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Thermogravimetric studies of $Y_1Ba_2Cu_3O_{7-x}$ superconductors

V. SRIDHARAN, D. RAVICHANDRAN, S. SRINIVASAN, S. SIVASANKARAN,
L. GIRIDHARAN, K. SURESH, T. NAGARAJAN
Materials Science Centre, University of Madras, Chepauk; Madras 600 025, India

A. RAMAN
Department of Mechanical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

The synthesis conditions and oxygen stoichiometry were determined using a thermogravimetric analyser. The kinetics of oxygenation at different temperatures and at different atmospheres were studied. The oxygenation kinetics were found to be sensitive to porosity of the material. The appropriate oxygenation temperature was found to be 400 °C. For oxygenation temperatures below 400 °C, the oxygenation occurs by a nucleation and growth process, whereas for higher temperatures it is diffusion limited.

1. Introduction

Discovery of 40 K superconductors by Bednorz and Müller [1] and 90 K superconductors by Wu *et al.* [2] triggered enormous amounts of research work, owing to their important electrical and magnetic properties. However, it was soon established that these properties sensitively depend on cationic/anionic non-stoichiometry and the presence of secondary phases that form during preparation. In the case of $YBa_2Cu_3O_{7-x}$ compounds, the critical current density, J_c, is drastically affected by the presence of low-melting $BaCuO_2$ compound along the grain boundaries. The structure [3], the electrical and superconducting properties [4] were found to depend not only on the oxygen stoichiometry but also on the ordering of the oxygen atoms in the basal plane. Hence determination and control of oxygen stoichiometry is of prime importance for the formation of high-quality superconductors.

Usually oxygen stoichiometry was determined by wet chemical methods [5, 6, 7] or from the weight loss of the sample in the presence of a hydrogen atmosphere at an elevated temperature [4]. Apart from the fact that the former technique requires typically 80 mg sample and it cannot be applied for oxygen stoichiometry less than 6.5, both techniques are destructive.

Using thermogravimetric analysis (TGA), Langer and Dichiara have studied the stability of $YBa_2Cu_3O_{7-x}$ under different atmospheric conditions [8]. From their isothermal studies it is seen that 500 °C isothermal annealing leads to higher oxygen stoichiometry compared to that at 400 °C. From neutron studies, Jantsch *et al.* [9] estimated the occupation number for O(1) and O(5) atoms and the thermal parameters of O(1) as a function of temperature. It was found that the occupation number of the O(1) atom begins to fall rapidly at 500 °C with a corresponding increase in the value of the O(5) atom. In addition, the thermal parameter of the O(1) atom anomalously increases in this temperature range. These results indicate that diffusion of the oxygen atom starts around 500 °C.

Oxygenation kinetics in dense $YBa_2Cu_3O_{7-x}$ compound was investigated by O'Byran and Gallagher [10]. From their TGA studies it was seen that for an isothermal annealing temperature of 600 °C or less, the weight of the sample continued to increase even after 7 h annealing. Hence they concluded that in these temperature ranges, oxygenation was not complete and also the kinetics was slower. At higher oxygenation temperatures they found that the parabolic law holds good up to 60% of the reaction after which the reaction becomes slower due to a topochemical mechanism. From the microscopic studies they found evidence for enhancement of oxygenation due to micro/macro cracks.

Alford *et al.* studied the effect of porosity on J_c [11]. They found that for 10% porosity, J_c sharply increased by an order of 10 and decreased on further increasing the porosity. They attributed this to the sample becoming impermeable to oxygen due to the high density of the sample, leading to lower oxygen stoichiometry.

However, the effect of porosity/cracks and oxygen partial pressure on the kinetics of oxygenation in these compounds remains unclear. With this in mind, TGA studies of the oxygenation of porous $YBa_2Cu_3O_{6.1}$ were carried out under two different oxygen partial pressures.

2. Experimental procedure

For the isothermal studies, sintered samples were prepared as follows. Stoichiometric amounts of Y_2O_3, $BaCO_3$ and CuO were mixed in an agate mortar for

3 h for better homogenization. This mixture was calcined at 900 °C for 12 h. The calcined powder was hand ground for 3 h in an agate mortar and pressed into small discs under a pressure of 6 ton. The pellets were sintered at 950 °C for 3 days with three intermittent grindings. Samples with an oxygen stoichiometry of 6.1 were prepared by vacuum annealing (better than 6×10^{-6} torr) at 700 °C for 8 h.

