Thermochimica Acta, 175 (1991) 207–213
Elsevier Science Publishers B.V., Amsterdam

KINETIC ANALYSIS OF SUPERCONDUCTING $YBa_2Cu_3O_7$ BY THERMOGRAVIMETRY IN HIGH VACUUM

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(Received 27 July 1990)

ABSTRACT

Superconducting $YBa_2Cu_3O_7$ was subjected to high vacuum thermogravimetry (TG) at various heating rates in the range from room temperature to 1000 °C. Two distinct weight-loss steps, each of which corresponds to the evolution of almost $1/2O_2$, were observed on the TG curve. The product following the first step was apparently the non-stoichiometric compound $YBa_2Cu_3O_{7-\delta}$. The rate equation for the first step was $d\delta/dt = k(1-\delta)$; the corresponding specific rate constant, k, was 1.8×10^{-3} s^{-1} at 490 °C, the activation energy, E_a, was 75 kJ mol^{-1} and the frequency factor, A, was 3.0×10^2 s^{-1}.

INTRODUCTION

Superconducting $YBa_2Cu_3O_7$ is characterized by possession of a labile oxygen atom, in contrast with other series of superconducting oxides of La, Bi and Tl. It is well known that oxygen plays an important role in the superconductivity because its amount is closely related to the positive hole concentration. There have been many extensive studies on the oxygen loss [1–4] and oxygen uptake [5] processes as a function of temperature and oxygen pressure, on the T_c change with oxygen amount [6,7], on the phase transition [8,9] and on the products [10,11]. However, no detailed kinetic data of the oxygen loss process has been reported, except for that on oxygen diffusion in highly densified polycrystalline specimens [12]. This is probably because the reverse (oxygen uptake) reaction is much faster than oxygen loss. To prevent the occurrence of the reverse reaction, thermogravimetric measurement in an oxygen-free atmosphere was attempted but the thermogravimetry (TG) curve obtained was still composed of both the forward and

0040-6031/91/$03.50

reverse reactions [4]. This may indicate that the diffusion of oxygen gas evolved from the specimen upon heating was incomplete in the presence of gas pressure. A TG measurement in high vacuum is needed to evaluate precise kinetic parameters.

EXPERIMENTAL

Preparation

Non-stoichiometric $YBa_2Cu_3O_{7-\delta}$ was prepared by sintering a disk made of a powdered mixture of Y_2O_3, $BaCO_3$ and CuO at 950 °C in air. The resulting product was heated up to near 600 °C in high vacuum ($\sim 10^{-5}$ Torr) and, once converted into the tetragonal phase, was slowly cooled down to room temperature under 1 atm of O_2 to reproduce the orthorhombic phase. Analytical results using the iodometric method showed that the two phases were $YBa_2Cu_3O_{6.1}$ and $YBa_2Cu_3O_{7.0}$, respectively.

TG measurement

The TG curve and its first differential (DTG) curve were obtained with a Shinku Riko TGD-1500 microbalance equipped with a DTG unit. About 100 mg of powdered sample in a platinum crucible was used for each TG run. In order to obtain high vacuum and a horizontal TG base line, the sample system was continuously evacuated with an oil diffusion pump through two vacuum vents located above and below the electronic balance unit of the TG apparatus. The basic pressure inside the system was 2×10^{-5} Torr and the maximum pressure during the TG measurement was 5×10^{-5} Torr.

RESULTS AND DISCUSSION

Decomposition behaviour of $YBa_2Cu_3O_7$ in vacuum

The TG–DTG chart obtained in high vacuum is shown in Fig. 1. There are two distinct weight loss steps of 2.1 and 1.9% in the temperature ranges 400–650 °C and 900–950 °C, respectively. The observed weight loss values correspond to the loss of approximately 1/2 mole of O_2 (theoretically 2.4%). The product of the first step, assigned as tetragonal $YBa_2Cu_3O_6$, reverted to the initial $YBa_2Cu_3O_7$ when exposed to 1 atm O_2 gas and cooled slowly. Both the oxygen loss and oxygen uptake processes in the $YBa_2Cu_3O_7$–$YBa_2Cu_3O_6$ system took place in a single step and were completely reversible. The product formed following the second step also reabsorbed oxygen

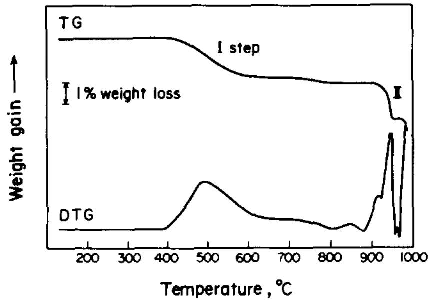

Fig. 1. TG curve and the first differential (DTG) curve of 112 mg $YBa_2Cu_3O_7$ at a heating rate of 5 °C min^{-1} in vacuum.

gas and almost recovered its starting weight when exposed to 1 atm O_2 gas and cooled slowly. However, the X-ray diffraction lines of the oxygen-reabsorbed product were completely different from those of $YBa_2Cu_3O_7$. When it was reheated in vacuum, about one mole of O_2 was lost in several steps. Typical TG behaviour of the product formed following the second step is shown in Fig. 2. These results indicate that the oxygen loss in the second step is accompanied by an irreversible destruction of the perovskite structure and that the processes of oxygen uptake and loss by nearly one mole of O_2 are probably achieved by alternating Cu(I) and Cu(II) valencies in the decomposition mixture. The second step is not available for kinetic analysis.

