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SINTERING KINETICS OF BaAl_2O_4

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ABSTRACT

Isothermal sintering of Monobarium aluminate (BaAl_2O_4) has been carried out by measuring shrinkage on firing of compacted pellets of -45 micron size powder samples at temperature of 1300, 1350, 1400 and 1450°C. The time dependence of linear shrinkage reveals volume diffusion as dominant mechanism of sintering. The apparent diffusion coefficient (D) of sintering has been calculated and its temperature dependence can be represented by the equation,

$$D = 8.04 \times 10^{-9} \left(- \frac{188,000}{R T} \right) \text{ cm}^2 \text{ sec}^{-1}$$

Introduction

In a powder compact, sintering increases the area of contact between the particles accompanying mass transfer. Diffusion is apparently the mechanism of mass transport in sintering of solids. The driving force for the sintering is the excess surface energy present in a powder as compared to single crystal of the same composition (1). Based on the path of diffusion, different mechanisms of diffusion such as vapour transport, surface, grain boundary and volume diffusion have been reported (1-4). Volume diffusion usually occurs at higher temperatures in which the atoms move through the lattices to the neck region and particles come closer causing shrinkage and densification. Sintering may

A = Al_2O_3 B = BaO C = CaO BA = BaAl_2O_4 CA = CaAl_2O_4

also bring microstructural changes and grain growth. Different diffusion models to determine the mechanism of sintering operating in the mass have been given (2-3). Most sintering experiments have been interpreted assuming that a single mechanism is responsible for the material transport. Slope of the plots of logarithm of shrinkage of a powder compact versus time has been used as an index of mechanism of material transport. According to the model of Kuczynski (2), Kingery and Berg (3), when the value of the slope is near to 0.4, volume diffusion is the predominant mechanism of material transport. In the present paper the sintering kinetics of BA powder compact has been studied by measuring shrinkage and diffusion coefficient was calculated (4) using equation ,

$$\frac{\Delta L}{L_0} = \left(\frac{20 \gamma a^3 D}{\sqrt{2} K T} \right)^{2/5} r^{-6/5} t^{2/5}$$

Where $\Delta L/L_0$ is linear shrinkage, t is time, r is average radius of particles taken, γ is the surface energy, T is sintering temperature and K is Boltzman constant. a is the atomic volume of diffusing species and calculated (5) using equation ,

$$a^3 = \frac{1}{3} \frac{\text{molecular weight}}{\text{density}} \frac{1}{N}$$

Where N is the Avogadro number. The temperature dependence of diffusion coefficient has been used to calculate activation energy of diffusion.

Experimentation

Monobarium aluminate was prepared by repeated firing and grinding of equimolar quantity of AR grade BaCO_3 and Al_2O_3 at 1450°C (6). Formation of pure BA was confirmed by XRD. Powdered BA having particle size -45 micron was pressed in the form of pellets of diameter 1.5 cm and thickness around 0.32 cm by taking 1.0 gm of powder and using a hydraulic press at the pressure around 1000 kg/cm^2 . The pellets were kept for about 30 minutes at the specified pressure.

Sintering was carried out in a microprocessor based rapid heating high temperature furnace at $1300, 1350, 1400$ and 1450°C for the time duration of 5 to 120 minutes. Pellets were invariably oven dried at 100°C for 3 hours before firing. The rising rate of temperature was maintained 5°C/min . After soaking the pellets were removed from furnace and kept in dessicator at the room temperature. The linear shrinkage was measured using Vernier Calliper having least count of 0.02 mm .

Results and Discussion

The shrinkage isotherms of -45 micron particle size powder compacts sintered at 1300, 1350, 1400 and 1450°C are shown in Fig 1. It can be seen that the rate of linear shrinkage increases with increase in sintering temperature. At 1350°C a shrinkage of 13.0 percent is obtained in 30 minutes. The linear shrinkage obtained in 30 minutes at 1300, 1350, 1400 and 1450°C, are approximately 11.2, 13.0, 14.7 and 16.5 percent respectively. Sintering of -45 micron monocalcium aluminate (CA) powder compact reported (7) at 1400, 1420, 1440, 1460°C, a shrinkage of 5.60, 8.22, 9.60 and 12.0 percent respectively in 30 minutes soaking.