Thermogravimetric studies were carried out using a Perkin–Elmer TGA7 with a sensitivity of 0.1 μg. The atmosphere was switched from one gas to another using a gas selection accessory. A Perkin–Elmer high-temperature differential thermal analyser DTA4, was used to estimate the melting points of the compounds. Structural studies were investigated using a high-resolution Guinier powder X-ray diffractometer. The diffractometer was fitted with a primary Quartz monochromator to select either K_{α_1} or K_{α_2}.

3. Results and discussion

3.1. Synthesis studies

Approximately 15 mg mixture of stoichiometric Y_2O_3, $BaCO_3$, and CuO was loaded into TGA and subjected to the following heat treatment under oxygen atmosphere: 50–950 °C at 10 °C min^{-1}, soaked at 950 °C for 60 min, and cooled to 50 °C at a cooling rate of 10 °C min^{-1}. The resulting thermogram is shown in Fig. 1. The mixture starts to rapidly lose weight from 750 °C onwards and at 950 °C the weight loss was 6.23%. After 60 min soaking, the total weight loss was 11.73%. Because $BaCO_3$ decomposes at 1450 °C [12], we attribute the observed weight loss of 11.73% at 950 °C to the formation of $YBa_2Cu_3O_{6.5}$ with simultaneous evolution of CO_2

$$1/2\,Y_2O_3 + 2\,BaCO_3 + 3\,CuO \rightarrow YBa_2Cu_3O_{6.5} + 2\,CO_2 \qquad (1)$$

On cooling from 950 °C to 50 °C, the weight pick-up was 1.28%. This increase in weight is due to oxygenation of $YBa_2Cu_3O_{6.5}$ to $YBa_2Cu_3O_7$. In this sample, single-phase formation was confirmed using X-ray diffraction studies (Fig. 2).

Hence in all the preparation procedures, 950 °C was chosen as the sintering temperature. Fig. 3 shows the differential thermal analysis of the compound prepared in this way and the melting point was estimated to be 1015 °C, which agrees quite well with the reported value [13]. This shows that the sample is devoid of any impurity phases, such as $BaCuO_2$, CuO, etc., which would otherwise show a low-temperature melting peak of $BaCuO_2$ at 940 °C or a lowering of the melting point of the superconducting compound due to the presence of CuO [13].

3.2. Oxygen stoichiometry determination

The usual wet chemical methods and weight loss of the study under a hydrogen atmosphere, suffer from

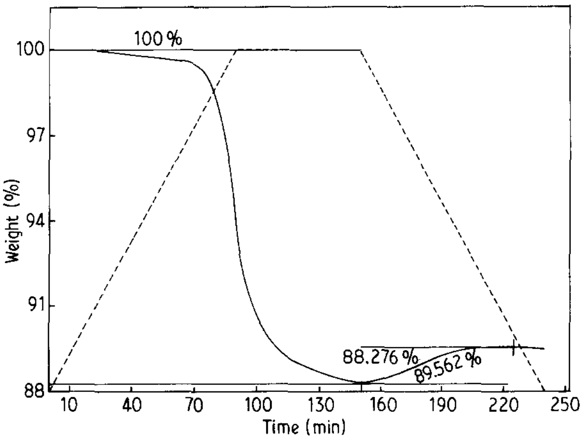

Figure 1 TGA thermogram of a stoichiometric mixture of Y_2O_3, $BaCO_3$ and CuO under an oxygen atmosphere. (– – –). The temperature profile.

