APPLICATION OF NEUTRON DIFFRACTION NDE TO HIGH-TEMPERATURE

SUPERCONDUCTING COMPOSITES*

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INTRODUCTION

Since the discovery of superconducting materials with relatively high transition temperatures (T_C), there has been a considerable effort both to understand the reason for the high T_C and to improve the mechanical properties, (the latter has been a limiting factor for practical applications). The $YBa_2Cu_3O_{7-\delta}$ (YBCO) compounds have received considerable attention because of their high T_C and high upper critical magnetic field [1-3]. Additions of silver have recently been shown to improve the mechanical properties (toughness and strength) of these compounds [4]. Furthermore, the addition of the Ag can improve the conductive path between grains of superconducting YBCO and possibly help reduce the "weak-link" effect [5]. Note that whereas the addition of a low-volume fraction of silver does not adversely affect the superconductivity the introduction of transition metals to YBCO can have a detrimental effect on the superconducting properties. Also, the addition of silver has a minimal affect on the stress free lattice spacing. During fabrication of YBCO/Ag composites, differential thermal expansion upon cooling can lead to potentially troublesome residual stresses. Since the Ag contracts more than the YBCO, good bonding between the ceramic and silver could lead [6] to tensile stresses in the silver and compressive stresses in the YBCO for relatively small percentages of Ag. These residual stresses could lead to premature failure of the composite, debonding of the YBCO and Ag, and/or microcracking, which will affect the flow of superconducting current and the life expectancy of components made from this material. An understanding of the nature and magnitude of these stresses will help improve the design of these composites.

Neutron diffraction is a powerful method for measuring bulk residual strains, from which residual stresses can be calculated [7]. Neutrons can provide a bulk measurement because they can penetrate deeper than X-rays. In the present work, the Intense Pulsed Neutron Source (IPNS) and General Purpose Powder Diffractometer (GPPD) at Argonne National Laboratory were used to measure the residual thermal strains in YBCO composites. The neutron diffraction measurements have been used to assess (a) the magnitude of the thermal residual tensile stresses in the Ag, (b) the role of Ag in creating bulk stresses in the YBCO, (c) the occurrence of yielding in the Ag, and (d) the effect of

variations in Ag content on the strain of the composite constituents and on the YBCO stoichiometry.

Sample Preparation

Samples discussed here are fabricated from a mixture of YBCO and Ag powders, with 0, 15, 20, and 30% Ag by volume. The YBCO powder was made by solid-state reaction of the constituent oxides Y_2O_3, CuO and BaO. Powders of Y_2O_3, CuO, and $BaCO_3$ were mixed in appropriate proportions and were wet ball milled for approximately 12 h. The dried powder was calcined at 890°C for 24 h and then crushed into fine powder. The calcination and grinding procedures were repeated three times. After milling, the calcined powder had a measured average particle size of ~5 μm. The phase composition of YBCO powder was confirmed by X-ray analysis. The composites of YBCO with Ag were made by mixing various amounts (10-30 vol%) of Ag powder with YBCO powder. The Ag powder had a particle size range of 2-3.5 μm, as indicated by the supplier. Both YBCO and composite powders were formed into rectangular bars, (~5.1 x 0.6 x 0.3 cm) by uniaxial pressing in a steel die at 150 MPa. Rectangular bars of composite YBCO/Ag were sintered in flowing O_2 at 930°C for 4 h and then annealed for 8 h from 435 to 385°C. Examination of polished surfaces of sintered YBCO/15% Ag bar specimens by SEM showed that the Ag phase was randomly distributed in discrete globules. Furthermore, little or no preferred orientation of Ag was observed next to the YBCO. The density of the sintered specimens was observed to increase with increasing Ag content. A density of 95% theoretical was obtained at 30 vol% Ag content. The increase in density probably occurs because the Ag acts as a sintering aid. Examination of the fracture surface of a sintered specimen of YBCO/20% Ag showed a typical grain size of 15 μm. These grains are about twice as large as those for YBCO specimens without any Ag addition. This increase in grain size is believed to be due to the presence of a liquid phase formed as a result of Ag addition. The resistivity was measured by a conventional four-probe technique. The critical current density values were determined with a criterion of 1.0 μV/cm at 77 K and zero magnetic field.

Neutron Diffraction Using the Intense Pulsed Neutron Source

Thermal neutrons with velocities of up to 1000 m/s are of interest for neutron diffraction. At these energies, the wavelengths are on the order of the lattice spacing and Bragg's Law of diffraction can be applied. In the experiments described here, Bragg's Law is used first to determine the lattice spacing d for a particular hkl reflection from both YBCO and Ag averaged over a volume of the strain-free powder. The stressed composite fabricated from these powders is examined next. The lattice strain associated with the hkl plane of a given phase in the composite is given by

$$e = (d - d_0)/d_0 ,$$

where d_0 is the unstrained hkl spacing (powder) and d is the spacing for the composite.

