MASTER

MAGNESIUM OXIDE ENHANCEMENT OF SINTERING OF ALUMINA

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Although it is known that small quantities of MgO enhance sintering of Al_2O_3 , the process of enhancement has not been established. Sintering data for compacts of several oxides heated at various rates to a specific temperature show that the final density achieved in powder compacts is relatively insensitive to heating rates above about 2°C/s . Transmission electron microscopy studies of these compacts show evidence of dislocation generation in the sintering material in regions between adjacent particles. Sintering measurements of compacts of Al_2O_3 and MgO doped Al_2O_3 show that MgO contributes to the initial densification even when high heating rates are applied to the compacts. Comparison of the observed densification kinetics with those of a diffusion process shows that the experimental results are incompatible with a diffusion controlled process. It is proposed that MgO on the surface of Al_2O_3 particles increases the ease of dislocation motion and generation compared to pure Al_2O_3 . This enhancement improves the compact densification.

INTRODUCTION

It has long been known that addition of small amounts of MgO increases the density achieved in sintered alumina compacts. Coble¹ observed the effect and used it to develop high density, translucent alumina ceramics. However, the method by which MgO improves the material transport involved in the sintering is still not satisfactorily established. Jorgensen and Westbrook² deduced that MgO prevented grain growth in Al_2O_3 and thus enhanced sintering. However,

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Peelen³ has shown that MgO in Al₂O₃ in quantities which have the greatest effect in enhancing densification causes increased grain growth. Stein et al.⁴ have shown that MgO does not segregate at the grain boundary in Al₂O₃.

At the Oak Ridge National Laboratory, sintering studies have been interpreted to indicate that dislocation movement may be an important method of material transport in many sintering situations.⁵⁻⁷ Experimental sintering measurements have now been extended to include Al₂O₃ and Al₂O₃-MgO. In this paper the basic arguments for material transport by dislocation slip are reviewed and extended to the Al₂O₃-MgO system.

REVIEW OF DENSIFICATION KINETICS STUDIES

A remarkable sintering phenomenon can be observed when compacts of a fine particle size, crystalline powder are brought to a predetermined temperature at various heating rates. When there is no appreciable hold time at temperature the density achieved is largely unaffected by widely differing heating rates. An example of this phenomenon is illustrated by the data plotted in Fig. 1.⁵ In this case, the density attained by the thoria powder compacts heated to 1600°C decreases only slightly with increasing heating rate between 2°C/s and 21°C/s. Other examples of this almost constant end point density are shown in Fig. 2.⁶ The time for sintering at each temperature is inversely proportional to the heating rate. An interesting part of this phenomenon is the point at which the almost constant end point ceases to exist, i.e., if the heating rate is low enough the density achieved increases significantly with reduced heating rate. This is illustrated in Fig. 2 for sintering of ZrO₂ at heating rates below 5°C/s. For the case of thoria powder compacts, this increase does not occur until the heating rate is below about 1°C/s.

Diffusion controlled material transport causing densification in sintering can be volume diffusion, grain boundary diffusion or dislocation slip limited to where the slip is controlled by diffusion processes. None of these diffusion controlled processes, however, would have the temperature-time-densification response observed above. The fact that these experimental results are incompatible with a diffusion controlled process suggests a need for identifying other mechanisms of material transport in the sintering process. The only known process or mechanism whose characteristics agree with the experimental results is dislocation transport of material occurring by slip which is not diffusion controlled.⁷

OBSERVATION OF DISLOCATIONS IN SINTERING

The plausibility of considering a dislocation slip contribution to material transport is increased by experimental observation of dislocations produced during sintering. It has been found that if small

Fig. 1. Density of ThO₂ compacts brought to temperature at different heating rates.

