

On the sintering kinetics of titania doped ceramic lanthanum chromite

K P BANSAL, S KUMARI, B K DAS and G C JAIN

Division of Materials, National Physical Laboratory, New Delhi 110 012, India

MS received 9 February 1981; revised 9 March 1981

Abstract. The sintering behaviour of lanthanum chromite with the addition of 1 to 3 wt% TiO₂ was studied. Densification was examined as a function of sintering temperature and TiO₂ concentration. The results showed that pure LaCrO₃ could not be densified to > 75% of the theoretical density, while the densities exceeding 90% of the theoretical were achieved with 3 wt% titania addition at 1600° C.

Metallographic study reveals a normal grain growth following the rate equation $D^2 - D_0^2 = kt$. Activation energies both for densification and grain growth have been estimated to be $\approx (80 \pm 5)$ k cal/mole in case of 3 wt% TiO₂ addition.

Keywords. Activation energy; densification; grain growth; lanthanum chromite; sintering kinetics.

1. Introduction

Ceramic lanthanum chromite has been emphasized by many workers (Meadowcroft 1969, 1972, 1973; Anderson *et al* 1977, 1978) as the most promising candidate material for MHD systems. Attempts have been made (Leslie Group and Anderson 1976; Bansal *et al* 1980) to prepare dense lanthanum chromites by the addition of certain dopants such as SrCO₃ and calcia stabilized Zirconia. Incorporation of magnesia (George and Karkhanawala, 1979) has also been tried to obtain a highly dense and electronically conducting material. St. Jacques *et al* (1974) have also studied the effect of various additives on the grain growth of La (Sr) CrO₃.

The primary difficulty encountered in the sintering of LaCrO₃ appears to be the volatilization of chromium in oxidizing atmosphere similar to problems identified in the sintering studies of Cr₂O₃ and MgCr₂O₄ (Halloran *et al* 1974, Anderson 1974). Callister *et al* (1979) have recently achieved better sintering of Cr₂O₃ with the aid of TiO₂. The present study of sintering kinetics and grain growth of LaCrO₃ with the addition of TiO₂ was also taken up with an aim of improving upon its sinterability.

2. Experimental

The material was prepared employing usual ceramic fabrication techniques. Reagent grade La₂O₃, Cr₂O₃ and TiO₂, in appropriate amounts, were wet mixed by ball milling for 24 hr and the resulting mixture was dried in an oven. The powder was pressed and pre-fired overnight at 1400°C in nitrogen atmosphere. The pre-fired powder was

dry ball milled again for 24 hr to get a particle size of $< 1 \mu\text{m}$. The powder was then sieved and granulated by means of PVA (Poly Vinyl Alcohol) as binder, and pressed at 8000 psi in the form of discs (14 mm diameter and 4 mm thickness).

The tablets so obtained were fired at temperatures ranging from 1500°C to 1600°C in air for different times. Density measurements were done by water immersion technique (ASTM-71), and for microstructure observations, polished tablets were chemically etched in boiling orthophosphoric acid for a few minutes.

3. Results

3.1 X-ray diffraction analysis (XRD)

The Debye Scherrer x-ray diffractograms of pure and titania doped powder samples of LaCrO_3 , were obtained. Pure LaCrO_3 sample exhibited single phase having an orthorhombic perovskite structure with $a_0 = 5.479 \text{ \AA}$, $b_0 = 5.513 \text{ \AA}$, $c_0 = 7.756 \text{ \AA}$, which compares favourably with the published data (Khattak and Cox 1977). The titania doped samples also showed an orthorhombic perovskite lattice structure with a slightly different lattice constants, $a_0 = 5.477 \text{ \AA}$, $b_0 = 5.511 \text{ \AA}$, $c_0 = 7.752 \text{ \AA}$.

3.2 Densification and activation energy for densification

The influence of TiO_2 on the densification behaviour of LaCrO_3 is presented in figure 1, which is a plot of sintered density versus TiO_2 concentration at various sintering temperatures; the sintering time being 8 hr. At 3 wt% TiO_2 addition, the sintered density sharply increases to $> 90\%$ (of the theoretical) while pure LaCrO_3 cannot be densified $> 75\%$ (of the theoretical).

