The effect of processing parameters on the environmental stability of YBaCuO superconductor

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The effect of processing parameters on the environmental stability of YBaCuO superconductor was studied by exposing the pellets to a constant level of relative humidity for periods up to 2000 h. Various annealing treatments and compaction pressures, including hot pressing, were utilized to fabricate the pellets. T_c measurements, Auger electron spectroscopy, energy-dispersive X-ray analysis, scanning electron and optical microscopy were employed to characterize the degradation. Samples coated with a polyimide material were also included in the study to determine its utility as a moisture barrier. Results indicated that a slow anneal (41 h) in flowing oxygen produces samples that are far more stable compared to the ones annealed rapidly (9 h) in air. The pellet compaction pressure does not appear to significantly affect the degradation characteristics of the material. The hot-pressed samples showed considerable degradation within 800 h of exposure. The polyimide was found to be ineffective in inhibiting the attack of the humid environment.

1. Introduction

The yttrium, bismuth, and thallium-based high transition temperature (T_c) supeconductors are ceramic materials; hence they lack the mechanical properties common to metals, making their processing more difficult. The high-T_c superconductors are very brittle and suffer from a high degree of porosity. In order to overcome the poor mechanical properties, techniques such as powder-in-tube [1], molten oxide processing [2], explosive fabrication [3], hot and cold extrusion [4], and powder metallurgy [5] have been applied. Hot pressing and hot-isostatic pressing (HIP) [6–9] have been used to form denser specimens. In spite of some successes using the aforementioned techniques, degradation of these materials upon exposure to the humid environment [10–13] as well as other aqueous solutions [14–16] continues to be a problem. Even though several studies have focused on the effect of processing conditions on parameters such as T_c, magnetic susceptibility and oxygen stoichiometry [17–20], the direct impact of the fabrication procedures on the environmental stability has not been thoroughly studied.

The objectives of the current study were to investigate the effect of process parameters on the degradation patterns of YBaCuO (YBC) superconductors upon exposure to humidity. Samples prepared using various techniques and conditions were used in the study. A long-term study was initiated in which YBC pellets were exposed to a constant level of relative humidity for various time intervals. A preliminary study was also performed to assess the suitability of polyimides as a moisture barrier. Polyimides were chosen because of their increasing usage in the semiconductor industry as an alternative to photoresist solutions during photolithographic fabrication of thin-film devices. Polyimides offer an increased resistance to attack from acidic etchants.

2. Experimental procedure

Five different types of sample were used for this study, out of which three batches were fabricated in-house. A conventional mixing, grinding and sintering procedure similar to the basic recipe proposed by Cava et al. [21] was followed. Appropriate amounts of Y_2O_3, $BaCO_3$ and CuO were combined to yield $YBa_2Cu_3O_{7-x}$ or a 123 stoichiometry. The ground powder was sintered at 950 °C for 15 h in air and allowed to furnace-cool to room temperature. After the sintered powder was reground, it was pressed into pellets using different compaction loads. Table I shows the sample diameters, compaction pressures, and the resulting densities. The annealing timetables followed for the various batches are shown in Tables II and III.

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TABLE I Sample density as a function of processing conditions

Sample batch	Sample diameter (mm)	Processing technique	Sample density (%)
A	12.7	Cold-pressed at 1.4×10^3 MPa	40
B	6.5	Cold-pressed at 1.4×10^3 MPa	50
C	6.5	Cold-pressed at 3.5×10^2 MPa	45
CPS	12.7	Cold-pressed at 55.2 MPa	74.4
HP	25	Cold-pressed at 2.1×10^3 MPa; hot-pressed at 13.8 MPa (975 °C)	> 99

Samples in batches B and C were annealed simultaneously in the same oven, and all samples were allowed to furnace-cool to room temperature over a period of 24 h.

The two remaining types of sample were obtained from Eastman Kodak Co. (Rochester, New York). These included (i) hot-pressed (HP) and (ii) regular cold-pressed-sintered (CPS) pellets. The HP pellet, fabricated by isostatically pressing the powder in a rubber mould at 3×10^5 psi (2.1×10^3 MPa), was green in colour. The green pellet was then embedded in fused MgO and hot-pressed at 975 °C in an alumina die. An axial load of 2000 psi (13.8 MPa) was applied during the high-temperature dwell. The pellet was cooled to 450 °C at a rate of 2 °C min^{-1}, held there for 3 h under oxygen, and finally cooled to room temperature. The pellet received from Eastman Kodak was cut into several smaller pieces for the study using a slow-speed saw (Buehler Isomet) fitted with a rotary diamond blade with methanol as the lubricant. This technique proved to be very effective to section the pellets in the desired dimensions. The hot-pressed samples took much longer to cut than their less dense counterparts.

