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Microstructure near 2 1 1 phase in high Jc MTG YBCO

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The microstructures of MTG YBCO near 2 1 1 phase clusters inside the sample are studied by means of transmission electron microscopy. The results indicate that crystal defects around 2 1 1 phase are closely related to the distance between 2 1 1 particles (d_{211}). With the decrease of d_{211}, the twin spacing increases. Simultaneously, the thickness of the twin boundary decreases. When d_{211} is less than 0.51 μm, there are almost no defects between 2 1 1 particles. According to the established crack model, the mechanism of the appearance of a defect-free-zone is explained. The relationship between d_{211} and Jc is discussed in this paper.

1. Introduction

High Jc is necessarily required for all potential applications of high Tc superconductors. Although it is quite high in single crystal thin films, the Jc values in polycrystalline bulk materials and wires are not sufficiently high. Experimental results indicate that the current carrying capacity of polycrystalline bulk materials is limited by the weak link behaviour of the grain boundary. Several efforts to reduce weak links and improve Jc have been reported [1, 2, 3]. Murakami *et al.* [4] first found the existence of 2 1 1 phase in QMG $YBa_2Cu_3O_{7-x}$ samples and attributed the increase of Jc to the flux pinning of fine 2 1 1 precipitates distributing in the 1 2 3 matrix. Recently, Jin *et al.* [5] compared the size and distribution of 2 1 1 precipitates in high Jc materials with those of low Jc materials and found no apparent differences.

Another opinion on the effect on Jc was the twin boundary theory. It was suggested that critical current was related to the existence of a twin boundary which acted as an internal Josephson junction and a flux pinning centre. The identification of this relation led to an experimental attempt to control the twin density. Unfortunately this attempt has not provided a low microtwin density bulk superconducting specimen [6]. When Shi *et al.* [7] investigated twin boundary in $YBa_2Cu_3O_{7-x}$, they found Jc increased as the twin spacing d increased; in other words, if d increased, the thickness of the twin boundary decreased. As the thickness of the twin boundary was approximately equal to the coherence length of the superconductor, the pinning strength reached a maximum; in this case Jc got to its highest value.

Analysis of the results listed above shows that there are great differences in the mechanisms which affect the critical current density, such as 2 1 1 phase; the role it played as a flux pinning centre and its effect on the thickness of the twin boundary are still unclear.

This research probed the relationship of Jc behaviour and crystal defects around 2 1 1 phase based on transmission electron microscopy (TEM) observations, an interpretation of the existence of twin boundaries, stacking faults, and a defect-free-zone related to the distance between two 2 1 1 particles d_{211} was given. Twin boundary spacing d dependence of (d_{211}) was also studied.

2. Experimental details

$YBa_2Cu_3O_{7-x}$ pellets made by solid state reaction were put into a furnace with a temperature gradient of 15 °C cm^{-1} and kept at 1100 °C for 5, 10, 15 min respectively. The samples were cooled quickly down to 1030 °C, then cooled slowly from peritectic temperature (1030 °C) to 980 °C at a rate of 0.5 °C h^{-1}. After this slow cooling course, the samples were cooled from 980 °C to 600 °C at a rate of 50 °C h^{-1} and annealed in flowing oxygen at 600 °C for 100 h. Eventually, the samples were cooled to room temperature at the rate of 50 °C h^{-1} and the MTG samples were obtained. The M–H hysteresis loops (81 K, H//C) for MTG samples were measured by using vibrating sample magnetometer, model 155. All samples were of identical shapes and the applied fields were normal to the longest axis of the samples being measured. Jc values were determined by using the Bean critical state model. TEM micrographs of the a–b plane were performed on a Philips EM 420 electron microscope.

