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Technical Note

Comparison of different TEM sample preparation methods for $YBa_2Cu_3O_{7-\delta}$ type materials

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Abstract. — Four different TEM specimen preparation methods, ultramicrotomy, powder suspension, ion-milling and electropolishing, have been described and compared for diverse $YBa_2Cu_3O_{7-\delta}$ samples. Based on TEM observations, defects introduced by these preparation methods are shown. The advantages and disadvantages for each method are discussed.

1. Introduction

For both aspects of fundamental research and domains of applications, the understanding of microstructures in high T_c superconducting oxides is essential. Transmission electron microscopy (TEM) is the most powerful tool to investigate the properties of microstructures and therefore has been used frequently in the study of high T_c superconducting ceramics. TEM however needs thin samples, typically 100 nm thick for conventional two-beam method and for energy dispersive spectroscopy (EDXS) analysis while only 10-20 nm thickness is required for high-resolution (HREM) imaging and for energy-loss spectroscopy (EELS) analysis. Depending on the thinning techniques either artificial defects or surface erosion could be introduced [1] especially for high T_c oxides which are complex and metastable [2-5]. These preparation effects could sometimes lead to results wrongly interpreted as representation of the original materials. So identification of non-intrinsic defects has its importance.

In this paper we will report, based on our observations, the advantages and disadvantages of four TEM specimen preparation methods, i.e., ultramicrotomy, powder suspension, ion-milling and electropolishing, which have been applied on different types of superconducting $YBa_2Cu_3O_{7-\delta}$ materials.

2. Ultramicrotomy

In order to avoid weak-links which might be produced by grain boundaries or other "giant" defects, $YBa_2Cu_3O_{7-\delta}$ oriented powders embedded in epoxy resin have been used for magnetic measurements. Small $YBa_2Cu_3O_{7-\delta}$ powders of dimension between 10-20 μm (broken from large single crystal and selected through micro sieves) have been homogeneously distributed in an low velocity epoxy resin and then oriented by strong magnetic field thanks to the anisotropy in the normal state for $YBa_2Cu_3O_{7-\delta}$ [6]. The *c*-axes for these powders are therefore parallel to each other, which can be seen by the twin contrast (Fig. 1).

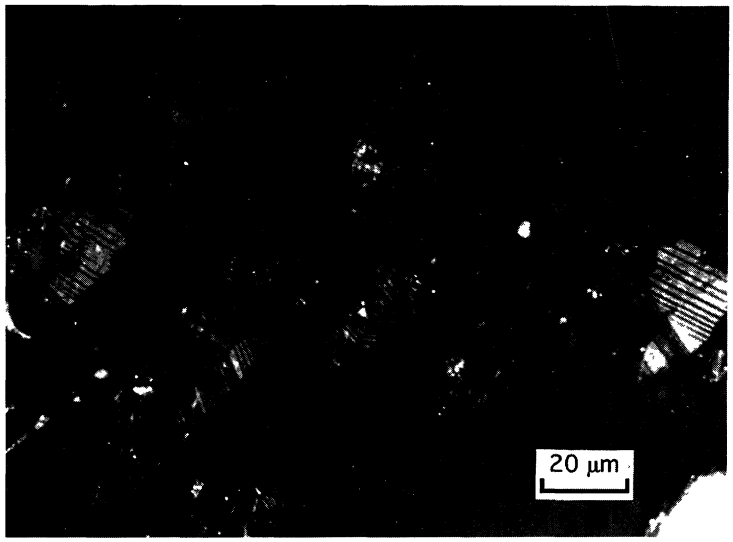

Fig. 1. — Polarized optical micrograph for oriented $YBa_2Cu_3O_{7-\delta}$ powders in epoxy resin

Ultramicrotomy has been performed on these $YBa_2Cu_3O_{7-\delta}$ oriented powders by cutting along their parallel basal *a-b* planes. The cutting angle for diamond knife is set to 50 ° and cutting speed is 0.2-0.5 mm/sec for a LKB 8800 Ultratome III.

