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Microstructural characterization of $YBa_2Cu_3O_7$ whiskers grown from the gas phase

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The microstructures of YBCO whiskers grown by *in-situ* high pressure RF magnetron sputtering in Ar–O_2 atmosphere on (1 0 0) MgO substrates at a temperature range of 650–720 °C were characterized by transmission electron microscopy. Two characteristic, plate-like, heavily twinned crystal and whisker shapes were formed during processing; elongated–hexagonal crystals with an average aspect ratio of 2 and long rectangular whiskers with aspect ratios from 5 up to 30 (length 60 μm). The growth direction for elongated-hexagonal crystals was [1 1 0]/[1 $\bar{1}$ 0] and for rectangular whiskers **a**/**b**-axis. In both cases the plate normal was parallel to the **c**-axes. At the beginning of processing a non-uniform **c**-axis oriented layer was formed on the MgO substrate followed by the initiation and growth of elongated–hexagonal crystal layer. Thereafter rectangular whiskers started to grow on it.

1. Introduction

Since the discovery of the high T_c superconductor materials [1], there has been an ensuing interest in microstructural characterization, alloy development, and process optimization of these materials with emphasis on property–structure correlations. An improvement of the materials' properties is useful for further theoretical understanding of superconductors and technological applications. Several processing routes have been studied to grow polycrystalline and single crystal bulk material and thin films [2–4]. However, very little work has been done to produce single crystal whiskers. The obvious advantage of whiskers is that they could be used for measurements where the disturbing effect of grain boundaries would be avoided and technologically, as a constituent in a superconductor composite material. If a reliable and high-yield process could be developed, it would solve many of the problems met in the technological application of present high T_c materials, and it would open up new high-tech applications.

This paper reports the characterization of YBCO whiskers grown by physical vapour deposition (PVD). The growth of whiskers from the gas phase is a well known phenomenon for ceramics deposited by chemical vapour deposition (CVD) methods [5–6]. Although PVD techniques have been used successfully to grow metallic whiskers [7–8], little work has been done on the growth of ceramic whiskers. The reason for this is that most of the work using PVD has been carried out at sputtering pressures and temperatures unfavourable for whisker growth. In the present studies suitable conditions for whisker growth have been used which has been previously discussed in an earlier paper [9]. The microstructures of whiskers were evaluated in the present study by transmission electron microscopy (TEM) and these observations were combined with the earlier X-ray diffraction (XRD) and scanning electron microscopy (SEM) results [9].

2. Experimental procedure

YBCO whiskers were grown by "*in-situ*" RF magnetron sputtering in Ar + 25%O_2 atmosphere at pressures of 27–67 Pa and at a substrate temperature of 650–720 °C on (1 0 0) single crystal MgO substrates as described in more detail previously [9]. The whiskers were shown by SEM to grow from a more or less continuous YBCO layer that formed initially on the substrate during growth. TEM analysis was carried out in ABT 002B and Jeol 4000 EX transmission electron microscopes operating at 200 kV and 300 kV acceleration voltages, respectively.

TEM specimens were prepared by removing the sputtered coating gently with a surgical knife and dropping the detached whiskers on carbon coated

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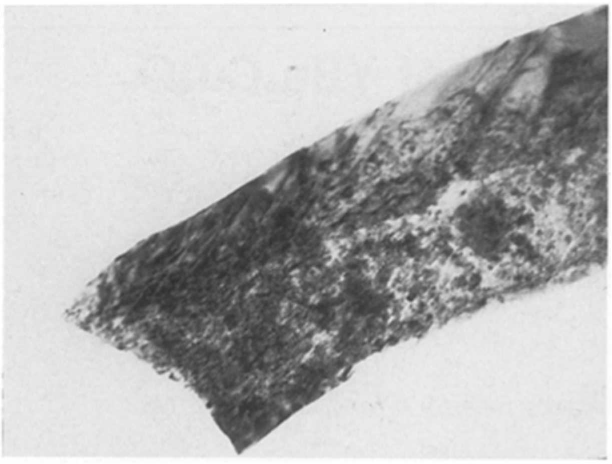

Figure 1 TEM BF-image from a curved whisker. Notice the nearly continuous change of direction on one side and the step-wise change on the other side.

