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Copper Whisker Growth from inside Sulfur-Doped $YBa_2Cu_3O_{7-x}$ Pellets

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We report on the growth of Cu whiskers (10 μm in linear transverse size) at the surface of a YBCO pellet, in a sulfur-rich atmosphere at a high synthesis temperature. Growth arises from inside the pellet since there is no Cu in the surrounding atmosphere. We present the experimental conditions and electron microscopic observations. We briefly propose a mechanism based on chemical considerations, in particular, a Cu reductive nucleation of the CuS phase at the surface of YBCO. Natural phenomena, laboratory findings, and computer simulation work (based on an Eden model) support this interpretation. © 1995 Academic Press, Inc.

I. INTRODUCTION

High critical current density superconductors (HJS) have come under intensive scrutinity in the past few years, but much progress is still needed to understand their chemical and physical properties. Doped HJS can elucidate both the effect of ions on the phase diagrams and the inherent mechanisms of synthesis. Additionally, the possibilities of improving the technological properties of the systems and of understanding the superconductivity mechanisms can be probed. The numerous possible substitutions cannot all be recalled, but for the following purpose, we only mention the attempts to substitute oxygen by other negative ions such as F, Cl, S, and SO_4^{2-} in $YBa_2Cu_3O_{7-x}$ (1–11).

It has been shown that sulfur can be, e.g., substituted for O in micrograins on YBCO polycrystalline ceramics (6–8). The observed insertion typically occurs at low synthesis temperatures. At elevated temperatures and under synthesis conditions to be mentioned below, we report an unusual phenomenon: the growth of Cu whiskers on the surface of a YBCO pellet in a sulfur-rich atmosphere.

Whiskers are well described in both the metallurgical and polymer industries, though some microscopic theory seems to be missing. They have unusual properties and, in particular, are used to strengthen composite materials (12, 13). The growth process is thought to start from an axial screw dislocation in the presence of supersaturation (14). However, much is still unknown about the basic process. In our case, the situation is apparently still more complicated: the growth arises from inside the pellet since there is no Cu in the surrounding atmosphere.

Recently, Cu-rich precipitates grown on the surface of *c*-axis oriented $DyBa_2Cu_3O_{7-x}$ thin films have also been observed (15). Apparently, strong oxidation conditions are required during the growth process in order to create nucleation sites at a film surface.

II. EXPERIMENTAL CONDITIONS AND RESULTS

The experimental conditions are similar to those used in our previous papers (5–9), where we prepared a nominal 123-YBaCuO pellet (1.8 cm in diameter, 2.5 g in weight) along a standard solid-state reaction route from stoichiometric amounts of 99.9% pure Y_2O_3, $BaCO_3$, and $CuCO_3 \cdot Cu(OH)_2$ and introduced very pure sulfur powder in a vacuum-sealed silica tube. The oxygen content of the initial YBCO pellet is approximately 6.5, as measured by iodometry and as determined from the *c*-lattice parameter obtained in an X-ray diffraction analysis.

Details of the thermal cycle have been given in Ref. (6). The temperature was raised at a rate of 15°C/hr to a temperature T_p = 550°C, at which the pellet was maintained for 48 hr. The silica tube was then extracted from the furnace and given time to cool to room temperature before opening.

The resulting materials have been studied by X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX).

The pellet apparently has a yellowish mold on the mantle. Optical microscopy showed that very fine fibers up to 1 mm in length grew on the pellet. In Fig. 1, the morphology and structure of the fibers, as observed from a scanning electron micrograph, are shown. The most important feature is the presence of entangled "whiskers" randomly distributed on the surface of the pellet. They look like wires sometimes twisted on themselves over several windings or forming flat platelets.