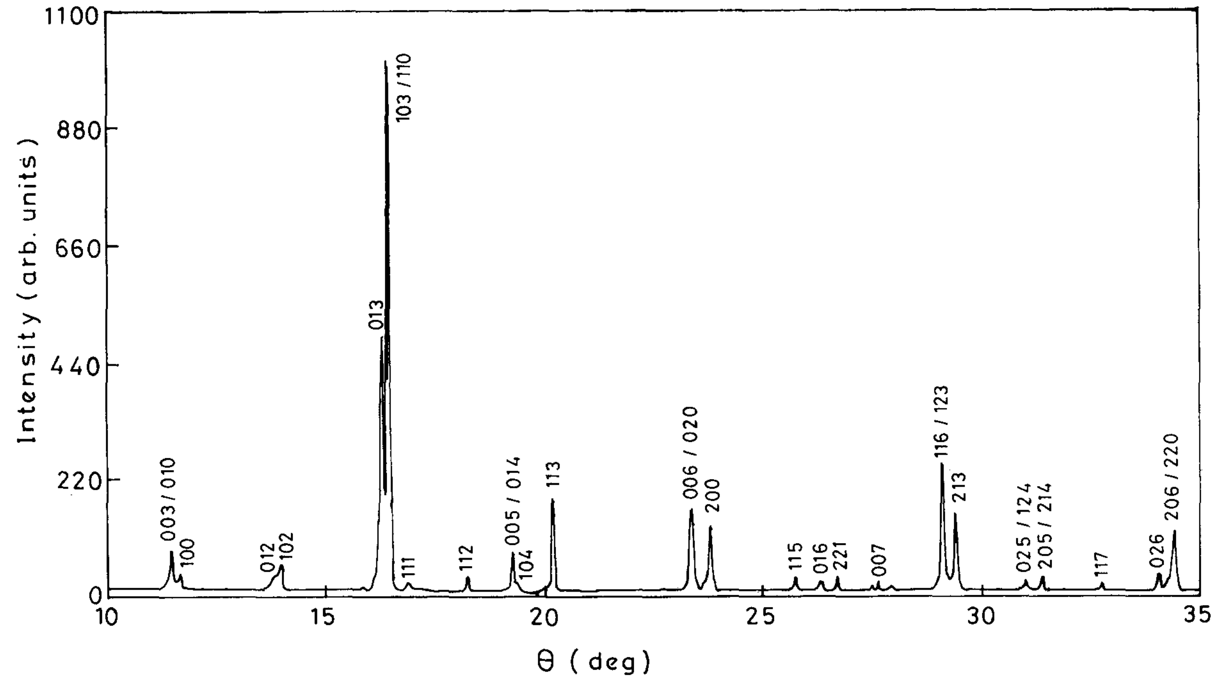

Figure 2 Powder XRD pattern of $YBa_2Cu_3O_7$.

TABLE I Oxygen stoichiometry of $YBa_2Cu_3O_{7-x}$ from thermogravimetric analysis and X-ray diffraction studies

Sample	TGA		XRD			
	Weight loss (%)	$7-x$	a (nm)	b (nm)	c (nm)	$7-x$
350 °C O_2 annealed	2.362	6.96	0.3827	0.3890	1.1683	6.908
450 °C vacuum annealed	1.735	6.70	0.3825	0.3875	1.1710	6.760
700 °C vacuum annealed	0.442	6.18	0.3857	0.3857	1.1825	6.165

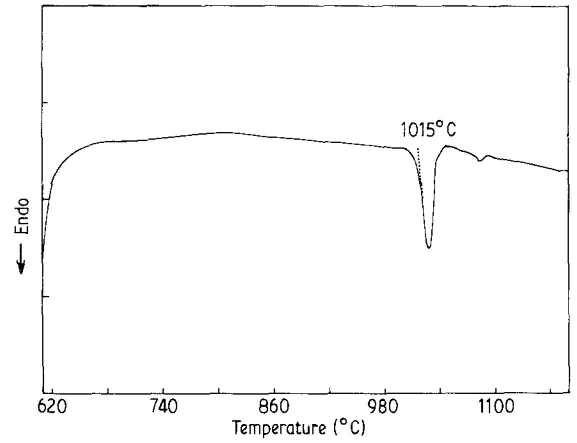

Figure 3 DTA thermogram of pure $YBa_2Cu_3O_{7-x}$ compound under an oxygen atmosphere.