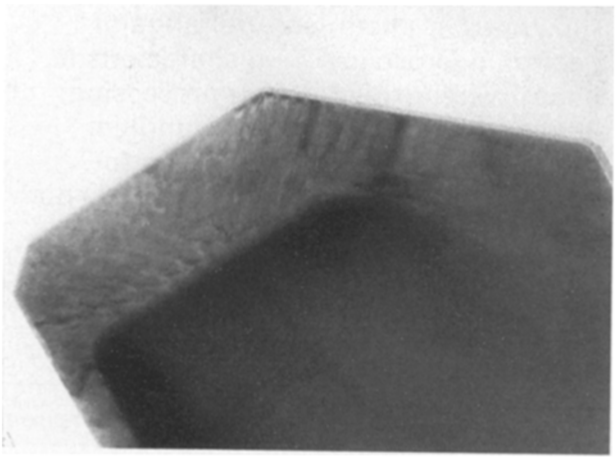

Figure 2 Hexagonal crystals elongated in the $[1\,1\,0]/[1\,\underline{1}\,0]$-direction. Notice that two crystals have stacked on each other in an assymmetrical way.

copper mesh grids. An additional thin carbon layer was deposited on the samples to ensure the permanence of the whiskers during handling. However this interfered with detail HREM studies and thus ion milling at 4 kV/0.3 mA for less than 10 min was done to remove some of the carbon. This resulted in some thin areas for HREM although most of the results presented in this study concentrates on conventional TEM analysis to clarify the crystal structure and whisker morphology and to explain a possible growth mechanism. Since the total number of whiskers suitable for TEM studies was fairly small statistical evaluations were not possible in the present study.

3. Results

Two characteristic whisker geometries were observed; elongated–hexagonal and rectangular with high aspect ratio. Two curved whiskers were also found but their significance in the growth process remained uncertain.

The observed curved whiskers were too thick for any detailed TEM and HREM studies even after ion milling. The average width and length values were of the order of 0.7 μm and 2 μm, respectively. The angular change of the side surface within a distance of 1.4 μm was about 37 degrees. On one side this change was continuous but on the other one it was discontinuous, i.e. the change took place in steps (Fig. 1). Electron diffraction studies did not reveal any correlation between the side surface steps and the unit cell axes **a** and **b**. The surface normals of these plate-like curved crystals were, however, always nearly parallel to the **c**-axis. This means that the growth has taken place mainly on **a**–**b** plane and having different growth rates in **a** and **b** directions. At this point it should be noticed that all studied crystals were heavily twinned and as the twinning in YBCO crystals takes place so that the two axes, **a** and **b**, change places, it is impossible to make any distinction between these two axes in a macroscopic crystal, and therefore the notation **a**/**b**-axis is used later on. In curved crystals the twins appeared always in the $[1\,1\,0]/[1\,\underline{1}\,0]$ directions, i.e. there was not any correlation to the directions of side surfaces. According to present TEM studies the internal stresses in curved whiskers were fairly high. This could be observed by taking BF-and DF-photographs from the same region under different imaging conditions and comparing them to each other. It was also noticed that the internal stresses in the continuously curved sides were higher than in the step-like sides.

All elongated–hexagonal crystals had nearly the same geometry, aspect ratio and **c**-axes parallel to the surface normal. Typical width and length values were 1 and 2 μm, respectively. In all studied cases two or three crystals had stacked onto each other so that all side surfaces were parallel, but the long ones were slightly displaced with respect to each other. This displacement was nearly constant, about 50 nm (Fig. 2). The elongated crystal direction was always $[1\,1\,0]/[1\,\underline{1}\,0]$, meaning that the growth must have taken place simultaneously along **a**- and **b**-axes and at a higher growth rate than along the short hexagonal axis. Like curved crystals, also elongated–hexagonal crystals were heavily twinned, but now the twinning had happened mainly in one direction. Only occasionally some perpendicular twins were observed.