Fig. 2. Density versus heating rate for powder compacts brought to temperature but not held at temperature. (The points for MgO are the average of several specimens.)

pieces of CaF_2 crystals are sintered to cleaved surfaces of CaF_2 , large concentrations of dislocation etch pits often occur around the sintering weld necks.⁸ Figure 3 shows an example of such etch pits in CaF_2 sintered at 1250°C for 30 min. Extensive testing showed that these dislocation concentrations resulted directly from the sintering experiment; they could not be identified as artifacts resulting from dropping small crystals on the larger crystal surface, handling deformation, or thermal shock. Geguzin⁹ found similar dislocation clusters around the weld necks when small crystals of LiF were sintered to the cleaved surface of LiF crystals. He described them as sintering rosettes. An example of Geguzin's sintering rosettes is shown in Fig. 4.

Fig. 3. Clusters of dislocation etch pits developed around weld necks of CaF_2 particles lightly sintered to CaF_2 crystals.

Transmission electron microscopy (TEM) provides another means of observing dislocations resulting from sintering processes. In these studies powder compacts were partially sintered by long term heat treatment at a relatively low temperature. For MgO powder compacts the partial sintering treatment was at 1450°C for 5 days. This produced a compact that would hold together during thinning for TEM examination. Partially sintered MgO at this stage did not contain any concentrations of dislocations. However, if the partially sintered compacts were heated to 2450°C and maintained only a short time, many massive concentrations of dislocations such as that shown in Fig. 5 were present.¹⁰ Extensive tests showed that the dislocations were not created by thermal stresses due to cooling or by mechanical deformation during handling.¹⁰ An example of dislocations generated during sintering of tungsten powder is shown in Fig. 6.¹¹

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Fig. 4. Sintering "rosettes" made by dislocation etch pits around weld neck on a LiF crystal. From Geguzin, ref. 9.

Fig. 5. Concentrations of dislocation etch pits were observed in partially sintered MgO. The annealed appearance of the dislocations shows they were present during high temperature treatments.

Fig. 6. Dislocation concentrations were found in W powder compacts after partial sintering.

These experimental tests indicate that the dislocations are generated during sintering. A possible, if not the only, conclusion is that the dislocations result from material transport by dislocation slip during the sintering process.

SINTERING OF Al_2O_3 -MgO

The initial densification of Al_2O_3 -MgO powder compacts occurring with heating at a uniform rate has been examined experimentally. High purity alumina powder of 0.3 μm average particle size was slurried in methyl alcohol containing dissolved magnesium acetate. The alcohol was evaporated with continuous stirring and the $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ remaining on the Al_2O_3 particles converted to MgO by heating the powder at 700°C for 1 h in air. As a control material in the sintering experiments, the Al_2O_3 powder was treated the same except for omission of $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ and acetic acid was added to obtain an equivalent effect on particle-particle interaction.

Powder compacts 6.35 mm diameter by about 3.8 mm high were obtained by cold pressing at 103 MPa (15,000 psi) without lubricants. The compacts were sintered in a refractory metal furnace with a thermocouple suspended just above the sample circle. The temperature of the samples was assumed to correspond to that indicated by a recording potentiometer activated by the thermocouple.

The first objective of this study was to compare the initial, fast sintering of Al_2O_3 compacts which contained MgO with the sintering of those which did not contain MgO. This was complicated by the fact that Al_2O_3 powder containing MgO and pure Al_2O_3 did not readily press to the same green density. However, almost exactly equivalent green densities (1.51 kg/m^3) were achieved by adjusting the amount of acetic acid added to the methanol slurry of Al_2O_3 . The fractional densification was always higher in Al_2O_3 -MgO samples.

Initial, nonisothermal sintering of these compacts was determined by heating them at a uniform rate to 1550°C with no appreciable hold at the maximum temperature. The Al_2O_3 and Al_2O_3 -MgO compacts were arranged alternately in a circle within the furnace during sintering. Results tabulated below are the average of two specimens in each case.