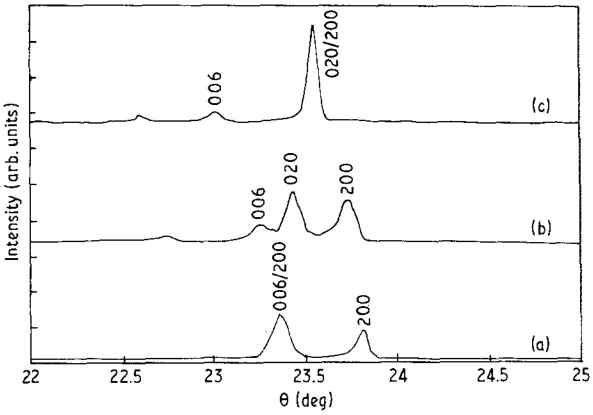

Figure 5 Powder XRD pattern of (a) 350 °C oxygen-annealed, (b) 450 °C vacuum-annealed and (c) 700 °C vacuum-annealed $YBa_2Cu_3O_{7-x}$ compound.

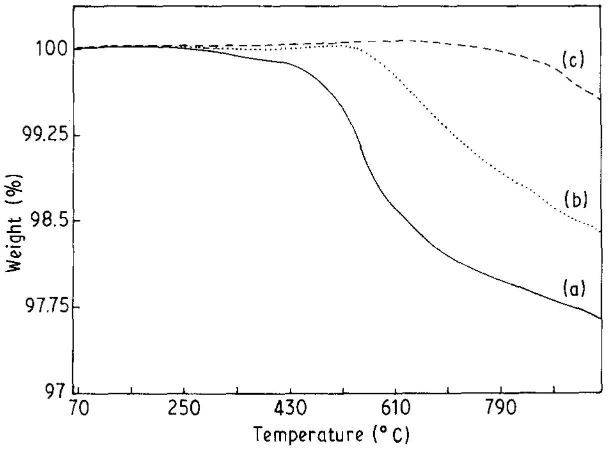

Figure 4 TGA thermogram of (a) 350 °C oxygen-annealed, (b) 450 °C vacuum-annealed and (c) 700 °C vacuum-annealed $YBa_2Cu_3O_{7-x}$ compound.

the fact that both methods are destructive. We adopted another method so that the sample can be reused after determination of oxygen stoichiometry. $YBa_2Cu_3O_7$ (Sample A) was prepared by the usual sintering methods, followed by 350 °C annealing for 12 h in an oxygen atmosphere and furnace cooled to room temperature. Samples with different oxygen stoichiometry were prepared by vacuum annealing at 450 °C (Sample B) and 700 °C (Sample C). The weight-loss studies were carried out from 50–950 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The resulting thermograms of the samples are shown in Fig. 4. While the 400 °C oxygen-annealed sample starts losing weight from 400 °C onwards, for vacuum-annealed samples, B and C, loss in weight is from 550 and 750 °C onwards, respectively. The weight loss of Samples A, B, and C at 950 °C was 2.362%, 1.735% and 0.442%, respectively. The oxygen stoichiometry of the starting materials was estimated using the following equation:

$$x = 1 - \frac{M_6 L}{100 M_O} \qquad (2)$$

where M_6 and M_O are the molecular weights of $YBa_2Cu_3O_6$ and the atomic weight of oxygen, respectively, and L is the total percentage weight loss at 950 °C.

The X-ray diffraction patterns of Samples A, B, and C recorded in the 2θ interval from 44°–50° are shown in Fig. 5. The lattice parameters were evaluated using a least-squares fitting technique and are tabulated in Table I. As the c-axis sensitively depends on oxygen stoichiometry, the latter can be estimated from the equation

$$7 - x = -5.205C + 67.724 \qquad (3)$$

The oxygen stoichiometry of Samples A, B and C using both lattice parameter and weight loss are compared in Table I. The results are in good agreement within the experimental resolution.

3.3. Kinetics of oxygenation

Vacuum-annealed samples with oxygen stoichiometry 6.1 were isothermal annealed in an oxygen atmosphere at 350, 400, 450 and 500 °C. Samples were brought to the isothermal temperature in 3 min using different heating rates. A nitrogen atmosphere was maintained during the initial ramping to the required isothermal temperature after which the atmosphere was switched over to oxygen with the gas flow rate of 50 cm^3 min^{-1}. In all the measurements approximately 2 mm × 2 mm (~ 15 mg) pellets were used to avoid any artefact in the measurements.

