diffraction with Rigaku D/max-ra Diffractometer with a resolution of $\pm$ 0.01. Cu$K\alpha$ radiation was used as the X-ray source.

3. Results and discussion

It is well known that the oxygen content in $YBa_2Cu_3O_{7-\delta}$ is extremely important for its superconductivity. Much work has been done to investigate the influence of oxygen on the structure and superconductivity of this compound. However, not much published work has been done on the influence of oxygen on the microstructural morphology of the sintered bulk sample. We have studied the microstructural morphology of the samples sintered in air and flowing oxygen atmosphere. Fig. 1a and b show the SEM photographs for Samples 1 and 2, respectively. It is obvious that the morphology of Sample 1 is very different from that of Sample 2. The microstructure of Sample 1 consists of large rectangular and rod shaped grains with wide grain boundaries. The grain sizes of Sample 2 are much finer and irregular in shape and the grain boundaries are not distinct. These facts indicate that the oxygen atmosphere during sintering has a marked effect on the morphology of the bulk sample. X-ray diffraction shows that both samples are of single phase orthorhombic perovskite structure.

As seen in Table I, the values of J_c are 160 and 375 A cm^{-2} for Samples 1 and 2, respectively. There might be three reasons leading to the differences in J_c of samples 1 and 2: (1) differences in the oxygen content in the Cu–O of the orthorhombic structure;

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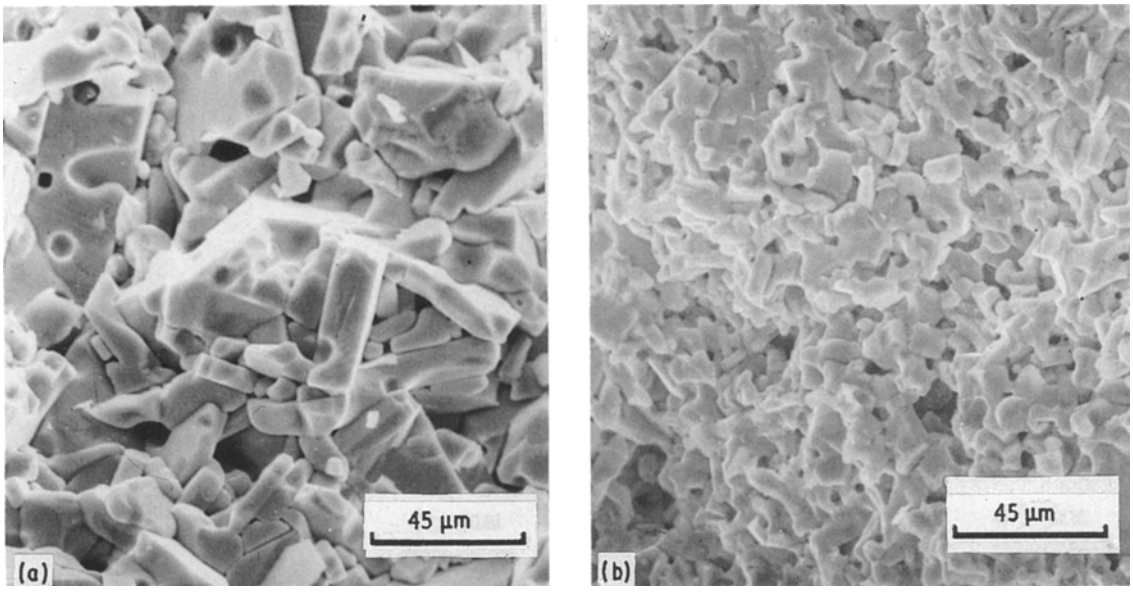

Figure 1 SEM photographs of Samples 1(a) and 2(b).

TABLE I Sintering conditions and superconducting properties of $YBa_2Cu_3O_{7-\delta}$

Sample No.	Sintering conditions			Pellet forming pressure, P ($kg\,cm^{-2}$)	T_c (K)	J_c ($A\,cm^{-2}$) (at 77 K)
	Powder reaction	Sintering of pellets	Low temperature annealing			
1[a]	910 °C–7 h + 935 °C–5 h	935 °C–12 h	–	3000	91.0	160
2	910 °C–7 h + 935 °C–5 h	935 °C–12 h	–	3000	90.0	375
3	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	3000	92.0	455
4	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	6000	91.5	480
5	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	9000	92.5	560
6	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	12000	93.0	625
7	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	15000	92.0	450
8	925 °C–8 h	925 °C–12 h + 935 °C–3 h	350 °C–60 h	18000	92.0	455

[a] Sintered in air.