The rectangular whiskers were frequently found grown together either directly, parallel to one another or with one situated perpendicular to the centre of the first one. Their shape was always very regular, plain normal parallel to **c**-axis, the average width of about 2 μm and length from 10 μm up to 60 μm. Typical TEM micrographs from rectangular whiskers are presented in Fig. 3(a) and (b). The long side surfaces were always parallel to the **a**/**b**-axis, i.e. the whisker growth had predominantly happened along one of the short unit cell axis. Just like elongated–hexagonal crystals, rectangular whiskers were also heavily twinned in one direction. Some regions also contained small, perpendicular twins. Their number was, however, fairly small. The average twin spacing, measured from several micrographs and whiskers, was 49 nm. This is in a good agreement with the reported correlation between microtwin spacing, d, and grain size, G (in μm);

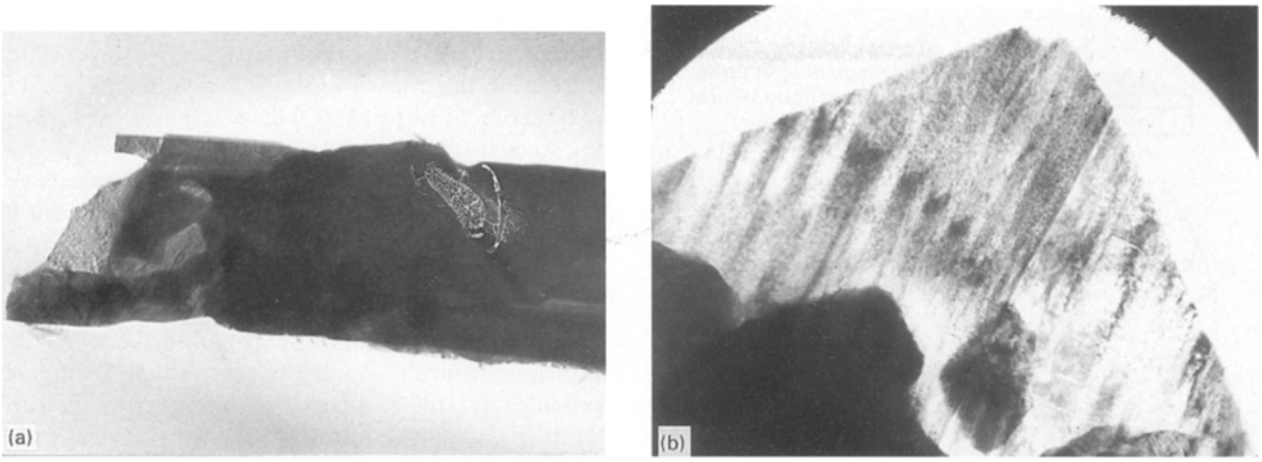

Figure 3 TEM BF-images from a long rectangular whisker: (a) general view with low magnification; (b) higher magnification from the tip area.

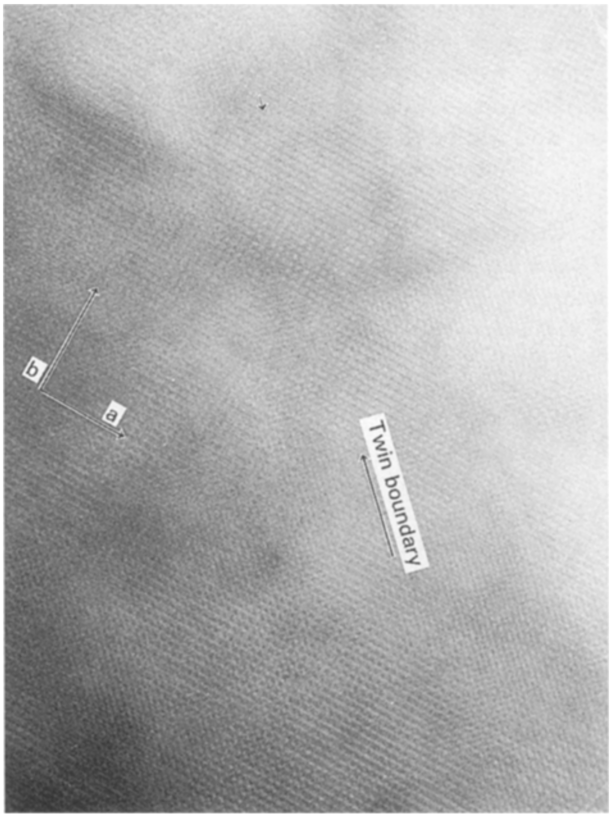

Figure 4 HREM-image from long, rectangular whisker. Twin boundary, as well as, **a**- and **b**-axes are indicated in the micrograph.