Fig. 6 shows the isotherms of the $YBa_2Cu_3O_{6.1}$ sample at different temperatures. The hump seen in first 3 min of these thermograms is due to the rapid heating rate (150 °C min^{-1}) employed during the initial period. It is evident from these thermograms that the 400 °C annealing leads to maximum weight pick-up indicating that 400 °C is a better oxygenation temperature, although the kinetics of oxygenation successively increases with higher isothermal temperatures. The weight pick-up of 2.16% at 400 °C corresponds to the formation of orthorhombic $YBa_2Cu_3O_7$. The X-ray diffraction pattern of the 400 °C oxygenated sample is similar to that shown in Fig. 2.

In general, the kinetics of oxygenation is much faster and also the weight saturates at much smaller annealing time compared to that given by O'Bryan and Gallagher [10]. Because we had sintered our samples at a lower temperature, 950 °C, this might have resulted in a porous material which is highly interconnected, as noted in [10]. These highly interconnected porous spaces form channels which are completely filled with oxygen. In this way the samples are "soaked" in the oxygen atmosphere. Interconnected porosity also offers a larger surface area for the oxygenation reaction. This is in contrast to the dense samples of O'Bryan and Gallagher, in which oxygenation can take place only across the external surface area and through the micro/macro cracks offering much smaller reaction area compared to the porous materials. Thus we can expect faster kinetics in the porous samples compared to dense samples. These results also support the findings of Alford *et al.* [11]. Also, the oxygen stoichiometry of the starting material was 6.1. The low oxygen stoichiometry acts as an additional driving force and, in general, the kinetics will be faster in this compound compared to that in samples with initial higher oxygen stoichiometry. The above two factors (interconnected porosity and low initial oxygen stoichiometry) led to faster kinetics as well as faster equilibration of the oxygen stoichiometry.

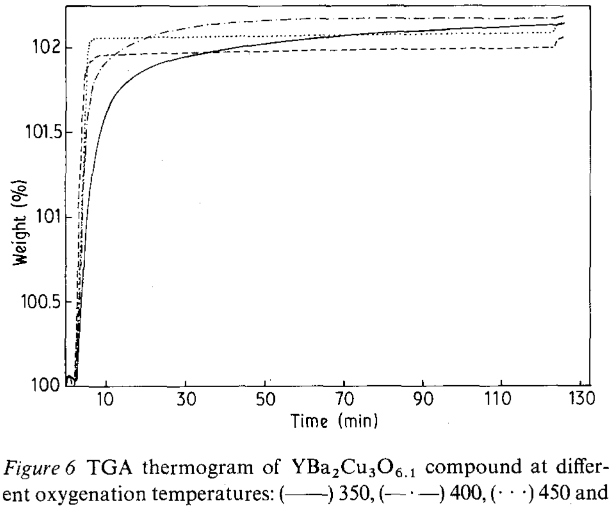

Figure 6 TGA thermogram of $YBa_2Cu_3O_{6.1}$ compound at different oxygenation temperatures: (——) 350, (— · —) 400, (· · ·) 450 and (– – –) 500 °C for 120 min under an oxygen atmosphere.

The thermograms could neither be fitted with the parabolic law corresponding to a diffusional mechanism nor with a power law equation corresponding to a nucleation and growth process. In all the thermograms, the fraction of reaction product, α, increases linearly with time, even up to a larger value of α. Fig. 7 shows a representative α versus t curve for the 500 °C isothermal annealing. The slopes of the corresponding thermograms increase with higher isothermal temperature, indicating faster kinetics.

In searching for a clue for the mechanism of oxygenation, approximately 15 mg finely powdered sample was oxygenated at 450 °C as in the heating schedule stated above. In Fig. 8 the corresponding thermogram is compared with that of the pellet. Interestingly, the following points were evident from this experiment.

(i) Oxygen stoichiometry is slightly smaller for the powdered sample compared to that of the pellet.