Thanks to the fact that the obtained thin $YBa_2Cu_3O_{7-\delta}$ crystallites are all in the same orientation, the cutting parallel to *a-b* plane is similar to a cleavage. Then the defect density created by the cutting will be lowered. The defect formation depends on the crystallite size. The crystallites with smaller dimension, e.g. 1μm, can be cleaved directly as the one in figure 2a, while bigger crystallites could not be well cleaved by one cutting because they were usually less perfect and the small angle deviation between cleavage plane and cutting direction became much serious. The large thin sections (10-20 μm) usually broke into many pieces as shown in figure 2b. Only the small pieces attached to the epoxy from the cutting side are suitable for observation. In order to avoid water, ethylene glycol is always used to float the obtained thin sections which were picked up onto grids of 700-1000 mesh.

Artificial dislocations produced by ultramicrotomy have been observed usually in the broken pieces. For the thin sections obtained by clean cleavage from smaller crystallites, this artifact is rarely found. These artificial dislocations can be distinguished from the intrinsic ones. They are

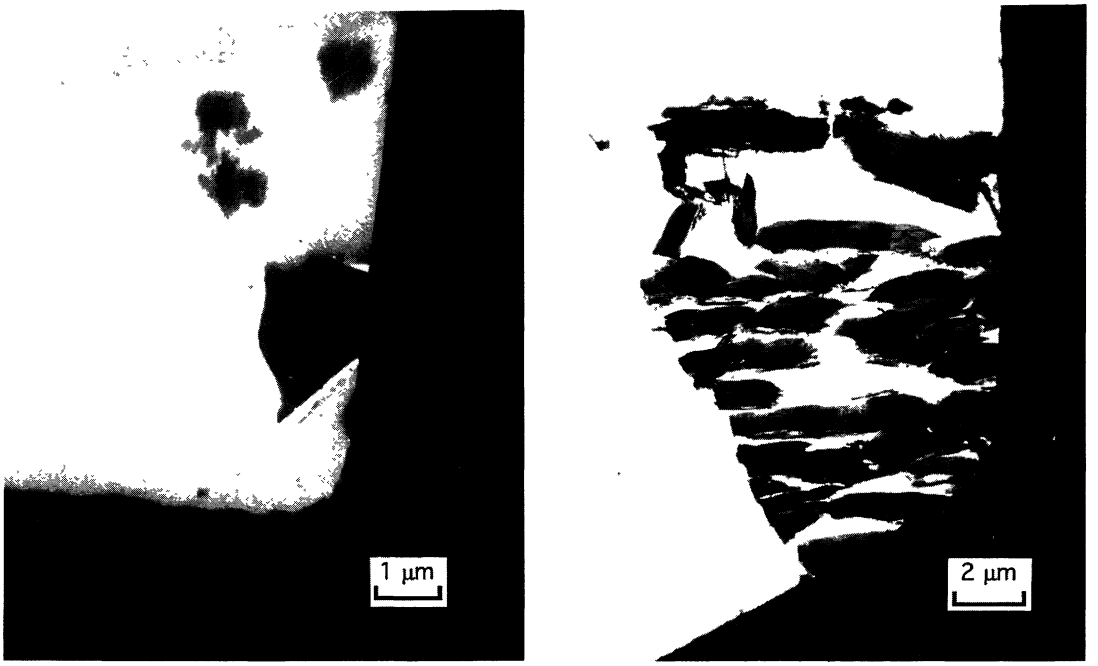

Fig. 2. — Thin flakes resulted by ultramicrotomy for small (a) and large (b) $YBa_2Cu_3O_{7-\delta}$ powders respectively.

generated by Frank-Reed mechanism [7] as seen in figure 3a. The Frank-Reed source located always in the cutting side which attached to epoxy resin. For artificial dislocations, their density decreased rapidly inside the crystallites. In contrary, the intrinsic dislocations showed no divergent behavior, one example is shown in figure 3b.

