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Thermosetting epoxy as a moisture-resistant coating for $YBa_2Cu_3O_7$

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Composites of $YBa_2Cu_3O_{7-x}$ and a thermosetting epoxy have been fabricated to study the effectiveness of the epoxy as a protective coating against aqueous decomposition of the oxide, and to determine the effects of the polymer on the oxide's superconducting properties. Reaction with water depletes the ceramic of barium, causes cracks perpendicular to the surface, and decreases the volume fraction of superconducting phase. Microstructural studies show that the epoxy coating is an effective barrier against the decomposition of $YBa_2Cu_3O_{7-x}$ immersed in 70° C water. In addition, resistivity and AC susceptibility measurements indicate that the epoxy has no deleterious effect on the superconducting transition temperature of the ceramic.

1. Introduction

Hermetic coating techniques to isolate ceramic superconductors from atmospheric moisture must be devised before any commercial applications of these materials can be realized. $YBa_2Cu_3O_{7-x}$ $(0 \leqslant x \leqslant 0.2)$ reacts with water to form Y_2BaCuO_5 (the semiconducting "green phase"), copper oxide, and barium hydroxide, accompanied by the evolution of oxygen and a reduction of the copper valence (from $\sim 7/3$ to 2). A pellet immersed in water at 75° C undergoes the reaction [1]

$$3H_2O(l) + 2YBa_2Cu_3O_7(s) \leftrightarrow Y_2BaCuO_5(s) + 3Ba(OH)_2(s) + 5CuO(s) + 0.5O_2(g)\uparrow \quad (1)$$

in 16 h or less. The barium hydroxide subsequently reacts with CO_2 to form $BaCO_3$. There is little doubt that this decomposition will occur at room temperature in ambient humidity over times that are short compared to the lifetimes of proposed applications, with deleterious effects on the volume fraction of superconducting phase and its ability to pass appreciable current densities.

The purpose of this work was to study the effectiveness of a thermosetting epoxy coating at inhibiting the degradation of $YBa_2Cu_3O_{7-x}$ by water. Also studied were the related issues of (1) the effects of the epoxy on the superconductivity of the ceramic and (2) the microstructural effects of the aqueous decomposition. Sintered pellets of $YBa_2Cu_3O_{7-x}$ were coated with epoxy. The superconducting transition temperatures (T_c) and a.c. susceptibility were measured on coated and uncoated pellets, before and after immersion in hot water. Microstructural studies of the reacted and unreacted samples were performed using the scanning electron microscope (SEM) with energy-dispersive X-ray analysis (EDAX).

The results showed that the epoxy used, a proprietary formula produced by Shell Development Company, was an effective moisture barrier. There was no evidence of degradation of the superconductor by the epoxy itself, and no evidence of reaction with water in regions that had continuous epoxy protection.

2. Experimental procedure

The epoxy used was EPON 9400 with EPON 9450 curing agent, proprietary developmental formulations of the Shell Co.

$YBa_2Cu_3O_{7-x}$ powder was synthesized by conventional solid state reaction of high-purity $BaCO_3$, CuO and Y_2O_3. After several grindings and firings, the powder was heated under flowing oxygen and cooled slowly to insure the proper oxygen stoichiometry for superconductivity. Pellets weighing 2 g were pressed from powder sieved to $< 45\,\mu m$, then resintered and annealed again slowly in oxygen. Details of the preparation have been reported elsewhere [2]. The pellets were approximately 85% dense.

For resistance measurements, the pellets were sectioned into parallelepipeds 1 mm × 3 mm × 12 mm. Four electrodes were attached to one face with silver paste. Four-point resistance measurements were performed from room temperature to 77 K on pellets before and after coating.

The pellets and the parallelepipeds were coated with epoxy by dipping. Curing was generally done at 105° C for 1 h. An exception was a series of coated pellets, for which the curing temperature was varied from 90 to 130° C in 10° C intervals to check for effects of curing temperature.

Coated and uncoated pellets were immersed in

70° C water for up to 4 h. To monitor the extent of decomposition of the ceramic, the pH of the water was recorded every 10 min. Similar tests were run on two epoxy blanks to determine any contribution to the pH changes from the epoxy.