The starting powder for the CPS pellets had an average particle size of approximately 0.11 mm and a stoichiometry of $Y_{0.98}Ba_{2.00}Cu_{3.00}O_{7-x}$ as confirmed by inductively coupled plasma spectroscopy. The 0.5 in. (12.7 mm) diameter pellets were compacted at room temperature by uniaxially pressing at 8000 psi (55.2 MPa). The pellet was then sintered for 3 h at 950 °C in oxygen and slow-cooled to room temperature in oxygen. These pellets had an onset T_c of 90 K.

In order to seek a material that could potentially behave as a moisture barrier, six samples from each of batches B and C were coated with Pyralin (PI-2703D) polyimide solution. Pyralin is manufactured by the Electronic Materials Division of DuPont Co. and is being used increasingly in the semiconductor industry as an alternative to photoresist solutions. The superconductor samples were dipped into the viscous solution and baked on a Teflon plate for 70 min at 105 °C to allow the polyimide to harden. The above step was carried out twice to obtain a uniform coating on both sides of the pellet.

All samples were placed in an in-house fabricated Plexiglass humidity chamber. A relative humidity

TABLE II Annealing cycle for batch A samples

Temperature (°C)	Time (h)	O_2 Flow
920	3	Off
700	2	Off
500	4	Off

Oven off/furnace-cool to room temperature

TABLE III Annealing cycle for batch B and C samples

Temperature (°C)	Time (h)	O_2 Flow
950	15	Off
950	1	On
900	1	On
800	1	On
750	2	On
725	2	On
700	1	On
600	1	On
575	1	On
550	1	On
525	1	On
500	1	On
450	1	On
400	12	On

Oven off/O_2 off/furnace-cool to room temperature

(RH) level of 85 ± 4% was maintained for the first 600 h of testing by adjusting the air and water flows. Tests longer than 600 h were continued at a level of 95 ± 5% relative humidity. A digital RH/temperature meter (Fisher Scientific C-78975) was utilized to monitor the humidity. The temperature in the Plexiglass chamber was the same as the ambient laboratory temperature. Preliminary studies were carried out on samples from batch A which were only exposed for short durations lasting up to 240 h. Samples from batches B and C were kept in the chamber for time periods shown in Table IV. A sub-batch from each sample type was retained in a vacuum desiccator as a control group, and another sub-batch was exposed to the ambient laboratory conditions for the entire duration of testing.

Each sub-batch consisting of six pellets was removed after the predetermined duration shown in Table IV and analysed using an Auger electron spectrometer (Perkin Elmer PHI 660), a cryostat for four-probe T_c measurements (APD Cryogenics HC-2), a scanning electron microscope (SEM, Jeol T300), an energy-dispersive X-ray spectrometer (EDS, PGT System 4 plus) and an optical microscope (Nikon Optiphot M). Results obtained before and after the exposure to humidity were compared to determine the extent of degradation.

Samples used for optical microscopy examinations were polished on a flock-twilled cloth with 0.3 μm alumina particle suspension in methanol. Final polish was achieved using 0.05 μm alumina suspension. Methanol was used as a lubricant instead of water to ensure that the pellets would not degrade in any way. Kerosene [22] and other non-aqueous media [23] have also been used for similar reasons by other groups. Only a slight finger pressure was required to hold the pellets against the polishing cloth, and a fine polished surface was achieved in 8 to 10 min. A highly polished surface is critical in order to observe the twinned microstructure of YBC crystals under polarized light.

TABLE IV Duration of humidity exposures for batch B and C samples

Sub-batch No.	Exposure Time (h)
1	31
2	72
3	170
4	264
5	360
6	600
7	840
8	1200
9	1680
10	2160
11[a]	2160
12[b]	2160
13[c]	2160

[a] Specimens coated with polyimide.
[b] Control samples kept in ambient laboratory environment.
[c] Control specimens kept under vacuum.

3. Results and discussion

The resulting densities of all samples as determined gravimetrically are shown in Table I. The density of CPS pellets was higher than those of batch A, B and C samples, even though the former were compacted at a lower pressure. This can possibly be attributed to the uniform particle size of the starting powder for the CPS pellets. Starting powders for the three batches, on the other hand, had a random particle size distribution.

