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Residual surface stress measurements in $YBa_2Cu_3O_x$ superconductors

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Abstract

XRD and residual surface stress ($\sin^2 \psi$) measurements were carried out on $YBa_2Cu_3O_x$ superconductors with varying oxygen stoichiometry ($6.3 < x < 7.0$). Slopes of the surface strain versus $\sin^2 \psi$ were plotted against oxygen content for certain reflections. Compressional surface stress has been found along the *c*-axis, while a tensile surface stress has been observed along the *ab*-plane. Both surface stresses were found to vary slightly with oxygen content. These findings qualitatively agree with a very small hydrostatic pressure effect on T_c for fully oxygenated $YBa_2Cu_3O_x$ ($x = 7$) compared to oxygen deficient material at the surface.

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Keywords: X-ray diffraction; $\sin^2 \psi$ analysis; Surface residual stress

1. Introduction

Optimization of the mechanical and superconducting properties of high-temperature superconducting materials continues to challenge physicists, material scientists and engineers. Microstructural defects are inherent in the manufacturing process of these materials. Residual stress may develop from certain operations (deformation, substitutions, heating, etc.) and will leave the material in a stressed condition even if all external forces have been removed. In this study, for example, residual surface stress was found to vary with changing the oxygen content in $YBa_2Cu_3O_x$.

The residual stress is usually measured either by mechanical relaxation, which is a very slow destructive method, or by X-ray diffraction, a relatively fast non-destructive method.

Two techniques are commonly used in X-ray analysis of stress in HTSC materials: line (width) profile analysis [1] and measurements of the shift in

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d-spacing [2,3]. The *d*-spacing shift analysis is more direct and easier to perform and commonly referred to as $\sin^2 \psi$ analysis. This technique requires obtaining the XRD diffraction pattern (θ–2θ scan) at different inclination angles, ψ. Using different inclination angles causes a shift in the peak position and some peaks may disappear from the diffraction patterns owing to preferred orientation. The shift is in principle, a measure of the residual stress [2–5]. The accuracy of this method increases when the analyzed peaks are selected at $\theta > \psi_{\max}$. Effectively, what is being measured is a surface stress to a depth of about 10 μm, which is the approximate average penetration depth of the X-ray beam [4].

The lattice constants in $YBa_2Cu_3O_x$ have been found to vary with the oxygen content (x). These changes are expressed in terms of orthorhombicity $(b - a)/(b + a)$ which decreases to zero near $x = 6.48$ where the structure becomes tetragonal. Basically, the orthorhombicity is a measure of the stress in the $a - b$, but gives no information about the stress along the *c*-axis, which is readily obtained using the $\sin^2 \psi$ analysis.

The objective of this paper is to use XRD pattern obtained at different inclination angles to investigate the residual surface stress introduced in $YBa_2Cu_3O_x$ upon changing the oxygen contents.

2. Experimental

To minimize the effects of sample processing on the residual stress, all samples were prepared under the same heat treatment and were pressed to the same pressure (5 tonne/in.^{2}). $YBa_2Cu_3O_x$ superconductors were prepared using a solid-state reaction technique [6]. Each desired oxygen content has been obtained using two sets of samples: by increasing the oxygen content in an oxygen-depleted sample and by reducing the oxygen content in a fully oxygenated sample. Samples have been annealed for different annealing times at 600 °C in nitrogen to reduce the oxygen or in oxygen to increase the oxygen contents. Samples were quenched to liquid nitrogen temperature using an argon gas cover. To reduce changes in oxygen contents at the surface, all magnetic and XRD measurement were performed immediately after preparation. The variation of the *c*-axis has been used to obtain the oxygen content in these samples. The oxygen content varied between 6.32 and 7.0 and transition temperature (T_c) in the range of 0.0–91.9 K.

A vibrating sample magnetometer PAR-4500 was used to measure the T_c by monitoring the magnetization response as the temperature increases in the presence of a low magnetic field (~20 Oe). These values have been found to agree with T_c values obtained using variation in the *c*-axis as a function of the transition temperature.

Structural refinement and stress analysis were performed by X-ray diffraction (XRD). XRD patterns were obtained using a computer-controlled Philips PW1700 diffractometer equipped with Cu Kα radiation operating at 40 kV and 30 mA. The XRD patterns for all samples with varying oxygen content were first indexed and refined (at zero inclination angle, $\psi = 0°$) to obtain the lattice parameters for each sample. The XRD patterns required for residual stress ($\sin^2 \psi$) measurements were obtained from the samples at three different inclination angles ψ (10°, 20° and 30°).