The cleavage mechanism leads to the formation of surface steps. It is interesting to note that the depths of surface steps are different in standard and deformed $YBa_2Cu_3O_{7-\delta}$ powders (Figs. 4a and 4b). The smaller depths comes from the high density of dislocations in the samples which have been deformed under high pressure [8].

Ultramicrotomy is usually thought unsuitable for microstructural studies, but it still works relatively well for oriented powders thanks to the cleavage mechanism here. Certain artifacts can reveal indirectly some useful information, e.g. for the case of surface steps.

3. Powder suspension

Powder suspension is the simplest method for preparation TEM specimens from bulk samples. Only a mortar and agate pestle are concerned. The $YBa_2Cu_3O_{7-\delta}$ bulk samples immerged in acetone or CCl_4 were crashed and gently ground to produce small chips suspended in acetone or CCl_4. With the help of an eyedropper, these thin micro crystalline grains were dispersed onto holey carbon film supported by Cu or Al grids.

This simple method has been applied to the majority of ceramics for high-resolution structure imaging [9,10]. However, this method is not very suitable for the studies of microstructural properties, except when the analyzed microstructure has rather high frequency of appearence.

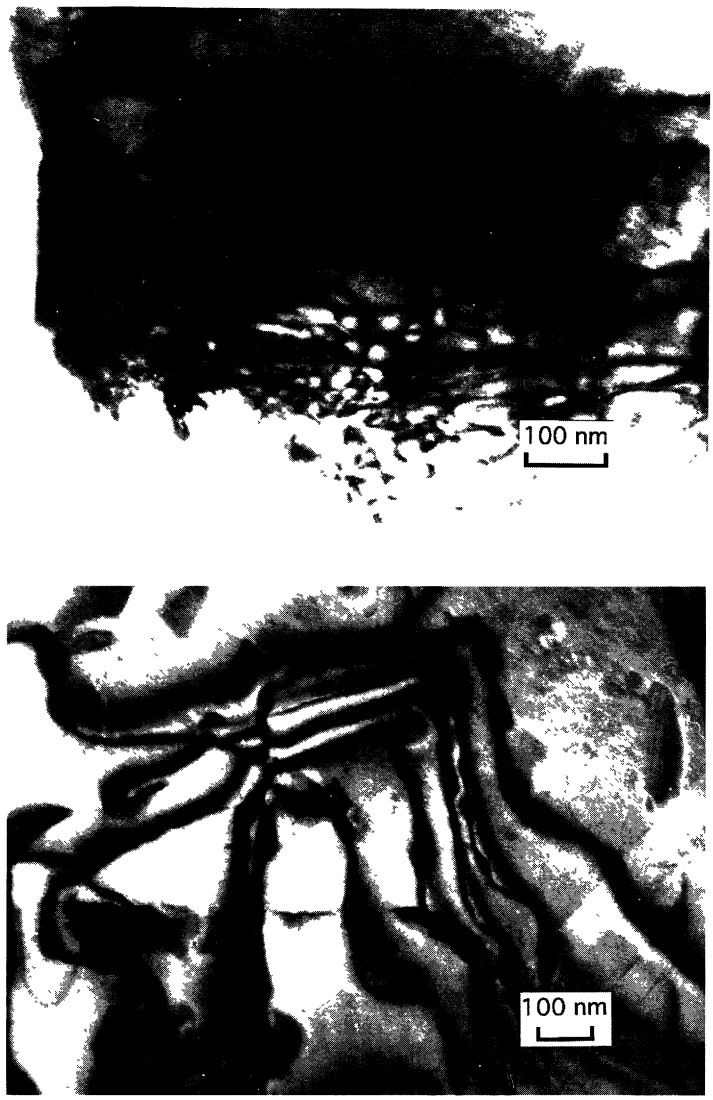

Fig. 3. — Artificial dislocations introduced by ultramicrotomy (a) and intrinsic dislocations of bulk (b).

