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Recrystallization of $YBa_2Cu_3O_x$ superconductors in vacuum

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$YBa_2Cu_3O_x$ ceramics were recrystallized in vacuum at high temperatures. Recrystallized layers consisting of small grains were observed near the surfaces of the original large-grain 1 2 3 ceramics. The small grains consisted of transformation twins and were identified to orthorhombic 1 2 3 using X-ray diffraction. As vacuum annealing time increased, the thickness of the recrystallized layer increased. The relationship between the thickness and the annealing time showed a linear relationship and an effective diffusion coefficient of $6.25 \times 10^{-10}\,cm^2 s^{-1}$ The recrystallized layer showed a critical temperature of 90 K.

1. Introduction

A high-T_c ceramic superconductor was discovered by Bednorz and Muller [1]. This discovery showed high-T_c superconductivity with the critical temperature of 35 K and opened a new field of oxide superconductors. The discovery of Y–Ba–Cu–O superconductor [2] with a T_c value of 93 K further stimulated the field, as liquid nitrogen could be used as a cooling agent, making possible practical applications of these superconductors.

A few studies reported observations of recrystallization phenomena in ceramics. Recently, a recrystallization phenomenon coupled with grain boundary migration was discovered in PLZT (Pb–La–Zr–Ti–O) ceramics after heat treatment in air [3]. These authors claimed that the Pb concentration changes in the solid-solution range of PLZT produced a sufficiently large diffusional coherence strain to induce the grain-boundary migration because of high vapour pressure of Pb at the heat-treatment condition. The grain boundary migrated to increase the boundary curvature, leaving behind a new solid solution having a different composition from the initial material, and the recrystallization occurred by nucleating new alloy grains from the specimen surface. Many studies have concentrated on microstructural modifications of high-T_c superconductors, because practical applications of these materials have been hindered by microstructural impurities and a random arrangement of the superconductor grains. However, recrystallization has never been reported in high-T_c superconductor materials to our knowledge.

This paper will report a recrystallization phenomenon observed in bulk $YBa_2Cu_3O_x$ (1 2 3) materials after heat treatment in vacuum. The objectives of this study are to study the microstructure of the recrystallized 1 2 3 materials, to determine the crystallographic phase of the new grains, to verify if the recrystallization phenomenon can be attributed to a diffusion process, and to test the superconducting transition temperature of the recrystallized grains.

2. Experimental procedure

We used a standard powder-processing technique for preparing $YBa_2Cu_3O_x$ (1 2 3) ceramics, which consists of mixing powders of Y_2O_3, $BaCO_3$, and CuO followed by solid-state reaction at high temperature. To obtain a complete reaction, it is necessary to use additional cycles of grinding, pelletizing and reaction. Appropriate amounts of powders were mixed and ground in an agate mortar for 1 h for each 10-g batch. 10 g pellets of the powder mixtures were pressed in a 1.75-cm steel mould at 20 MPa pressure. The pellets were reacted on a cleaved face of a single crystal MgO at 920 °C for 24 h. After the first reaction, the pellets were ground with an agate pestle and mortar for 30 min, and then repelletized for the second reaction following the same procedure as used for the first reaction. The pellets, after the second reaction, were ground with an agate pestle and mortar for 30 min. 2.5 g pellets of the precursor powder were pressed in a 1-cm steel mould at 80 MPa and sintered under flowing oxygen at 100 $cm^3\ min^{-1}$ on cleaved single-crystal MgO at 980 °C for 24 h with a final furnace cool to 450 °C, a 10-h hold at 450 °C, and a furnace cool to room temperature. Resulting pellets were sliced to 1-mm-thick bars using a diamond saw. The bars were vacuum ($\sim 10^{-4}$ Torr) annealed on cleaved single crystal MgO at 900 °C for various lengths of time, ranging from 1–50 h. After vacuum annealing at 900 °C, the furnace was backfilled with oxygen, and the bars were cooled to 450 °C under flowing oxygen at 100 $cm^3\ min^{-1}$, held at 450 °C for 10 h, and finally cooled to room temperature.

