Emanation thermal analysis of microstructural changes during interactions of high-T_c superconductors with the atmosphere [a]

Vladimir Balek [a] and Patrick K. Gallagher [b]

[a] *Nuclear Research Institute, 250 68, Řež (Czechoslovakia)*
[b] *Departments of Chemistry and Materials Science and Engineering, The Ohio State University, Columbus, OH 43210 (USA)*

(Received 4 December 1990)

Abstract

Emanation thermal analysis (ETA) was applied to obtain information on the microstructural changes occurring at the nanometer level during interaction of the high-T_c superconductor, $Ba_2YCu_3O_{7-x}$, with oxygen and hydrogen at elevated temperatures. The ETA curves in oxygen indicate differences in behavior between freshly conditioned samples and those which have been stored for several months in air. The ETA results provide valuable information additional to that obtained by traditional methods, e.g. TG, DTA and dilatometry.

INTRODUCTION

The ceramic high-T_c superconductors, especially $Ba_2YCu_3O_{7-x}$, degrade during storage due to interactions with the ambient atmosphere [1]. Thermogravimetry (TG) has been widely used to study the oxygen stoichiometry during reactions of this ceramic with oxygen and hydrogen and has been successful in predicting the superconducting properties of the material [1]. Thermodilatometry has enabled studies of bulk changes in the volume of sintered pellets to be made during their interactions as they were heated in various atmospheres [2]. These changes observed at the macroscopic level have their origins, however, at the microscopic (atomic) level.

The purpose of this paper is to demonstrate the usefulness of ETA for the study of these microstructural changes occurring during interactions of $Ba_2YCu_3O_{7-x}$ with oxygen and hydrogen. The ETA results are compared with earlier TG, dilatometry and X-ray diffraction results.

---

[a] Dedicated to Professor Hans-Joachim Seifert on the occasion of his 60th birthday.

EXPERIMENTAL APPARATUS AND PROCEDURES

Sample preparation

The $Ba_2YCu_3O_{7-x}$ was prepared from $BaCO_3$, Y_2O_3 and CuO which were mixed, calcined at $900°C$, remixed, pressed and then fired in oxygen at $975°C$. TG determined that the value of x was 6.98 ± 0.02 and EGA indicated that there was no carbonate remaining.

The sample to be studied by ETA [3] was labeled by absorbing trace amounts of ^{228}Th and ^{224}Ra as parent radioactive nuclides of ^{220}Rn inert gas atoms. The ^{220}Rn atoms are formed by spontaneous alpha decay according to the scheme

$$^{228}Th \rightarrow {}^{224}Ra \rightarrow {}^{220}Rn$$
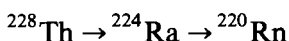
The radioactive parent nuclides of ^{228}Th (half-life = 1.9 y) serve as the permanent source of the daughter nuclide ^{220}Rn (half-life = 55 s). The Rn atoms are incorporated, due to the recoil energy, at a depth of approximately 80 nm from the surface of the powder particle. These Rn atoms are located at the structural defects, e.g. vacancy clusters, grain boundaries, etc., which can serve both as traps and paths for the diffusion of Rn atoms.

The labeled samples were stored for a month to form the maximum equilibrium amount of Rn atoms in the sample. Samples were preconditioned before each experiment by heating them in oxygen to $960°C$ and held for 20 min prior to cooling in oxygen at $2.5°C$ min^{-1}.
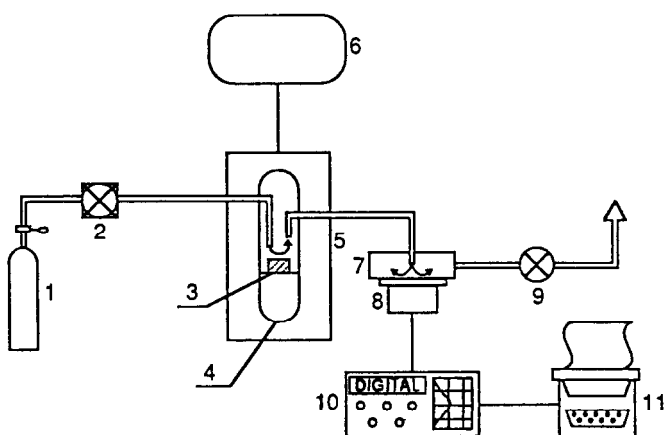

Fig. 1. Schematic diagram of the apparatus for emanation thermal analysis: 1, gas supply; 2, gas flow controller; 3, labeled sample; 4, sample holder; 5, furnace; 6, furnace controller; 7, measuring chamber; 8, radioactivity detector; 9, flow-rate meter; 10, counter; and 11, data processor and printer/plotter (ref. 4).