Before kinetic analysis for the first step can proceed, it is necessary to evaluate the reaction stoichiometry. The products formed in the course of the first step were examined by X-ray diffraction analysis for specimens with the compositions $YBa_2Cu_3O_y$ ($y = 6.73$, 6.52, 6.25 and 6.06) which were prepared by quenching partially decomposed samples obtained under the same conditions as for the high vacuum TG measurement. As shown in Fig. 3, there is not much difference in the unit cell parameters of the specimens

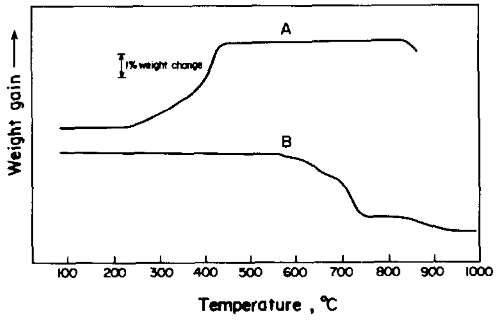

Fig. 2. TG behaviour of the product just after the second step of Fig. 1: A, oxygen uptake process of the product just after the second step, the TG being measured at a heating rate of 5 °C min^{-1} in 1 atm O_2 atmosphere; B, oxygen loss process of the product after the oxygen uptake process A when the TG was measured in vacuum.

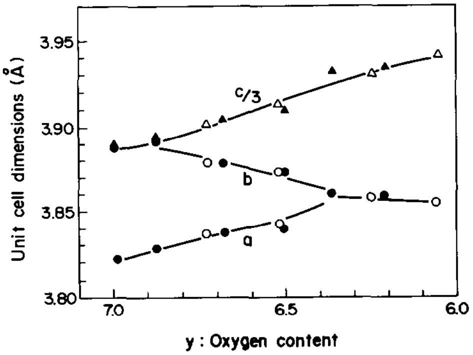

Fig. 3. The unit cell parameters of partially oxygen-desorbed products when $YBa_2Cu_3O_7$ was heated to the desired temperatures in vacuum (open) and those of the quenched samples after heating in air (filled).

prepared in vacuum and those prepared in air, indicating that the products in vacuum were also non-stoichiometric compounds. The X-ray diffractogram of the $YBa_2Cu_3O_{6.52}$ prepared in vacuum is quite different from that of a mechanical mixture of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ in equimolar ratio, as can be seen in Fig. 4; this provides additional support for the above consideration.

Kinetic analysis

On the basis of the preliminary experimental results which indicate that the product is non-stoichiometric $YBa_2Cu_3O_{7-\delta}$ in the range $0 < \delta < 1$, and because the corresponding TG–DTG curves were so smooth that the reaction apparently proceeds in a single mechanism, we assumed the following kinetic equations

$$d\delta/dt = kf(\delta) = A\exp(-E_a/RT)f(\delta) \tag{1}$$

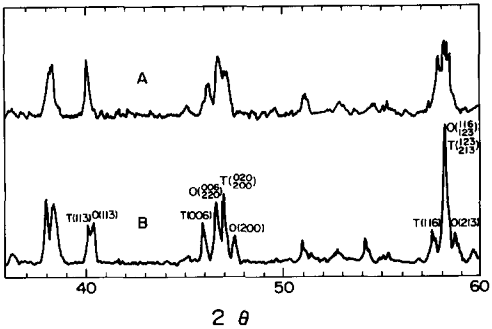

Fig. 4. X-ray diffractograms of $YBa_2Cu_3O_{6.52}$ (A) prepared in vacuum and of a mechanical mixture of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ in equimolar ratio (B), obtained using Cu Kα radiation.

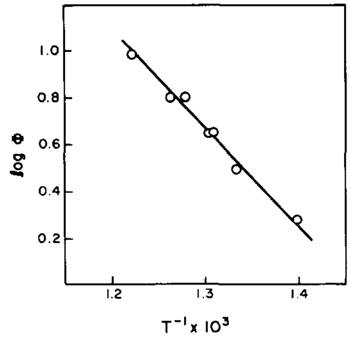

Fig. 5. Plot of log ϕ vs. T_m^{-1} for the first step.

where k is the specific rate constant, A the frequency factor and E_a the activation energy. The above expressions are possible only when k is kept constant with changes in δ. The rate $d\delta/dt$ is rewritten as

$$d\delta/dt = (d\delta/dT)(dT/dt) = (d\delta/dT)\phi \quad (2)$$

where ϕ is the heating rate, and therefore the following relation is obtained

$$\ln \phi + \ln(d\delta_c/dT) = \ln A - E_a/(RT_m) + \ln f(\delta_c) \quad (3)$$

Because the value of δ_c, at which $d\delta/dT$ becomes maximum, is independent of the heating rate and also because the value of $d\delta/dT$ is kept constant with different heating rates [13], the plots of ln ϕ against $1/T_m$ should give a straight line with slope $-E_a/R$, where T_m is the temperature at which the rate becomes maximum. The values of T_m were obtained experimentally from the DTG peaks when the heating rates were changed in the range 1–15 °C min^{-1}. The plot of log ϕ against $1/T_m$ for the first step is shown in Fig. 5. A straight line was obtained and from its slope, the activation energy was calculated to be 75 kJ mol^{-1}.