3. Results

The XRD pattern obtained for the as-prepared fully oxygenated superconductor was found to have an orthorhombic structure with lattice parameters $a = 3.82(1)$, $b = 3.88(5)$, $c = 11.68(8)$, which is in general agreement with published data [7]. This sample is a superconductor with $T_c = 90.2$ K.

By contrast, the XRD pattern for the de-oxygenated ($x = 6.32$) sample gives a tetragonal structure which is not superconducting. As already noted for all of the samples studied, the oxygen content varied from $x = 6.32$ to 7.0 and T_c from 0.0 to 91.9 K. Also, for these samples, the results of the calculated structures were in agreement with published data for YBCO tetragonal and orthorhombic phases [7–11].

The variation in lattice parameters with oxygen content in YBCO materials has been the subject of extensive investigation by many research groups [7–10]. The variation of the *c*-axis with oxygen content has been found to decrease linearly as the oxygen content increases [7,8]. Independent literature data obtained by iodometric titration, X-ray diffraction analysis and oxygen weight loss [7,9,10] were used to fit a linear relationship relating the oxygen content and *c*-axis length. This is compiled from the *c*-axis and the oxygen content data obtained by Vanderah et al. [9], Parks and co-workers [10] and Jorgensen et al. [7] and applying a linear fit to obtain the following:

$$x = 73.47 - 5.701c \tag{1}$$

with a reliability of fit = 0.98, where x is the oxygen content and c is the lattice parameter of the *c*-axis. The relation was used to obtain the oxygen content for each sample after obtaining the refined value of the *c*-axis from the XRD patterns. The variations of the refined values for a and b parameters with oxygen were in good agreement with the literature data [7,8,10].

In an effort to obtain the residual surface stress caused by changing oxygen content, XRD patterns were obtained for each $\psi = 0^\circ$, 10°, 20° and 30° inclination angles and used to obtain the shift in *d*-spacing for each sample. Elasticity theory relates the strain (ε) to the relative variations in *d*-spacing according to the following relation [4,5]:

$$\varepsilon = \frac{d_\psi - d_{\psi=0}}{d_{\psi=0}} = \left(\frac{1+\nu}{E}\right)\sigma_\psi \sin^2\psi \tag{2}$$

where E is Young's modulus and ν is Poisson's ratio.

The variations in residual surface stress (σ_ψ) are reflected as changes in the slopes in ε versus $\sin^2\psi$ representation. From this data the slopes for (0 0 6) and (1 1 5) planes obtained for samples with different oxygen content are presented in Fig. 1. Within the accuracy of our measurement in the orthorhombic phase, the residual surface stress along the *c*-axis (0 0 6) is compressive (bottom line) and for the mixed plane (1 1 5) it is tensile (top line). These results can be represented as changes in the surface stress versus the transition temperature T_c as shown in Fig. 2.

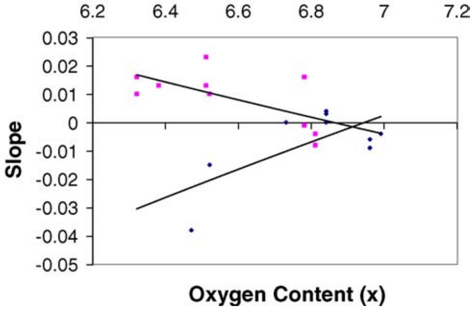

Fig. 1. Variation of slopes with oxygen content for (1 1 5) top and (0 0 6) bottom.

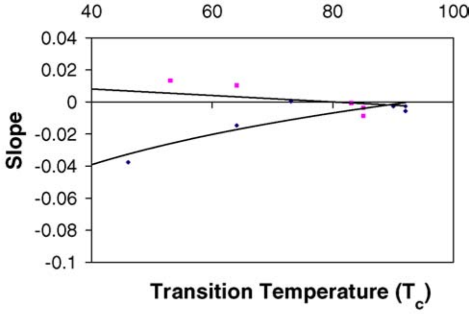

Fig. 2. Variation of slopes with transition temperature for (1 1 5) top and (0 0 6) bottom.