Densification of LaCrO_3 versus sintering time and temperature for 3 wt% TiO_2 addition (henceforth known as LCT-3 composition) is presented in figure 2. The activation energy for densification is calculated from the Arrhenius rate equation

$$\frac{1}{t} = K_0 \exp\left(-\frac{Q_D}{RT}\right), \quad (1)$$

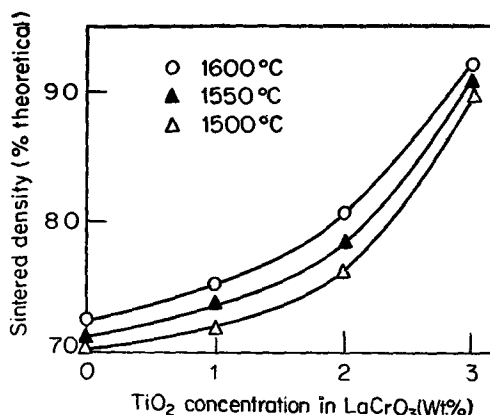


Figure 1. Sintered density as a function of TiO_2 concentration for LaCrO_3 sintered at various temperatures.

where t is the sintering time required for the desired densification; Q_D is the activation energy for densification which is computed to be $\approx (80 \pm 5)$ kcal/mole (figure 3).

3.3 Grain growth kinetics

Normal pore free grain growth is obtained for LCT-3 composition and presented in the photomicrographs (figure 4). Figure 5 shows a plot of grain size versus sintering time at various sintering temperatures. The variation of square of grain diameter with sintering time (figure 6) resulted in a straight line, and as such the grain growth follows a rate-equation:

$$D^2 - D_0^2 = kt, \quad (2)$$

where D_0 is the initial particle size and K is the rate constant.

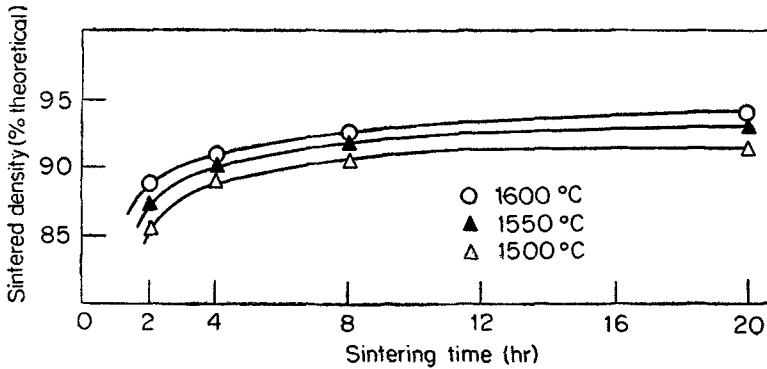


Figure 2. Sintered density versus sintering time plot for LCT-3 composition.

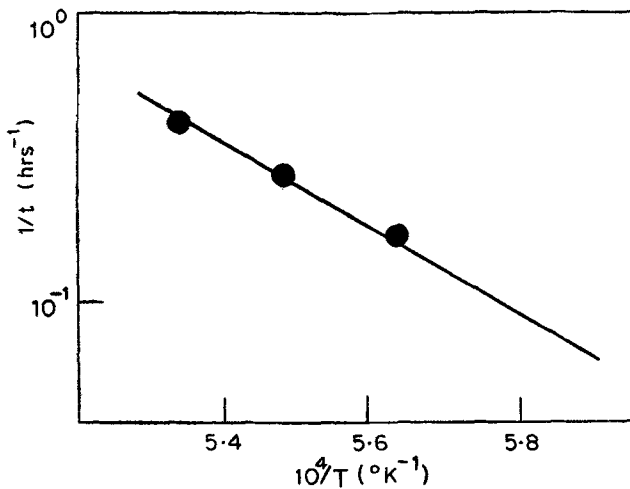


Figure 3. Arrhenius plot of densification rate constant for LCT-3 composition.