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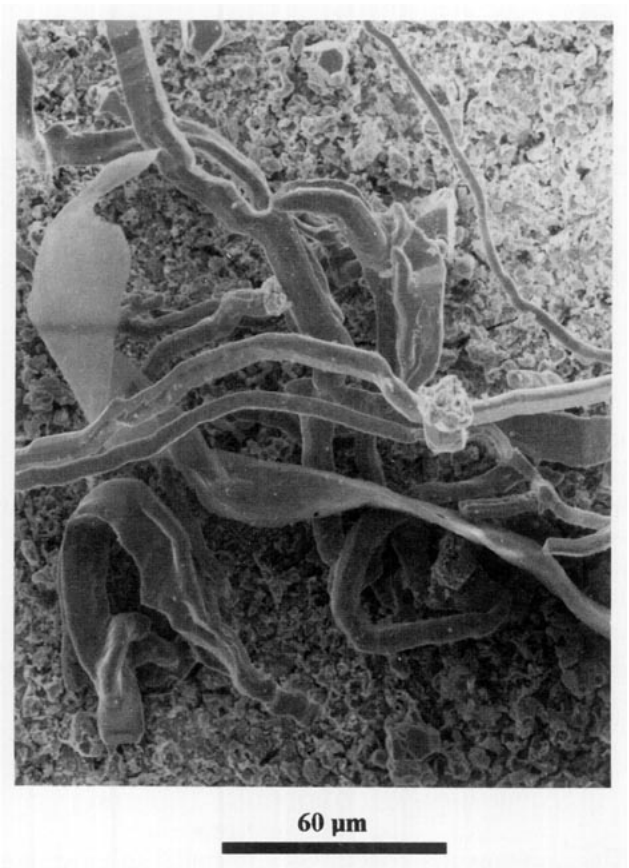

FIG. 1. Whiskers and platelets of Cu at the surface of a $Y_1Ba_2Cu_3O_{7-x}$ pellet after sulfurization.

Energy dispersive X-ray analyses were performed on the surface of the pellet with a LINK system (Oxford Instruments) using a so-called atmospheric thin window. The detectable elements are all those having an atomic weight greater than or equal to that of carbon. The data give the appropriate chemical composition of (i) the material at the top of the pellet, (ii) the whiskers, and (iii) the free whiskers surface in the vicinity of the whisker nucleation sites. The analyses undoubtedly show that the whiskers contain copper *only* and can be identified as *pure* copper filaments which can, in view of the experimental setup, *only* grow *from* the YBaCuO–S surface. The absence of oxygen is absolutely clear from the recorded data. Therefore, Cu oxydes which could form a crystalline structure consistent with the whisker cross section can be excluded. Furthermore, the reducing conditions make such a possibility unlikely. Finally we recall that the color of the whiskers is yellow and not black, which would be the case when an oxide was formed.

Figure 2 shows a rather symmetric cubic crystal with pentagonal facets. It can be considered, due to its size, to be an early stage of development of a Cu whisker. It has roughly a linear size of 1–10 μm. It is impossible to tell whether such crystals are large nuclei which are formed by the coalescence of smaller ones or whether they are the minimal size for (further) development. Very fine examination of the top surface of another nucleus-like crystal in Fig. 2 shows some contrast indicating some twins (T).

In Fig. 3, a more developed fiber is shown. The fiber is well developed (total length, 1 mm) but is twisted in the overall growth direction perpendicular to the mantel. A temperature gradient in the tube could have resulted in sulfur vapor convection. Some turbulence and gravity effects could thus lead to a crooked fiber. The size of the fiber cross section is the same near the middle of the fiber as at the nucleus in Fig. 2.

In Fig. 4, we present a view showing that all the fibers have roughly the same polygonal cross section (10 μm in linear transverse size). The configuration ratio is thus of the order 10^{-3} for a 1 mm length. Note that for carbon fibers most of the reported work mentions circular cross sections. As far as we know, the only exception is that of graphitized fibers obtained from carbon black at 3000°C, for which different morphologies are seen (17).