4. Discussion

It is relatively recent that attempts have been made to measure the residual stress in HTSCs [1–3,16]. However, extensive study on the effect of residual stress should be made to achieve more systematic understanding of growth mechanisms, process technology, weak links, fracture mechanisms, etc. For YBCO material, residual surface stress measurements show a small change in the residual surfaces stress for (0 0 *l*) planes and mixed planes (*h k l*) with increasing oxygen content. These findings can be understood in view of occupation of the O(1) and O(5) sites. In the tetragonal structure, a and b lattice constants are equal, and the O(1) and O(5) sites are equally occupied. As oxygen is added to the structure and at a critical value ($x = 6.48$), a phase transformation occurs to form the orthorhombic structure with the O(1) sites that occupy the one-dimensional chain along the *b*-direction and leave the O(5) sites empty. The lattice constant b increases while the lattice constant a decreases. As a result, strain in the *ab*-plane would be expected to increase along with the residual stress at the surface. The increased strain in *ab*-plane, would then be expected to be combined with a decrease in the lattice parameter along the *c*-direction. It is common to all residual stresses in isotropic solids that a tensile stress in one direction is balanced with a compressive stress in another. However, YBCO is highly anisotropic with T_c and *c*-axis lattice parameter dependant on oxygen content and the arrangement of oxygen vacancies in the Cu–O chains.

Results obtained from the (0 0 6) reflection indicate that as the oxygen content changes, the slope remains negative corresponding to a compressional surface stress. The variation in compressional surface stress may be the result of small changes in the *c*-axis parameter or attributed to the arrangement of oxygen vacancies and oxygen atomic order–disorder within the lattice structure [12–15]. Similarly, XRD reflections obtained from mixed Miller indices (*h k l*) indicate that a positive slope is present that corresponds to the presence of surface residual tensile stress. Again, the variation in slope with oxygen content may be a consequence of changes to the *a* and *b* lattice parameters or the re-arrangement of oxygen within the crystal *ab*-plane configuration. Also, the role played by YBCO's microstructure was not studied in this work and the effect of, i.e. grain boundaries, twins, dislocations and the like on residual surface stress can be significant.

Ultimately, the atomic structure–surface stress relationship is of interest in understanding and controlling the internal bulk material and interfacial residual stress state for YBCO. It is well known in metallic systems that certain crystallographic planes and directions can be favored for slip by deformation (i.e. the orthorhombic *c*-axis (0 0 1) planes in Ga or the tetragonal *ab*-axis (1 1 0) planes in β-Sn) [17]. However, in YBCOs the behavior is similar to a brittle ceramic material with covalent and ionic type bonding, where deformation and slip systems are not commonly found or expected in these material systems. As a consequence, new approaches may be necessary to improve their mechanical properties (such as fracture toughness) in order to make them viable for industrial applications. Therefore, further understanding of the role that residual stress plays in regards to this materials structure, properties and defects is necessary, and perhaps new combinations can be explored such as were recently found for α + β-sialons to toughen silicon nitride ceramics [18].

5. Conclusions

YBCO samples of different oxygen content were prepared by annealing in O_2 and N_2 gases for different times at 600 °C. X-ray diffraction patterns at different inclination angles were obtained for all samples and for the relation between surface strain and $\sin^2\psi$. Slopes of the surface strain versus $\sin^2\psi$ that are proportional to the residual surface stress were plotted against oxygen content for certain reflections (0 0 6) and (1 1 5) in the orthorhombic phase. Different behaviors for the two reflections (0 0 6) and (1 1 5) were noted and attributed to compressional and tensile surface stresses. The surface stress along the *c*-axis is compressional with varying oxygen content while the residual surface stress in the *ab*-plane is tensile. This may explain the hydrostatic pressure effect for oxygen-deficient YCBO compared to a very small (nearly zero) effect for fully oxygenated material ($x = 7$) at the surface.

Several shortcomings were encountered in using this technique. First, XRD peaks were found to disappear at higher inclination angle due to preferred orientation. Second, there is separation of the residual surface stress in the *ab*-plane. Third, the X-ray $\sin^2\psi$ analysis technique only evaluates surface stress. Improvement in using this technique can be achieved by lowering the degree of preferred orientation in the samples, using additional smaller inclination angle, ψ, preparation of thinner samples and/or removal of surface layers for thick samples to probe for surface-to-bulk stress effects and stress gradients as a function of depth.

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