The activation energy for grain growth is estimated following the rate equation

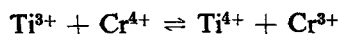
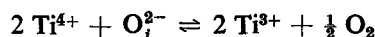
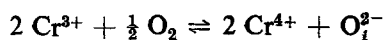
$$K = K_0 \exp\left(-\frac{Q_G}{RT}\right), \quad (3)$$

where Q_G is the activation energy for grain growth, and it comes out to be $\approx (80 \pm 5)$ kcal/mole (figure 7).

4. Discussion

The rate of grain growth is decided by the rate at which a curved grain boundary approaches its centre of curvature, which is controlled by the bulk diffusivity of the slowest moving ion in ceramics. The densification rate is on the other hand controlled by the rate of pore removal. Various mechanisms like bulk diffusion, surface diffusion and evaporation-condensation, etc have been proposed for pore removal during sintering. The same values of activation energies for densification and grain growth in the present case indicates that the same mechanism, *i.e.* the bulk diffusion of the slowest moving ion, controls the rate of densification and grain growth (Stuijts, 1968). The diffusion of cations found at interstitial sites is known to be faster than that of oxygen ions. The activation energy of grain growth and densification can thus be considered as the activation energy for self diffusion of oxygen ions in the perovskite lattice.

An additive may enhance the sintering of a material such as LaCrO_3 , by stabilizing the oxidation state of the host cation so that the volatile species are not formed, and by modifying the defect structure of one or both host sublattices to accelerate diffusion of the component ions. It is well known (Anderson, 1977, 1978) that the evaporation of Cr from LaCrO_3 by oxidation of Cr^{3+} to Cr^{4+} leads to poor densification. Any additive that can stabilize Cr as Cr^{3+} would give better densification. Addition of TiO_2 leads to such stabilization by the following reactions (George and Karkhanawala, 1979):



Since the ionic radius of Cr^{3+} ion (0.69 Å) is almost equal to that of Ti^{4+} ion (0.68 Å), Ti^{4+} can be easily accommodated substitutionally on the Cr^{3+} sublattice. However, such a substitution will lead to the creation of cation vacancies on the Cr-sublattice in accordance with valency-charge balances. Presence of cation vacancies will in turn give rise to faster pore mobility if there is a separate path for oxygen diffusion, *i.e.* through the gaseous phase. A possible mechanism of grain growth by increased pore mobility in the presence of the excess cation vacancies has been suggested by Yan and Johnson (1978), and has explained the grain growth promotion in TiO_2 doped Mn-Zn ferrites, for the increased pore mobility results

