Journal of Alloys and Compounds 495 (2010) 570–573

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Densification kinetics of ZrO_2-based ceramics using a master sintering curve

Ricardo Caruso [a], Nadia Mamana [a], Edgardo Benavidez [b,*]

[a] Laboratorio de Materiales Cerámicos (FCEIyA–UNR–CONICET), Av. Pellegrini 250–(2000) Rosario, Argentina
[b] Departamento Metalurgia/DEYTEMA – Facultad Regional San Nicolás (UTN), Colón 332 – (B2900LWH) San Nicolás, Argentina

ARTICLE INFO

Article history:
Received 11 July 2008
Received in revised form 29 October 2009
Accepted 10 November 2009
Available online 16 December 2009

Keywords:
Ceramics
Sintering
Thermal expansion
Thermal analysis

ABSTRACT

With the aim to know the densification kinetics of ZrO_2-based ceramics a master sintering curve for ZrO_2 containing 3 mol% Y_2O_3 was constructed. Zirconia (3 mol% Y_2O_3) powders were prepared by a chemical method and then they were uniaxially pressed at 200 MPa. A green density 36% of theoretical density was obtained after pressing. The shrinkage-temperature curves were obtained by dilatometric runs at different constant heating rates: 5 °C/min and 10 °C/min up to 1500 °C. Dilatometric data were used to construct the master sintering curve (MSC) with an energy of sintering $Q = 500$ kJ/mol between 600 and 1100 °C. The results of this study can be used to predict the shrinkage/densification level of ZrO_2 powders, and by this way to design a heat treatment to obtain a bulk ceramic with a predetermined density.

1. Introduction

Yttria stabilized zirconia ceramics (YSZ) exhibit high values of fracture toughness, mechanical resistance and ionic conductivity. Due to these properties, YSZ materials are used in different industrial applications such as cutting tools, valve guide, abrasive tools, solid oxide fuel cells (SOFC), oxygen sensors, etc [1–3].

Nanocrystalline ceramics exhibits a high surface area providing a high driving force for sintering. In this manner, the activation energy of sintering is reduced and a lower temperature of sintering can be employed. However, nanocrystalline particles promote grain growth which is an undesired mechanism because degrade the properties of YSZ products [4]. Usually, the grain growth occurs in the last stage of sintering. Therefore, to control the densification process, avoiding grain growth, it is necessary to understand the sintering process of this oxide.

Su and Johnson [5,6] have developed the master sintering curve (MSC) concept to predict the densification behavior using a minimum of preliminary experiments, regardless of the heating profile.

The MSC theory is derived from the combined-stage sintering model [7] that relates the linear shrinkage rate of the compact (dL/dt), at any time, to grain boundary (D_b) and volume (D_v) diffusion coefficients, the surface energy (γ) and some microstructural parameters such as the atomic volume (Ω), the mean grain size (G), and scaling parameters for volume (Γ_v) and grain boundary diffusion (Γ_b):

$$-\frac{dL}{L\,dT} = \frac{\gamma\,\Omega}{kT}\left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b\ \delta D_b}{G^4}\right) \tag{1}$$

For isotropic shrinkage:

$$-\frac{dL}{L\,dT} = \frac{d\rho}{3\rho\,dt} \tag{2}$$

where ρ is the bulk density.

By assuming that only one diffusion mechanism, either volume diffusion or grain boundary diffusion, is dominant during the sintering process, then Eq. (1) can be written as follow:

$$\frac{d\rho}{3\rho\ dt} = \frac{\gamma\,\Omega\,\Gamma(\rho)D_0}{kT[G(\rho)]^n}\exp\left(-\frac{Q}{RT}\right) \tag{3}$$

where D_0 is the diffusion coefficient for the dominant diffusion mechanism, Q is the apparent activation energy, R is the gas constant, and n is a constant dependent on the diffusion mechanism.

Based on previous studies, in Eq. (3) it was assumed that the microstructural functions (G and Γ) depends only on density.

