JOURNAL OF MATERIALS SCIENCE 25 (1990) 3508–3512

Studies on the influence of lanthanum oxide on the sinterability of chromium(III) oxide

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The mechanism of sintering in chromium(III) oxide in the presence of varying amounts of lanthanum oxide under firing conditions which simulate a controlled reducing atmosphere, has been investigated. The investigation is based on isothermal shrinkage measurements at different temperatures. The data suggest that the vapour-phase transport mechanism becomes predominant with evidence of a grain-boundary diffusion process.

1. Introduction

Chromium(III) oxide, because of its high melting point (2260 ±25° C) and high electrical conductivity [1–3], which make it useful in high corrosive environments as well as at elevated temperatures, has been in great demand over the past several years. In addition, the oxide has also been found to possess excellent thermal shock resistance to enhance its applicability. However, hindrance of its sintering due to the change in oxidation state producing the volatile phases, is well known. Several investigators have studied the sintering of Cr_2O_3 under varied conditions. In these studies, the oxygen partial pressure has either been unknown or too high [4–7]. In the study of Hagel *et al.* [4] p_{O_2} was actually unknown because of the use of graphite holders, although they reported $p_{O_2} \simeq 1.3 \times 10^{-5}$ atm. While repeating these experiments, without using graphite boats, Anderson [5] found p_{O_2} to be $\simeq 10^{-5}$ atm, but failed to reproduce the observed data. Halloran and Anderson [8] studied the dependence of p_{O_2} on the initial sintering of chromia and their results have confirmed the data of Ownby and Jungquist [9]. Other workers, such as Stone and Lockington [10], have used powder reductants such as carbon to promote sintering with some success and their results emphasize the role of grain boundaries on sintering. Densification of Cr_2O_3 has been found to be enhanced in neutral or reducing atmospheres [4, 11] and this has occurred by both evaporation–condensation and by volume diffusion mechanisms. Several transition metal oxides [12, 13] have been used as sintering aids but with the exception of TiO_2, none has been found to be effective. Roy *et al.* [14] indicated that the sintering mechanism is predominantly a grain-boundary diffusion with simultaneous occurrence of a vapour transport process in the presence of varying amounts of MgO.

The present investigation deals with the study of isothermal sintering kinetics of Cr_2O_3, based on isothermal shrinkage measurements in the presence of varying amounts of La_2O_3 at different temperatures. The conditions during firing simulate a controlled reducing atmosphere with a very low p_{O_2}, which is the consequence of the formation of carbon monoxide from graphite granules used around the sintering bed. From the kinetic data, the probable mechanism of mass transport has been suggested. The fracture surface of the densest specimen obtained in the present study has been examined under a scanning electron microscope (SEM) for grain growth, crystal habit and vapour-phase growth.

2. Experimental details

Chromium(III) oxide used in the study was high-purity grade (Thomas Baker, London, 99.9% purity). The particle size distribution of the Cr_2O_3 powder determined by Sartorius sedimentation balance is shown in Fig. 1. Extrapure $La_2(Co_3)_3$ (99.9% purity, SISCO Research Laboratory, India) was used as the source of La_2O_3.

For the doped samples, a weighed amount of $La_2(CO_3)_3$ was suspended in distilled water and mixed with the preweighed Cr_2O_3. This mixture was stirred continuously with a magnetic stirrer for about 6 h for

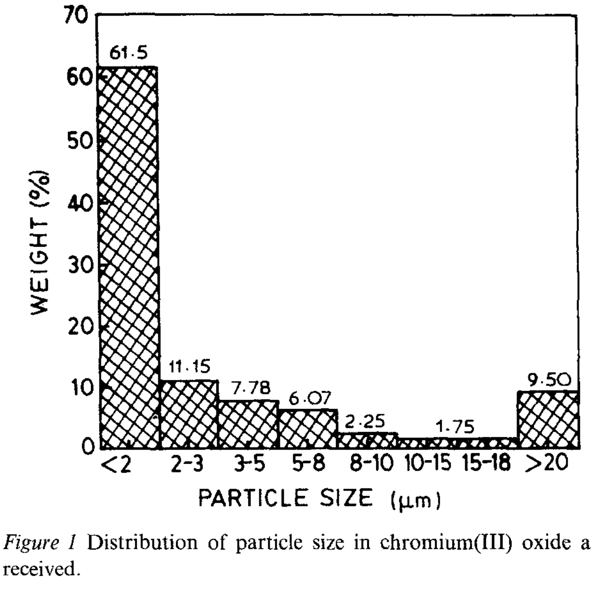

Figure 1 Distribution of particle size in chromium(III) oxide as-received.