3. Results and discussion

Fig. 1 shows the microstructures of MTG samples. The results indicate that the forms of defects are closely related to the distance between 2 1 1 particles (d_{211}). By measuring a great number of d_{211} values, we find an interesting feature which can be described by cutting d_{211} into three regimes:

1. $d_{211} \leq 0.51$ μm. In this area, there are almost no defects between two 2 1 1 particles (Fig. 1a). Although we have not found whether the emergence of a defect-free-zone can improve Jc or not, the method of

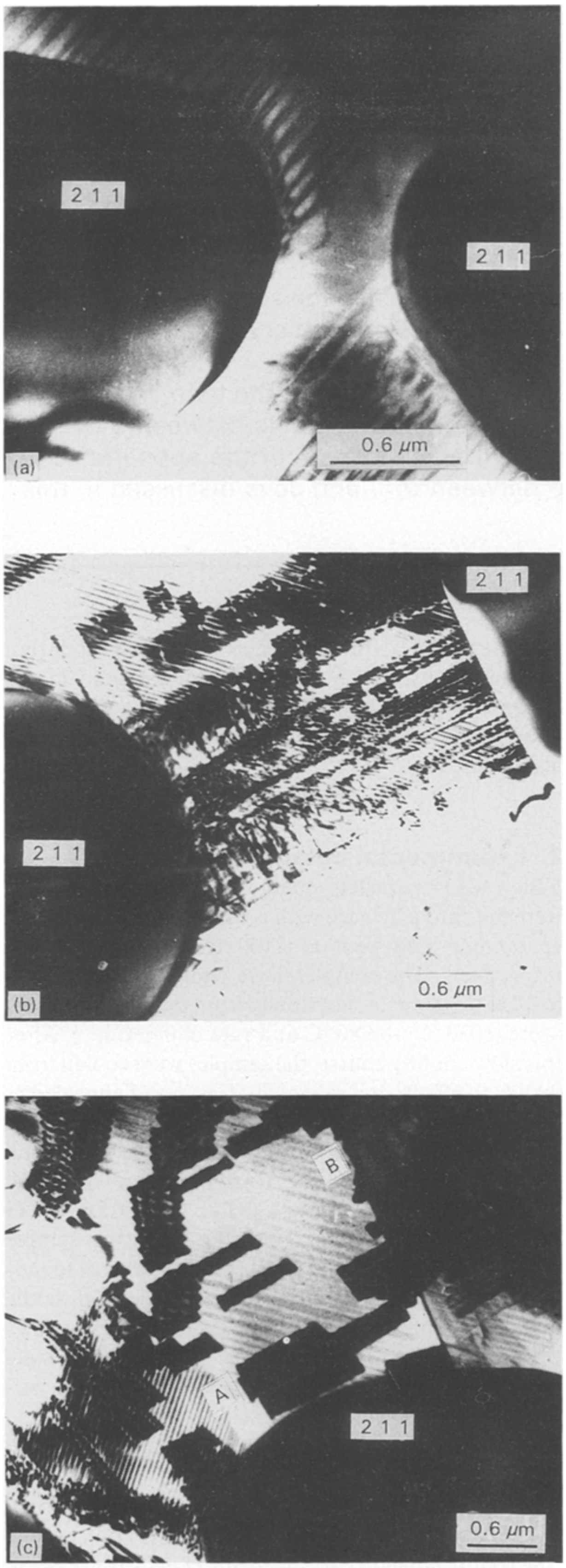

Figure 1 TEM photographs of MTG $YBa_2Cu_3O_{7-x}$ samples showing different distances between 2 1 1 particles. (a) $d_{2\,1\,1} \leqslant 0.51$ μm; (b) 0.51 μm $< d_{2\,1\,1} \leqslant 2.86$ μm; (c) $d_{2\,1\,1} > 2.86$ μm.

obtaining a perfect crystal by controlling $d_{2\,1\,1}$ is of importance and effective.

2. 0.51 μm $< d_{2\,1\,1} \leqslant 2.86$ μm, the parallel (1 1 0) twins and a few stacking faults are induced. The twin boundary spacing d is in the range of 1000–1500 Å (Fig. 1b).