Of the various $f(\delta)$ models proposed for solid state reactions, we chose $f(\delta) = (1-\delta)^n$ as the most appropriate from the TG and DTG curvatures. The plot was made using the conventional kinetic analysis method developed by Freeman and Carroll [14] and is shown in Fig. 6. Although there was some scatter in the plot, the measured data can be fitted by a linear relationship with the intercept very close to unity. Therefore, we assumed that the first step is governed by unimolecular decay law

$$d\delta/dt = k(1-\delta) \quad (4)$$

The specific rate constant k was calculated as 1.8×10^{-5} s^{-1} at 490 °C by putting $d\delta/dT = 7.8 \times 10^{-3}$ K^{-1}, evaluated from the TG curvature at $\delta = 0.5$ when $\phi = 5$ °C min^{-1}, into the equation

$$k = (d\delta/dT)/(1-\delta) \quad (5)$$

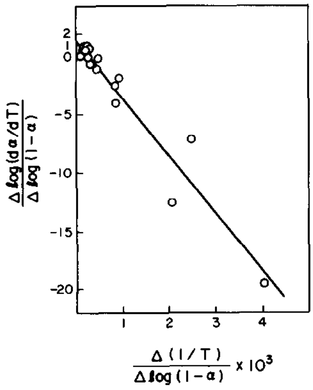

Fig. 6. Freeman–Carroll plot for the first step.

from eqns. (2) and (4). The frequency factor, A, was calculated to be 3.0×10^2 s^{-1} by putting $E_a = 75$ kJ mol^{-1}, $k = 1.8 \times 10^{-5}$ s^{-1} and $T = 763$ K into the Arrhenius equation.

The kinetic parameters obtained provide the following insights into the mechanism of the oxygen loss process. The oxygen evolution in the first step seems to occur at random in the bulk and the specific rate constant does not apparently depend on the δ value because most of the reaction is governed by a unimolecular decay law. Surface reaction, diffusion-controlled-type reactions and nucleation-and-growth-type reactions are excluded; this differs from the previous result [12] that the chemical diffusion constant of oxygen depends on the δ value. This difference may be attributed to the very different experimental conditions in the present and earlier studies. The low activation energy, resulting in a low frequency factor of 10^2 s^{-1} compared with $kT/h(\sim 10^{14}$ $s^{-1})$, and the non-dependence of δ on the specific rate constant might suggest that the electronic state in the Cu–O bond in question is delocalized.

REFERENCES

1 K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa and K. Fueki, Jpn. J. Appl. Phys., 26 (1987) L1228.
2 J.P. Burger, L. Lesusur, M. Nicolas, J.N. Daou, L. Dumoulin and P. Vajda, J. Phys. (Paris), 48 (1987) 1419.
3 M. Kikuchi, Y. Syono, A. Tokiwa, K. Oh-ishi, H. Arai, K. Hiraga, H. Kobayashi, T. Sasaoka and Y. Muto, Jpn. J. Appl. Phys., 26 (1987) L1066.
4 H.G. Langer and R.A. Dichiara, Thermochim. Acta, 133 (1988) 33.
5 A. Hanic, I. Horvâth and L. Galikova, Thermochim. Acta, 143 (1989) 123.
6 C.N.R. Rao, P. Ganguly, K. Sreedhar, R.A. Mohanram and P.R. Sarode, Mat. Res. Bull., 22 (1987) 849.
7 P. Monod, M. Ribault, F. D'Yvoire, J. Jegoudez, G. Collin and A. Revcolevschi, J. Phys. (Paris), 48 (1987) 1369.

8 F. Izumi, H. Asano and T. Ishigaki, Jpn. J. Appl. Phys., 26 (1987) L617.
9 Y. Nakabayashi, Y. Kubo, T. Manako, H. Igarashi and M. Yonezawa, Jpn. J. Appl. Phys., 27 (1988) L64.
10 F. Izumi, H. Asano, T. Ishigaki, E. Takeyama-Muromachi, Y. Uchida, N. Watanabe and T. Nishikawa, Jpn. J. Appl. Phys., 26 (1987) L1214.
11 Y. Morioka, A. Tokiwa, M. Kikuchi, Y. Syono and K. Nagase, Solid State Comm., 70 (1989) 1127.
12 K. Kishio, K. Suzuki, T. Hasegawa, T. Yamamoto, K. Kitazawa and K. Fueki, J. Solid State Chem., 82 (1989) 192.
13 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
14 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.