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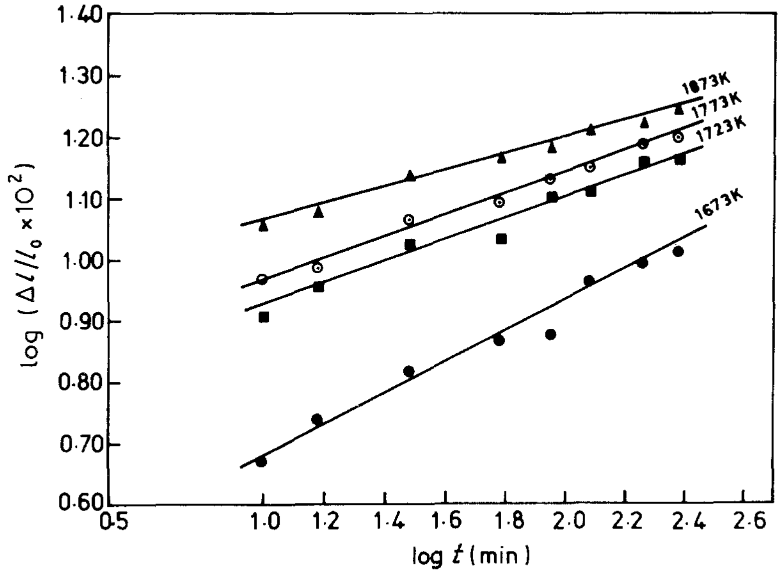


Figure 2 Plot of logarithm of percentage linear shrinkage against logarithm of time for specimen C000. (●) 1673 K, (■) 1723 K, (⊙) 1773 K, (▲) 1873 K.

homogenization. The mixture was carefully dried. The powders were then calcined at 873 K to liberate the CO_2 gas. The dried material was further wet ground and converted to square pellets by applying a pressure of 122 MPa using a hydraulic press to produce a more uniform green compaction density of about 3.33 g cm^{-3}. The density used to compute the per cent theoretical density of both pure and doped material was 5.21 g cm^{-3}.

Pellet samples (1.54 cm × 1.54 cm × 0.7 cm in size) were placed inside a sealed alumina crucible packed with graphite granules to avoid oxidation during sintering. The sintering was carried out at 1673, 1723, 1773 and 1873 K with soaking times ranging from 10 to 240 min in each case. The rate of heating was 373 K h^{-1}. The samples were cleaned and measured for various properties. The data reported in this paper were evaluated on the basis of two experiments.

3. Results and discussion

Kinetic parameters such as the n-value and activation energy calculated for different compositions studied, and temperatures used for their sintering, are given in Table I. Figs 2 to 6 show the plots of percentage relative shrinkage against time (min) on a log–log scale for the different specimens. The plots are based on the equation suggested by Johnson and co-workers [15–17]

$$\log\left(\frac{\Delta L}{L_0} \times 10^2\right) = \log K_T + n \log t \qquad (1)$$

where K_T is a temperature-dependent constant, $\Delta L/L_0$ is the relative linear shrinkage, t is the time and n is an exponent whose value varies with the mechanism of material transport. n is calculated from the slope of the plot while $\Delta L/L_0$ at $t = 1$ gives K_T. Using an Arrhenius equation, plots of $-\log K_T$ against reciprocal temperature $(1/T)$ for different samples are shown in Fig. 7. The slope of these plots gives $Q/2.303R$ from which Q, the activation energy, is calculated. The calculated values of n reveal that although they range between 0.1 and 0.24, the average value is 0.15. It has been pointed out by others [18, 19] that n varies from 0.32 to 0.47 depending on the relative importance of grain-boundary and volume diffusion in the material transport. Singu [20] has also shown that the