ETA apparatus

Figure 1 shows schematically the ETA apparatus used [4]. Approximately 300 mg of the labeled samples were heated in the alumina crucible in flowing oxygen or hydrogen (40 ml min^{-1}) at a heating rate of 5°C min^{-1}. The ETA results are represented as the temperature (time) dependence of the radon release rate, E, (in relative units) normalized to the rate of radon formation in the sample by the decay of Ra atoms.

RESULTS AND DISCUSSION

Interaction with oxygen

Figure 2 shows the ETA curve for the preconditioned sample during heating in oxygen together with the results from TG [5] and dilatometry [2] obtained independently. As indicated in curve 1 of Fig. 2, the TG data show that the onset of weight loss due to evolution of oxygen starts at about 350°C and continues to decomposition above about 1050°C. The dilatometric data (see curve 2 in Fig. 2) indicate that the increase in the rate of thermal expansion corresponds with the onset of weight loss. The rapid rate of expansion decreases at the orthorhombic to tetragonal transformation.

These changes of macroscopic parameters fit fairly well with the changes of microstructure at the nanometer level as indicated by the diffusion of Rn atoms (atomic size = 0.38 nm). The ETA curve shown in Fig. 2 (curve 3),
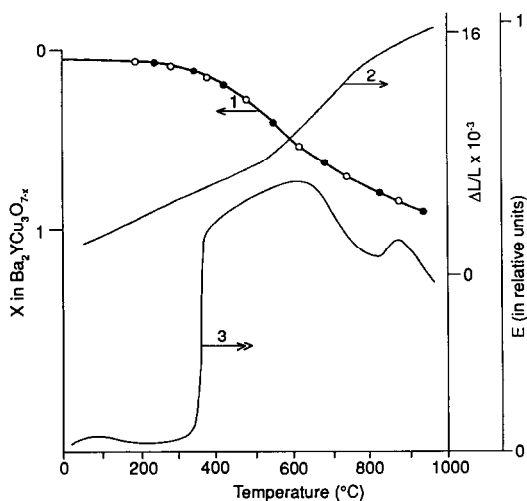

Fig. 2. Thermoanalytical curves for $Ba_2YCu_3O_7$ heated in O_2: curve 1, TG at 1°C min^{-1} (ref. 5); curve 2, dilatometric trace at 1°C min^{-1} (ref. 2); and curve 3, ETA-conditioned sample at 5°C min^{-1}.

indicates the onset temperature of the sample's change in microstructure associated with loss of oxygen. This onset value is 385°C. The rapid increase of the Rn release rate in the narrow temperature range (385–415°C) indicates the sudden formation of many new paths for the diffusion of Rn. However, the slower rate of Rn release after 415°C indicates either that the ability to form rapid diffusion paths has been exhausted or that there are an increased number of sites formed which are capable of trapping the Rn atoms.

A randomization of the oxygen ions in the *ab* planes around 700°C which leads to a change from orthorhombic to tetragonal symmetry, initiates a strong decrease in the release rate of Rn atoms, presumably by the same mechanisms as described above. This is consistent with the decreased rate of thermal expansion for the lattice which also occurs at this temperature.

Above about 1000°C, the rate of Rn release slows in anticipation of melting and decomposition.

Interaction with hydrogen

The TG and ETA curves for $Ba_2YCu_3O_{7-x}$ are presented in Fig. 3. The onset of weight loss in the TG (curve 1) corresponds well with the rapid increase in the rate of Rn release. Nevertheless, it should be mentioned that this onset temperature of about 280°C is approximately 100°C lower than that observed for the interaction with oxygen. It can be seen from the TG that the decomposition beginning when $x = 1.0$ occurs shortly before 500°C in hydrogen. This corresponds with the temperature where the decrease in the rate of Rn release is indicated in Fig. 3, curve 2. The peak during the initial rise in rate occurring at about 400°C on the ETA curve, may be associated with the orthorhombic to tetragonal transformation.

The changes occurring during heating beyond 500°C indicate morphological changes accompanying the decomposition to a multi-phase mixture. The general trend is that associated with a decrease in surface area as would be expected from the formation of copper metal.
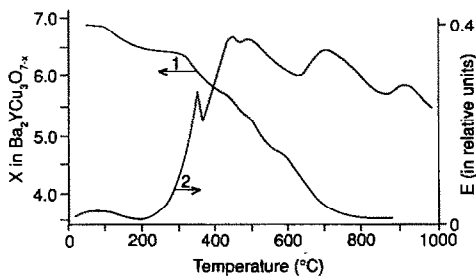