(2) the difference in orientations of the grains; (3) the effect of grain boundaries. According to [9] the oxygen content could be estimated by the difference of lattice parameters $(b-a)/b$. The values were determined by X-ray diffraction and are 0.0178 and 0.0180 for samples 1 and 2, respectively, and the difference is within experimental error. The superconducting volume fraction of the two samples was estimated by a.c. magnetic susceptibility and no obvious difference was found between them. Therefore (1) cannot be the main reason. As there is no marked difference in X-ray diffraction patterns for the two samples this excludes (2) as the reason for the difference. The main reason must be the effect of grain boundaries. We attributed the difference in J_c between the two samples mainly to the different microstructures of the samples. The widths of the grain boundaries shown in Fig. 1a are about 1 μm, this results in very poor links between the grains and is responsible for the low J_c. The grain boundaries shown in Fig. 1b seem to be much narrower and the grain sizes much smaller than those shown in Fig. 1a. This may account for a better connection for the superconducting path in Sample 2 leading to a comparably larger J_c. We suggest that the lack of oxygen during sintering and cooling process not only reduces the oxygen content in the crystal but also results in larger grain sizes and wider grain boundaries. Both will lower the value of J_c.

We have further studied the influence of the sample densities in terms of the pellet forming pressures P. Fig. 2 illustrates J_c against P for Samples 3 to 8. It is shown that with $P < 12\,000\,kg\,cm^{-2}$, J_c increases linearly with P, but when P exceeds $12\,000\,kg\,cm^{-2}$ J_c drops sharply. J_c seems to keep constant with further increases of P as shown in Fig. 2. Generally, the higher the pressure the higher should be the density of the

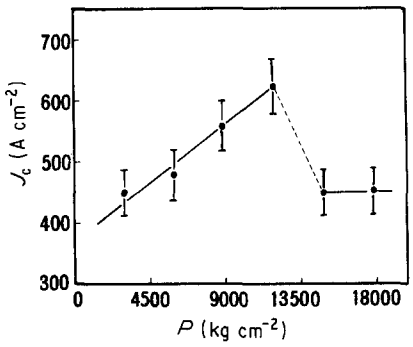

Figure 2 J_c against the pellet forming pressure P.

pellet. Thus from this experiment, it can be conjectured that in the range of $P = 3000$–$12\,000\ \mathrm{kg\,cm^{-2}}$ the effect of density is predominant, J_c increases with the increase of P. But when the density becomes so high that oxygen is difficult to absorb into the sample during cooling and low temperature annealing, the fraction of superconducting volume in the sample becomes less and subsequently leads to a low J_c.

SEM photographs of Samples 3, 6 and 8 are shown in Fig. 3a, b and c. It is obvious that the higher the pressure, the finer is the microstructure, but even with the finest microstructure, the thickness of the grain boundaries is still quite wide (Fig. 3d), of the order of 0.1 μm in width, that is much larger than the superconducting coherent length. The material is therefore weakly linked and the critical current density is naturally very low.

The effect of pressure on the orientation of the grains is studied by X-ray diffraction analysis. The six samples are essentially of single phase orthorhombic structure with small amounts of unidentified phases. They are all partially oriented with the c axis normal to the pellet surface as reported by Kumakura *et al.* [10]. Fig. 4 shows the X-ray relative intensity peaks of (0 0 6) (0 2 0) and (2 0 0) for the six samples with different P. It can be seen that for lower values of P the