0022–2461

The microstructure of cross sections of the samples was observed and the thicknesses of the recrystallized layers were measured using an optical microscope with polarizer. Phases of the original and the recrystallized bar samples were determined using X-ray diffraction (XRD). The superconducting transition temperatures were measured using a d.c. four-point probe method. Four contacts were made of Ag epoxy, and temperatures were measured using a diode.

3. Results and discussion

Fig. 1a shows a typical polarized light image of the microstructure of a cross section of a 1 2 3 sample annealed in vacuum at 900 °C for 17 h. The image consists of two regions. The central region of the sample consists of typically large 1 2 3 grains (average grain size = 51 μm). The 1 2 3 grains show twin structures in the polarized light. The outside layer near the surfaces of the sample consists of recrystallized fine grains. Even though the image shows a limited area of the cross section, due to the magnification of the microscope used in this study, the interface between the fine grain layer and the original large grain area appears not to be flat but to have a saw-tooth structure. Because of the limited magnification of the optical microscope used in this study, it was impossible to observe whether the fine grains also show twin structure. To increase the size of the recrystallized grains, a bar sample was annealed at 900 °C for 50 h.

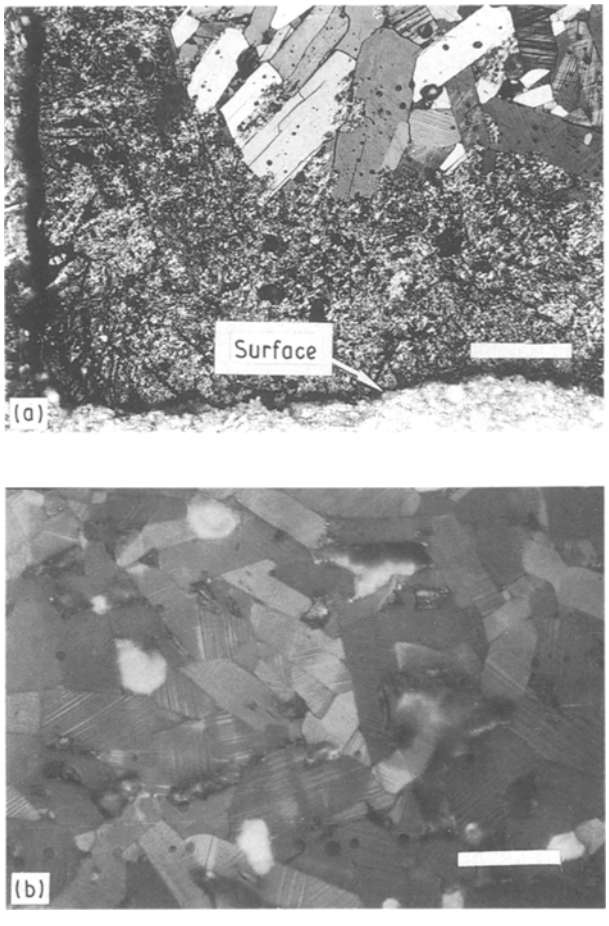

Figure 1 Polarized light images of $YBa_2Cu_3O_x$ samples vacuum annealed at 900 °C for (a) 17 h, bar = 50 μm; (b) 50 h, bar = 20 μm.

The microstructural observation of the cross section of the sample showed that the whole cross section of the sample consisted of recrystallized small grains (average grain size = 8.8 μm) compared to the original sample. Fig. 1b shows a polarized light image of the microstructure. The morphology of the small grains is similar to that of the original large 1 2 3 grains, and the small grains also show twin structure, which may indicate that the small grains are orthorhombic 1 2 3.