3. $d_{2\,1\,1} > 2.86$ μm, the twins are perpendicular to each other and the twin boundary spacing d decreased to 300–900 Å. The stacking faults increase in size (Fig. 1c). In both Fig. 1b and c, the stacking fault fringes are again visible but the partial dislocations bounding the stacking faults are invisible. We have applied the invisibility criteria for the stacking fault fringes ($\mathbf{g.b}$ = integer) and the partial dislocations ($\mathbf{g.b} = \pm 1/3$) to the observed contrast behaviour. Since these partial dislocations are observed to glide, they must be partial dislocations of Shockley type.

It should be emphasized that all the TEM photographs shown here are based on statistics from much experimental data. They are highly representative of extensive microscopic observations.

Fig. 2 shows the Jc values of samples heated at 1100 °C for different intervals of time against applied magnetic field. The results show the sample treated at 1100 °C for 10 min has the highest critical current density. After TEM observation of 2 1 1 particles in this sample, we find most of the $d_{2\,1\,1}$ values fall into the range of 0.51–2.86 μm. For samples kept at 1100 °C for 5 min and 15 min, $d_{2\,1\,1} > 2.86$ μm and $d_{2\,1\,1} < 0.51$ μm are dominant respectively.

It has been well established that the values of Jc are determined by the flux pinning strength; the fluxoids are pinned mainly by grain boundaries. Generally the pinning strength reaches a maximum as the average diameter of the pinning centre is approximately equal to the coherence length of the superconductor. In high Tc superconductors the coherence length is very short, estimated for the Y-system to be 31 Å in the a–b plane and 43 Å along the c axis [7]; therefore, the size of effective pinning centres is reduced to a much smaller level. We acknowledge that different heat treatment techniques will affect the alignment of textured superconductivity grains, connectivity between grains and grain sizes, however, these factors play little part in the

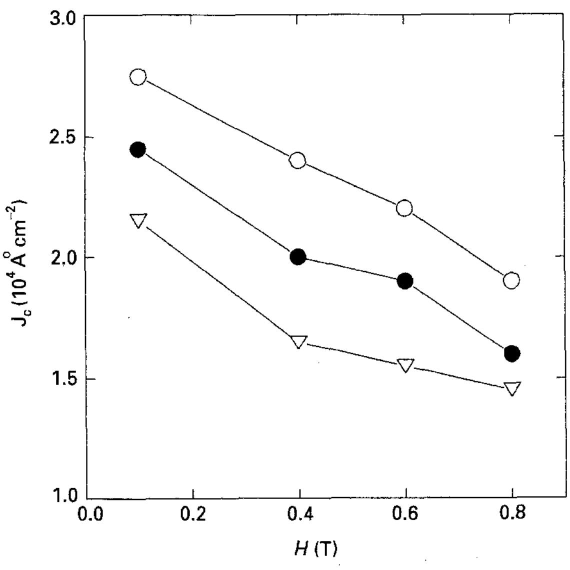

Figure 2 The relation of critical current density with magnetic fields of MTG samples (81 K, H//C) under three different processes. (○) 10 min at 1100 °C; (●) 6 min at 1100 °C; (▽) 15 min at 1100 °C.

difference in Jc values, especially when the magnetic fields are applied. This is due to the very small coherence length of oxide-type high-Tc superconductors and those factors mentioned above have almost no effects on pinning force. The possible pinning centres in high Tc materials have been identified as a twin boundary whose thickness is in the range of coherence length. With twin spacing d increasing, the thickness of the twin boundary decreases. When the thickness is equal to the size of coherence length, Jc increases to a high level.

