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Problems of Obtaining Highly Textured HTSC Coatings

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Abstract

Bi-containing "2201" and "2212" high temperature superconductor (HTSC) coatings have been obtained on silver substrates and wires using solution techniques. At different thermal conditions at least two structure modifications of the "2201" precursor phase are formed. These modifications have different morphology, chemical composition and crystal structure. Features of the transition between the phases mentioned are discussed. Needle-like grains of the 2201 high temperature phase are shown to be textured along the wire axis. HTSC coatings of 2212 composition replicate the texture of the precursor phase 2201.

1 Introduction

For practical applications, superconducting wires and tapes are needed with critical current densities of about $10^4 - 10^5\,\mathrm{A/cm^2}$ at $T = 77\,\mathrm{K}$ in magnetic fields above 1 T.

The present paper reports some novel features of the kinetics of HTSC phase growth in coatings on curved surfaces. This problem is closely related to structural changes in theses materials. The solution of this problem will permit to obtain textured structures with high critical current densities.

2 Experimental

Specimens obtained as thick film coatings ($10-20\,\mu$m) deposited on silver wires were used for this investigation.

The coatings were prepared using a modified sol-gel route [1]. The coated wires were annelaed in air at 760 – 860 °C. The annealing time was varied from 1 to 56 hours. After annealing, the specimens were quenched to room temperature. Coatings such obtained were dense and practically free from pores.

Since the results of thermal treatment of the compounds studied depend on initial composition, the composition was kept constant during the experiments and equal to the stoichiometric ratio of the components. The concentration of cations in solution and in the coatings were tested both prior to and after thermal treatment using plasma atomic absorption and atomic emission spectroscopy [2].

Structural X-ray examination was performed on a D-500 diffractometer (Siemens) with CuK_α radiation. The results were processed using the software package "fit". Phase morphology and phase microchemistry were inspected with an JSM-820 electron microscope with an attached "Link-1000" microanalytical system. Concentrations errors, expressed in equivalent units, were Bi - 0.02, Sr - 0.03, Cu - 0.06, and Ca - 0.04.

3 Results and Discussion

Theoretical considerations based on elasticity theory show that the growth of needle-like crystals in thick coatings on cylindrical surfaces occurs non-uniformly in different directions. The free energy of such crystals has a minimum if the growth takes place with the longest axis along the cylinder generatrix. The probability of such growth rises with increasing cylinder curvature.

During the initial step of the experiment, an amorphous oxide-containing coating is formed with a composition similar to the Bi-containing "2212" HTSC [3]. Solid phase reactions stimulated by a thermal treatment result in the growth of crystallites within a precursor phase and, later, within the 2212 phase [3].

As was mentioned already, the crystallites formed within the Bi_2O_3-SrO-CaO-CuO-containing superconducting phase are equiaxed and small-sized and would therefore not have been oriented. This obstacle could be overcome by means of preliminary formation of precursor crystallites with needle habitus, achieving their uniform orientation and their transformation into superconducting 2212 and 2223 phases in the course of a thermal treatment. The final crystallites are supposed to inherit the orientation of the precursors and, consequently, their texture.

If the pyrolysis is accompanied by partial melting of the oxide coating, strontium and calcium cuprates

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Fig. 1. Electron microscopy image of needle-like crystals of Sr and Ca cuprates in the coating on an Ag wire.

Fig. 2. Electron microscopy image of cuprate decay and beginning formation of 2212 phase.

will be formed at the first stage of thermal treatment. These cuprates grow as needle-like crystals, reaching a length of the order of 400 μm, which are oriented along the cylinder generatrix. An electron microscopy image of such crystals is shown in Fig. 1. The crystals shown were grown on a silver wire with 0.5 mm diameter.

X-ray examination and electron microscopic studies indicate that the coating which surrounds the growing cuprate crystals maintains its status quo as a mixture of oxides, although the calcium and strontium content within this part of the coating appears to be reduced. Prolonged thermal treatment results primarily in the formation of the 2201 phase. It is followed by 2212 phase development, which is produced as a result of diffusion of elements between the cuprates and 2201 phase areas. A microphotograph of a zone where this process took place is reproduced in Fig. 2.

