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PASSIVATION OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SINGLE CRYSTALS BY FLUORINATION TREATMENTS*

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Summary

The passivation layer which is formed on the surface of single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by fluorination has been studied using various techniques. The amorphous nature of the layer has been established by transmission electron microscopy, its thickness and composition have been determined using Auger electron spectroscopy, and the influence of fluorination on ESR properties has been pointed out.

1. Introduction

The discovery of high- T_c superconductors has led to great activity in the search for new materials with improved characteristics.

Numerous studies have been devoted to the influence of cationic and anionic substitutions on the superconductivity onset. After debate on a possible increase of T_c by substitution of fluorine for oxygen in the crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, most authors now agree that the materials obtained from solid state reactions between oxides and fluorides do not exhibit any improvement of the critical temperature and, in fact, show even lower conductivities [1 - 7].

We have previously pointed out that atmospheric degradation of ceramics of high- T_c oxides could be prevented by low-temperature fluorine gas treatment [8]. A fluorination mechanism has been proposed, which can account for both fluorine analysis and weight uptake. Improvements in the

Meissner effect-shielding effect cycles have been achieved by further annealings. Other fluorinating reagents have been used, such as CF_4 [9] and NF_3 [5, 10].

We report here the procedure for formation and characterization of the fluorination layer obtained by fluorine gas treatment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals.

2. Experimental details

2.1. Crystal growth procedure

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ does not melt congruently in air or in oxygen at normal pressure. A peritectic decomposition occurs at about 1020°C in air. The flux method has therefore been chosen for crystal growth [11]. Attempts with "standard" fluxes such as borates or lead-based solvents were unsuccessful.

Crystal growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was performed from BaCuO_2 - CuO - $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compositions in which partial melting takes place in the temperature range 960 - 1000°C . Gold crucibles were chosen, in spite of their weak dissolution in the melt, because of the ease of separation of the single crystals [12].

For example, a mixture of CuO , BaCuO_2 and presynthesized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the ratio 62.5:32.8:4.7 (mol.%) was placed in a gold crucible which was then placed in a larger gold crucible. The thermal cycle was as follows: heating to 970°C at 60°C h^{-1} , maintenance at this temperature for 24 h and then cooling to 700°C at 3°C h^{-1} and from 700°C to room temperature at 60°C h^{-1} . When melting occurs, the melt overflows the inner crucible because of its high wetting properties and growth takes place in the outer crucible.

Thin platelets of up to $10\text{ mm} \times 6\text{ mm}$ and thickness 0.01 - 0.3 mm could be removed mechanically from the flux. Typical flux-grown $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals are shown in Fig. 1. Well-developed faces were shown by Laue photographs to correspond to the (001) plane. Resistivity and susceptibility

Fig. 1. Flux-grown crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

measurements confirm that the superconductivity onset of the crystals takes place in the 85 - 92 K temperature range.

2.2. Fluorination procedure

Fluorination was carried out between 20 and 100 °C in an experimental set-up previously built in our laboratory, using handling procedures described in ref. 13. The crystals were placed in a nickel boat. The reaction tube was evacuated and then filled with 1 atm of non-diluted fluorine gas. When the reaction temperature was reached, the crystals were kept in a moderate flow of fluorine for 5 h and allowed to stand overnight under 1.3 bar fluorine pressure. No colour change or weight uptake were noticed.

It should be noted that destruction of the crystals occurs when fluorination is carried out at higher temperatures, *i.e.* above 200 °C. This behaviour is similar to that previously observed for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics. In this case, the resulting compound is a yellow amorphous (oxy)fluoride, and no BaF_2 peak is detected, at least for $T_{\text{F}_2} \leq 300$ °C [14, 15].

2.3. Physical characterization

The crystals were characterized before and after fluorination using various physical techniques: X-ray diffraction, transmission electron microscopy (TEM), Auger electron spectroscopy (AES), electron spin resonance (ESR) and magnetization measurements. For TEM experiments, the equipment was a JEOL 1200 CX, with an accelerating voltage of 120 kV. The samples were ground and deposited onto a carbon grid. The AES measurements were performed using Physical Electronics 590 equipment with an accelerating voltage of 3 kV. The absorbed current was about 50 nA for scanned surfaces of $200 \times 200 \mu\text{m}^2$ to reduce possible migration of fluoride ions during the analysis.

ESR experiments were carried out on a Bruker ER 200 tt X-band spectrometer with a continuous flow cryostat. Magnetic fields were measured using a Bruker NMR probe gaussmeter.