A.c. susceptibility measurements were performed between 43 K and room temperature on pure sintered pellets and coated pellets, both before and after immersion in hot water. The apparatus consisted of two air-cored transformers with a turn ratio of 1 : 2, which were placed in an aluminium holder. This holder was mounted on a cold head (CTI-Cryogenics Model 22). Measurements were conducted in a vacuum chamber. The sample was placed inside one of the transformers and the second transformer was left empty. The two primaries (connected in series) were excited with a 10 Hz signal. The voltages that developed across the secondaries were then applied to a differential amplifier. The output, amplified by 20 000 ×, was applied to a lock-in amplifier. The lock-in amplifier, which was synchronized with the 10 Hz signal, yielded the amplitude of the recorded differential voltage. In plotting the results, the 20 000 × amplification was factored out to give the true voltage difference between the transformers.

After water exposure, coated pellets were sectioned perpendicular to the coated faces, polished with SiC and diamond paste with high-purity ethanol as a lubricant, and vapor-coated with palladium for SEM examination (JEOL 35CF). (Fracture surfaces were also examined, with essentially identical results.) Semiquantitative EDAX chemical analysis was performed in various regions of the specimens to determine the nature and extent of any decomposition observed.

3. Results and discussion

3.1. Effect of epoxy on superconductivity

Resistivity results are shown in Fig. 1. An uncoated sample, the same sample coated with epoxy and cured for 48 h at room temperature, and a coated sample cured at 120° C for 1 h showed virtually identical resistance characteristics, with superconducting onsets at 90 K and very sharp drops to zero resistance (total transition widths $\leqslant 2$ K). However, these measurements can only measure the lowest-resistance path between electrodes and cannot provide information regarding the bulk.

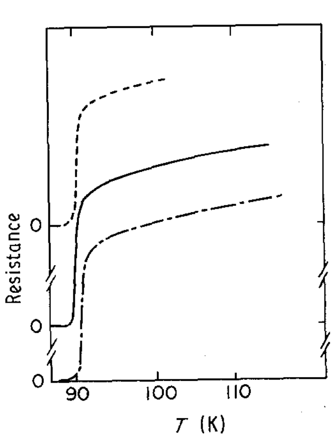

Figure 1 Resistance versus temperature in three $YBa_2Cu_3O_{7-x}$-based samples. (– – –) Standard sintered pellet. (——) Sintered pellet coated with epoxy, cured at room temperature for 48 h. (–·–·–) Sintered pellet coated with epoxy, cured at 120° C for 1 h.

A.c susceptibility measurements indicate T_c as the onset of diamagnetic behaviour (that is, an abrupt increase in ΔV between the measuring coils). Fig. 2 shows curves from several samples. $T_{c,onset}$ was 91 ± 1 K for all samples: uncoated and coated pellets, before and after exposure to hot water. This attests to the fact that this technique will measure T_c of the superconducting fraction of the sample, regardless of its distribution.

The magnitude of the diamagnetic response (ΔV in Fig. 2) indicated the amount of superconducting material. Within experimental uncertainty, the epoxy coating by itself had no effect on the susceptibility. However, ΔV decreased markedly for the uncoated pellet after 30 min in hot water. It is especially noteworthy to contrast the coated sample after 5 h in 70° C water, showing a diamagnetic response virtually identical to that of the pure uncorroded pellet, to the uncoated pellet after just 1/2 h in 70° C water, with its diamagnetic response at 43 K reduced by 50%.

The slopes of the curves at 43 K, the minimum temperature measured, may indicate a possible difference between the coated and uncoated samples, in that ΔV for the pure pellet may increase at lower temperatures, whereas the coated pellets appear to have saturated.

One obstacle to detecting any slight chemical reaction between the epoxy and the superconductor in this study was the relatively small interfacial area between the two phases. A powder–epoxy mixture provides more intimate mixing and therefore a greater likelihood of observing any interaction. Such mixtures have been extensively studied, both by us and many other research groups, since our report of alignment of the powder in a magnetic field while the epoxy cures [3]. We have observed no change in T_c and no chemical or microstructural signs of interaction in the SEM. There has been only one report [4] of a slight deleterious interaction; but considering the chemical sensitivity of $YBa_2Cu_3O_{7-x}$ properties, especially with respect to oxygen loss [5], this subject requires more detailed study.