Large thin areas are not expected from this method and electron transparent regions are usually limited around edges of the chips. The selection of representative microstructures is often arbitrary and also time-consuming. The statistic or quantification of defects is nearly impossible. Less frequent defects, such as grain boundaries and intergranular regions, can only be found by chance. Furthermore additional deformation could be introduced during hand crashing and grinding. Nevertheless, this method can be used for quickly first-eye glances.

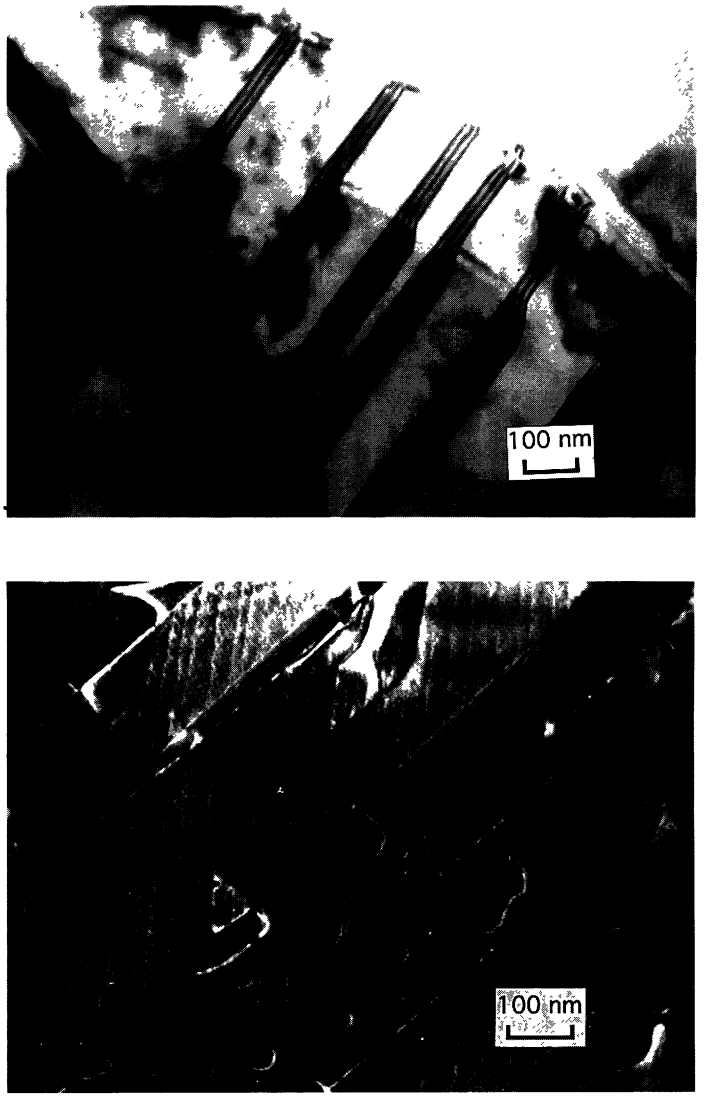

Fig. 4. — Surface steps by ultramicrotomy in standard (a) and deformed (b) $YBa_2Cu_3O_{7-\delta}$ powders.

4. Ion-milling

The ion-milling method is one part of a standard TEM specimen preparation procedure. It is usually applied to $YBa_2Cu_3O_{7-\delta}$ single crystals as well as to thin films. Original samples were first cut by a disc saw to a disc of 3 mm diameter. The thinning procedure is first performed by hand polishing from one side of single crystals down to 150 μm thick with stepped polishing papers (the finest polishing powders are 1/4 μm). Then it follows by dimpling/grinding from another side of the crystals down to less than 50 μm. The last step of thinning is performed by ion-milling with a Gatan 600 DuoMill^{TM} from both sides of crystals mounted onto a liquid N_2 cooling stage. The bombardement angle is usually set to 15 °. The voltage and current for Ar ion flow are 5 kV and

50 mA respectively. The ion flow is cut automatically by a laser sensor as soon as perforation appears.