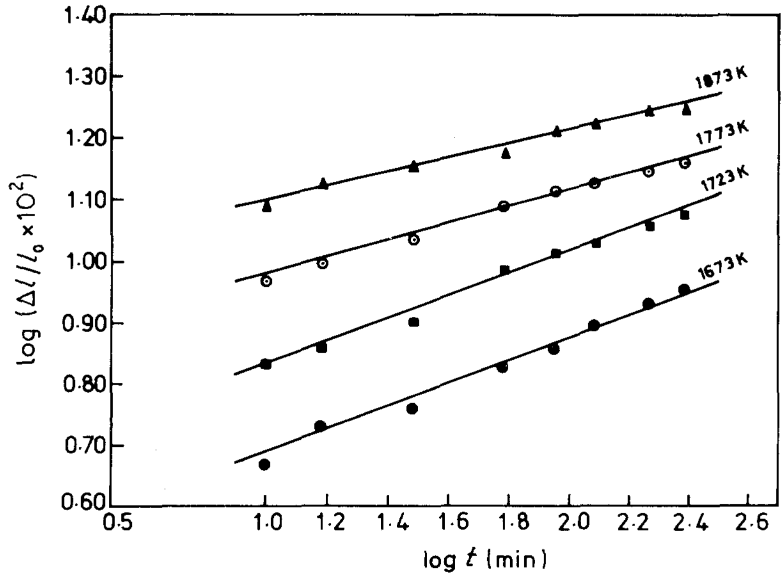


Figure 3 Plot of logarithm of percentage linear shrinkage against logarithm of time for specimen CL010. (●) 1673 K, (■) 1723 K, (⊙) 1773 K, (▲) 1873 K.

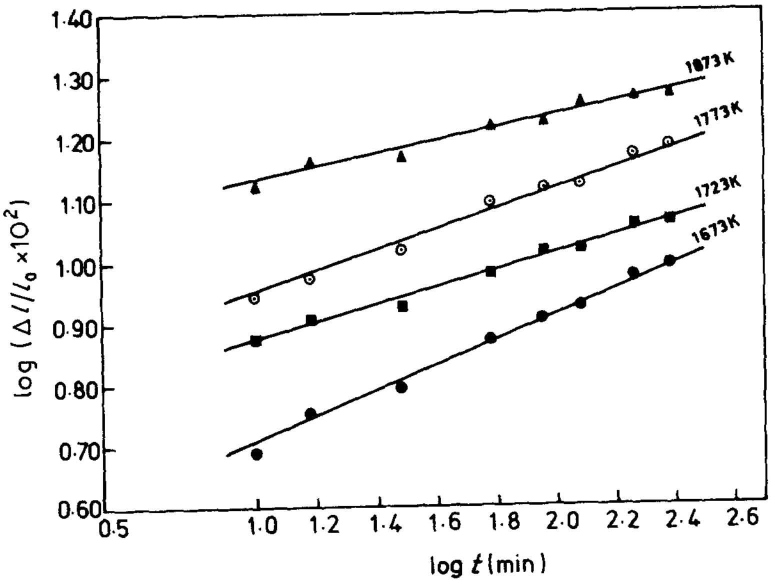


Figure 4 Plot of logarithm of percentage linear shrinkage against logarithm of time for specimen CL025. (●) 1673 K, (■) 1723 K, (⊙) 1773 K, (▲) 1873 K.