3. Results and discussion

The presence of a fluorination layer has been established from TEM photographs obtained on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals fluorinated at $T_{\text{F}_2} = 20$ °C and $T_{\text{F}_2} = 100$ °C. This result is shown in Fig. 2 for a sample treated at $T_{\text{F}_2} = 100$ °C. Besides the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ substrate, a fluorinated layer can be observed. The amorphous nature of the layer formed on the surface of the oxide is clearly supported by the electron diffraction pattern (Fig. 2b). It can be seen that the fluorination layer is about 5000 Å thick in

Fig. 2. (a) TEM image of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal fluorinated at $T_{F_2} = 100^\circ\text{C}$ (1, substrate; 2, fluorination layer). (b) Electron diffraction pattern of the amorphous layer.

Fig. 3. Fluorine, oxygen and carbon AES profiles: (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal fluorinated at $T_{F_2} = 20^\circ\text{C}$; (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal fluorinated at $T_{F_2} = 100^\circ\text{C}$. Fluorine and oxygen AES profiles: (c) sample (a) annealed for 4 h at 350°C , in vacuum; (d) sample (a) annealed for 3 h at 550°C in air; (e) sample (b) annealed, 3 h at 550°C in air.

this part of the sample, a larger value than those generally deduced from AES profiles (see Fig. 3). The nature, composition and origin of the small grains in this layer have not been yet identified.

The thickness and composition of the amorphous layer formed at the crystal surface have been determined from Auger electron maps. For experiments at $T_{F_2} \leq 100^\circ\text{C}$, the crystal surface is fluorinated and a layer a few hundred ångströms thick is formed. Concentration profiles of fluorine and oxygen are shown in Fig. 3 for two different fluorination temperatures. At the outer surface of the layer, the fluorine to oxygen ratio is dependent on the reaction temperature: it increases with increasing T_{F_2} . For instance, at $T_{F_2} = 100^\circ\text{C}$ (Fig. 3b) the outer surface appears to be mostly formed of fluoride species.

Mohotonic decrease of fluorine concentration in the material is observed. Such behavior was previously found for similar experiments carried out on sintered ceramics of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Because of the open porosity and grain size inhomogeneity, the interface between the amorphous layer and the superconducting oxide in such materials was greatly extended [8].

When left in moist air, the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals deteriorated strongly in hydrolysis reactions with carbonation [16]. From

Fig. 4. X-Band ESR spectrum (4.2 K) of flux-grown crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ fluorinated at $T_{F_2} = 100^\circ\text{C}$.

AES profiles, the presence of carbon contamination can be detected to depths of several thousand ångströms. The protective properties of the fluorination treatment is illustrated in Fig. 3a, b, in which the thickness of the carbon-containing layer has been reduced to a few tens of ångströms.

To estimate the stability of the passivation layer, various annealings have been performed on the fluorinated crystals. After annealing for 4 h at 350°C in vacuum, the amorphous layer remains practically unchanged, as shown in Fig. 3c for a crystal prefluorinated at $T_{F_2} = 20^\circ\text{C}$. On the other hand, when the crystals are heated in air for 3 h at 550°C , the stability of the passivation layer is dependent on the temperature of the fluorination pretreatment; when $T_{F_2} = 20^\circ\text{C}$, fluoride ions almost completely vanish from the surface (Fig. 3d), whereas only a slight reduction of the thickness of the layer is noticed for $T_{F_2} = 100^\circ\text{C}$ (Fig. 3e).

As mentioned in many papers dealing with ESR in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics, no localized Cu^{2+} signal is observable in pure superconducting samples, whereas microwave absorption is observed at zero field [14]. This absorption has been attributed to the granular character of these ceramics (Josephson junctions). Microwave absorption has also recently been observed on single crystals [17] and attributed to twin boundaries. ESR experiments on as-grown $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals of dimensions $1 \times 1 \times 0.1 \text{ mm}^3$ show no Cu^{2+} signal or microwave absorption, which may indicate a limited number of Josephson junctions (domain walls). Treatment at $T_{F_2} = 100^\circ\text{C}$ gives rise to an anisotropic ESR signal corresponding to Cu^{2+} ($g_{\parallel} = 2.21$, $g_{\perp} = 2.05$) in a powdered (or disordered) state. This signal probably arises from the oxyfluorinated surface layer. Weak microwave absorption is observed at zero field, indicating that the bulk is still superconducting.

4. Conclusions

As previously shown for ceramics, the degradation process of single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in moist air is inhibited by fluorine gas treatment at

low temperature. This property can be ascribed to the formation of an amorphous (oxy)fluorinated layer at the surface. An XPS study is in progress on these materials to clarify the nature of bonding involved in the passivation layer.

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