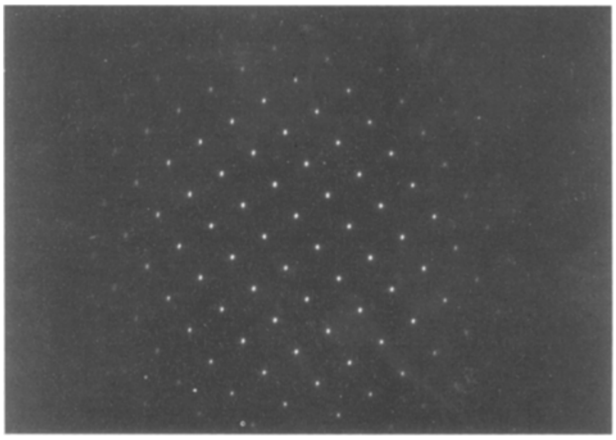

Figure 5 Electron diffraction pattern from a long rectangular whisker. The beam direction is $[0 0 \bar{1}]$.

$d \approx 0.033 G^{1/2}$ [10], i.e. if we take $G =$ whisker width $=$ 2 μm, the formula yields $d = 46.6$ nm. The thinned areas of the ion beam treated sample, where more detailed investigations were possible, were shown to be nearly defect free. A typical HREM-image is shown in Fig. 4.

Electron diffraction studies of curved, elongated–hexagonal and rectangular whiskers showed that they all were single crystalline with an orthorombic crystal structure and had always the **c**-axis parallel to the plane normal. When large area diffraction patterns were recorded, a strong contribution of twins could be observed. This effect was used in detailed twin analysis confirming that the direction of twin plane was $[1 1 0]$ and $[1 \bar{1} 0]$. The lattice parameters, calculated as the average values from 20 diffraction patterns, were $a = 0.379$ nm and $b = 0.385$ nm. An electron diffraction pattern, taken from a long rectangular whisker is shown in Fig. 5.

4. Discussion

The observed whisker geometries and the main axis, as well as, the initial stage of the coating are presented schematically in Fig. 6. At the initial stage of deposition, a thin, non-uniform layer with thicknesses from 0 up to 30 nm is formed on the (1 0 0) single crystalline Mg-substrate. According to reported XRD-studies [11] the **c**-axis of this layer settles perpendicularly to the substrate surface, and if conditions are favourable it continues to grow in this way. In the present study, however, relatively high substrate temperatures, 650–720 °C, and high sputtering pressure values, 22.6–66.6 Pa, were used, and this led into a situation in which the normal layer growth was replaced by the growth of plate-like crystals (shape 2) and whiskers (shape 3). As mentioned in the result presentation some curved crystals (shape 1) were also observed, but because of their small number they could not be regarded as characteristic products of the process. All

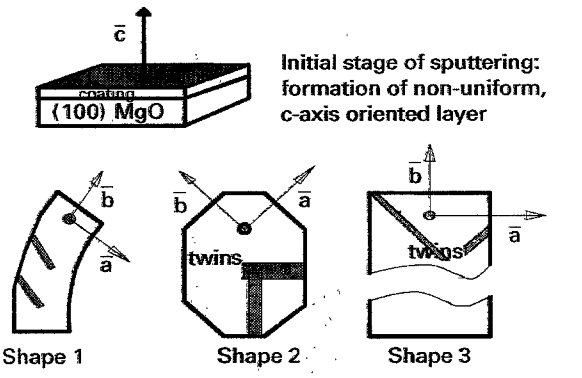

Figure 6 Schematic presentation of the crystal and whisker shapes observed in the present study. Also the first stage of coating formation is presented.

crystals and whiskers were elongated in one direction; shape 3 whiskers along **b**/**a**-axis, shape 2 crystals along $[1\,1\,0]/[1\,\bar{1}\,0]$ direction and shape 1 flakes so that in the final stage the **b**/**a**-axis had become parallel to the side surface. This means that the growth rates and directions have been different for different shapes.