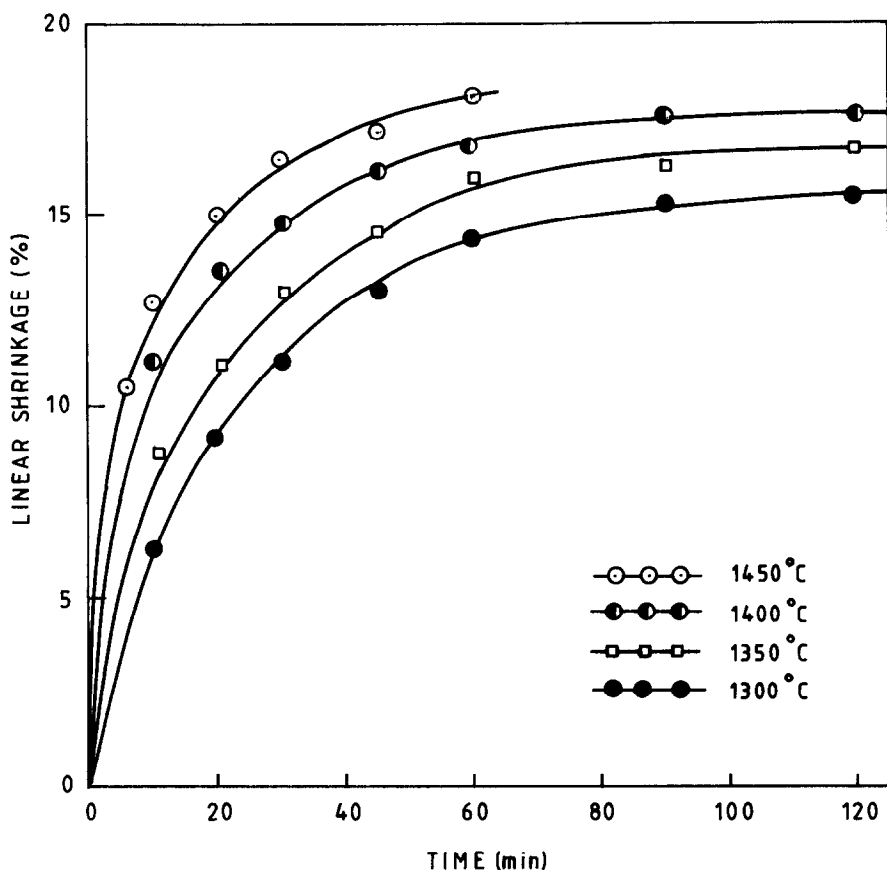


FIG 1. Shrinkage isotherms of BA compacts

In order to determine the mechanism of diffusion log-log plot of linear shrinkage vs time was plotted (Fig 2) which indicates the slope in the range of 0.28 to 0.5 at all sintering temperatures. It is thus clear that the volume diffusion is the predominant mechanism of diffusion in sintering of BA compact.

Apparent diffusion coefficient was calculated from the shrinkage equation using surface energy 1000 ergs/cm^2 (8), density 4.11 and r taken as 15 micron as the average diameter of the particles. The diffusion coefficients were calculated using the slope of Fig 2 in early period ie. for the lower time durations (5-60 minutes) for all the temperatures where linear relationship is followed.

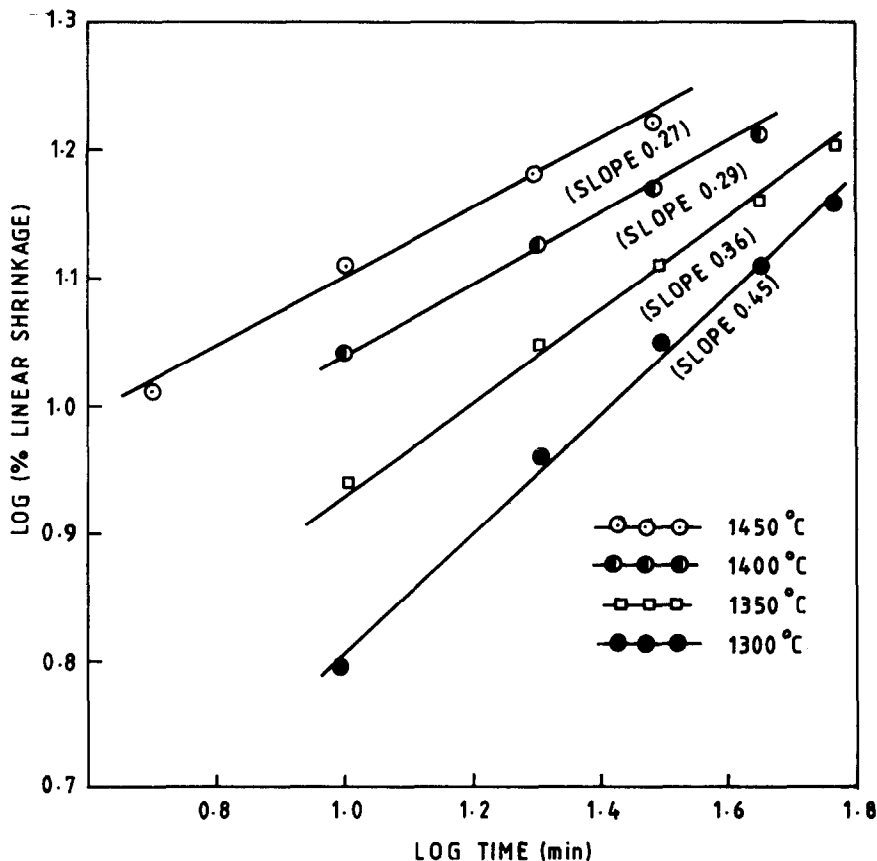


FIG 2. Log-Log plot of shrinkage versus time

Calculated values of the apparent diffusion coefficient are given in Table 1. It was observed that diffusion coefficient increases with increase in temperature of sintering.

The temperature dependence of the diffusion coefficient is shown in Fig 3 by plotting a curve between $\log D$ vs $1/T$ ($^{\circ}\text{K}$) which reveals a straight line relationship, the slope of which was used to calculate the activation energy.

Activation energy of apparent diffusion is 188 Kcal/mole. Sintering kinetics of CA powder compact (7) have indicated the activation energy of apparent diffusion to be 167 Kcal/mole. The diffusion coefficient dependence on temperature is shown in Fig 4. It can be seen that values of diffusion coefficient of BA sintering were comparable to that for CA (9). A comparison of

TABLE 1

Diffusion coefficient at different temperatures

Temperature °C	Diffusion coefficient cm ² /sec	Activation energy Kcal/mole
1300	3.38x10 ⁻⁹	188.00
1350	5.16x10 ⁻⁹	
1400	8.91x10 ⁻⁹	
1450	11.20x10 ⁻⁹	

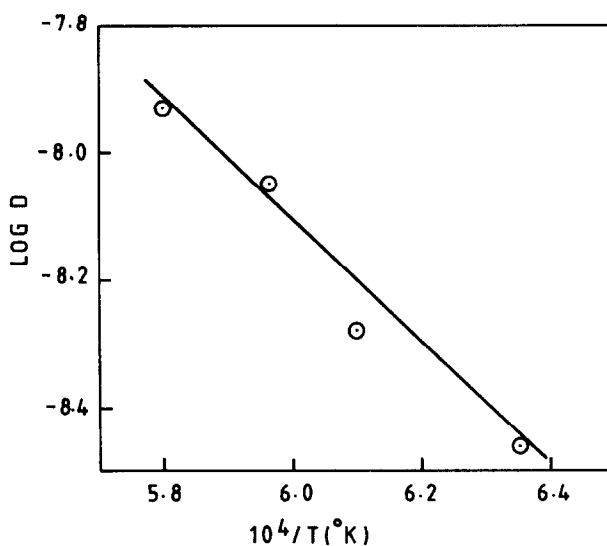


FIG 3. Temperature dependence of diffusion coefficient

apparent diffusion coefficients with interdiffusion coefficients (10) of reaction between BaO and Al₂O₃ in formation of BaAl₂O₄ shows higher values of interdiffusion coefficient.

Conclusions

1. Linear shrinkage at 1300, 1350, 1400 and 1450°C for time duration of 30 minutes is found to be approximately 11.2, 13.0, 14.7 and 16.5 % respectively indicating the increase in rate of linear shrinkage with sintering temperature.

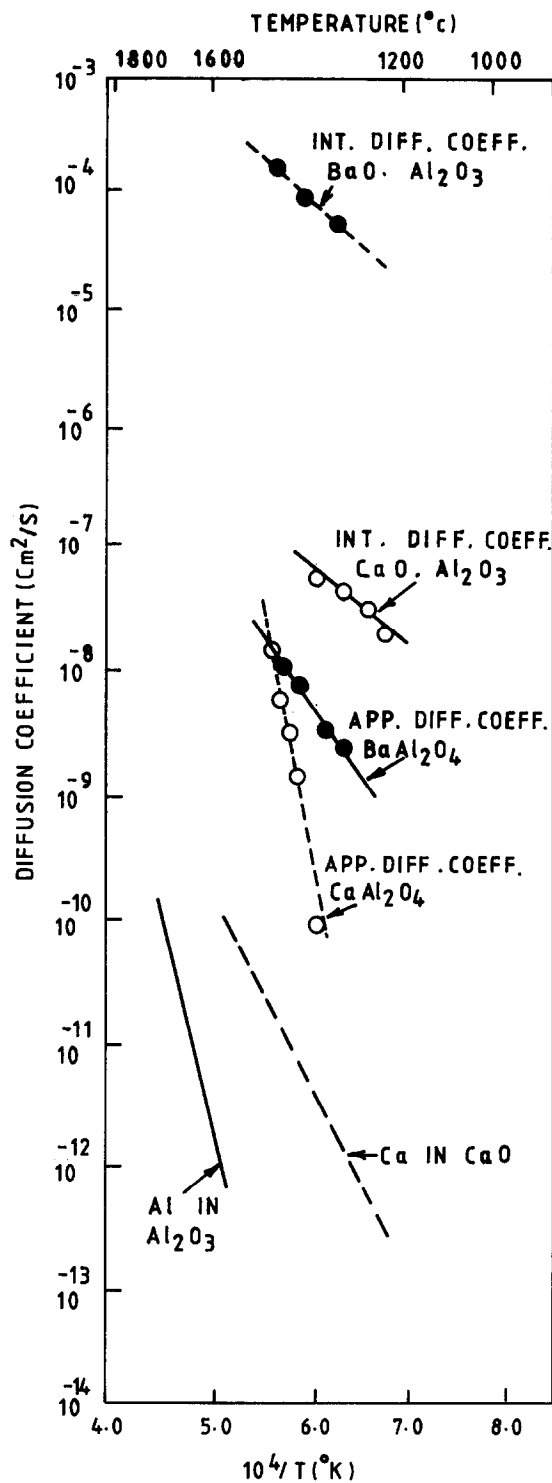


FIG 4. Temperature dependence of the diffusion coefficient

2. Volume diffusion is the predominant mechanism of sintering and diffusion coefficient increases with temperature. A comparison of apparent diffusion coefficient with the interdiffusion coefficient indicates the higher values of interdiffusion coefficient.
3. Activation energy for the sintering of BA was calculated to be 188.0 Kcal/mole.
4. Diffusion coefficient values calculated for sintering of BA were found comparable to those reported for CA.

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