The ion-milling method can produce electron transparent areas as large as several tens of microns in dimensions. For such a wide region many kinds of defects are observed simultaneously and thus representative microstructural features can be obtained. The statistical analysis of defects is therefore possible. Figure 5 shows a typical image of twin boundaries, dislocations and a sub-grain boundary which is composed of grain-boundary-dislocation networks (see Ref. [11]). This sub-grain boundary passes through the observed region, probably over the entire crystal.

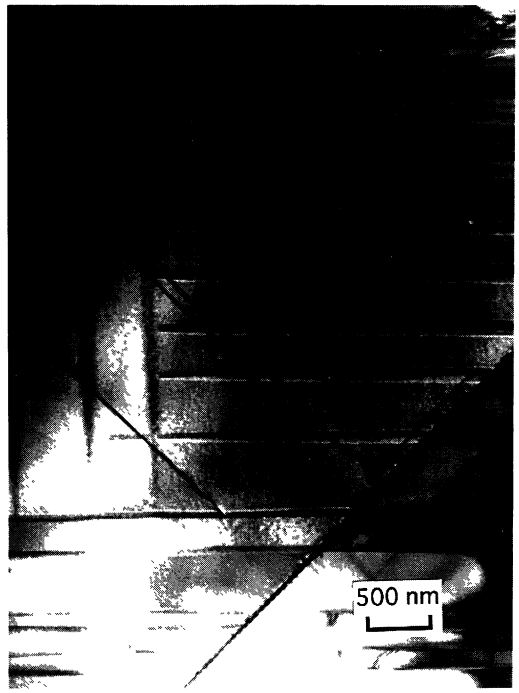

Fig. 5. — Representative microstructure for a $YBa_2Cu_3O_{7-\delta}$ single crystal prepared by ion-milling.

However, this method presents disadvantages not merely due to its complexity and time-consuming preparation. Although cold stages have always been used during the entire ion-milling process to reduce the formation of point defects, bombardment damage could still be observed sometimes. The irradiation by Ar ions produces small surface defects which produce a rough morphology for the foil surface, as shown in figure 6. Invisible irradiation damage exists also in the clean surface as evidences by LeGoues *et al.* [12], who found that Cu_2O precipitation nucleates on ion-milled surface under O or He ion irradiation. The increase of the stacking-fault size after ambient conservation has been observed in the ion-milled samples [11].

Moreover, effect irradiation from ion-milling produces underived changes for twin configurations. In thinner regions near holes, twin boundary densities have been found higher than those in the nearby thicker regions (see Fig. 7a), and the well-known oxygen-vacancy-ordering superstructure [13] has also been observed by electron diffraction in the same regions (see Fig. 7b). This

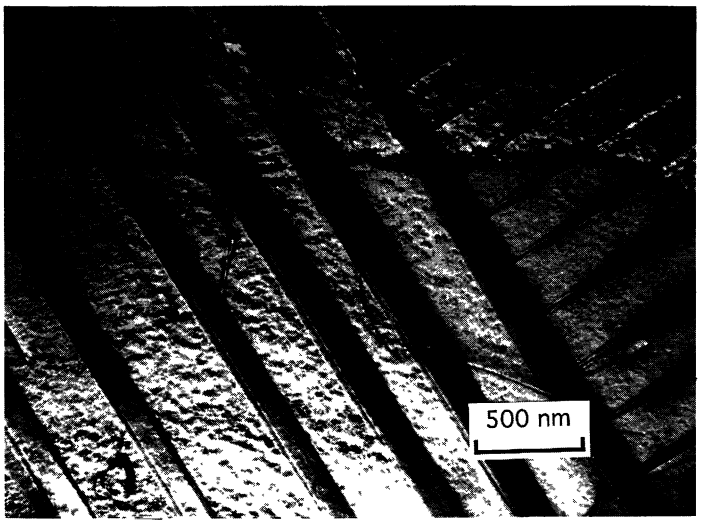

Fig. 6. — Surface roughness in a $YBa_2Cu_3O_{7-\delta}$ single crystal from ion-milling.