The Eq. (3) can be rearranged and integrated to obtain:

$$\int_{\rho_0}^{\rho}\frac{[G(\rho)]^n d\rho}{3\rho\ \Gamma(\rho)} = \int_0^t \frac{\gamma\,\Omega D_0}{kT}\exp\left(-\frac{Q}{RT}\right)dt \tag{4}$$

* Corresponding author. Tel.: +54 3461 420830; fax: +54 3461 420820.
E-mail address: ebenavidez@frsn.utn.edu.ar (E. Benavidez).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.11.080

The right-hand of this equation, depends on the Q and the thermal history (time–temperature profile):

$$\Theta(t, T(t)) = \int_o^t \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt \quad (5)$$

While the left-hand of Eq. (4) depends on the microstructural and materials properties.

$$\Phi(\rho) = \frac{k}{\gamma\ \Omega D_0} \int_{\rho_0}^{\rho} \frac{[G(\rho)]^n d\rho}{3\rho\, \Gamma(\rho)} \quad (6)$$

The relationship between density and Θ-function is defined as the master sintering curve (MSC). It is noted that there is a unique MSC for a given powder and process.

It is possible to construct a MSC for a given powder using the final (or theoretical) density and the shrinkage obtained from dilatometry.

In previous works, the MSC has been applied to sintering studies of different oxide ceramics, such as: ThO_2 [8], ZnO [6,9], Al_2O_3 [6], $BaTiO_3$ [10], and TiO_2 [11].

In the present work, the linear shrinkage of ZrO_2–3 mol% Y_2O_3 compacts was monitored by a dilatometer. These data were used to construct the master sintering curve to different heating rates up to 1100 °C corresponding to a unique sintering mechanism valid to about 0.7 relative density of YSZ powders.

2. Experimental

To produce ZrO_2–3 mol% Y_2O_3 powder, the YSZ chemical solution was obtained by stirring zirconium n-propoxide (70% in propanol) and yttrium acetate with nitric acid. The PH of solution was 5. Gelification of solution was obtained adding distilled water. The powder was obtained by drying the gel at 100 °C in air. The dried powder was pulverized in a mortar with pestle. Finally, the organic components were burning by heating at 500 during 1 h. Previously to be pressed, the powder was pulverized in a mortar with pestle again.

As obtained YSZ powder was pressed uniaxially at 200 MPa. The green compacts were 3.4 mm in length and 5.1 mm in diameter. Green density of compacts was obtained by geometrical method.

The linear shrinkage was monitored in a horizontal dilatometer (Theta Instruments Inc., Dilatronic) used in standard form. The runs were effected at constant heating rates (CHR) of 5 °C/min and 10 °C/min in static air, up to 1500 °C.

Dilatometric data were used to determine the density (ρ) applying the following equation [12]:

$$\rho = \frac{1}{(1-(dL/L_0))^3}\rho_0 \quad (7)$$

where dL/L_0 is instantaneous linear shrinkage, L_0 is the initial length of compact, and ρ_0 is the green density.

Relative density was calculated by $\rho_r = \rho/\rho_t$. The theoretical density (ρ_t) was assumed: $\rho_t = 6.00\ g/cm^3$ [13].

The microstructure of samples after dilatometric runs up to 1500 °C were observed by atomic force microscopy (AFM) using a Nanotec Electronica equipment.

3. Results and discussion

Fig. 1 shows the complete dilatometric curves running at 5 °C/min and 10 °C/min. In both runs the onset of densification/shrinkage process start about 550 °C. The maximum level of shrinkage was 28% of L_0 and it was attained at 1500 °C. At this temperature, the maxima relative densities were 0.95 and 0.98 at 5 °C/min and 10 °C/min, respectively.

By this, to obtain a high final density (95–98%) a considerable dimensional change would occur due to low initial packing (green density = 36% ρ_t).