Formation of plate-like HTSC crystallites on the elongated cuprate crystals can also be observed. During the thermal treatment, the previously amorphous coating turns into the textured HTSC phase. The block structure of such a coating is presented in Fig. 3.

It should be emphasized again that this texturing is achieved due to the inheritance of the axial orientation of the precursor crystallites.

The perpendicular orientation of the c-axis of the HTSC plates results from the fact, that these grow parallel to the oxide layers. Their thickness is of the same order or even smaller than their lateral dimensions, the direct reason of texturing being surface effects. The phenomenon described occurs independent of the substrate shape (curved or flat).

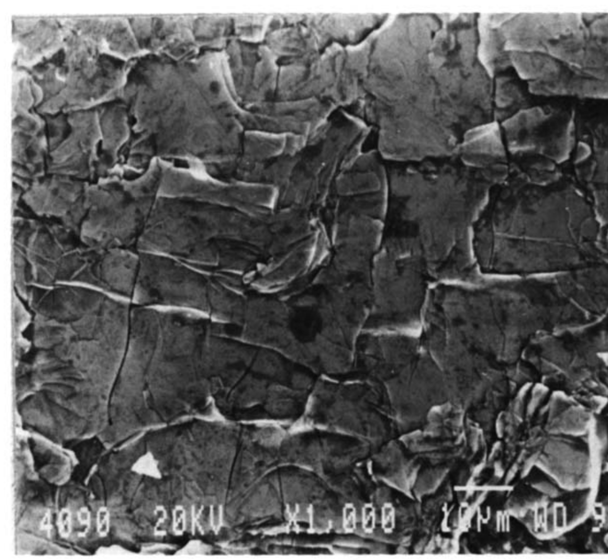

Fig. 3. The block structure of 2212 coating on an Ag wire.

Thus, the possibility of creation of textured HTSC coatings deposited onto curved surfaces by means of preliminary deposition of precursor phases has been proven. We note, however, that the proposed approach based on the preliminary growth of cuprates cannot be regarded as technologically perfect. The reason is that the "dissociation" of cuprate crystals which are large enough proceeds too slowly. Even prolonged thermal treatment does not result in full elimination of the cuprates, which may be an admixture negatively influencing the critical currents.

Below, we present a new alternative procedure for depositing HTSC coatings on curved surfaces. We found that the growth of non-equiaxed crystallites appears possible also in the 2201 oxide system, which could serve as precursor phase for HTSC. The results of structural and morphological investigation of various structures, which can be conventionally characterized as 2201-phase related, are described below.

With respect to the varied conditions of the deposition process (pyrolysis) and of the thermal treatment, two kinds of 2201 phase are distinguished: a high-temperature phase (designated phase I) formed at 840 – 870 °C, and a low-temperature phase (designated II) formed below 800 °C. In the intermediate temperature range, biphase coatings are obtained.

The low-temperature phase II is tetragonal with lattice parameters $\mathbf{a}$ = 5.390 Å, $\mathbf{c}$ = 24.571 Å, phase I is orthorhombic with $\mathbf{a}$ = 5.444 Å, $\mathbf{b}$ = 5.290 Å, $\mathbf{c}$ = 24.485 Å. X-ray diffraction patterns of the (200) lines of samples annealed for 24 h at different temperatures are reproduced in Fig. 4. (It should be noted here, that variations of the pyrolysis conditions permit to obtain either textured or non-textured products; the patterns presented in Fig. 4. were obtained during testing of non-textured samples).