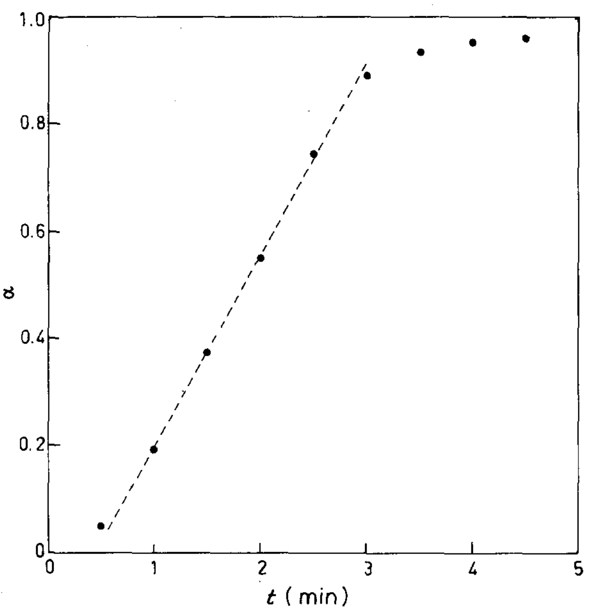

Figure 7 α–t plot for the 500 °C oxygenated sample. (– – –) A guide for the eye.

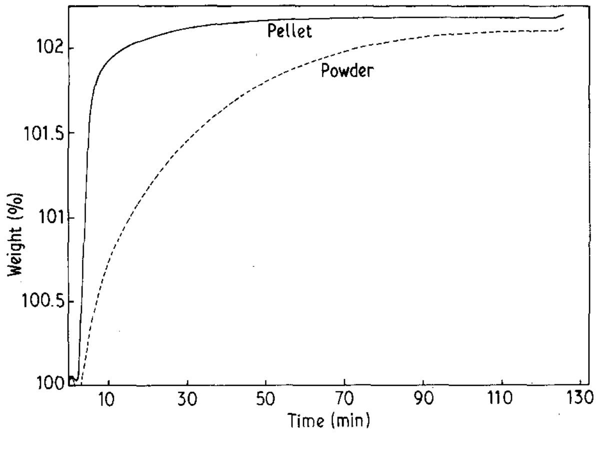

Figure 8 TGA thermogram of $YBa_2Cu_3O_{6.1}$ oxygenated at 400 °C for (——) small pellets and (– – –) fine powder.

(ii) Importantly, for the powdered sample the kinetics is slower right from smaller values of α.

The second point excludes a topochemical mechanism for retardation of kinetics, because its effect is felt only for large values of α, typically greater than 0.7. If the oxygenation is by a diffusion process one would expect faster kinetics and also higher oxygen stoichiometry in the powder sample than in the pellet. On the other hand, if the mechanism of oxygenation is by nucleation and growth, then the reaction wavefront should be able to move freely across the sample. This is quite possible in the case of the sintered pellet. In the case of the powdered sample, with smaller particle size, the wavefront is largely impeded in its movement so that the kinetics becomes slower. Hence slow kinetics in the powdered sample is a clear indication of a nucleation and growth mechanism, at least at this oxygenation temperature.

In order to investigate the effect of oxygen partial pressure on the kinetics of oxygenation, we carried out similar isothermal studies with 50% nitrogen and 50% oxygen. The corresponding thermograms are shown in Fig. 9. Weight pick-up under this atmospheric condition is always less than that of 100% oxygen atmosphere.

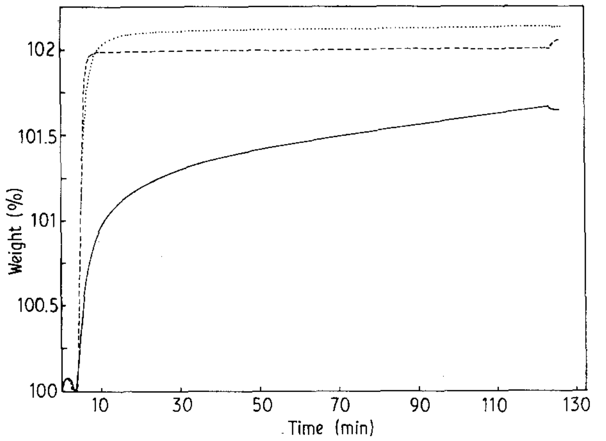

Figure 9 TGA thermogram of $YBa_2Cu_3O_{6.1}$ compound at different oxygenation temperatures: (——) 350 (· · ·) 400 and (– – –) 450 °C for 120 min under a 50% N_2 and 50% O_2 atmosphere.