The curves in Fig. 1 exhibit the highest percentage of shrinkage between 600 °C and 1100 °C (from 0% to 22% of initial length). In this range, more shrinkage was obtained when the heating rate was 5 °C/min, because the pellet is exposed to sintering for a longer time. However, between 1100 °C and 1350 °C, the level of contraction was similar regardless heating rate. In the range 1350–1500 °C it

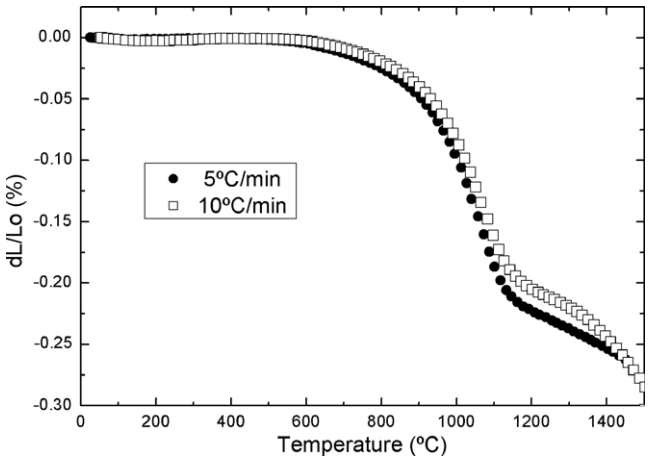

Fig. 1. Dilatometric curves of ZrO_2–3 mol% Y_2O_3 compacts run at 5 °C/min and 10 °C/min.

is observed a higher shrinkage rate when the sample is heating at 10 °C/min. These facts are observed in Fig. 2, where it is plotted both relative density and densification rate vs. temperature.

From Fig. 2 it can be observed that the maximum shrinkage rate move to higher temperature (from 1096 °C to 1114 °C), when the heating rate is increased from 5 °C/min to 10 °C/min. In both cases, these temperatures (1096 °C and 1114 °C) correspond to a density about 66% of theoretical density.

By using experimental data and Θ-function, activation energy values between 100 and 600 kJ/mol were chosen to construct ρ_r

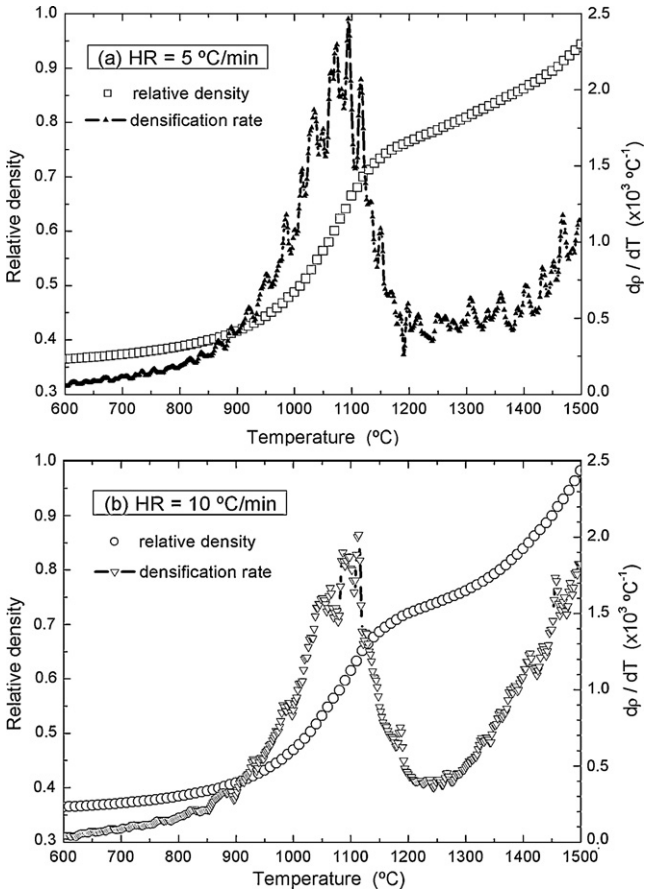

Fig. 2. Heating rate effect on both density and densification rate of YSZ powder compact.

