Y–Ba–Cu–O ceramics interaction with H₂O

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Abstract. Effect of water vapour on the YBa₂Cu₃O_{7-x} ceramics of different density has been studied using Auger electron and X-ray photoelectron spectroscopy. The initial period of decomposition of this compound when exposed to H₂O is accompanied by Ba(OH)₂ deposition on the ceramic grain surface and partial reduction of copper to Cu₂O in the oxide. With this barium diffuses to free surfaces of ceramic grains. Degradation of HTSC ceramics proceeds by increase of thickness of the changed layer on free surfaces of grains. Violation of the initial composition may at first lead to some improvement of transitional characteristics T_c and ΔT_c and with their subsequent degradation, the transition width ΔT_c is in particular broadened. Dense ceramics possess higher resistance to a humid atmosphere.

1. Introduction

Degradation of HTSC ceramics YBa₂Cu₃O_{7-x} in a humid atmosphere is explained by decomposition of initial compound with precipitation of Ba(OH)₂, CuO and O₂ (Yan *et al* 1987).

2. Experiment

We have studied the variations of the elemental composition of the YBa₂Cu₃O_{7-x} ceramic grains after 20 days of its exposure in a hygrostat with 76% humidity. Samples with density ranging from 4.9 to 5.9 g/cm³ were prepared by hot pressing. YBa₂Cu₃O_{7-x} powder was prepared by solid-phase synthesis.

Auger-electron and X-ray photoelectron spectra of the sample surface were analysed using LAS-600 and XPS-800 (Riber and Kratos Cos respectively). Characteristics of the transition into the superconducting state were determined by temperature dependences of electrical resistance using the d.c. four-probe method.

3. Results and discussion

The surface of the samples, held in the hygrostat, was covered with a thin layer of greyish substance. According to the Auger-spectroscopy data, this layer consists of barium compound but does not contain copper. Yttrium is oxygen-deficient relative to the initial composition. Analogous data were obtained while studying fresh break of degenerated ceramics. However, the degree of variation of the grain surface composition in the depth of the samples was found to be much less.

Some results of the depth profile analysis of the ceramics using Auger-spectra, obtained on etching the surface of the samples as well as their breaks with Ar⁺ ions of the energy of 4 keV and etching rate of 4 Å/min, are shown in figures 1 and 2. It can be seen that in the layers that did not react with water vapour (~ 1200 Å), concentration of

Figure 1. Relative intensity of the Auger-spectrum of barium (584 eV) depending on the time of etching. (a) reference sample, surface and break identically, (b) surface and (c) break of a degenerated sample.

Figure 2. Relative intensity of the Auger-spectrum of oxygen (510 eV) depending on the time of etching. (a) reference sample, surface and break identically, (b) surface and (c) break of a degenerated sample.

barium and oxygen (as well as copper and yttrium, not shown in figures 1 and 2) corresponds to the level of the reference sample and is close to the stoichiometric ratio for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. With increase in the ceramic density from 4.9 to 5.9 g/cm³ the thickness of the degenerated layer on the ceramics grain surface decreases from ~ 1200 to ~ 100 Å.

Thus when H_2O affects the ceramics a migration of barium atoms from the depth of the ceramic grains to their surface takes place. Degradation of HTSC proceeds due to the change of composition of the grain surface layers near their free surfaces (pores, cracks and outer sides of the sample) and in sintered contacts of grains where the probability is initial deviation from stoichiometry $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and impurity localization (Antonova *et al* 1987). Increasing the ceramic density strengthens its resistance to the effect of water vapour.

This was also confirmed by electrical resistivity studies. Thus, after exposure to a humid atmosphere under equal conditions the electrical resistivity of the samples with density below 5.0 g/cm³ acquired a form which is typical for semiconductors. But a levitation effect in the magnetic field was observed. The ceramics up to a density of 5.4 g/cm³ remained superconducting at a significant change of the transition parameters and for samples with a ceramic density of 5.9 g/cm³ some improvement of the transition characteristics was observed (figure 3).

Grain surface investigation in the dense samples of the HTSC ceramics revealed no increase in concentration of barium atoms, i.e. the degradation processes does not propagate into the bulk of the sample at high density of the ceramics.

The effects noted can be explained using the suggested mechanisms of degradation of HTSC ceramics with migration of barium atoms towards the grain surface. Since the stoichiometric compound YBa₂Cu₃O_{7-x} has the highest temperature of the SC transition, deviation from the stoichiometry results in T_c decrease and broadening of ΔT_c . This is due to the displacement of the low-temperature part of the curve $\rho = f(T)$ at the relative stability of the transition onset position (see figure 3). If we assume that

Figure 3. HTSC ceramics resistivity vs temperature density. (a) 4.9 g/cm³, (b) 5.2 g/cm³ and (c) 5.9 g/cm³; (---) original samples, (—) after water vapour effect.

localization of the initial powder of the phase with the deviation of the stoichiometry relative to barium, i.e. $\text{YBa}_{2+y}\text{Cu}_3\text{O}_{7-x}$ type compound, that blocks the SC transition is greater, the deviation is stronger from the stoichiometry and that is one of the reasons for the absence of transition (on the transport current) in the nonsintered samples of a rather pure powder $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Antonova *et al* 1987; Antonova *et al* 1989). On prolonging the heating period for such samples a gradual increase of the transition temperature T_c , and narrowing of the transition width, ΔT_c , are observed (as in Antonova 1989) due to a gradual elimination or at least lowering of the barium concentration gradient over the ceramic grain. However, on the sintered grains the barium excess will be preserved in this case and diffusion of barium atoms to the surface of such contacts under exposure to H_2O will lead to the “cleaning” of the contact composition, i.e. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x} \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ process will take place resulting in deformation of the dependence $\rho = f(T)$ in the case of dense ceramics. During further development of the barium diffusion process, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x} \rightarrow \text{YBa}_{2-z}\text{Cu}_3\text{O}_{7-x}$ transformation occurs according to this model, followed consequently by the lowering of T_c and broadening of the transition (see figure 3) up to a complete loss of the superconducting properties. The water vapour effect on the HTSC ceramics for a rather short time improves its transition characteristics irrespective of the ceramic density.

Analysis of the X-ray photoelectron spectra of the studied samples showed (figure 4) that in the degenerated layer of all the samples which underwent the water vapour effect, copper was partially reduced to Cu^{1+} , with this the Cu^{1+} content in the degenerated layer of a fresh break of the ceramics with the density of 4.9 g/cm^3 was up to 50% of the total amount of copper. Heating of such degenerated samples at 920°C for 5 hr in air or in oxygen-saturated atmosphere restores the composition of the grain surface to the initial $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The characteristics of the transition are also partially restored.

Figure 4. X-ray photoelectron spectrum of the $\text{Cu}_{2p_{3/2}}$ shell: (—) original, (---) a degenerated sample.

4. Conclusions

Our results indicate that water effect on HTSC ceramics ($YBa_2Cu_3O_{7-x}$) proceeds in the surface boundary layers over their free surfaces with deposition of $Ba(OH)_2$ on these surfaces and partial reduction of copper in the oxide from CuO to Cu_2O with the release of a part of oxygen. The course of these processes is accompanied by the barium atom diffusion to the free surfaces of the ceramic grains and their contacts. Almost an equal relation of the concentrations of Cu^{2+} and Cu^{1+} is observed in the degenerated layer. The degradation process of the ceramics results in increase of the degenerated layer thickness on free surfaces of the ceramic grains.

References

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