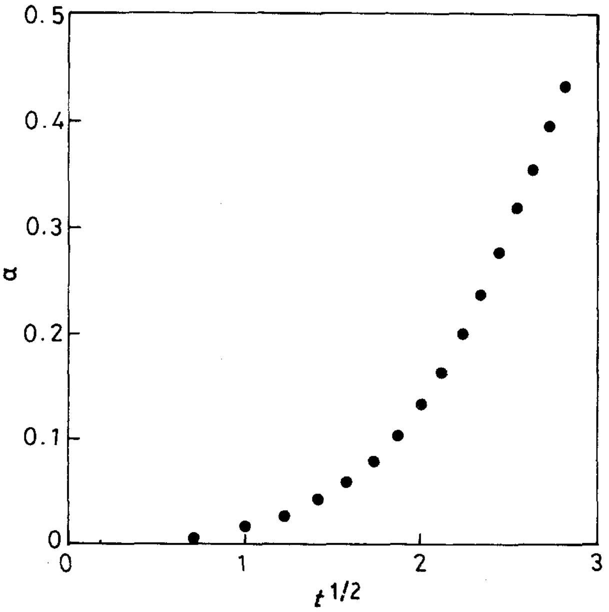

Figure 10 α–$t^{1/2}$ plot for the 350 °C oxygenated sample under a 50% N_2 and 50% O_2 atmosphere.

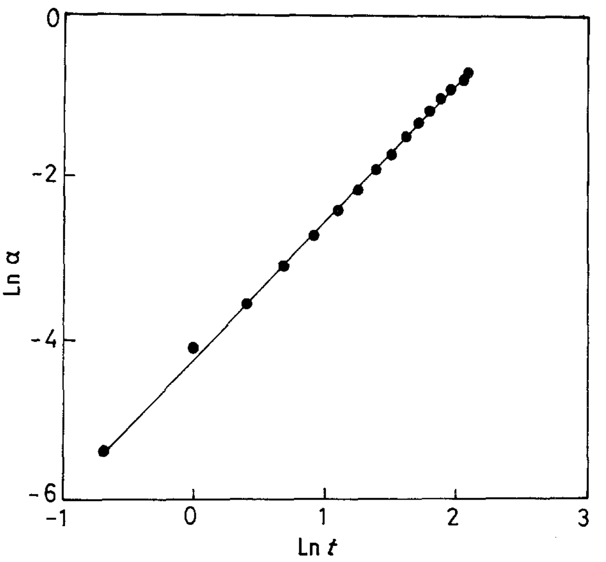

Figure 11 Plot of $\ln \alpha$ versus $\ln t$ for the 350 °C oxygenated sample under a 50% N_2 and 50% O_2 atmosphere.

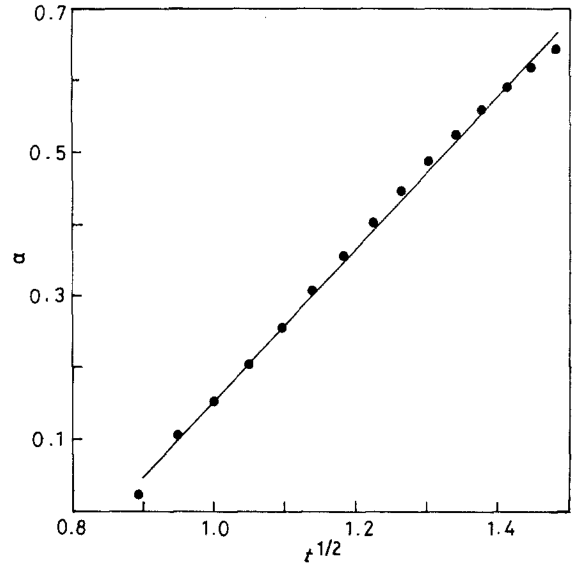

Figure 12 α–$t^{1/2}$ plot for the 400 °C oxygenated sample under a 50% N_2 and 50% O_2 atmosphere.