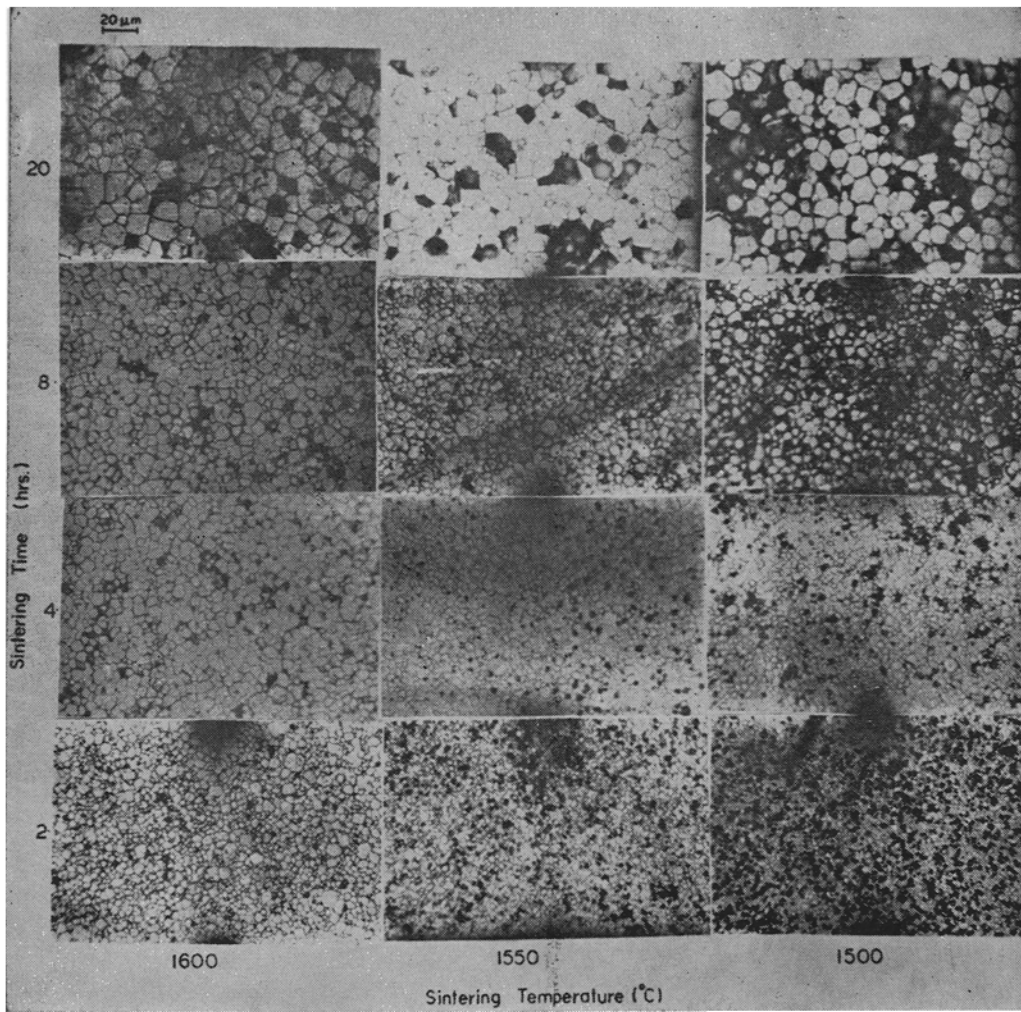


Figure 4. Microstructure of lanthanum chromite doped with 3 wt% TiO_2 (LCT-3 composition) sintered at various temperatures for different times.

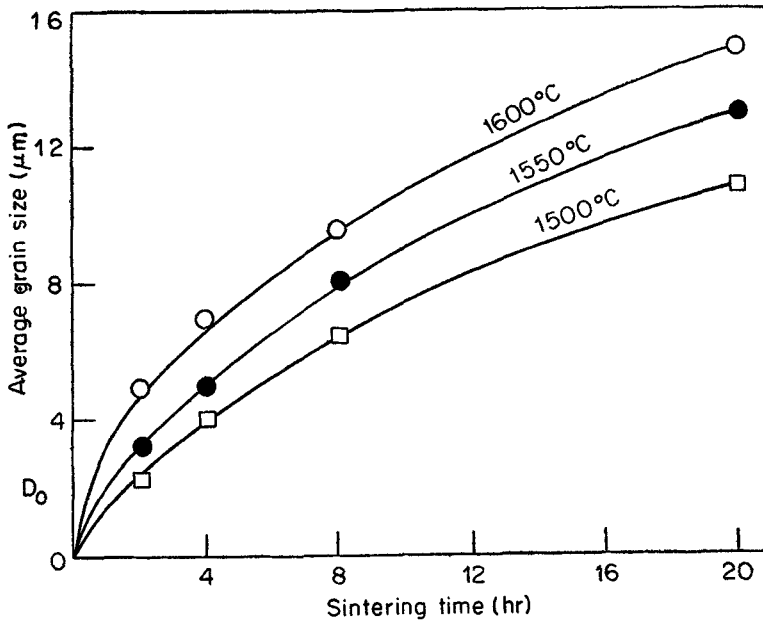


Figure 5. Grain growth isotherm for LCT-3 composition.