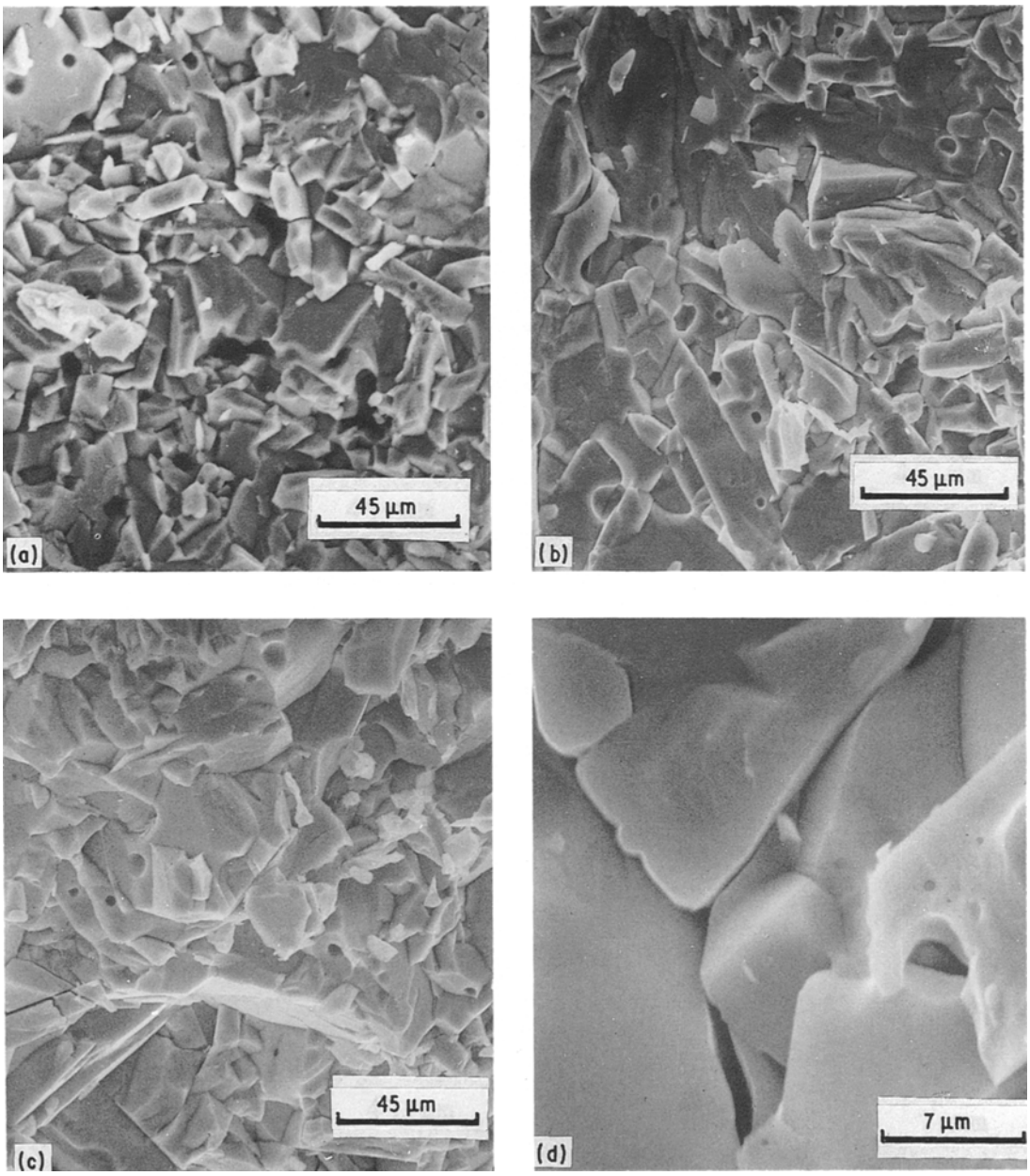

Figure 3 SEM photographs of Samples 3(a), 6(b) and 8(c). (d) High magnification SEM photograph of Sample 6.

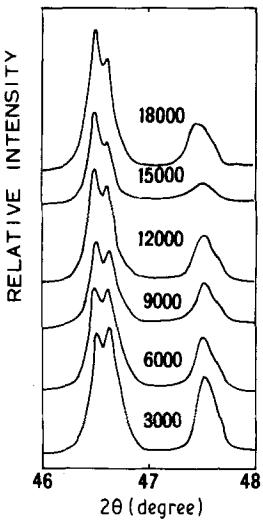

Figure 4 The relative intensities of the X-ray diffraction peaks (0 0 6) (0 2 0) and (2 0 0) for samples 3 to 8. The curve labels are values of P (kg cm^{-2}).

(0 2 0) peak is higher than the (0 0 6) peak, when P increases, the relative peak heights are reversed. This phenomenon may reflect the dependence of the fraction of preferred orientation of the grains with the pellet forming pressure. However, the dependence of J_c on P shown in Fig. 2 can not simply be explained by the effect of the preferred orientation of the grains in the sample. If the effect of orientation is dominant in determining J_c, then one would expect that the J_c of Sample 7 to be largest among all the samples, because the ratio of peaks (0 0 6) to (0 2 0) for Sample 7 is the greatest. But it is not the case, one could perhaps argue that the low J_c of Sample 7 might result from the lack of oxygen due to the high density of the sample. However, one could not explain why the J_c of Sample 8 is not lower than that of Sample 7. Although there is a possibility that the orientation of the grains may affect the grain sizes, no correlation between them has been found. Recently, Zhang [11] reached the same conclusion based on a calculation of a simple model. From the above results, we suggest that the effect of the grain boundaries on J_c is more important than that of the orientation of the grains.

The YBaCu oxide superconductor is a granular material, the term "grain boundary" means the boundary between "single crystals" within the sintered sample. The single crystals are not perfect; there are twins and mosaic structures forming sub-boundaries. These boundaries will also have a marked effect on J_c, which is now being studied by transmission electron microscope.

4. Conclusion

The bulk $YBa_2Cu_3O_{7-\delta}$ samples have been sintered under different conditions. These samples have been studied by SEM, X-ray diffraction and electric measurements. The results show that the morphology of the sample and its superconductivity are strongly dependent on the sample sintering conditions. The oxygen atmosphere during sintering can influence not only the crystal structure of the sample but also the grain sizes and the widths of the grain boundaries. The pressure used to press the pellets is closely related to the resultant grain orientation. For the samples prepared by solid state reaction of powders, the grain boundaries are the most important factor in determining J_c.

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