The microstructure of the hot-pressed samples was remarkably different from the CPS pellets as determined by SEM. Typical scanning electron micrographs for these samples are shown in Figs 1 and 2. The highly twinned, elongated grain structure of the hot-pressed pellet, which is almost 100% dense, is shown in the polarized-light optical micrograph in Fig. 3. In measurements made at Eastman Kodak, the
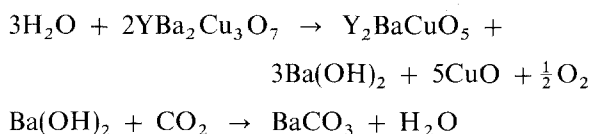

Figure 1 Scanning electron micrograph of hot-pressed YBaCuO superconductor.

Figure 2 Scanning electron micrograph of cold-pressed-sintered YBaCuO superconductor.

Figure 3 Polarized-light optical micrograph of hot-pressed YBaCuO superconductor before exposure to humidity, showing a high degree of twinning (× 423).

hot-pressed pellet exhibited virtually zero diamagnetism, a fact that has been attributed to poor oxygenation of the sample. The extremely high density of the sample made it difficult for oxygen to diffuse into the bulk of the material.

The T_c, as shown in Fig. 4, for batch A samples was lower than that of batch B and C samples shown in Fig. 5. Batch B and C samples had an onset T_c of 91 K with a very sharp transition width of less than 2 K. The only difference in the processing conditions for the batch A and batch B samples was the annealing procedure. No oxygen was used during any portion of the heat treatment, and temperatures were cycled more rapidly for batch A as indicated in Table II. These results imply that the compaction load is probably not an important factor in determining the T_c of the superconductor.

Samples from batch A were exposed for periods lasting only 10 days at 85% RH, since signs of degradation were apparent within the first 10 h of exposure. Formation of corrosion product was even more obvious after a three-day exposure. Tentacle-like growth, such as that shown in Fig. 6, was observed on several areas of the sample. The reaction products were identified using EDS and high-resolution X-ray dot mapping. The tentacle-like features were clearly identified to be barium-rich and deficient in copper and yttrium. Even though carbon and oxygen were not detected due to the limitation of the beryllium-window X-ray detector, it can be assumed that the product formed is barium carbonate. The most likely reaction that occurs, as proposed by Yan et al. [24], when YBC material comes in contact with water or humidity is as follows:

$$3H_2O + 2YBa_2Cu_3O_7 \rightarrow Y_2BaCuO_5 +$$
$$3Ba(OH)_2 + 5CuO + \tfrac{1}{2}O_2$$
$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

According to this reaction, barium reacts with water to form barium hydroxide, which subsequently reacts with the atmospheric carbon dioxide to form barium carbonate. A non-superconducting phase with a 211 stoichiometry is also formed in the process. Although there was evidence of precipitate formation, X-ray diffraction scans performed by Yan et al. [24] indicated no phase change from orthorhombic to tetragonal.

T_c measurements for batch A samples performed after the five-day exposure showed a negative slope above the transition temperature as seen in Fig. 7. This behaviour is characteristic of the formation of semiconducting phases in the material and has been reported by other groups also [25, 26].

The long-term humidity exposure studies performed on batch B and C samples yielded very encouraging results. Only minor surface degradation of the superconducting pellets was observed, even after exposures as long as 2000 h. The superior resistance of

Figure 5 Resistance versus temperature behaviour for slowly annealed batch B sample shows the sharp transition width and zero resistance at 86 K.