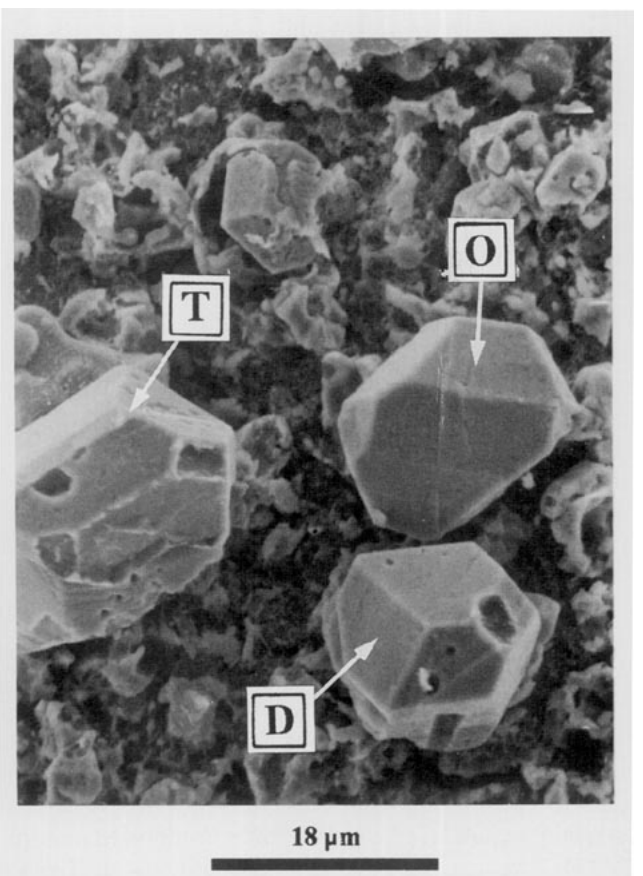

FIG. 2. Small crystallite of Cu at the surface of a $Y_1Ba_2Cu_3O_{7-x}$ pellet after sulfurization: (D) dodecahedron; (T) twin; (O) octahedron.

FIG. 3. Whiskers of Cu at the surface of an $Y_1Ba_2Cu_3O_{7-x}$ pellet after sulfurization in the vicinity of the nuclei of Fig. 2.

FIG. 4. Whiskers of Cu at the surface of a $Y_1Ba_2Cu_3O_{7-x}$ pellet after sulfurization showing the cross-section uniformity and slip lines.

III. DISCUSSION

Copper crystallizes in the cubic crystal system ($Fm3m$, $a = 0.36077$ nm). The most common crystal forms are the cube, the dodecahedron, and the octahedron. Numerous other forms derived from these basic ones occur in nature. Note that copper exhibits twin structures on the (111) plane, in agreement with the spinel law (18).

On the YBCO surface, rhombic dodecahedrons (D), emphasized by an arrow in the figure, are typically observed. Such a morphology is illustrated in Fig. 5a. Other forms are also observed in Fig. 2: a twin (T), in agreement with the spinel law (drawn in Fig. 5b), and an irregularly shaped octahedron (O).

Wire-like copper crystals are observed in nature (19a), have an elongated form along the triad axis, and are generally grown from a basic dodecahedron associated with prehnite, which is an orthorhombic layered structure with the general formula $Ca_2Al_2Si_3O_{10}(OH)_2$. Wire copper crystals are also found in sulfurating primary ores (as found in Kipushi, Shaba Province, Zaïre) (19b).

It is worth noting that such very specific conditions are also present in our system: (i) an orthorhombic (YBCO)