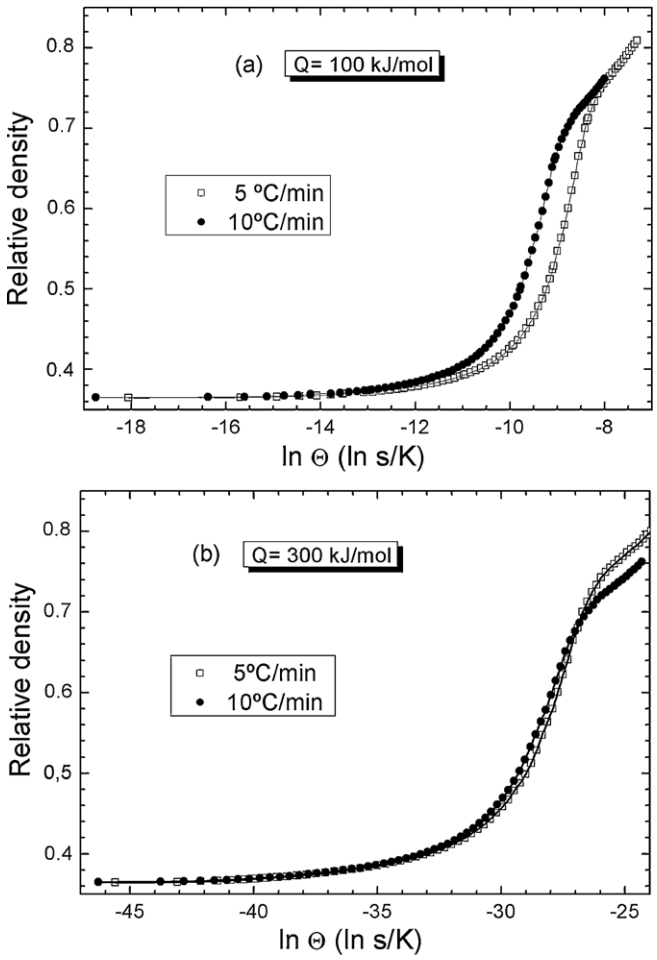

Fig. 3. Master sintering curve for YSZ powder compact at different values of *Q*.

vs. ln Θ curves. When the correct value of *Q* has been given, the two curves would converge to a single curve. If the curves did not converge, a new value of *Q* is chosen and the process is repeated.

As examples, the MSC curves constructed at 100 and 300 kJ/mol are shown in Fig. 3a and b, respectively.

The best convergence occurs at around $Q = 500$ kJ/mol (range: $\rho_r = 0.36$–0.70). From the knowledge of activation energy of sintering for YSZ between 600 and 1100 °C, the MSC has been constructed and it is shown in Fig. 4. From these data it is suggested that the

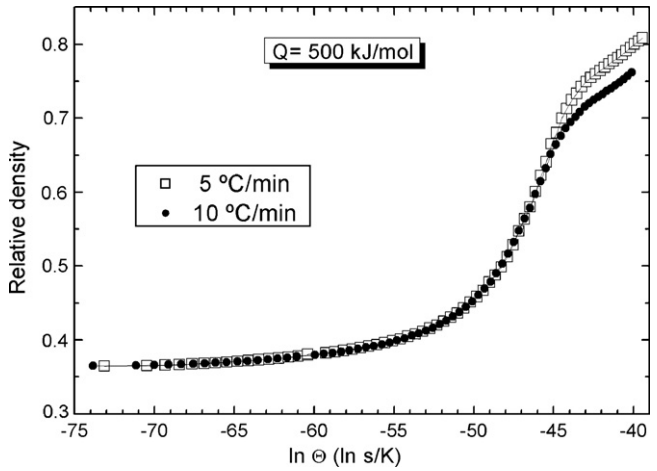

Fig. 4. Validation of master sintering curve for YSZ powder compact.

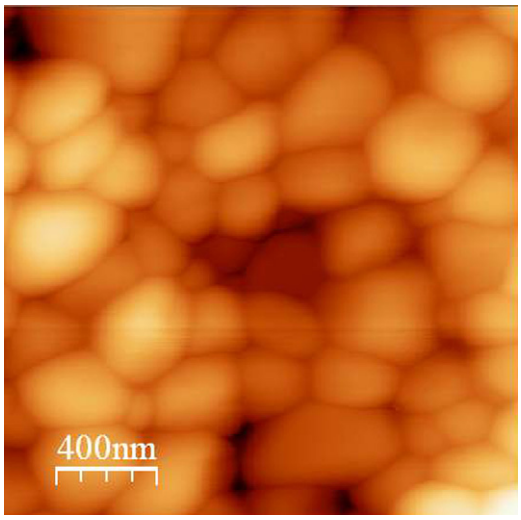

Fig. 5. AFM micrograph of YSZ compact after heating at 1500 °C (heating rate = 10 °C/min).

sintering kinetics is conduced by one densification mechanism up to a relative density about 0.70. At higher level of density probably the microstructure coarsening became operative [14,15].