Fast neutrons from the IPNS are moderated and produce beams at various instruments such as the GPPD, which is used for powder diffraction experiments. The GPPD is about 20 m from the target. Neutrons are detected with banks of ^{3}He proportional counters (140 total) encircling the sample chamber on a 1.5-m scattered flight path, at 20°, 30°, ±60°,

±90°, and ±148° relative to the neutron forward direction. Lattice spacings can be measured to an accuracy of ±0.0002 Å. The main advantage of the pulsed source is that many diffraction peaks can be measured at the same time. Results reported here combine the data from the 90° and 148° detectors.

Experimental Results

Figure 1 shows the average bulk strain at room temperature in the Ag as a function of volume percent Ag in the composite and the crystallographic direction. The Ag diffraction peaks for which data are presented are clearly isolated from the YBCO diffraction peaks. The potentially complex loads and the relatively large error in absolute measurement of strain makes it difficult to reach any conclusions by comparing strains in various crystallographic directions. However, there is a trend toward decreasing Ag strain as the Ag volume fraction increases (the relative error in strain between samples of varying Ag content is about half the uncertainty in the absolute values). The strain, however, is expected to be proportional to the difference between the thermal expansion coefficient of Ag and that of the composite (which increases with increasing Ag) [8]. The difference between the thermal expansion coefficients of Ag and YBCO is about $2 \times 10^{-6}/°C$. An increase in Ag content from 15% to 30% should increase the composite coefficient of expansion by about 2%. The observed decrease in strain is much larger than can be explained by the ~2% change in thermal expansion coefficient. It is possible that the strain is relieved by creep, microcracking or that the Ag is yielding. Analysis of the diffraction peak full-width-at-half-maximum (FWHM) shows insignificant broadening, which is consistent with little or no yielding. The Ag hydro-static stress calculated from the strain values and the Ag bulk modulus ranges from 130 ± 65 MPa for 30% Ag to 229 ± 65 MPa for 15% Ag. These relatively low values also support the conclusion that no yielding of the Ag occurs. Another possible explanation for the low strain in the 30% Ag material is that the silver content is so large that it is not surrounded by enough YBCO to keep the Ag in tension. If this were true,
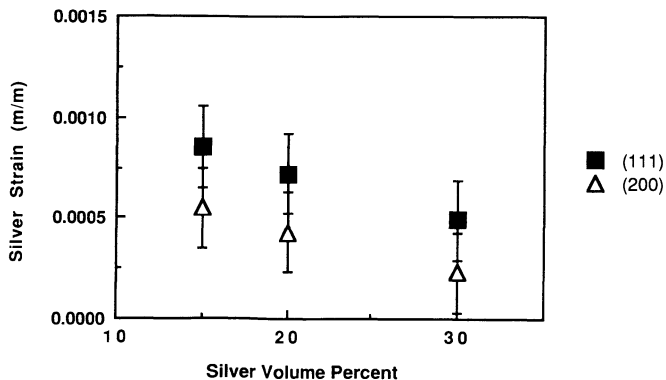

Fig. 1. Room-temperature tensile strain in Ag as a function if Ag content in $YBa_2Cu_3O_{7-\delta}$/Ag composite and crystallographic direction.

the YBCO would not experience significant compressive stress, on the average.

Measuring strains in the YBCO is difficult because the stoichiometry can change with Ag content. Thus the shifts in YBCO diffraction peaks may not be solely the result of strain. Figure 2 shows the change in the diffraction pattern with Ag content for several Ag and YBCO peaks. The pattern for the 30% Ag composite is clearly different from the others and indicates a nearly tetragonal structure. Destructive analysis, combined with X-ray diffraction analysis of sections of a 30% Ag sample [4], shows that the stoichiometry for the 30% sample changes gradually from $\delta = 0.1$ at the outer surface (orthorhombic superconducting phase) to $\delta \sim 0.8$ near the center of the specimen (non-superconducting tetragonal phase). This finding is consistent with the observation that the 30% Ag sample shows a dramatic decrease in critical current density as compared with samples with 0, 15, and 20% Ag content.