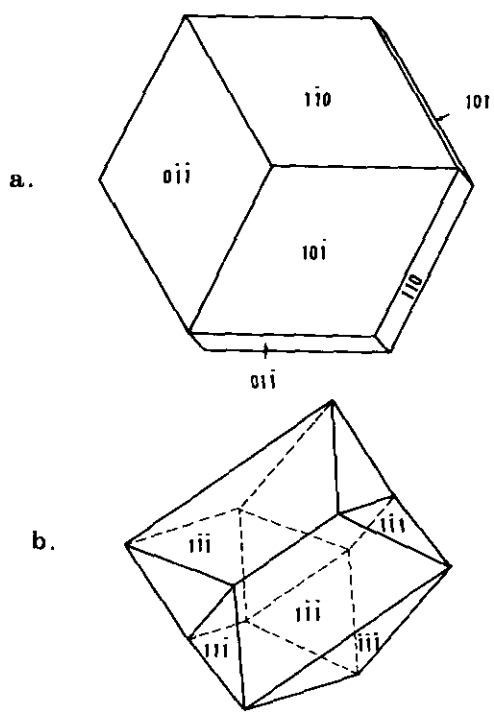

FIG. 5. Growth faces of (a) a rhombic dodecahedron and (b) a twinned dodecahedron.

layered structure used as the support and (ii) a reducing sulfurating atmosphere.

This whisker microstructure is also very similar to the dendritic deposition of copper, observed at the cathode surface in a solid electrochemical cell $Cu/Rb_4Cu_{16}I_7Cl_{13}/Cu$ during the copper (I) titration reaction (20). The copper platelets therein possess slip lines in the microstructure just as in our system (Fig. 4). The growth process is related to the penetration of the reductive nucleation sites *into* the solid electrolyte during the titration reaction.

In our case, and by analogy, a possible origin of the filaments can be attributed to the formation of copper reductive nucleation (Cu (1)) sites created at the pellet surface and induced by the reductive (electro)chemical decomposition of the CuS phase. Such a covellite phase has been observed at the surface of 123-YBCO under lower temperature synthesis conditions of a sulfur atmosphere (6).

Usually, catalytic seeding of the substrate results in germs or nuclei from which a layer or compound grows. However, there is no deposition process here; it is basically germination.

More important, to our opinion, is the morphology of the crystal. To describe it, Tanaka and Matsuoka (21) constructed a phase diagram to show the physicochemical conditions under which a crystal would grow to a given spatial dimensionality. The diagram relates the differences in dipole moments between two components to the difference between the heat of fusion (of the crystallizing compound) and the heat of crystallization (of the mixture). The area where one-dimensional crystals grow lies very far (in arbitrary units!) from the origin of the coordinates. This shows that extreme conditions are necessary for whisker growth.

It is of interest to recall the modern physical point of view describing a growth process. The growth of filaments has been frequently studied in recent years both from a thermodynamic point of view (22) and from a kinetic point of view, with the help of simulation work (16). In the first case, a macroscopic approach is followed, using the free energy instability of a surface due to the presence of competing "forces" (e.g., surface tension, gradient of concentration). In the second case, various models have been proposed, such as the Eden model, the diffusion-limited aggregation model, and their multiple variants (16). In the latter cases, the growth is simulated by a deposition process from a bath *toward* a "seed." Geometrical, rather than chemical or physical, properties are calculated (16).

Under appropriate conditions, snowflakes with dendrites, or more irregular ("fractal") structures, are obtained. Nevertheless, a pure whisker situation is rarely (if at all) encountered. However, from our simulation work, which we give explicitly in Appendix A, it appears that an extreme and anisotropic *dipole–dipole coupling* value (rather than the dipole moment values of Ref. (21) must act on the growing elements to obtain an anisotropic structure like a whisker.

The "inner" growth process which is encountered here can be trivially simulated along an Eden model by considering a finite (semiopened), strictly one-dimensional chain situation (23) and "pushing" from the inside (from the "seed") the added elements. However, this leaves the "external" tip in an unchanged state; i.e., there is no spiral growth, which only occurs in a three-dimensional situation.

The situation is indeed more complex here because a whisker is not truly one-dimensional. In fact, it is likely a growing spiral emerging from the substrate (22). The top of the tip reflects the symmetry of Cu, and the cross-section size thus merely reflects the basic size of the YBCO grains. Therefore, the simulation data in Appendix A refers to a two-dimensional case. The order of magnitude of the coupling strength is hereby given, and hence is apparently a first insight into microscopic considerations for whisker growth of the type presented here.