In the earlier paper [9] the authors suggested that growing whiskers have to rotate their growth direction by 90° from that of the **c**-axis oriented layer. Any explanation was not given how this, as such fairly strange rotation can happen. The reason for this was that at that time there were available only preliminary results of microstructural studies. The present studies, however, gave us a good basis to work out this explanation. When studying the observed shapes, presented in Fig. 6, and comparing them into the SEM photographs taken from the early and later stages of the crystal and whisker growth [9], it can be seen that shape 2 is the dominating feature in the early stage of crystal growth, but in the later stage they are mainly replaced by the shape 3 whiskers. This suggests that shape 2 crystals must have started their growth directly from the **c**-axes oriented layer so that the two competing growth directions, along **a**- and **b**-axis, form an angle of 45° with respect to the substrate surface and the **c**-axes of the growing crystals is parallel to the surface. As the rotation of **c**-axis by 90° is difficult to explain merely on crystallographical basis and as any crystals indicating such rotation were not observed in the present study, it is assumed that shape 2 crystals nucleate directly on the non-uniform **c**-axis oriented initial YBCO layer owing to the process conditions favouring high nucleation and growth rates. This growth mechanism is supported by the earlier SEM studies showing that a thin porous layer is formed between substrate and shape 2 crystal layer. At first it was, however, believed to indicate only non-uniform nucleation and growth on the substrate surface, but now the present results favour the above mentioned mechanism where the fast nucleation of shape 2 crystals on the initial YBCO layer lead to the development of a porous layer between them. These nucleation sites were not detected in the present study, and the reason is straightforward; the specimen preparation technique, detaching method, is so "gentle" that it can loose only outreaching crystals, not those which have started the formation of the shape 2 crystal layer. After nucleation the growth of shape 2 crystals takes place in direction $[1\,1\,0]/[1\,\bar{1}\,0]$. This was a little bit surprising since it means simultaneous growth along **a**- and **b**-axis and so far the thin film growth has been reported to take place either along the **c**- axis or **a**/**b**-axis. On the other hand the existence of these two competing directions, **a** and **b**, explains why one of them becomes later on the dominating one and leads finally to the growth of shape 3 whiskers. As the transition from shape 2 crystals into shape 3 whiskers provides 45° tilt of **a**/**b**-axis with respect to the substrate surface, it will mean that the whiskers should be seen in an inclined position in SEM photographs. Restudying the SEM results presented in the earlier work ([9], Fig. 4), it could be seen that this was the case.

Although the present studies revealed the main microstructural features of YBCO crystals and whiskers grown from the gas phase, there are still some open questions concerning the details of growth mechanisms and thus further studies are being carried out and will be reported in the future.

5. Conclusions

The results of the present study can be summarized as follows:

1. YBCO crystals and whiskers are growing on single crystalline (1 0 0) MgO substrate during high pressure RF magnetron sputtering at the temperature range 650–720 °C.
2. Two characteristic crystal and whisker shapes are formed during processing; elongated–hexagonal crystals (shape 2) and long rectangular whiskers (shape 3). Both are plate-like with surface normal parallel to the **c**-axis, and heavily twinned.
3. Shape 2 crystals have grown simultaneously along **a**- and **b**-axes and are thus elongated in the $[1\,1\,0]/[1\,\bar{1}\,0]$-direction. The average aspect ratio is two.
4. Shape 3 whiskers have grown on shape 2 crystals along **a**/**b**-axis. The aspect ratio varies from 5 up to 30.
5. The initiation and growth of shape 2 crystals is proceeded by formation of a non-uniform, thin layer with **c**-axes parallel to the surface normal of the substrate material.

Based on the above conclusions it is evident that the high sputtering gas pressures have promoted random scattering of the vapour phase species and high deposition rates such that crystals and whiskers with similar morphologies as bulk single crystals grow from the melt indicating a preferred growth of the YBCO. Further work to continue to understand the growth process during sputtering and to improve the crystal quality is being continued.

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