effect shows the sensibility of twin domain to the irradiation damage, which is similar to the electron beam heating effect observed by several authors [14-16]. The *in situ* twin structure evolution produced by ion-irradiation has also been revealed by Ruault *et al.* [17]. Therefore in TEM sutdies of the twin boundary structure and of the oxygen-vacancy-ordering, this artifact from ion-milling should be taken into account in addition to the electron beam heating effects.

High-resolution works are more sensitive to these surface artifacts and/or thickness effects related to ion-milling. For the very thin areas near edges, which would otherwise suitable for HREM structure images, the surface defects became dominant for our single crystalline specimens. The sensitivity of high-resolution imaging on the ion-milled samples has also shown by Chrisholm and Smith in their study of grain boundaries, where the grain boundary dislocation cores have changed under short exposure to the electron beam even in the relative thicker regions [18].

5. Electropolishing

The electropolishing method was not applied to the preparation of TEM specimens for superconducting oxides due to their sensitivity to water until Kestel has found a non-acid electrolyte [19]. This entirely alcohol-based electrolyte is composed of LiCl and $Mg(ClO_4)$ in a solvent containing butyl cellusolve and methyl alcohol in appropriate proportions. A single jet polishing at 150K was performed by Wheeler [20], on thin $YBa_2Cu_3O_{7-\delta}$ flakes (70 μm) obtained by cleaving a thick singel crystal. The sample is turned over at mid-time of thinning. Samples obtained with this method were successfully used for electron irradiation experiments, $YBa_2Cu_3O_{7-\delta}$ samples showed a good stability of the structure (especially for twins) under 300 to 1000 KeV electron beam and no electron irradiation defects appeared during observation [21]. We have also used a variant of this technique for $GdBa_2Cu_3O_{7-\delta}$. In this case the thin flakes for electropolishing are more difficult to obtain and the electropolishing was performed with double jet on relatively thick samples (200 to 400 μm). Nevertheless, the thinning procedure is rather quick, typically two or three minutes for crystals with initial thickness of 200 μm. The jet flow was immediately cut off