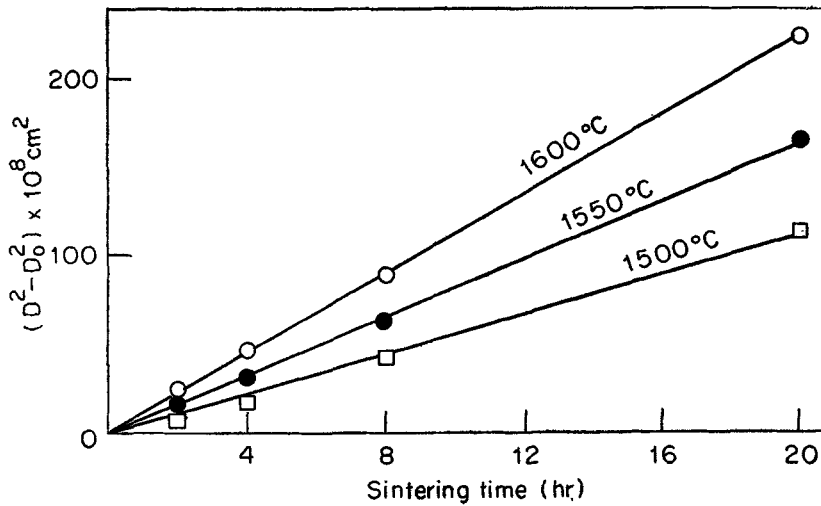


Figure 6. Plots of the equation $D^2 - D_0^2 = kt$ for LCT-3.

in higher grain size. Hence the addition of TiO_2 leads to higher densification and increased grain growth rate in LaCrO_3 .

5. Conclusions

(i) 3 wt% TiO_2 additions improves the sintering of LaCrO_3 and densities $> 90\%$ of the theoretical value are achieved.

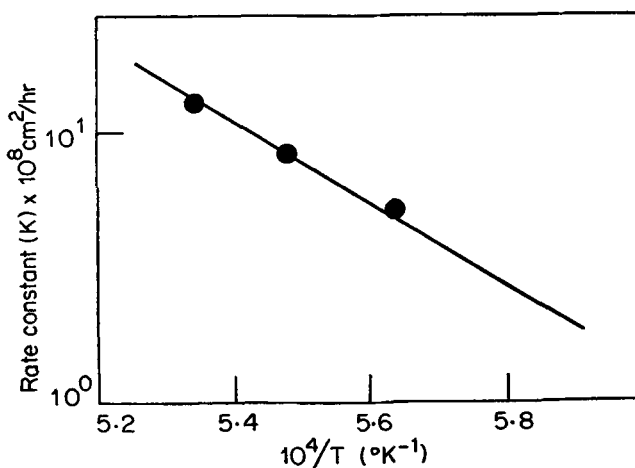


Figure 7. Arrhenius plot of rate constant K versus $(1/T)$ for LCT-3 composition.

(ii) Enhanced densification of LaCrO_3 with the addition of titania is best explained as due to the creation of cation vacancies.

Acknowledgements

One of the authors (KPB) wishes to acknowledge UGC for extending financial assistance in carrying out the present work. The assistance of Mrs U Dhawan in taking x-ray diffractograms is gratefully acknowledged.

References

- ASTM Designation 1971, C20-70 Parts 13 6.
- Anderson H U *et al* 1977, 13th Rare Earth Conf. Olgebay Park W. Vir, Oct. 16
- Anderson H U 1978 Processing of crystalline ceramics (New York: Plenum) 467-77
- Anderson H U 1974 *J. Am. Ceram. Soc.* **57** 34
- Bansal K P, Kumari S, Das B K and Jain G C 1980 Communicated to *Tran. J. Brit. Ceram. Soc.*
- Callister W D *et al* 1979 *J. Am. Ceram. Soc.* **62** 208
- George A M and Karkhanawala M D 1979 Symp. Sintering & Sintered Products BARC, Oct. 29-31
- Halloran J W and Anderson H U 1974 *J. Am. Ceram. Soc.* **57** 150
- Khattak C P and Cox D E 1977 *Mat. Res. Bull.* **12** 463
- Leslie Group and Anderson H U 1976 *J. Am. Ceram. Soc.* **59** 449
- Meadowcroft D B 1969 *Br. J. Appl. Phys. Ser. 2* 1225
- Meadowcroft D B 1972 *Energy Conversion* **8** 185
- Meadowcroft D B 1972 *Energy Conversion* **12** 145
- Meadowcroft D B 1973 Conf. on Strontium Containing Compounds, Halifax, Canada
- St. Jacques R G, Moise A and Yerouchalmi D 1974 *J. Canad. Ceram. Soc.* **43** 23
- Stuijts A L 1968 Ceramic Microstructures Chap. 19 (New York: John Wiley)
- Yan M F and Johnson Jr D W 1978 *J. Am. Ceram. Soc.* **61** 342