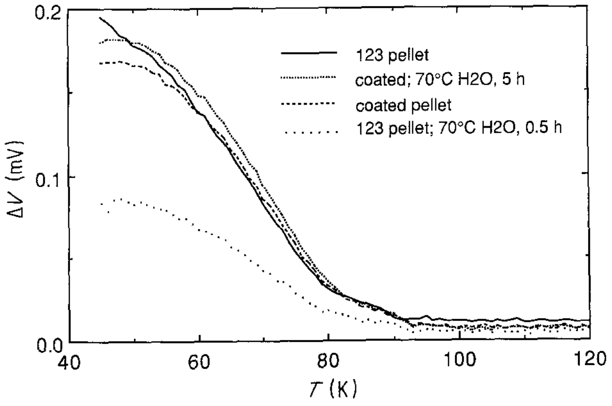

Figure 2 A.c. susceptibility measurements for epoxy-coated and uncoated $YBa_2Co_3O_{7-x}$ ("123") pellets, before and after exposure to hot water.

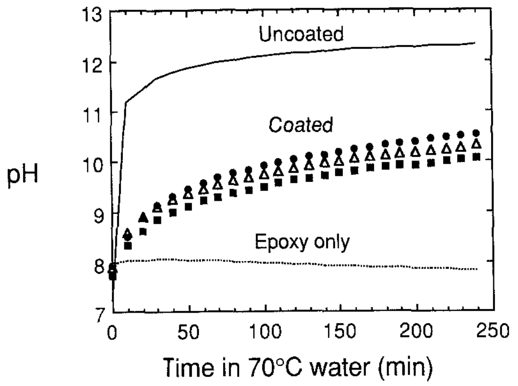

Figure 3 pH of solution during reaction of distilled water with $YBa_2Cu_3O_{7-x}$ pellets at 70° C. Top: uncoated. Middle: coated with epoxy cured for 1 h at the following temperatures: (■) 130° C; (△) 110° C; (●, ——, – – –) 120° C. Most, if not all, of this evidence of decomposition in coated samples can be attributed to discontinuities in the epoxy coating. Bottom: the epoxy without $YBa_2Cu_3O_{7-x}$.

3.2. Effectiveness of epoxy as a moisture barrier

Fig. 3 shows the pH measurements during reaction of the samples in 70° C water. The uncoated sample shows a rapid rise in pH as $YBa_2Cu_3O_{7-x}$ reacts with water to form (among other compounds) dissolved $Ba(OH)_2$, which raises the pH [1]. Such a curve is not a simple indicator of the extent or kinetics of the reaction, since $Ba(OH)_2$ will react with CO_2 to form insoluble $BaCO_3$, and the kinetics of this latter reaction will affect the dissolution rate of the superconductor. The leveling off seen in Fig. 3 does not indicate completion of the reaction, but rather the achievement of a steady state between the dissolution of the superconductor and precipitation of $BaCO_3$.

The polymer coated samples show a much slower rise in pH, and have apparently not reached steady state after 4 h. Most, if not all, of this evidence of decomposition in coated samples can be attributed to interruptions in the epoxy coating. All coated pellets had regions that were uncoated or only thinly coated (Fig. 4). There was no consistent trend with curing temperature. This is most likely attributable to the variations among these samples in coating thickness as well as continuity of the coating. A more uniform coating would provide a more effective barrier to water.

SEM with EDAX microanalysis was performed on some of the polymer-coated samples to examine the microstructures and chemistries of the reacted pellets. Fig. 4 shows two polished sections near the surface of the same coated pellet (cured at 130° C for 1 h) after 4 h in 70° C water. The top photo shows a region coated with ~ 100 μm of epoxy; the bottom photo shows a region which was essentially uncovered by epoxy.

The reacted surface was characterized by three layers:

1. At the surface, white precipitates which analyse as rich in barium indicated the presence of precipitated $BaCO_3$.
2. Immediately below the surface, a layer ~ 150 μm thick was observed. It was distinguished in microstructure from the interior of the pellet by finer and less faceted grains, less distinct grain boundaries, and lower porosity. The lower porosity indicates that the volume of the reaction products is higher than that of the starting oxide. This region was mechanically very weak, crumbling under light pressure. Cracks existed perpendicular to the exposed surface and extended inward, stopping at the boundary with the next region. This layer analysed as Cu-rich and Ba-deficient (see below).
3. The unreacted interior of the pellet showed the faceted, ~ 10–30 μm, platelike grains characteristic of $YBa_2Cu_3O_{7-x}$ derived from solid-state reaction [2]. (Compare to Fig. 4, top.) EDAX analyses were within experimental error of the 17 : 33 : 50 ratio of the superconducting compound.