Since the lattice spacings for the three principal directions of YBCO are known as a function of stoichiometry, it is possible to estimate the diffraction peak shift resulting from strain (for some diffraction lines) by correcting for stoichiometry. For example, since the (111) diffraction peak is a single peak and the shifts are unambiguous, we can predict the change in the spacing of the (111) plane as a function of stoichiometry from the relationship

$$1/d_{111}^2 = 1/a^2 + 1/b^2 + 1/c^2,$$

where the values of a, b, and c as a function of d are determined by neutron diffraction [9]. The value of d for YBCO in the present composites was estimated by comparing relationships that are primarily due to stoichiometry and not strain with those of materials with known d (Fig. 2). Lattice parameter estimates for strain-free YBCO (111) as a function of Ag content are presented in Fig. 3. We have assumed that the addition of 15% Ag does not significantly change the stoichiometry of YBCO. The stoichiometry of the 30% Ag sample is assumed to be nearly tetragonal (bulk average), and the 20% Ag sample is assumed to be intermediate in stoichiometry between 15% and 30% Ag samples [10]. These assumptions are consistent with Fig. 2. The lattice parameter is predicted to increase as the stoichiometry approaches the tetragonal phase (with increasing Ag content). However, experimentally, the spacing for the (111) planes decreases as the Ag content increases from 15% to 20%, indicating an average compressive stress in the YBCO (Fig. 3). This result is in qualitative agreement with expectations, since the Ag strain is tensile. At 30% Ag, the difference between measured and stress-free lattice spacing indicates negligible YBCO strain. This finding is consistent with the low strain measured for Ag in the YBCO/30% Ag composite, and is probably a result of additional creep of the composite which can vary with stoichiometry [11].

DISCUSSION

We have shown that neutron diffraction techniques can be applied to YBCO composites to measure residual strains in the constituent parts caused by differential thermal contraction after fabrication, and to determine the effect of Ag on stoichiometry (and thus on the critical current density). We have observed residual tensile strains in Ag as a function of crystallographic direction; these strains range from as high as 0.085% in 15% and 20% Ag samples to as low as about 0.02% in a 30% Ag sample. Compressive strains in the YBCO (111) crystallographic direction were estimated by correcting for the diffraction peak shift due to

D-SPACING (Å)

1.908   2.037   2.166

(020)
(006)
(200)   **(113)**

0% Ag

(105)
(114)

15% Ag   **Ag (200)**

NEUTRON COUNTS

20% Ag

30% Ag

Fig. 2. Neutron diffraction spectrum of $YBa_2Cu_3O_{7-\delta}/Ag$ as Ag volume
fraction varies from 0 to 30%. The YBCO (200), (020)/(006),
(105)/(114), and (113) lines and the Ag (200) lines are shown.

2075

changes in stoichiometry with Ag content. The estimated compressive-strain values vary from 0.04% (15% Ag) to 0.09% (20% Ag) to 0.01% (30% Ag), with an uncertainty of about 0.03%. The decrease in strain in YBCO is consistent with the decrease in Ag strain and may be due to variation in creep properties of the composite which is sensitive to stoichiometry. The presence of significant average tensile strain in the Ag, particularly for 15 and 20% Ag samples, indicates good interface bonding between YBCO and Ag.

Strains were also measured at liquid nitrogen temperatures with only small changes in strain detected. The absence of any relaxation of strain suggests little or no cracking occurred as the temperature was lower to superconducting transition.
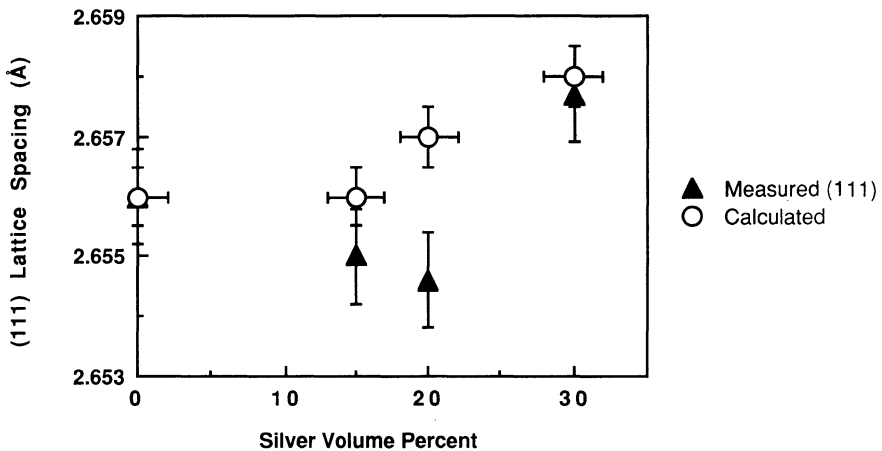
Fig. 3. Calculated and experimentally measured lattice spacing for the $YBa_2Cu_3O_{7-\delta}$ (111) plane as a function of stoichiometry.

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