At the start of heating the sintered sample to 1100 °C in order to decompose 1 2 3 phase into 2 1 1 phase, the 2 1 1 particles are very small; thus the distance between 2 1 1 particles which remain in the 1 2 3 matrix as a result of an incomplete peritectic reaction at about 1000 °C is very large ($d_{211} > 2.86$ μm). The 2 1 1 phase has no apparent effect on the original twin boundary. The twin spacing d is in the range of 300–900 Å, but the twin boundaries are thick enough. Simultaneously acting as weak links they reduce the Jc values. As the keeping time increases to 10 min, 2 1 1 phase increases, d_{211} decreases to a range of 0.51–2.86 μm, twin spacing d increases to 1000–1500 Å, the thickness of the twin boundary becomes smaller and is equal to the coherence length of the superconductor. Therefore, these twin boundaries form effective flux pinning centres and improve Jc markedly. When the keeping time at 1100 °C is longer than 15 min, the 2 1 1 phase increases in size. After the peritectic reaction, the 2 1 1 precipitates reach large values in size and volume fraction and result in the reduction of superconducting phase; thus Jc values are reduced. However, the reduction of Jc is not remarkable (Fig. 2); the authors believe that it is due to the existence of a defect-free-zone in front of the 2 1 1 phase ($d_{211} < 0.51$ μm).

We propose the use of a crack model to explain the formation of a defect-free-zone in MGT $YBa_2Cu_3O_{7-x}$. In 1963, Bilby *et al.* [8] proposed a model for a shear crack that has an associated plastic zone consisting of a linear array of dislocations which are coplanar with the crack; Ohr *et al.* [9] have applied the technique of *in situ* TEM to observe directly the dislocation structure in the plastic zone of advancing cracks in thin-foil specimens of stainless steel single crystals. The same phenomenon was also discovered in Cu [10], Ni [11], Al [12], Mo [13], W [14] etc. in subsequent years.

For MTG $YBa_2Cu_3O_{7-x}$, at the primitive formation stage of 2 1 1 phase, the 2 1 1 embryos keep a good coherence or semicoherence with the matrix. This relation makes a strong internal stress which most likely acts on the triple point grain boundary, therefore, some cracks will be formed near the stress-concentrated zone. There, a defect-free-zone appears in front of the crack top and several dislocations accompany it ahead. Ohr *et al.* measured the defect-free-zone sizes in some pure metals and found the sizes to be in the range of 2–10 μm [13].

We suggest there are two cracks in $YBa_2Cu_3O_{7-x}$ ceramic and their relative sites can be roughly described as in Fig. 3. As the 2 1 1 embryos grow the cracks taper off; simultaneously the defect-free-zone

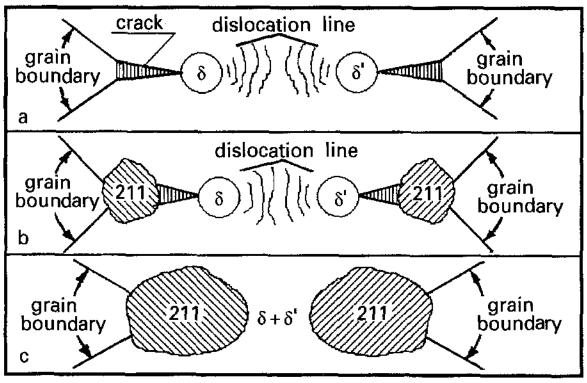

Figure 3 Formation process of the defect-free-zone between 2 1 1 phase particles. (a) Primitive stage of forming 2 1 1 phase; (b) beginning precipitation and segregation of 2 1 1 phase; (c) fully precipitated 2 1 1 phase.

δ and δ′ get close and the number of defects drops gradually (see Fig. 3b). At the end of the 2 1 1 precipitating process, the 2 1 1 particle separates from the matrix and forms an incoherent relation which ensures the system is in a low energy or equilibrium state, the δ and δ′ close up, the cracks disappear completely (see Fig. 3c). From Fig. 1a, we can still find some remaining dislocations which are in the form of inverse pile-up.

The mechanism of the formation of a defect-free-zone described above obtains support from Murakami *et al.*'s experimental results in which they found the appearance of 2 1 1 phase reduced the number of cracks in QMG $YBa_2Cu_3O_{7-x}$ superconductor [15].

4. Conclusion

The distance between two 2 1 1 particles is an important parameter which influences not only the forms of crystal defects but the twin spacing d. Critical current density is closely related to the twin spacing d and a higher Jc can be attained by controlling the d_{211} values.

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