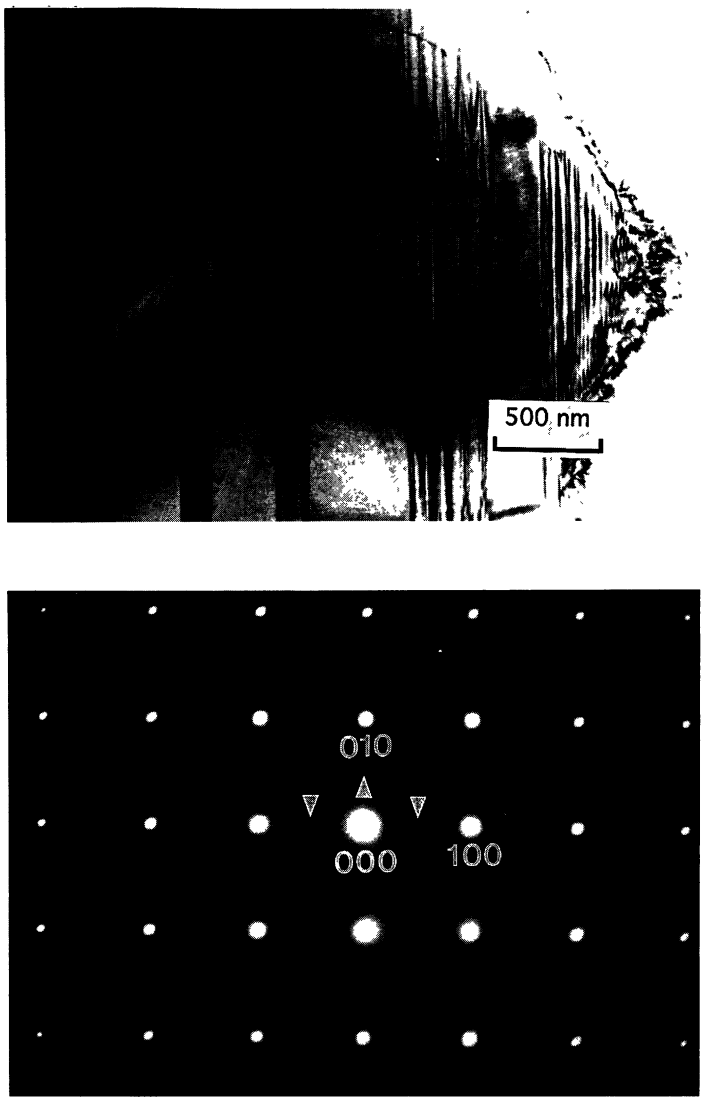

Fig. 7. — Increased of twin boundary density (a) and appearance of oxygen-vacancy-ordering (b) in thin regions (near a hole) by ion-milling for a $YBa_2Cu_3O_{7-\delta}$ single crystal.

by an photo-electric sensor when the first perforations appeared. Lacquer was used to mask the surrounding regions.

This rapid method has two advantages over the other methods, especially over ion-milling. The first advantage is to reduce the effect of mechanical treatment in removing the outer layers, the second one is that no heat has been involved here. Thus we can get ideal TEM samples nearly free from both mechanical and thermal modifications of original bulk samples. Figure 8a shows the overlapping of two orthogonal groups of twin boundaries in a same region. This high stressed configuration keeps its original form in thin foil. In particular no change of twin boundary density is observed here, in contrary to the ion-milling.