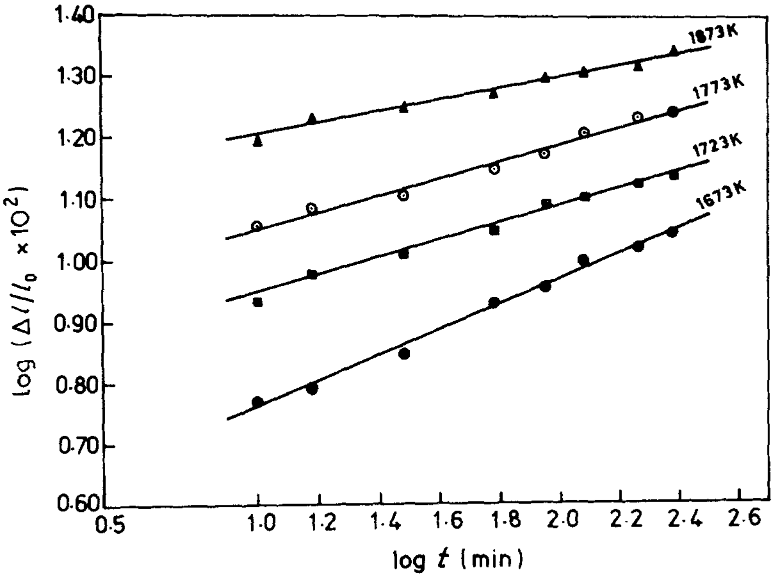


Figure 5 Plot of logarithm of percentage linear shrinkage against logarithm of time for specimen CL050. (●) 1673 K, (■) 1723 K, (⊙) 1773 K, (▲) 1873 K.

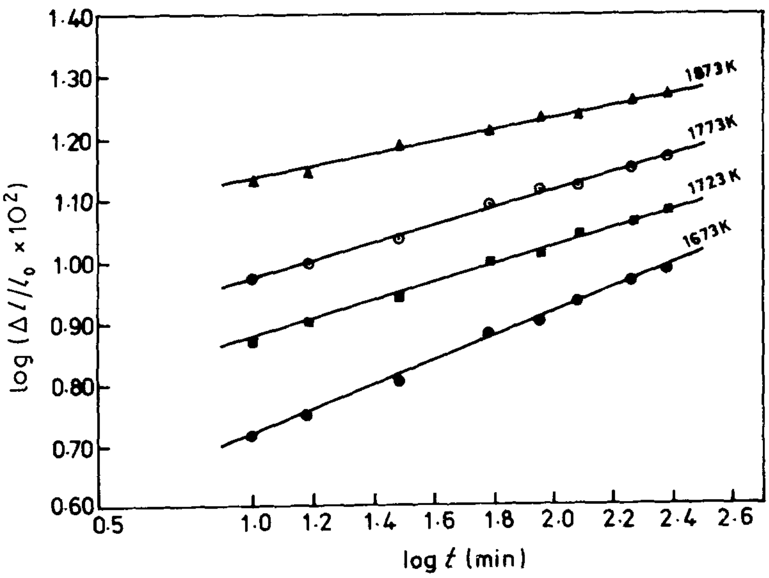


Figure 6 Plot of logarithm of percentage linear shrinkage against logarithm of time for specimen CL100. (●) 1673 K, (■) 1723 K, (⊙) 1773 K, (▲) 1873 K.

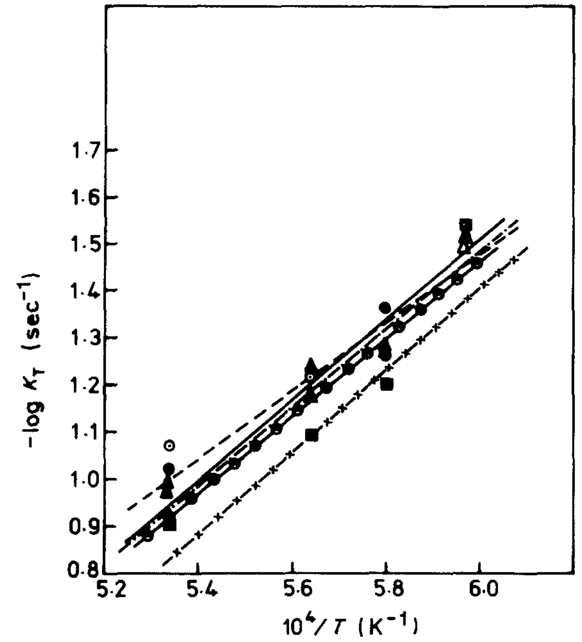


Figure 7 Plot of negative logarithm of densification rate constant against reciprocal temperature (K^{-1}). (⊙) C000, (●) CL010, (▲) CL025, (×■×) CL050, (⊖△⊖) CL100.