Heating Rate	Density, kg/m^3	
	Al_2O_3 -300 ppm MgO	Al_2O_3
2°C/s	2.11	2.08
3°C/s	2.03	1.98
4°C/s	2.03	2.01

These experimental differences are small but are thought to be significant as the initial sintering enhancement by MgO was observed in 43 separate sinterings. Al_2O_3 with MgO contents of 1000 ppm and 3000 ppm sintered to essentially the same density as the 300 ppm sample during these experiments. It is of interest to review results of sintering for 1 h at 1600°C in an argon atmosphere:

Sample Composition	Density Units (kg/m^3)	% TD
Al_2O_3	3.83	96.5
Al_2O_3 -300 ppm MgO	3.92	98.7
Al_2O_3 -1000 ppm MgO	3.89	98.0
Al_2O_3 -2000 ppm MgO	3.89	98.0

Densification of Al_2O_3 -300 ppm MgO powder compacts all pressed from the same powder preparation the same day are shown in Fig. 7 as a function of heating rate. These data do not show as large a disagreement with predictions based upon diffusion controlled processes as the ThO_2 data in Fig. 1, but do indicate that the densification kinetics are incompatible with the predictions for a diffusion controlled sintering model. The limited slip available on other than the basal planes may prevent Al_2O_3 compacts from exhibiting as small a change in density with heating rate as cubic ThO_2 . In Fig. 7 the

Fig. 7. The comparison of a diffusion controlled densification (curve A) and experimental measurements illustrates the incompatibility of initial $\text{Al}_2\text{O}_3\text{-MgO}$ densification with a diffusion controlled process.

density expected if sintering was controlled by a volume diffusion process is included as shown by curve A. This curve was obtained using the Kingery-Berg equation for volume diffusion:¹²

$$\frac{\Delta V}{V_0} = \frac{-3n}{8} \left[\frac{80 \gamma a^3 D}{r^3 k T} \right]^{4/5} t^{4/5}$$

where

- V = volume of compact,
- n = average number of contacts per sphere,
- γ = the surface energy,
- a = the atomic radius,
- D = the self-diffusion coefficient of the slower species,
- r = sphere radii,
- k = the Boltzmann constant,
- T = the absolute temperature,
- t = the time.

For reasonable values of r and the other parameters, the extent of densification indicated by the formula is less than that achieved

in the initial fast densification of Al_2O_3 compacts, but by force fitting the results to agree with that obtained experimentally for $1/2^\circ\text{C/s}$ heating rate, curve A of Fig. 7 was obtained.*

ANALYSIS OF RESULTS

Two conclusions can be drawn from the experimental results: 1) the initial densification of Al_2O_3 is improved by small amounts of MgO ; 2) during the sintering occurring as the temperature is increased, the densification kinetics do not agree with those expected for diffusion controlled densification, i.e., the densification rates during fast heating (short times at temperature compared to slower heating conditions) are faster than diffusion processes will allow.

In interpreting the results, consider the effect of surface coatings on dislocation slip. Westwood and coworkers have demonstrated that small amounts of many surface additives affect the ease of dislocation slip in both metals and ceramics.^{13,14} Figure 8 from Westwood's work shows the effect of additives on glide of edge dislocations in MgO crystals. It has been observed that initial sintering densification kinetics, while incompatible with diffusion controlled processes, are in good agreement with the characteristics expected for dislocation motion where it occurs without much assistance from diffusion processes.⁷ These considerations strongly suggest that MgO on the Al_2O_3 particles increases the ease of dislocation slip, and the improved dislocation slip contributes to material transport which accounts for the MgO enhancement of sintering of Al_2O_3 .

Fig. 8. These curves taken from Westwood et al.¹⁴ illustrate the extensive effect that small amounts of surface coatings can have on ease of dislocation slip.

*The force fitting was accomplished by adjusting the pre-exponential term. The final temperature of 1823 K was used as if it were the continuous temperature and the time, t , was time above 1000°C .

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