The reacted zone contrasted with the coated surface (Fig. 4a), which showed only the original $YBa_2Cu_3O_{7-x}$ microstructure [2]. It can also be seen in this sample that epoxy has penetrated the ceramic, filling the pores as deep as 200 μm below the surface. (Filled pores appeared flat and were a uniform dark gray. Unfilled pores, seen at the bottom of the photo, showed more surface contrast at the grain edges, and features on the pore walls were visible.) This indicates that the epoxy–superconductor surface energy favours wetting of the ceramic. This is consistent with other

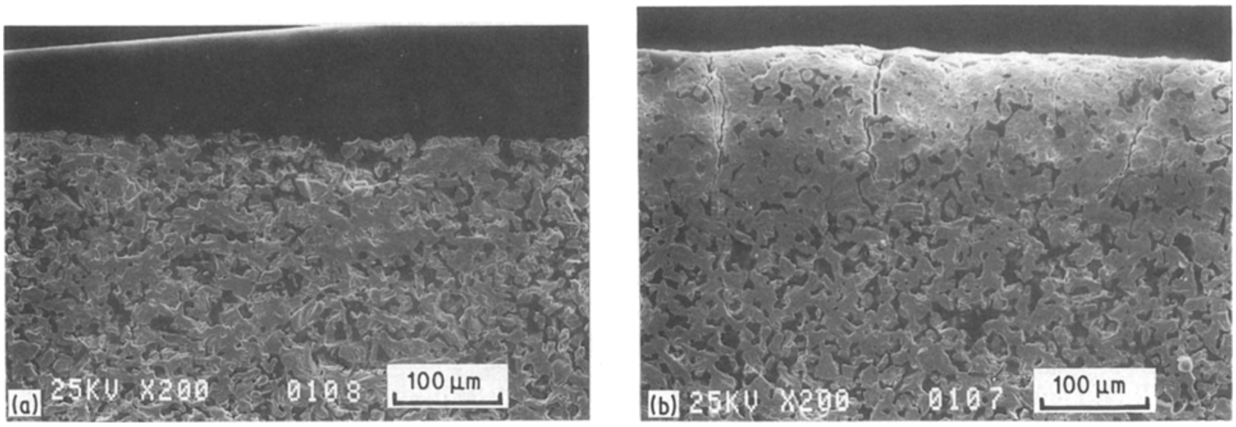

Figure 4 SEM micrographs of a $YBa_2Cu_3O_{7-x}$ pellet, coated with epoxy, cured for 1 h at 130° C, and immersed in 70° C water for 4 h. (a) Region with continuous epoxy coating. (Top surface of epoxy is visible at upper left.) (b) Region without epoxy coating.

