

## Sintering and crystal growth of magnesia in the presence of lime and forsterite

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**SUMMARY.** The densification of pure magnesia was examined along with mixtures containing 0.5 and 1.0 mol % of calcium oxide and forsterite. The sintering behaviour at temperatures between 1400 and 1800 °C was studied and measurements made of changes in shrinkage, porosity, bulk density, and grain size for sintering times of up to 8 h at sintering temperature. It was found that both the 0.5 and 1.0 mol % additions enhanced the sintering of pure magnesia in the temperature range 1500–1700 °C. Increased grain growth was found for mixtures containing forsterite but little change occurred for mixtures containing lime. Examination of the grain growth data showed that the mixtures obeyed a relationship: Time at temperature  $\times$  Constant = (grain size)<sup>n</sup>, where  $n = 2$  for the grain growth of pure magnesia and mixtures containing lime, but  $n = 3$  for mixtures of magnesia with additions of a silicate such as forsterite. A value of 78 kcal/mole was obtained for the grain growth of pure magnesia, which agrees with other researches.

The extent of the solubility of lime in periclase for each lime–magnesia mixture at each temperature was also examined using electron probe analysis and related to the sintering behaviour observed for these mixtures.

**INTEREST** in magnesia stems from the wide use of this oxide as a refractory in the steel-making industries. Because of its high melting point (2800 °C) and resistance to the high-temperature corrosive and erosive conditions in steel-making furnaces, large quantities of this material are used for the hearth, which contains the molten metal and its slag.

Commercially available magnesia refractories now approach a high level of MgO content, where the main impurities are the oxides CaO and SiO<sub>2</sub>, which are present as silicates. Lesser impurities are Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and traces of oxides such as B<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub>.

In the CaO–MgO–SiO<sub>2</sub> system as given by Levin (1964) there are a range of silicates that can coexist with a magnesia phase at high temperature: forsterite, monticellite, merwinite, dicalcium silicate, and tricalcium silicate. The silicates, monticellite, merwinite, dicalcium silicate, and tricalcium silicate have been examined after sintering in the presence of a magnesia phase by Spencer and Coleman (1969) and it has been found that these silicates do affect the sintering and crystal (or grain) growth of magnesia in the temperature range 1400–1800 °C. The silicates are either molten within this temperature range, or decompose liberating free CaO, which dissolves in the periclase phase leaving a silicate system having a lower CaO/SiO<sub>2</sub> ratio.

In this system, only the phases forsterite and lime can be considered as solid phases in the range of temperatures 1400–1800 °C. This paper presents information on the densification and crystal growth of magnesia, magnesia–forsterite, and magnesia–lime mixtures during sintering at these temperatures.

*Raw materials*

*Magnesia.* The source material for this oxide was the oxalate prepared via the nitrate obtained from magnesium metal of stated purity 99.97%. Upon calcination of the magnesium oxalate in platinum crucibles at 800 °C for 5 h a pure magnesium oxide was obtained having the following impurities, when analysed by spectroscopic techniques: Al 3, Ca 4, Cu 3, Fe 4, K 3, Mn 4, Na 2, Ni 1, Pb 1, Si 2 ppm (total 27 ppm). Other metals were sought but not detected.

*Forsterite.* Pure precipitated silica (> 99.9% SiO<sub>2</sub>; X-ray amorphous) was dried at 250 °C and used to make the forsterite addition. The correct molar amounts of the dried magnesia and silica were fired (as pressed pellets) for 3 h at 1650 °C and then quenched to room temperature. The fired pellets were ground with an agate pestle and mortar to pass through a 300 B.S. sieve. This powder was examined by X-ray diffraction techniques to ensure that the reaction of the raw materials was complete and that forsterite was formed. This procedure has been previously used successfully by Spencer and Coleman (1969) to prepare the other silicates in the CaO–MgO–SiO<sub>2</sub> system for the determination of their densities.

*Lime.* The addition of lime to magnesia was made using Analar grade calcium carbonate that had been dried at 250 °C.

*Mixture preparation.* Mixtures of magnesia with 0.5 and 1.0 mol % of forsterite or lime were prepared by repeatedly passing the material through a 300 B.S. sieve, and formed into pellets by pressing at 10 ton/in<sup>2</sup>, using a few drops of carbon tetrachloride as a lubricant to prevent lamination. These levels of addition, which correspond to 0.73 and 1.45% SiO<sub>2</sub> or 0.69 and 1.38% CaO, were chosen to give compositions approaching those of commercially available magnesia refractory materials.

*Experimental details*

*Sintering procedure.* The pellets were sintered in air in a horizontal alumina tube furnace for 0.1, 1, 2, 4, and 8 h at each of the following temperatures: 1400, 1500, 1600, 1700, and 1800 °C. Five pellets of each mixture were sintered at a constant heating rate of 300 °C per h. A thermocouple was placed on each side of the pellets within the furnace and one thermocouple in their centre. Up to and including 1700 °C, the control of the sintering temperature was within ±2 °C difference between the three thermocouples. For sinterings at 1800 °C, the control of the sintering temperature was considered to be better than ±5 °C.

*Determination of densities and volumes:* The pressed pellets were weighed to ±0.001 g. Their volumes were determined by weighing to within ±0.02 g immersed in mercury, using the 'mercury balance' method; this corresponds to ±0.004 g/cm<sup>3</sup> in the bulk densities and ±0.005 cm<sup>3</sup>/g in the bulk volumes calculated from these determinations.

After sintering, the pellets were reweighed as accurately as before, and then impregnated with xylene under vacuum. The sintered bulk volume and apparent solid volume of the pellets were determined by weighing to within ±0.001 g immersed in

xylene, and in air still impregnated with xylene. This enabled the apparent porosities of the pellets to be calculated. Knowing the true densities (Spencer and Coleman, 1969*b*) of the silicates, the true porosities of the sintered mixtures can also be calculated. The values presented in this paper are the average of at least 10 pellets (i.e. 2 sinterings of 5) and in some cases 15 pellets (i.e. 3 sinterings). Results of pellets that were severely cracked were ignored, and results of sinterings that gave doubtful data were repeated. Strict control of the pressed bulk densities of the pellets was observed. Only those pellets that had bulk densities that came within the range  $1.58 \pm 0.02 \text{ g/cm}^3$  were sintered, all pellets with different densities to this were rejected.

*Preparation for microscopic examination.* The sintered pellets were impregnated under vacuum with a polystyrene resin and allowed to set slowly in air. They were ground on carborundum papers and with diamond paste to a  $1 \mu\text{m}$  finish.

*Measurement of grain size.* The 'random intercept' method of Fullman (1953) was used to determine the mean grain diameter  $D$ . For random straight lines drawn across a section of a microstructure composed of equal spherical grains, he showed that  $D = 1.5l$ , where  $l$  is the average length of the intercepts of individual grains on the lines. This method is considered valid if the range of grain size is not too wide as in this research.

The polished surfaces, after etching, of three pellets from each sintering treatment were photographed under the microscope. