

Modeling of the Effect of MgO and ZrO₂ on Sintering of Alumina

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Abstract

This research studies the effect of MgO and ZrO₂ as additives in sintering Al₂O₃ . The experimental results are modeled using (L² _ regression) technique , sintered density and grain size rate measurements were accounted by utilizing experimental results of undoped , MgO doped and ZrO₂ doped alumina impregnated with spherical large pores in final stage of sintering . The effect of each additive is inhibition of the grain growth and increasing the densification rate which enhances the kinetics of densification and the removal of large and small pores.

Introduction

Alumina ceramic (Al₂O₃) is a hard refractory ceramic, which has been used in high temperature, structural and substrate applications because of its good strength and low thermal expansion coefficient . Nevertheless , like other mono lithic ceramics, Al₂O₃ is aptto suffer from low ductility and low fracture toughnees[I].

Doped samples were studied fro the influence of varying the grain growth rate of the alumina , MgO is a strong solid-solution grain growth inhibitor in high purity alumina [2] , and ZrO₂ when added in high enough concentrations, is an even strong second-phase grain growth inhibitor [3] .

The intension of this study to was model mathematically the densification and grain size rate of doped Al₂O₃ system using regression modeling technique utilizing MgO and ZrO₂ as additives seperately.

Theoretical background

The pores are classified into two basic types, there are the so-called matrix or first-generation pore and the second type, large so-called second-generation pores which originate from particulate agglomeration and particulate packing irregularities within the powder compact [4]. The large pores are always more difficult to eliminate large voids for two basic reasons. First, simple kinetics dictates a longer time to fill a larger void by diffusion [5], second a large pore can be thermodynamically stable depending on the value of dihedral angle and pore size : grain size ratio (for a given dihedral angle and pore size, there is a critical grain size above which the pore is unstable and can sinter), while below where it is stable and can not sinter.

The models which are used in this study have simplifying assumptions in order to perform the calculations.

- 1) Pore shrinkage is controlled by lattice diffusion
- 2) The grain size is fixed at the critical grain size which was taken to be 0.68 times the pore size [6].
- 3) The pores are assumed to be spherical with no thermodynamic barrier for shrinkage [4,7].

The large-pore volume will start to decrease (once the critical grain size is reached), the matrix grain growth rate (dG/dt) can be given by [8]

$$\frac{dG}{dt} = \frac{13.4}{N} M_p G \gamma_b \epsilon \left(1 - \frac{G}{G_{max}}\right) \dots (1)$$

Where N is the number of pores surrounding each grain, M_p is the average pore mobility, G is the grain size, γ_b is the grain boundary energy, ϵ is the grain growth rate factor and (G/G_{max}) is the ratio of average grain size over maximum grain size.

The densification rate (dp/dt) depends on the diffusion coefficient responsible for densification (D_{lattice} or D_{boundary}) and the grain size [9].

$$\frac{d\rho}{dt} = C D / G^n \dots (2)$$

where C is a constant and D is the diffusion coefficient.

The grain size exponent, n, is 3 for lattice- diffusion controlled densification which is used in this study [5].

In this study (reported in Ref [5]). Ultra-high-purity α -alumina powder for which the manufacturer claimed a (99.995%) purity size of powder was 0.45 μ_m and 97% of the particles were less than 1 μ_m .

The following three compositions were chosen for this study (i) pure alumina ; (ii) 250-ppm-MgO-doped alumina , and (iii) Al₂O₃ +10 Vol % ZrO₂ . Large mono size pores were introduced in to each composition by incorporating latex spheres (5.6 μ_m) into the powder mix before sintering .The ratio of the sphere volume / the sum of the sphere volume and the solid volume in each composition was (5%) .The powder was cold-pressed into pellets of approximately the same green density (47.5%) using a high-purity alumina punch and die set . The pellets calcined at 1000^oc in air for 48 h , large pores were produced after calcination as a result of burning out of the latex spheres.

The processing procedure for all composition was kept as consistent as possible to ensure similar initial microstructures . Sintering was conducted under flowing nitrogen gas in a furnace heated with graphite elements, the specimens were heated at a constant rate of (60^oc/min) up to the sintering temperature of 1620^oc (oxygen partial pressure < 10⁻¹¹ atm <10⁻⁶ pa).

Regression modeling technique

The equation of L²_ regression which is used in this study can be express as follows [10]

$$X = (A^T A)^{-1} A^T b \dots\dots\dots(3)$$

where A is the matrix , A^T is the transpose of matrix A , b is random observation and X is the fixed part of equation but unknown.

The integral form of the grain growth rate equation (1) [4].

$$\ln G_{t+\Delta t} - \ln G_t = \frac{13.4}{N} M_p Y_b \varepsilon (1 - \frac{G}{G_{max}}) \Delta t \dots\dots\dots(4)$$

and the integral form of densification rate equation (2)

$$\rho_{t+\Delta t} - \rho_t = \frac{CD}{(1 - n)} G^{(1-n)} \Delta t \dots\dots\dots(5)$$

After simplifying the integral expression for equation (4) and (5) we get a suitable form of equation (3) that can be adopted to L²_ regression .

$$\ln G_{t+\Delta t} = z_1 (1 - \frac{G}{G_{max}})t + Y_1 \dots\dots\dots(6)$$

$$\rho_{t+\Delta t} = Z_2 G^{(1-n)} t + Y_2 \dots \dots \dots (7)$$

Where Z_1 is the grain size rate parameter and equals to $[\frac{13.4}{N} M_p Y_b \varepsilon]$, Z_2 is the densification rate parameter and equals to $[CD / (1-n)]$, Y_1 is the grain size rate coefficient and equals to $[\ln G_t - z_1 (1 - \frac{G}{G_{max}}) t_o]$ and Y_2 is densification rate coefficient and equals to $[P_t - Z_2 G^{1-n} t_o]$

The grain size and density value were measured using model of L² Regression (see-Ref II)

Results and Disussion

Figs . (1) and (2) showed the effect of MgO and ZrO₂ doped alumina which have a large (□ 5 μ_m) model spherical pores on the density date as a function of time at 1629^oc . As can be seen that both MgO and ZrO₂ increased the desification rate of Al₂O₃ . ZrO₂ had more effective in enhanced densification rate than MgO . The calculatedion by model sintered densites of sample with ZrO₂ addition was ranged between [92 and 97.9%] and for samples with MgO addition was ranged between [91 and 97.2 %] .

The ZrO₂-doped samples did reach a slightly higher density than the MgO-doped samples , however , this does imply that a fraction of the pores were indeed thermodynamically unstable and cabable to shrink . Such pores would be able to shrink at a faster rate than those in the MgO – doped samples due to smaller grain size and associated faster kinetics.

Fig (3) and Fig (4) are showed the grain size versus time date for MgO-doped , and ZrO₂-doped aluminas which imregnated with large (□ 5 μ_m) model spherical pores at 1620 °c . MgO and ZrO₂ were very effective in inhibiting grain growth in the system (ZrO₂ more so than MgO), the grain sizes for undoped and MgO-doped samples well beyond the critical grain size and the large pores do not readily disapper even when thermodynamics is permitting .

The degree of grain growth inhibition was faster with the ZrO₂-doped samples , where the small grain size of these samples showed that not all the pores were necessarily thermodynamically unstable for any reasonable lenght of sintering time.

In Table (1) we can see the grain size rate parameter of doping samples increases , this can be explained in terms of the number of pores which increase with doping and this may naturally decreases densification rate parameters .

Table (2) lists the grain size rate coefficient and densification rate coefficient, the doping lowers both the densification and grain size rate coefficient respectively where the dopant particles may form barriers along the diffusion path and reduce the densification

Conclusion

The modeling technique shows that the calculated results using L^2 Regression technique agrees with experimental results, and MgO-doped alumina impregnated with large pores have effective in inhibiting grain growth rate and increases the densification rate, while the effect of ZrO₂ doped alumina was faster than MgO, ZrO₂ doped samples have more effective in enhanced densification and inhibition the grain growth rate.

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Table (1): Grain size and densification rate parameters in three case , undoped, MgO-doped and ZrO₂-doped alumina impregted with large model pores

	Undoped	MgO-doped	ZrO ₂ -doped
Grain size rate parameter (Z ₁)	90.583	93.964	94.651
Densification rate parameter (Z ₂)	1.574	1.102	0.578

Table (2): Grain size and densification rate coefficent in three case , undoped , MgO-doped and ZrO₂ –doped alumina impregnated with large model pores

	Undoped	MgO-doped	ZrO ₂ -doped
Grain size rate coefficient (Y ₁)	0.00559	0.00511	0.00238
Densification rate coefficient (Y ₂)	4.397	0.6562	0.0604

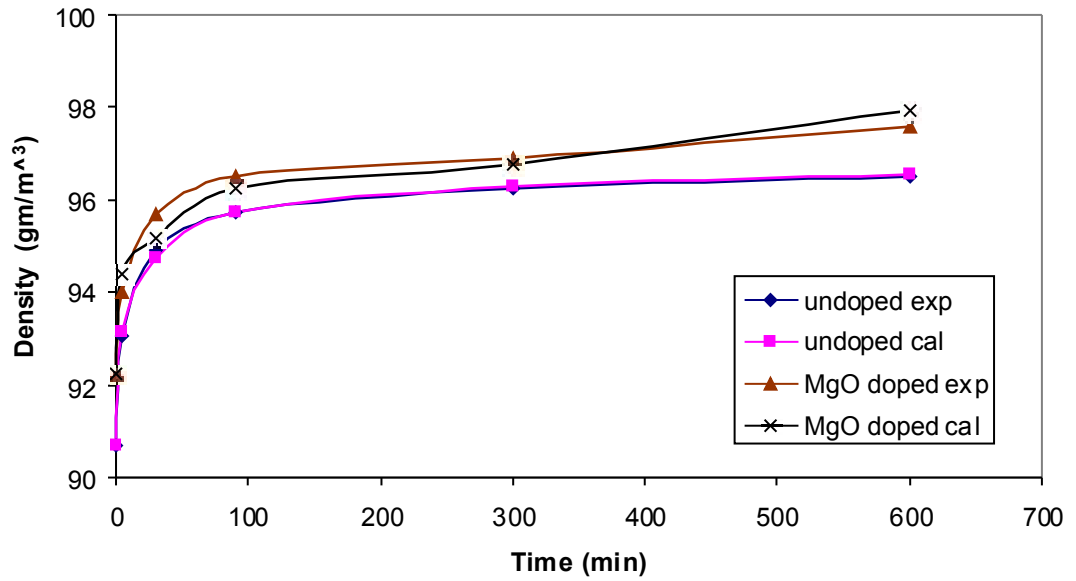
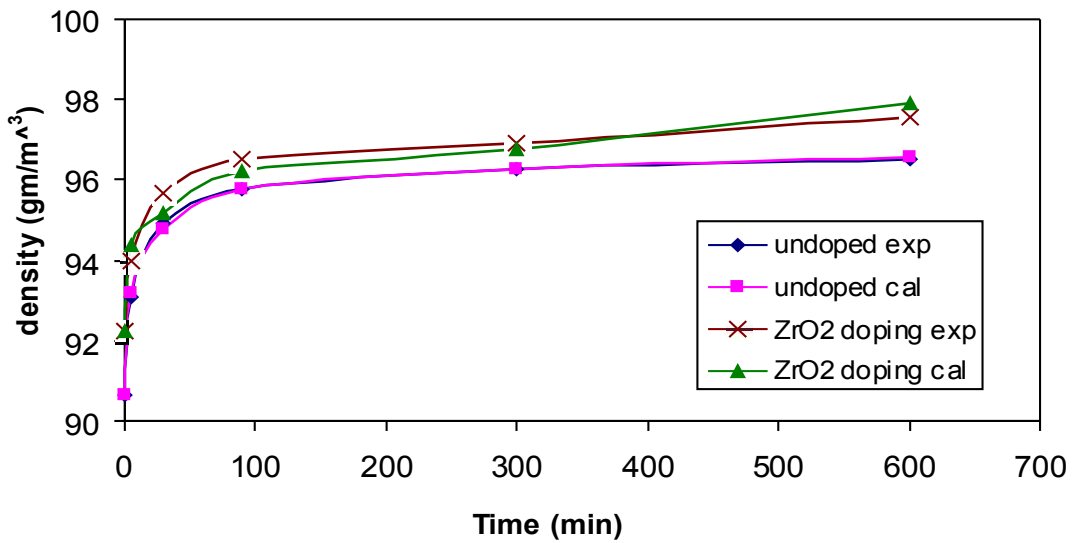


Fig (1) Density data of undoped and MgO doped aluminas impregnated with large pores as a function of time



Fig(2) Density data of undoped and ZrO₂ doped aluminas impregnated with large pores as a function of time