Figure 6 Scanning electron micrograph of batch A sample after 72 h exposure, showing formation of tentacle-like barium-rich corrosion product.
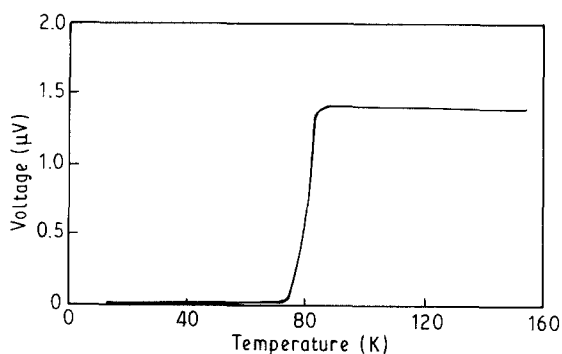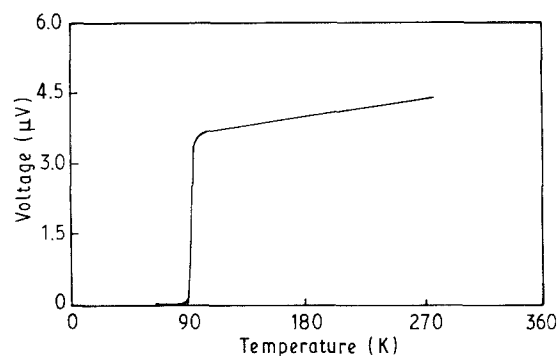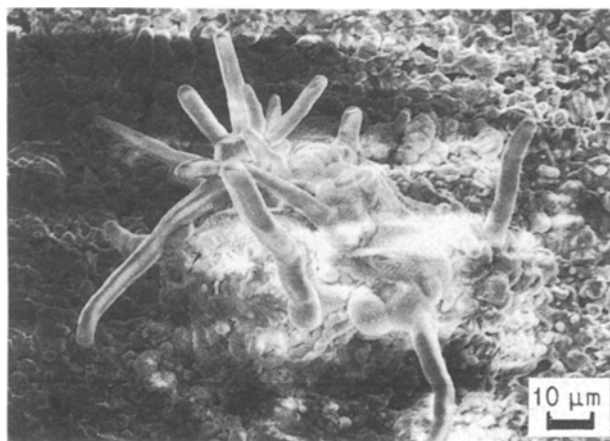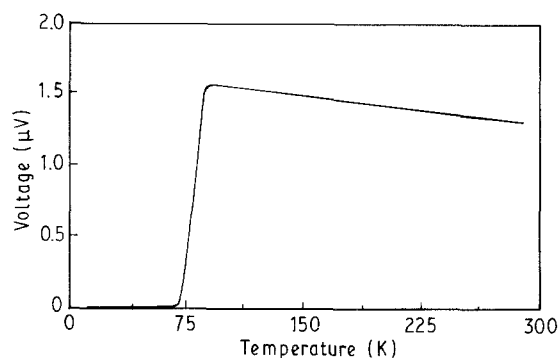
Figure 4 Resistance versus temperature behaviour for a rapidly annealed oxygen-deficient batch A sample which shows that the sample never achieved zero resistance.

Figure 7 Resistance versus temperature behaviour for batch A sample after 120 h humidity exposure; the negative slope above T_c indicates a semiconducting behaviour.

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these pellets is best exemplified by the resistance versus temperature plot shown in Fig. 8. It can be seen that no significant change occurred in the T_c or the transition width until 1200 h of exposure, after which a slight negative slope is observed. On the other hand, the T_c curve for the batch A samples displayed a semiconducting behaviour after being exposed to humidity for only 120 h. The semiconducting nature of the T_c curve probably implies an orthorhombic to tetragonal transition for only a part of the sample since the actual T_c did not change, but the difference of an order of magnitude in the time required to observe the formation of semiconducting phases in the samples is indicative of the improved characteristics of batch B and C samples.

Other analytical techniques used did not indicate any significant changes in the degradation parameters for batch B and C samples either. Some $BaCO_3$ formation was observed on the surface of the samples, but the rate and extent of this reaction was significantly slower than in the case of batch A samples. Localized crystallographic cracking, as shown in the backscattered electron image of a polished sample in Fig. 9, was evident though, after a 2000 h exposure. (The dark areas in the micrograph correspond to the unpolished areas of the sample.) Post-exposure EDS analyses did not demonstrate any significant change in sample compositions. The behaviour of batch B and C samples upon exposure to humidity was essentially similar even though they were compressed at two different loads. They were, however, subjected to the same annealing treatment.