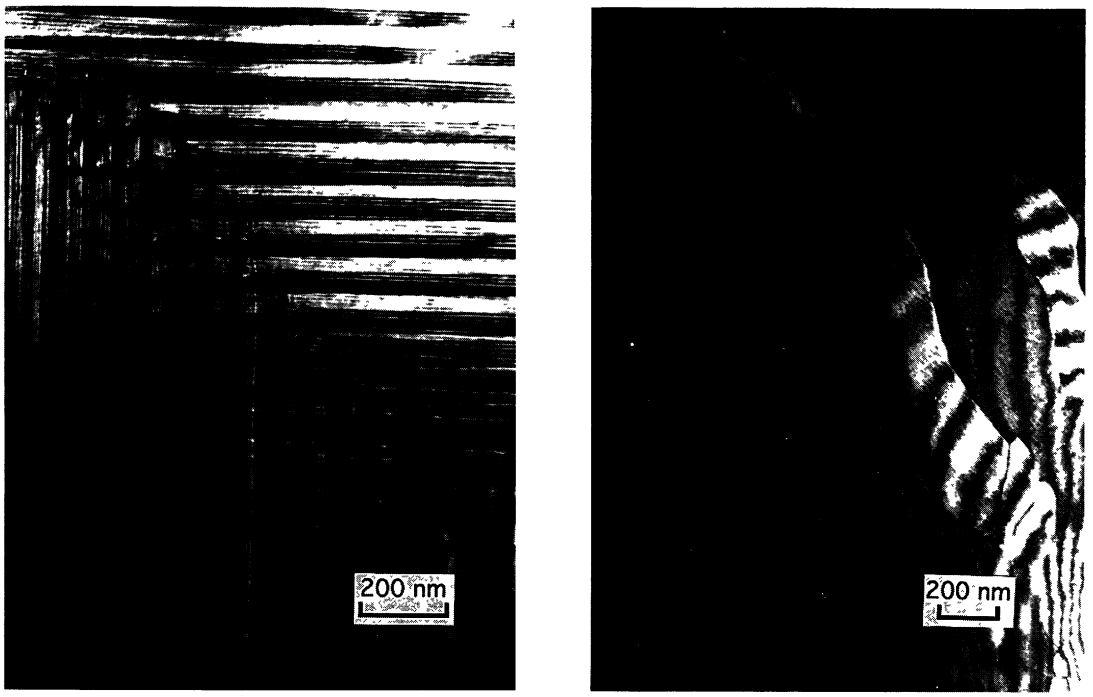

Fig. 8. — (a) The overlapping orthogonal twin boundaries have been well preserved by electropolishing but dislocations are widely dissociated when they reach foil surfaces (b).

However, this method still has its special problems in $GdBa_2Cu_3O_{7-\delta}$ samples. It is difficult to obtain very clean free surfaces and, during HREM observations of defect clusters created by ion implantation, we have noted that the relative thinner regions have changed much quicker than in the other samples under bright electron beam. This makes it almost impossible to take HREM images. In the thicker regions, dislocations were found dissociated unusually wide when they reach the surface of thin foils as shown in figure 8b. This observation implies that there exists a chemically active surface layer. These surface active layers lead to a rapid amorphisation of the thin regions. This intrinsic drawback of electropolishing reduces seriously the application field for this useful method if the thin foil surface cannot be completely cleaned.

6. Summary

We can summarize all major aspects of these four TEM specimen preparation methods for diverse YBaCuO type materials as follows:

6.1 ULTRAMICROTOMY. — This method can only be used with caution in the case of dilute powders of small dimension embedded in epoxy resing. In our case these $YBa_2Cu_3O_{7-\delta}$ powders were oriented by a strong magnetic field along parallel c-axes, thus the cutting along the common (001) planes is practically a cleavage process and artificial dislocations which would be otherwise very serious could be minimized and also distinguishable due to their special configurations which are different from the intrinsic dislocations. Surface steps, which are the by-products of the cutting/cleavage, could exhibit some microstructural characters.

6.2 POWDER SUSPENSION. — This method is the most simple one and it is often used for high-resolution works or merely for a quick first-eye glance. Usually no artifact is introduced by this method, however, large uniform thin areas could not be easily obtained from this method. The study of defect statistics is impossible. Important microstructural features for YBaCuO such as grain boundary and other intergranular/interfacial structures are likely not to be found.

6.3 ION-MILLING. — Ion-milling is a method frequently used for $YBa_2Cu_3O_{7-\delta}$. It produces large electron transparent areas which are suitable for many types of electron microscopy studies. Representative microstructural features can thus be obtained. However, surface defects from ion irradiation are introduced here whatever they are visible or not. Moreover, increase of twin boundary density and appearance of oxygen-vacancy-ordering are observed on thin areas near the holes. These artifacts should be considered in the high-resolution imaging, in particular when the twin structure of YBaCuO type materials is the major object of interest. And this method is prohibited in the case of irradiation damage evolution studies.

6.4 ELECTROPOLISHING. — This method could not be applied to YBaCuO type materials until a non-acid entirely alcohol-based electrolyte was found. No mechanical or thermal influence is introduced during preparation and large electron transparent areas can also be obtained. But for samples with non perfectly cleaned free surfaces, the relatively thinner regions were found to amorphize very quickly under a strong electron beam and thus not suitable for HREM investigation. Active surface layers resulting from the chemical reaction during the thinning procedure are thought to be the reason for the observed unusually wide dissociation of dislocations. These artifacts can limit the utilization of this method.

Acknowledgements.

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