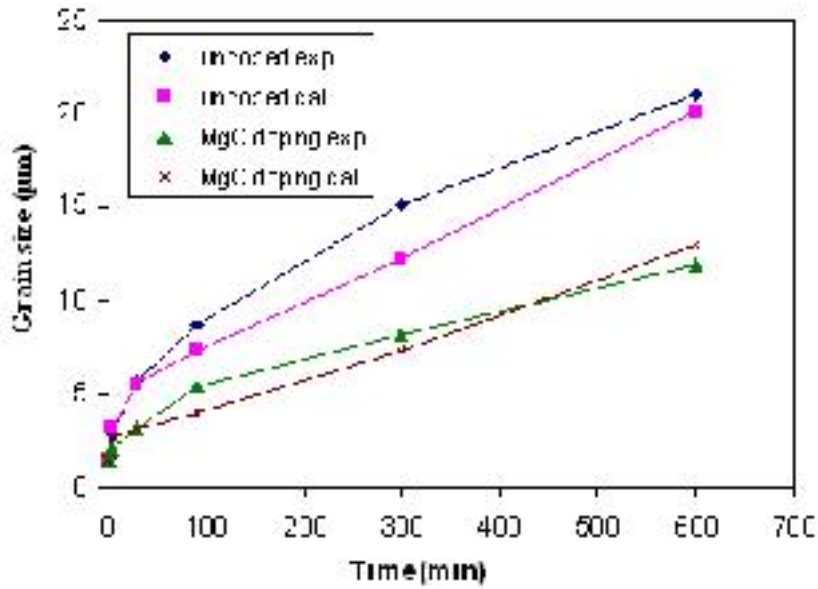


Fig. (3) Grain size of undoped and MgO-doped aluminas impregnated with large spherical pores as a function of time

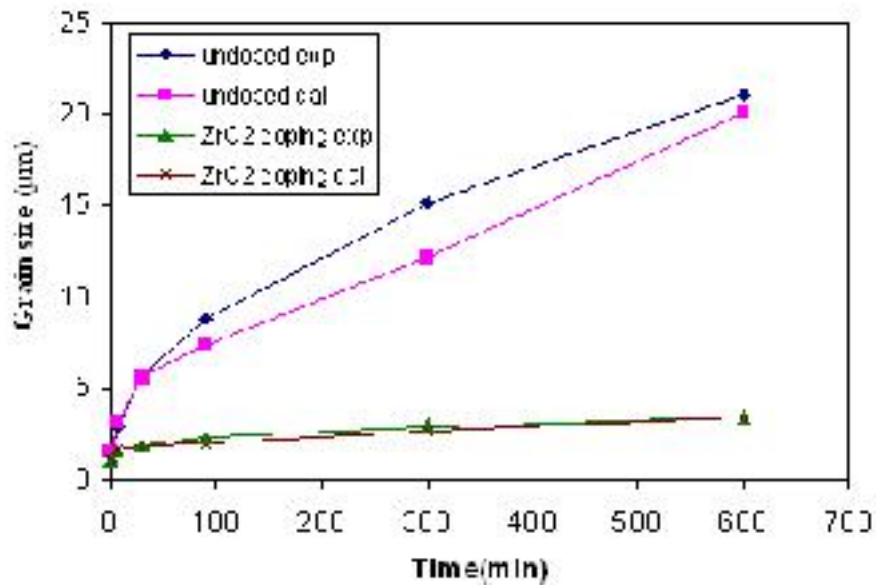


Fig. (4) Grain size of undoped and ZrO₂-doped aluminas impregnated with large spherical pores as a function of time

أنموذج تأثير MgO و ZrO₂ في تليبيد الالومينا

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الخلاصة :-

درس تأثير اضافة MgO, ZrO₂ في تليبيد الالومينا. تم نمذجت النتائج التجريبية بأستخدام تقنية L2-Regression، وحسب معدل كثافة التليبيد والحجم الحبيبي بأستخدام نتائج تجريبية للألومينا غير مطعمة، المطعمة ب MgO والمطعمة ب ZrO₂ والمشبعة بالفجوات الكبيرة في المرحلة النهائية من عملية التليبيد. ان تأثير نوعي التطعيم هو منع النمو الحبيبي وزيادة معدل التكاثر حيث زيادة حركيات التكاثر وحركة الفجوات الكبيرة والصغيرة.