Fig. 3. Thermoanalytical curves for $Ba_2YCu_3O_{7-x}$ heated in H_2: curve 1, TG at 10°C min^{-1} in 15% H_2/85% N_2 (ref. 6); and curve 2, ETA conditioned sample at 5°C min^{-1} in 100% H_2.
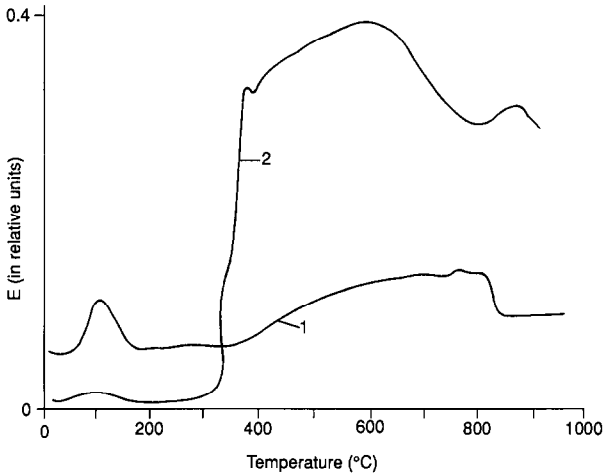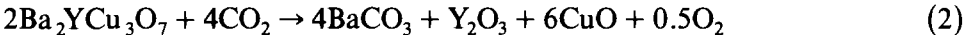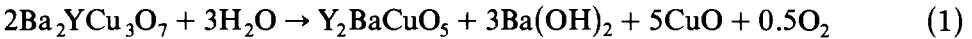
Fig. 4. ETA curves for $Ba_2YCu_3O_7$ heated at $5°C$ min^{-1} in O_2: curve 1, unconditioned; curve 2, conditioned (see text).

Interaction with moisture and CO_2 after storage in air

Serious degradation of the superconducting properties has been observed and attributed to reactions with moisture and carbon dioxide in the atmosphere [1,7,8]. The moisture can lead to the reduction of Cu^{3+} and formation of $Ba(OH)_2$ according to eqn. (1). The interaction with carbon dioxide forms highly stable $BaCO_3$, as indicated in eqn. (2), or, in the presence of moisture, by reaction with the $Ba(OH)_2$ formed by reaction (1)

$$2Ba_2YCu_3O_7 + 3H_2O \rightarrow Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + 0.5O_2 \qquad (1)$$

$$2Ba_2YCu_3O_7 + 4CO_2 \rightarrow 4BaCO_3 + Y_2O_3 + 6CuO + 0.5O_2 \qquad (2)$$

The unreacted chemisorbed moisture and carbon dioxide are evolved around $100°C$ leading to a peak in the ETA curve shown in Fig. 4, curve 1, for the unconditioned sample. The presence of the $Ba(OH)_2$, $BaCO_3$ and other corrosion products at the surface and in the grain boundaries apparently impedes the release of Rn atoms during the loss of oxygen above $400°C$. Since this rate is so diminished, the change normally observed during the orthorhombic to tetragonal transformation is obscured. Heating above about $960°C$ for some time is necessary to regenerate the uncontaminated superconductor, as shown in Fig. 4, curve 2. This regeneration is presumably due to decomposition of the $BaCO_3$ with concomitant reformation of $Ba_2YCu_3O_{7-x}$.

CONCLUSIONS

1. The initial loss of oxygen from the conditioned sample indicates the abrupt formation of sizable diffusion paths for the Rn atoms (atomic size $= 0.38$ nm).

2. Randomization of the oxygen vacancies to form tetragonal symmetry markedly reduces the mobility of Rn atoms in the material studied.

3. The ETA method demonstrates clearly the differences in thermal behavior between the sample exposed to atmospheric degradation and the same sample after reconditioning by heating in oxygen to 960°C.

4. Reduction by hydrogen speeds up the processes described in points 1 and 2 above so that they are complete by about 500°C. Above that temperature the compound decomposes forming a multi-phase mixture with concomitant reduction in the rate of Rn release.

REFERENCES

1 P.K. Gallagher, Thermochim. Acta, 174 (1991) 85.
2 H.M. O'Bryan and P.K. Gallagher, Adv. Ceram. Mat., 2 (1987) 642.
3 V. Balek, Thermochim. Acta, 22 (1978) 1.
4 V. Balek, J. Therm. Anal., 35 (1989) 405.
5 P.K. Gallagher, Adv. Ceram. Mat., 2 (1987) 632.
6 P.K. Gallagher, H.M. O'Bryan and G.S. Grader, Thermochim. Acta, 137 (1989) 373.
7 M.F. Yan, R.L. Barnes, H.M. O'Bryan, P.K. Gallagher, R.C. Sherwood and S. Jin, J. Appl. Phys. Lett., 51 (1987) 532.
8 P.K. Gallagher, G.S. Grader and H.M. O'Bryan, Mat. Res. Bull., 23 (1988) 1491.