The hot-pressed (HP) and the CPS pellets obtained from Eastman Kodak exhibited behaviour that was quite contrary to that of batch B and C samples. Within 800 h of exposure, the HP samples experienced an obvious swelling effect, implying an excess intake of water. Fig. 10 shows the degraded HP sample covered with barium precipitates after an 840 h exposure. A thin, self-standing, greyish-coloured film of the corrosion product actually delaminated from the surface of the HP sample. EDS spectra of this film indicated the presence of barium only. EDS analysis of a fractured surface of the HP sample showed a lesser degree of degradation, indicating that the corrosion is localized at the surface of the sample. Some of the original microstructure was still discernible underneath the
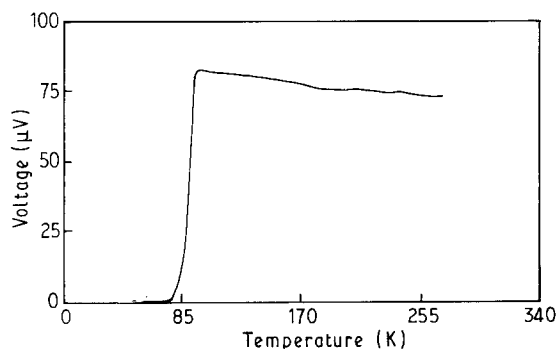
corrosion product. The extent of degradation in the case of the CPS pellet was not as extreme as the HP sample, but formation of reaction product on the surface was quite evident.

Auger electron spectroscopy was used to confirm the composition of precipitates and to determine the depth of attack as a function of exposure time. No significant change was observed in the composition of batch B and C samples when compared to the original scans. The degraded samples from these batches showed only small, localized areas of carbon concentration, which would indicate the formation of $BaCO_3$ on the surface only. Auger depth profiles for even the 1200 h exposure did not show much carbon, implying once again that no bulk decomposition of barium had occurred. Typical Auger depth profiles obtained by sputtering with 3 kV Ar^+ ions for 30 min are shown in Figs 11 and 12. The carbon peak intensity for the batch B sample in Fig. 11 is much smaller than that for the hot-pressed sample in Fig. 12. This indicates that the hot-pressed sample had a greater amount of $BaCO_3$ on the surface than the batch B sample. In both cases, however, the carbon does not extend into the bulk of the material. Auger studies performed by Nakahara et al. [27] on in situ-fractured samples indicated segregation of carbon along all fracture
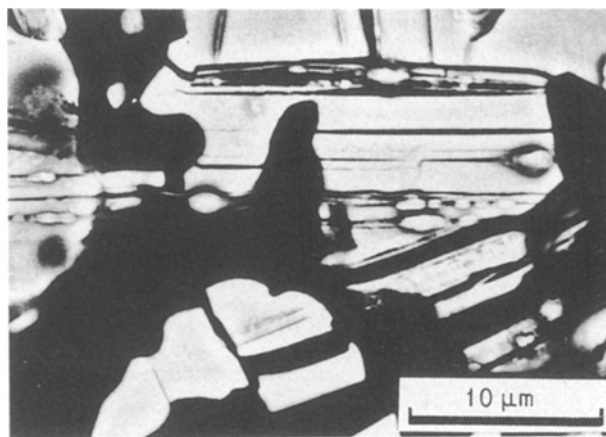

Figure 9 Backscattered SEM image of batch B sample, showing crystallographic cracking after 2000 h of exposure.

Figure 10 Scanning electron micrograph of hot-pressed sample surface after 840 h exposure, showing the barium precipitates.
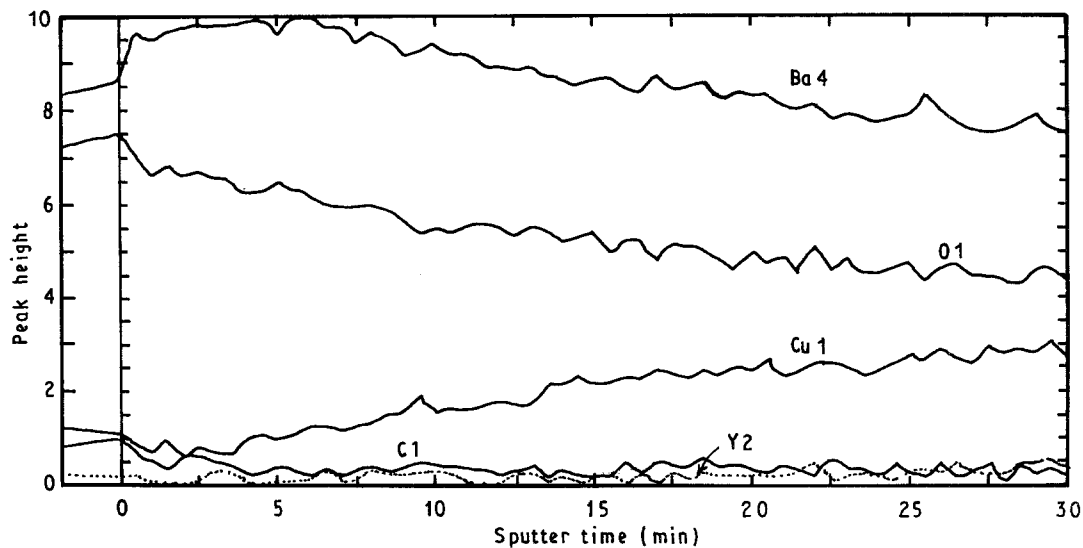