TABLE I Kinetic data for the sintering of chromium(III) oxide in the presence of different wt % lanthanum oxide

Sample no.	Composition (wt %)	Temperature (K)	*n*	Activation energy, *Q* (kJ mol^{-1})
C000	0.00	1673	0.24	139.7
		1723	0.18	
		1773	0.18	
		1873	0.14	
CL010	0.10	1673	0.20	153.6
		1723	0.19	
		1773	0.15	
		1873	0.12	
CL025	0.25	1673	0.22	150.6
		1723	0.14	
		1773	0.18	
		1873	0.11	
CL050	0.50	1673	0.21	161.9
		1723	0.15	
		1773	0.14	
		1873	0.10	
CL100	1.00	1673	0.21	150.6
		1723	0.16	
		1773	0.15	
		1873	0.11	

slope is increased by concurrent surface diffusion and decreased by vapour transport.

In the light of these findings, one may conclude that the mechanism operative in the sintering of Cr_2O_3 in the presence of varying amounts of La_2O_3 is predominantly a vapour-phase transport process with concurrent contribution from grain-boundary diffusion. Earlier, Stone [21] pointed out that the diffusion mechanism became important particularly in non-stoichiometric Cr_2O_3. Further, it is also observed that the sintered specimen obtained in this study contained a black mass which can be highly polished but on pulverizing, turns distinctly green. This observation is also in accord with that of Stone [21] and Roy *et al.* [14]. Lastly, the relatively low activation energy (140 to 162 kJ mol^{-1}) found for the present system possibly indicates the predominance of vapour-phase transport. It is interesting to note that the log shrinkage against log time plots for each specimen at different

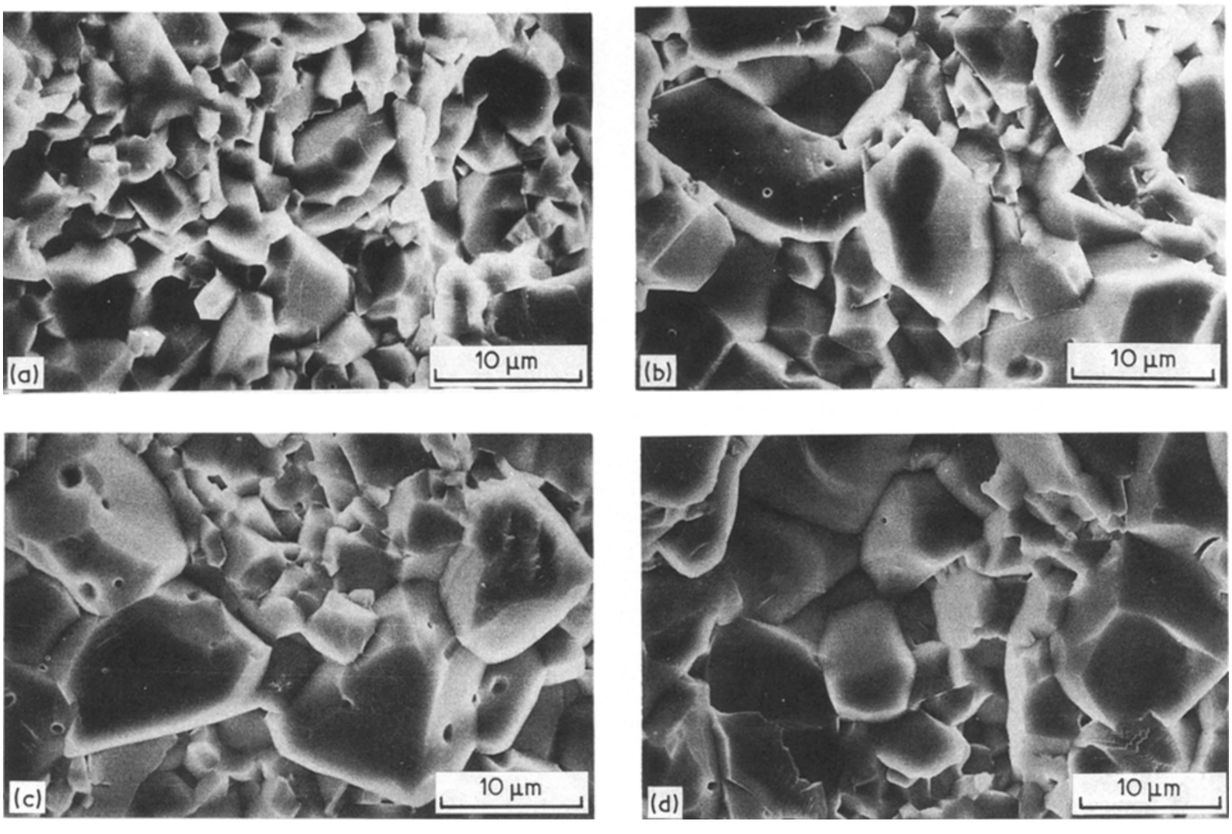
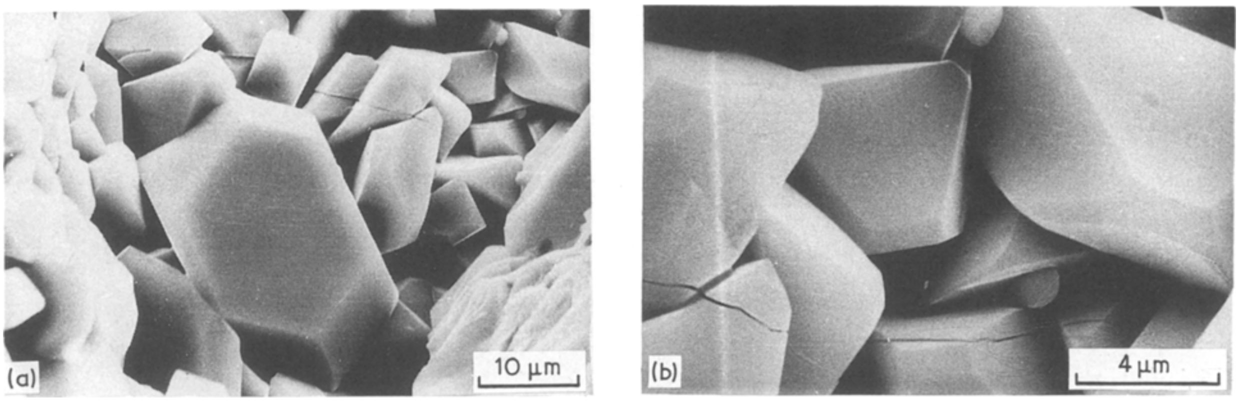