Fig. 2 shows the XRD patterns of original and vacuum-annealed $YBa_2Cu_3O_x$ specimens. Fig. 2a is a typical XRD pattern for the powder of an original sample. The pattern is well matched to the published pattern of the orthorhombic 1 2 3 phase. Fig. 2b shows an XRD pattern of an original bar sample. Except for several unseparated peaks, major peaks are well matched to the published peaks of the orthorhombic 1 2 3 phase. The reason why several peaks were not separated was due to the possible presence of preferred orientation due to directional pressing of powders. Fig. 2c shows the XRD pattern of the surface of a bar sample annealed in vacuum at 900 °C for 50 h. Major

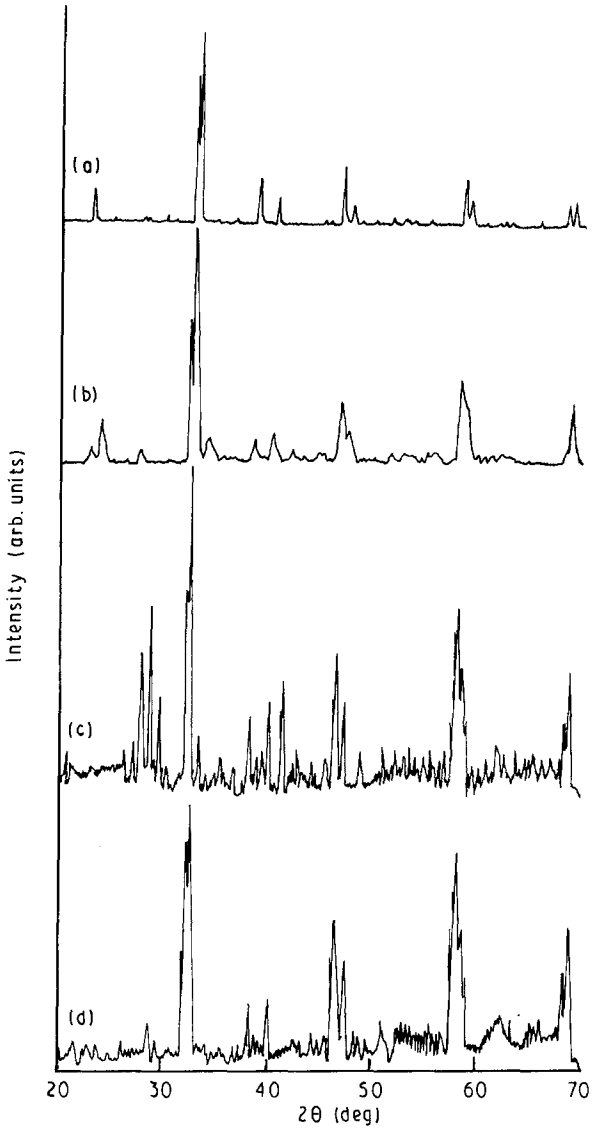

Figure 2 XRD patterns of $YBa_2Cu_3O_x$ samples. (a) Powder; (b) bar sample before vacuum annealing; (c) an original surface; (d) a surface after being ground off ~ 0.1 mm layer of a bar sample annealed in vacuum at 900 °C for 50 h.

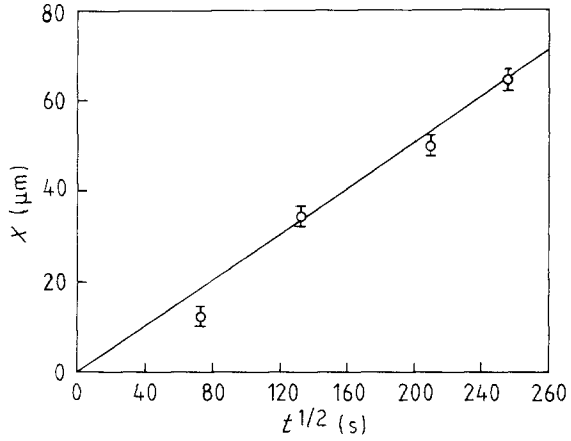

Figure 3 Relationship between recrystallized layer thickness and square root of annealing time for samples annealed in vacuum at 900 °C.