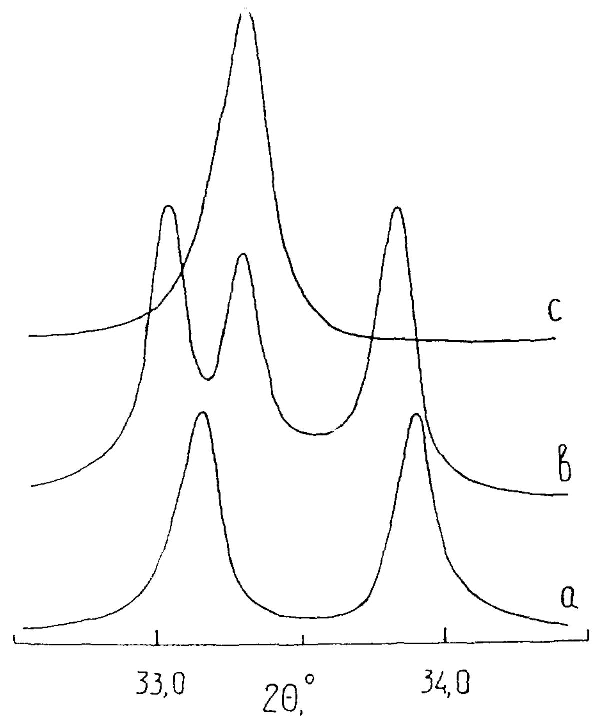

Fig. 4. X-ray diffraction patterns (200) for different "2201" phases. Annealing temperature: (a) 860 °C, (b) 840 °C, (c) 760 °C.

It can be observed, that the samples annealed at 860 °C and 760 °C are single-phase (patterns 4a and 4c). Annealing at 840 °C obviously leads to a two-phase coating (pattern 4b).

The grains of the low-temperature phase appear to be plate-like and are almost equiaxed within the plane perpendicular to the $\mathbf{c}$ axis. When the pyrolysis temperature was equal to or above 840 °C, a very high degree of texturing is observed. Grains of the orthorhombic high-temperature phase are needle-like, highly anisometric (length 30 – 40 μm, diameter ~ 1 μm), neighbouring crystallites tending to be parallel to each other.

Besides their distinguishing structural and morphological features, phases I and II have different chemical composition. Microanalysis gives evidence for the following concentrations of bismuth and strontium in phase II crystallites: Bi 2.27 ± 0.02, Sr 1.70 ± 0.03 per 1 atom of Cu. Within the range of temperatures studied, the Bi/Sr ratio does not depend on temperature. Thus, we conclude that the tetragonal modification of the 2201 phase is characterized by rigorous stoichiometric equilibrium between Bi and Sr.

In the high-temperature phase, the Bi and Sr concentrations are approximately 2 (Bi 2.09 ± 0.02, Sr 1.93 ± 0.03) to 1 atom Cu. These values were shown to be independent of the duration of the thermal treatment. Since the temperature interval in which the orthorhombic phase is formed is very narrow, we cannot conclude definitely whether the bismuth and strontium concentrations are temperature dependent.

Following the formation, each of the phases appeared to exist within a definite temperature range. The transformation temperature is near 840 °C. Since the chemical composition of the two phases is different, the phase transition takes place according to a diffusion mechanism associated with the decomposition of the solid solutions. It is seen that the transition from orthorhombic to tetragonal is accompanied by precipitation of Ca and Sr cuprates. At the reverse transition, the cuprates are dissolved in the tetragonal phase.

Thus it appears evident, that similar to HTSC coatings formed from needle-like cuprate crystals, textured coatings obtained in this case are the result of geometric effects. Thermal treatment has to be carried out in such a way that HTSC formation is preceded by the generation of needle-like orthorhombic phase. In this case, the coating in its final state is textured both by $\mathbf{c}$ axis orientation normal to the surface and in the $\mathbf{a} - \mathbf{b}$ plane since the morphology of the 2201 phase is inherited by the HTSC phase.

HTSC coatings on silver wires with 0.55 mm diameter are characterized by $T_c = 80\,\mathrm{K}$ and a critical current density $J_c = 10^5\,\mathrm{A/cm^2}$ at 4.2 K, measured by a contactless method.

4 Conclusions

1. The influence of a geometrical factor (the substrate curvature) stimulates the perfect texture of the superconducting Bi-based coatings.
2. To obtain a high degree of texturing of Bi-2212 superconductors, the solid state reaction should be carried out through the intermediate orthorhombic 2201 phase.
3. Highly textured Bi-containing coatings on curved metallic substrates (wires) are highly promising as the basic method for a future technology for wires and cables.

References

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