Figure 8 Scanning electron micrographs of fracture surfaces of specimen CL050 sintered at different temperatures with fixed soaking time (240 min): (a) 1673 K, (b) 1723 K, (c) 1773 K. (d) 1873 K.



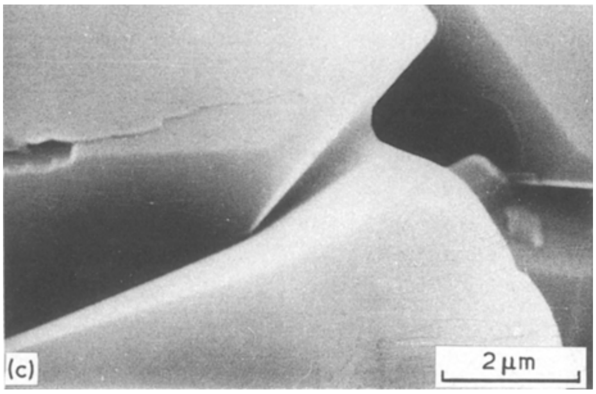


Figure 9 Scanning electron micrographs of fracture surfaces of specimen CL050 sintered at 1873 K with fixed soaking time (240 min): (a) vapour-phase growth of very fine loosely packed crystals of Cr_2O_3 at localized spots, (b) recrystallized Cr_2O_3 grains exhibit perfect tetrakaidecahedral habit, (c) neck growth between Cr_2O_3 grains.

temperatures are linear but not completely parallel, a situation similar to that in the MgO system [14]. The n-value decreases with increasing sintering temperature. It reveals that the vapour-phase transport mechanism becomes predominant at higher temperatures which also cause a lowering of the activation energy. However, in the lower temperature range, the higher n-value might suggest that grain-boundary diffusion at that temperature predominates over vapour-phase transport.