IV. CONCLUSION

In conclusion, we recall that we have presented results on copper whisker growth on $YBa_2Cu_3O_{7-x}$ material under a sulfurating atmosphere. Such a process has been discussed in terms of a reductive nucleation of copper from CuS at the surface of the YBCO pellet. The findings have been compared with those obtained from other laboratories or from synthesis under conditions found in nature. The growth of whiskers has been briefly reviewed from thermodynamic and kinetic points of view. In the latter case, a modified Eden model has been proposed in order to take into account an anisotropic dipole–dipole-like interaction. This shows that extreme conditions are necessary for whisker growth. An order of magnitude of the coupling strength has been given here for the first time.

APPENDIX A

Anisotropic Eden Model as a Paradigm for Whisker Growth

The simulation work which we have used for obtaining whisker-type crystals is based on a generalized anisotropic Eden model (16). It belongs to the class of "magnetic Eden models" (23). In the Eden model, a seed is placed on a lattice and a set of identical quantities are randomly glued to it according to given probability rules. The process leads to a compact cluster for which all the

properties are not yet fully understood (16). We have used the same basic idea but placed the seed on a substrate, i.e., at the origin of axes defining coordinates of a semi-infinite square lattice such that the growth can only occur for $y > 0$ or along the x-axis. An anisotropic selection rule for the choice of the growth site has then been imposed.

The growth sites next to the seed on the substrate are each given a sticking probability $\exp(p_x N_x)$ and the site on the top of the seed a probability $\exp(p_y N_y)$. The parameters p_x and p_y are the growth parameters, while N_x and N_y are the numbers of occupied sites next to the considered growth site in the x and y direction, respectively. The probabilities are renormalized between 0 and 1. The choice among one of the three first growth sites next to the seed is obtained from a random number generator which selects the appropriate probability segment. At the second step there are either five or six possible growing sites. The one selected is also chosen by considering all the growth probabilities and selecting one through a random number generator. It is clear that the most favored sites are those corresponding to the largest probability of growth. However, in this nonequilibrium kinetic process unfavorable sites are sometimes chosen.

In Fig. 6, we show the results of growth processes for a total of 800 "atoms" when $p_x = 0$ and for various p_y's ($p_y = 4, 6, 8, 10$). When p_x is almost equal to p_y the growth process leads to rather compact clusters with some vacancies. For a large difference between p_x and p_y with $p_x < p_y$, the growth leads to a whisker-like situation, as shown. If $p_x > p_y$, the growth results in regularly filling up successive layers on the substrate.

A three-dimensional simulation would lead to a lengthier computation time without bringing any supplementary insight to the process. The above result seems to be the first quantitative indication of the relative strength of anisotropic bonding for whisker growth.

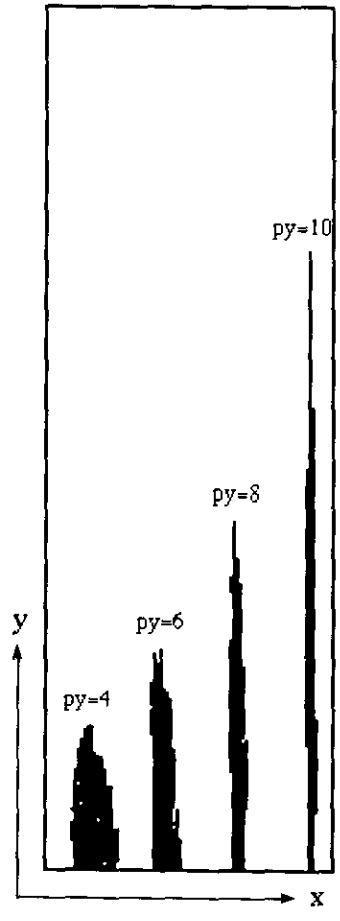

FIG. 6. Simulation of whisker growth in the anisotropic Eden model; see text for parameter definition.

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