Figure 8 Resistance versus temperature behaviour for batch B sample after 1200 h exposure to humidity.

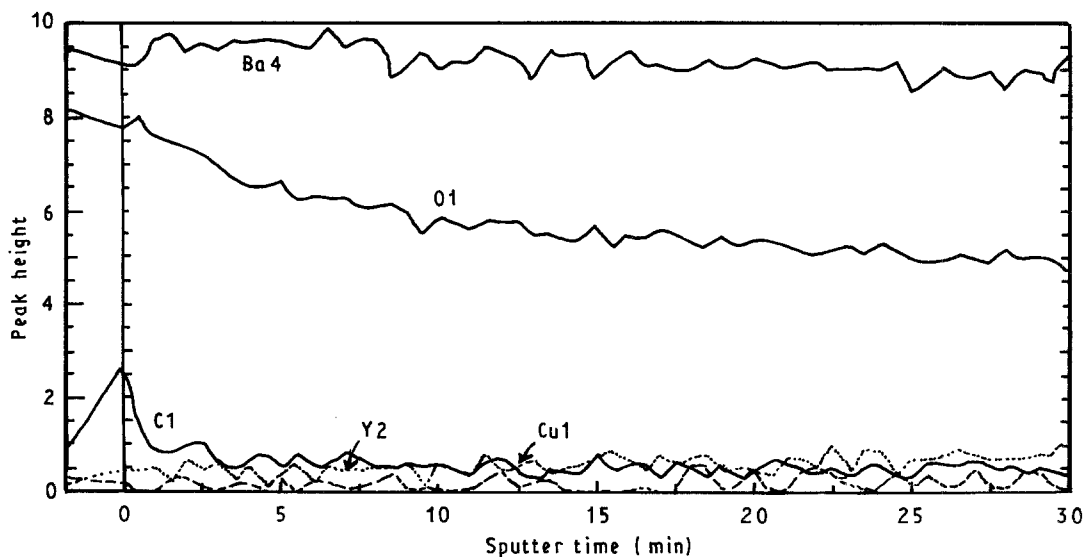*Figure 11* Auger depth profile for batch B sample after 1200 h humidity exposure.

Figure 12 Auger depth profile for hot-pressed sample after 860 h exposure to humidity.

surfaces that cracked in an intergranular manner. There was a direct correspondence between carbon-free areas and the transgranular fracture surfaces. Depth profiling results also indicated that carbon did not extend much below the surface of the samples.

The extensive use of polyimides in the semiconductor industry lends them to be a prime choice for a moisture barrier. Results from this study, however, indicated that the particular polyimide material used was not suitable for this purpose. The coated samples underwent severe cracking and the clear, shiny polyimide showed a brown discoloration at the conclusion of a 2000 h exposure. The most likely reason for the samples to crack is that stresses were caused by the shrinkage of polyimide which also led to delamination of the coating. The cracking and degradation of the samples were observed after only 1200 h of exposure to humidity, after which they got progressively worse. The control samples, held in vacuum and in the ambient conditions, showed surface cracking only, but no delamination of the polyimide layer or bulk crack-

ing, even after 3300 h. Further studies will be required to substantiate the long-term feasibility of polyimide materials as protective coatings.

4. Conclusions

The results indicated that the annealing cycle is extremely critical in determining the ultimate quality of the superconductors, which includes their resistance to environmental degradation. It has been seen that samples cycled slowly through the prescribed temperature range under flowing oxygen underwent virtually no degradation. On the other hand, pellets pressed under the same compaction pressure, but annealed much more rapidly in an oxygen-deficient atmosphere, showed very poor characteristics and started degrading within 10 h of exposure. The hot-pressed pellets did not perform very well either and showed severe surface degradation. This study indicated that polyimide materials may not be suitable for long-term applications as a moisture barrier.

Acknowledgements

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