Maximum densification of 99.05% theoretical density has been observed for the La_2O_3-doped (0.5 wt %) Cr_2O_3 specimen. Grain growth and pore morphology have also been studied from SEM fractographs. In this system, a significant amount of grain growth has been observed during sintering. The gradual increase in grain size with increasing sintering temperature from 1673 to 1873 K with fixed soaking time (240 min) and 0.5 wt % La_2O_3 concentration is shown in Fig. 8. It may be noted that trapped pores are diminished with increased sintering temperature. These figures also indicate that for dense specimens, the fracture mode is always transgranular. Fig. 9a reveals the vapour-phase growth of very fine loosely packed crystals of Cr_2O_3 at localized spots. It may also be noted that the recrystallized Cr_2O_3 grains exhibit perfect tetrakaidecahedral habit (Fig. 9b). Fig. 9c shows a clear indication of neck growth during sintering.

4. Conclusions

The present study of isothermal sintering kinetics of chromium(III) oxide in the presence of varying concentrations of La_2O_3 indicated that the vapour-transport mechanism becomes predominant at higher temperatures. However, in the lower temperature range, the grain-boundary diffusion mechanism plays a more important role. The sequence of microstructural change suggests that vapour transport and grain-boundary diffusion controlled mechanism might have been operative. Grain growth and pore morphology are dependent on the temperature and time of isothermal soaking.

References

1. D. B. MEADOWCROFT and F. G. HICKS, *Proc. Brit. Ceram. Soc.* **23** (1972) 33.
2. R. F. HUANG, A. K. AGARWAL and H. U. ANDERSON, *J. Amer. Ceram. Soc.* **67** (1984) 146.
3. G. M. CROSBIE, G. J. TENNENHOUSE, R. P. TISCHER and H. S. WROBLOWA, *ibid.* **67** (1984) 498.
4. W. C. HAGEL, P. J. JORGENSEN and D. S. TOMALIN, *ibid.* **49** (1966) 23.
5. H. U. ANDERSON, personal communication (1971).
6. H. E. N. STONE, *Metallurgia* **74** (1966) 151.
7. *Idem, ibid.* **76** (1968) 152.
8. J. W. HALLORAN and H. U. ANDERSON, *J. Amer. Ceram. Soc.* **57** (1974) 150.
9. P. W. OWNBY and G. E. JUNGQUIST, *ibid.* **55** (1972) 433.
10. H. E. N. STONE and N. A. LOCKINGTON, *J. Mater. Sci.* **2** (1967) 112.
11. L. L. HENCH, PhD thesis, Ohio State University (1964).
12. S. N. ROY and S. K. GUHA, *Trans. Ind. Ceram. Soc.* **44** (1985) 49.
13. W. D. CALLISTER, M. L. JOHNSON, I. B. CUTLER and R. W. URE Jr, *J. Amer. Ceram. Soc.* **62** (1979) 208.
14. S. N. ROY, S. R. SAHA and S. K. GUHA, *J. Mater. Sci.* **21** (1986) 3673.
15. D. L. JOHNSON and I. B. CUTLER, *J. Amer. Ceram. Soc.* **46** (1963) 541.
16. D. L. JOHNSON and T. M. CLARKE, *Acta. Metall.* **12** (1964) 1173.
17. L. BERRIN and D. L. JOHNSON, in "Sintering and Related Phenomena", edited by G. C. Kuezynski, N. A. Hooton and C. F. Gibbon (Gordon and Breach, New York, 1967) p. 445.
18. D. L. JOHNSON, in "Kinetics of Reactions in Ionic Systems", Vol. 4, edited by T. J. Gray and V. D. Frechette (Plenum Press, New York, 1969) p. 332.
19. M. K. PARIA, S. BASU and A. PAUL, *Trans. Ind. Ceram. Soc.* **42** (1983) 90.
20. P. H. SINGU, PhD thesis, North Western University (1967).
21. H. E. N. STONE, *Metallurgia* **77** (1968) 152.

Received 7 April
and accepted 28 September 1989