This *Q* value is in accord with Mazaheri et al. [14] who estimated a sintering activation energy of 485 kJ/mol to a ZrO_2–3 mol% Y_2O_3 powder.

Besides, Aglietti and co-workers [16] reported a sintering activation energy of 170 kJ/mol to zirconia powders with 8 mol% of Y_2O_3, using a sintering model based on a volume diffusion mechanism but applied to initial stage of sintering.

Fig. 5 shows the microstructure of YSZ compact after dilatometric run at 10 °C/min up to 1500 °C. The microstructure shows uniform distribution of YSZ particles in a dense particle packing. The mean grain size is about 300 nm suggesting that a low grain growth level has been developed even at 1500 °C.

This behavior has also been reported by Li and Gao [17] who suggested that the ion Y on the grain boundaries hinder the grain growth mechanism.

According to this slow grain growth, it is probable that volume diffusion could be the main sintering mechanism acting in the range 600–1100 °C.

4. Conclusions

The master sintering curve has been constructed for ZrO_2 containing 3% Y_2O_3 and it has been used to calculate the activation energy for sintering.

The sintering activation energy was found to be 500 kJ/mol, and it was valid up to a relative density around 0.70. To higher densities the coarsening mechanism was proposed.

It was observed a low grade of grain growth in the samples even heated at 1500 °C.

References

[1] S. Ran, L. Winnubst, W. Wiratha, D.H.A. Blank, J. Am. Ceram. Soc. 89 (2006) 151–155.
[2] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563–588.
[3] S. Somiya, N. Yamamoto, H. Yanagida (Eds.), Science and Technology of Zirconia III, The American Ceramic Society, Westerville, OH, 1986.
[4] H.T. Kim, Y.H. Han, Ceram. Int. 30 (2004) 1719–1723.
[5] H. Su, D.L. Johnson, J. Am. Ceram. Soc. 79 (1996) 3199–3210.
[6] H. Su, D.L. Johnson, J. Am. Ceram. Soc. 79 (1996) 3211–3217.
[7] J.D. Hansen, R.P. Rusin, M.H. Teng, J. Am. Ceram. Soc. 75 (1992) 1129–1135.
[8] T.R.G. Kutty, K.B. Khan, P.V. hedge, J. Banerjee, A.K. Sengupta, S. Majumdar, H.S. Kamath, J. Nucl. Mater. 327 (2004) 211–219.

[9] K.G. Ewsuk, D.T. Ellerby, B. DiAntonio, J. Am. Ceram. Soc. 89 (2006) 2003–2009.
[10] M.V. Nikolic, V.P. Pavlovic, V.B. Pavlovic, N. Labus, B. Stajanovic, Mat. Sci. Forum 494 (2005) 422–717.
[11] D. Li, S. Chen, W. Shao, X. Ge, Y. Zhang, S. Zhang, Mater. Lett. 62 (2008) 849–851.
[12] R.M. German, Sintering Theory and Practice, John Wiley and Sons, Inc., New York, 1996.
[13] R.P. Ingel, D. Lewis III, J. Am. Ceram. Soc. 69 (1986) 325–332.
[14] M. Mazaheri, A. Simchi, M. Dourandish, F. Golestani-Fard, Ceram. Int. 35 (2009) 547–554.
[15] F.F. Long, Ceram. Trans. 1 (1989) 1069–1083.
[16] G. Suarez, L.B. Garrido, E.F. Aglietti, Mater. Chem. Phys. 110 (2008) 370–375.
[17] W. Li, L. Gao, J. Eur. Ceram. Soc. 20 (2000) 2441–2445.