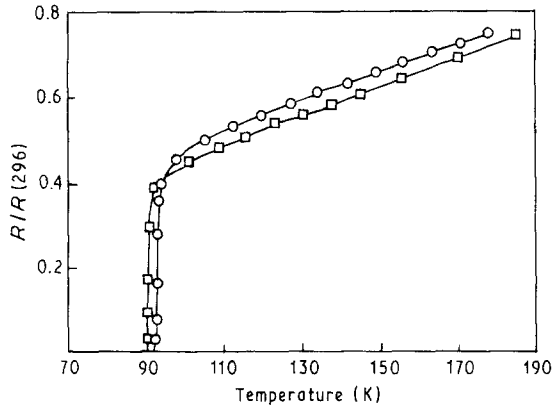

Figure 4 Temperature against relative electrical resistance for an original and a recrystallized $YBa_2Cu_3O_x$ sample. (○) original sample; (□) recrystallized sample.

peaks are fairly well matched to the published orthorhombic 1 2 3 peak, but extra peaks, which are well matched to the published peaks of $BaCuO_2$ (0 1 1) phase, are also observed in the pattern, which indicates that the surface of the vacuum annealed sample contains 0 1 1 impurities. Fig. 2d shows an XRD pattern of the vacuum-annealed bar sample after a ~ 0.1 mm layer was ground off from the original surface. The peaks representing 0 1 1 impurities were not observed in this pattern, but major peaks are well matched to the published peaks of the orthorhombic 1 2 3 phase. Compared to the peaks for the original sample (Fig. 2a, b), the peaks for the vacuum annealed sample showed small extra peaks on the sides of the major peaks. Those extra peaks were probably caused by partial lattice distortion due to improper stoichiometry or defects. The grains in the sample were recrystallized in vacuum, so that the lattice may be defective and be slightly different from the 1 2 3 lattice formed in air or oxygen atmosphere.

The $YBa_2Cu_3O_x$ ceramics may be depleted of oxygen in vacuum at high temperature, and diffusional coherence strains may be increased to a degree such that a recrystallization process, as in the case of the recrystallization of PLZT [3], occurs. Fig. 3 shows the relationship between a recrystallized layer thickness and the square root of annealing time for the samples annealed in vacuum at 900 °C. The figure shows a linear relationship, which is usually observed for the diffusion process, and an effective diffusion coefficient was calculated based on following the equation using a least-square-fit method.

$$X = \sqrt{(Dt)} \quad (1)$$

The value of the effective diffusion coefficient was 6.25×10^{-10} cm^2 s^{-1}. The nature of diffusing species controlling the recrystallization is not known in this study. The diffusion coefficient of oxygen ions was reported as $0.035 \exp(-1.3\,\text{eV}/kT^{-1})$ cm^2 s^{-1} for $YBa_2Cu_3O_7$ superconductor ceramics using electrical resistivity data near the tetragonal–orthorhombic transition temperature [4]. The diffusivity value in this study was two orders of magnitude lower than the value calculated using the reported diffusion coefficient at 900 °C (9.09×10^{-8} cm^2 s^{-1}). This discrepancy was probably due to the difference in diffusion processes controlling different phenomena. The resistivity changes were probably due to grain-boundary diffusion, in which the diffusion coefficient is much higher than that of the bulk diffusion for the recrystallization process.

Fig. 4 shows resistivity against temperature curves for original and recrystallized samples. The original sample shows zero resistance at 90 K; the recrystallized sample shows a little lower T_c than the original sample, but similar superconducting transition characteristics, which indicates that the recrystallized grains are superconducting orthorhombic 1 2 3 phase. This observation is well matched to the previous observations made in this study.

4. Conclusions

This study has shown that at high temperature, when $YBa_2Cu_3O_x$ (1 2 3) ceramics are annealed in vacuum, recrystallization occurs. Microstructural examination showed that recrystallized small-grain layers were formed from the surfaces of the original large grain 1 2 3 ceramics. The small grains consisted of transformation twins, which are always observed in orthorhombic 1 2 3 ceramics. XRD studies showed that the recrystallized small grains were orthorhombic 1 2 3. As vacuum annealing time increased, the thickness of the recrystallized layer increased. The relation between the thickness and the annealing time showed a linear relationship with an effective diffusion coefficient of 6.25×10^{-10} cm^2 s^{-1}. The recrystallized sample showed T_c of near 90 K, which is similar to an original orthorhombic 1 2 3 sample.

Acknowledgements

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