The thermogram for 350 °C isothermal annealing could not be fitted with the parabolic law, as is evident from Fig. 10. However, the 350 °C thermogram could be fitted with a power law equation (Fig. 11) up to $(d\alpha/dt)_{max}$. This clearly demonstrates that the oxygenation mechanism at this temperature is by nucleation and growth. However, for higher isothermal temperatures, 400 and 450 °C, thermograms could only be fitted with a parabolic law up to $\alpha = 0.75$ (Figs 12 and 13). Applicability of the diffusional mechanism up to large values of α, compared with O'Bryan and Gallagher, is due to the larger surface area of the porous material, so that topochemical manifestation sets in during the later part of the reaction.

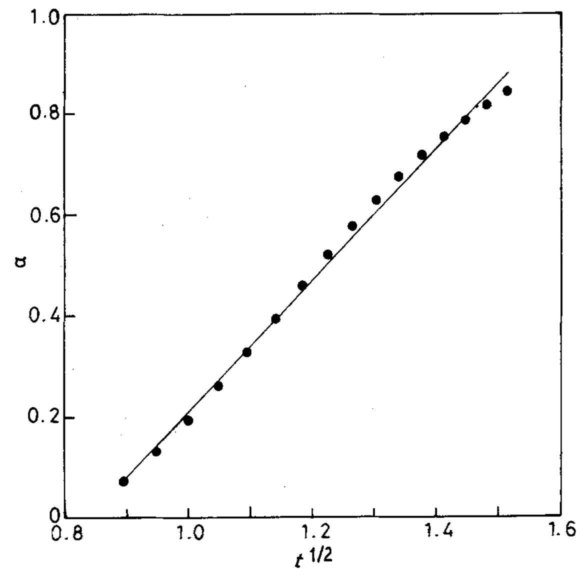

Figure 13 α–$t^{1/2}$ plot for the 450 °C oxygenated sample under a 50% N_2 and 50% O_2 atmosphere.

4. Conclusions

1. For a better oxygenation process, the sample must be relatively porous so that kinetics can be faster and results in high oxygen stoichiometry.

2. A 400 °C oxygen anneal is better for achieving high oxygen stoichiometry.

3. The kinetics of oxygenation is sensitive to oxygen partial pressure in addition to the oxygenation temperature.

4. Under a 50% nitrogen and 50% oxygen atmosphere, the oxygenation at 350 °C is by a nucleation and growth process and at still higher temperature it is diffusion limited.

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References

1. J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys. B* **64** (1986) 189.
2. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
3. J. D. JORGENSEN, D. G. HINKS, L. SODERHOLM, K. J. VOLIN, R. HITTERMAN, J. D. GRACE, I. K. SCHULLER, C. V. SEGRE, K. ZHANG and M. S. KLECFISCH, *Phys. Rev. B* **36** (1987) 3608.
4. R. J. CAVA, B. BATLOGG, C. H. CHEN, E. A. RIETMAN, S. M. ZAHURAK and D. WEDER, *ibid.* **36** (1987) 5719.
5. D. C. HARRIS and T. A. HEWSTON, *J. Solid State Chem.* **69** (1987) 182.
6. E. H. APPELMAN, L. R. MORSS, A. M. KINI, U. GEISSER, A. UMEZAWA, G. W. CRABTREE and K. D. CARLSON, *J. Inorg. Chem.* **26** (1987) 3237.
7. J. M. TARASCON and B. G. BAGLEY, *MRS Bull.* January (1989) 53.
8. M. G. LANGER and R. A. DICHIARA, *Thermochim. Acta* **133** (1988) 32.
9. S. JANTSCH, J. IHRINGER, J. K. MAICHLE, W. PRANDL, S. KEMMLER-SACK, R. KIEIMEL, S. LOSCH, W. SCHAFEE, M. SCHLICHENMAIER and A. W. HEWAT, *J. Less Common Metals* **150** (1989) 167.
10. H. M. O'BRYAN and P. K. GALLAGHER, *J. Mater. Res.* **3** (1988) 619.
11. N. McN, ALFORD, W. J. CLEGG, M. A. HARMER, J. D. BRIDALL, K. KENDALL and D. H. JONES, *Nature* **332** (1988) 58.
12. C. WEAST and M. J. ASTLE, "CRC Handbook of Chemistry and Physics" (CRC Press, Florida, 1981).
13. F. LICCI, P. TISSOT and H. J. SCHEEL, *J. Less Common Metals* **150** (1989) 210.

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