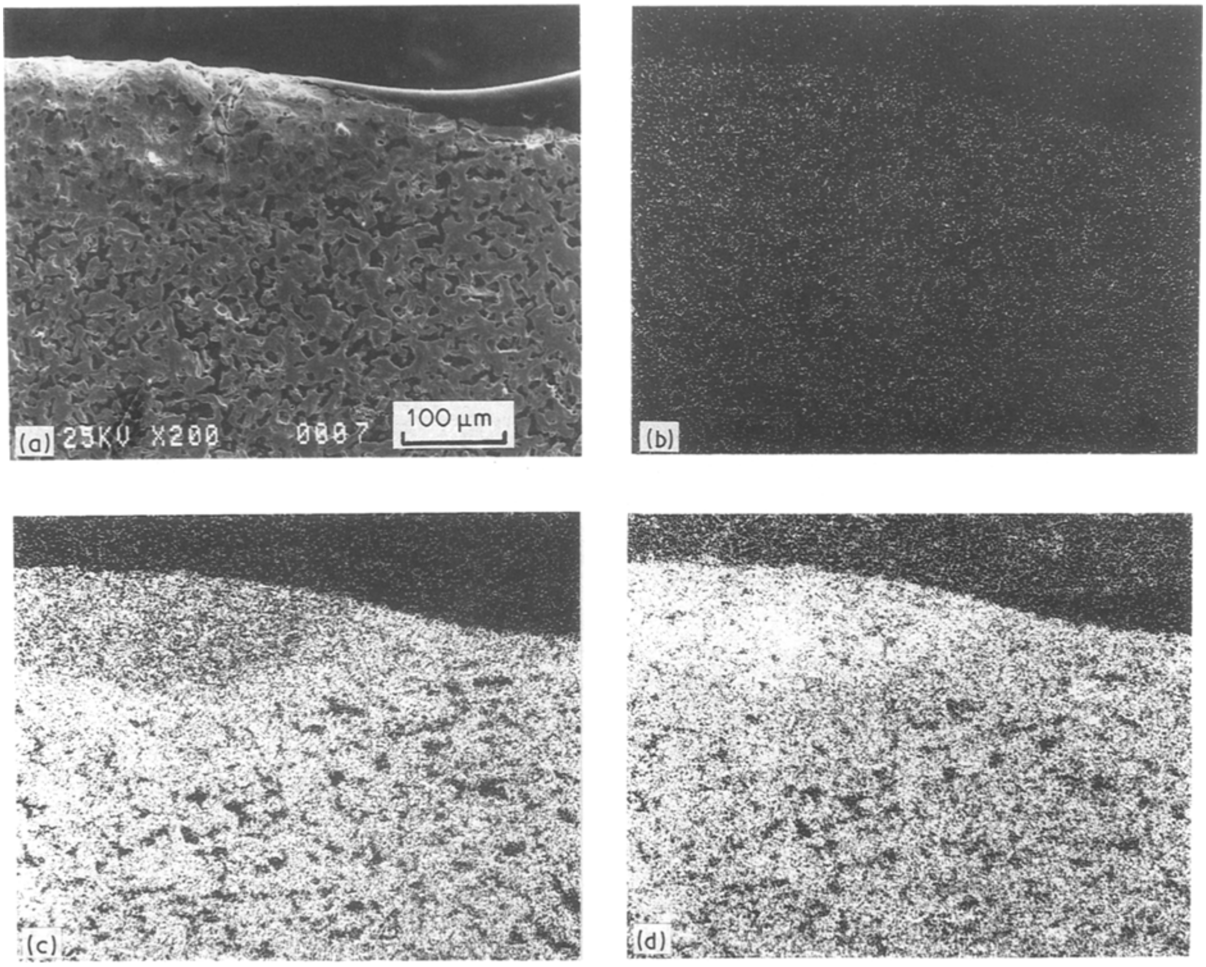

Figure 5 $YBa_2Cu_3O_{7-x}$ pellet with partial epoxy coating (same pellet as Fig. 4). (a) secondary electron image. (b) Y dot map. (c) Ba dot map. (d) Cu dot map.

observations by our group that $YBa_2Cu_3O_{7-x}$ powder dispersions in epoxy are continuously coated by the polymer. While not by any means conclusive, the absence of a visual change in the $YBa_2Cu_3O_{7-x}$ grains where they are in contact with epoxy argues for the lack of a gross chemical alteration of the superconductor by the epoxy.

Regions of the pellet where coated and uncoated regions are side-by-side (Fig. 5) confirmed the microstructural differences discussed above. The transition from unreacted to reacted ceramic coincides with the gradual thinning of the epoxy coating. Elemental dot maps for Y (Fig. 5b), Ba (Fig. 5c) and Cu (Fig. 5d) show that the reacted region is Ba-deficient. This is consistent with Equation 1 and Fig. 3; that is, the $Ba(OH)_2$ dissolves, raising the pH and depleting the ceramic of barium. However, on the basis of this mechanism, one would expect both the copper and yttrium concentrations to be unaffected. While this is true for yttrium, (Fig. 5b), there is an apparent enhancement of copper in the reaction region. This may be an artifact from the depletion of barium, since barium strongly absorbs the copper characteristic radiation generated in the specimen.

A crack or delamination of the epoxy in the thinly coated area is apparent in Fig. 5a, in contrast to Fig. 4a. It is not known whether this occurred during curing or during reaction with water, but such decohesion could be a limiting factor in the long-term effectiveness of epoxy coatings as moisture barriers for $YBa_2Cu_3O_{7-x}$.

4. Conclusions

It has been shown that an epoxy coating can greatly retard the aqueous decomposition of $YBa_2Cu_3O_{7-x}$. When decomposition was observed in coated samples, it could be attributed to incomplete or locally thin coatings; SEM/EDAX investigations of the coated pellets after 4 h in 70° C water showed no chemical or microstructural evidence of decomposition in regions where the polymer coating was uninterrupted.

From resistivity and a.c. susceptibility measurements, it has been shown that the T_c of epoxy-coated sintered bodies and of superconductor powders in epoxy matrices is unchanged from that of the pure superconductor (91 ± 1 K). The absence of indications of degradation of the superconductor by the epoxy bodes well for their use together in circuit board components or integrated circuits. It should be noted, however, that there are insufficient measurements at this stage to prove the complete absence of any interaction.

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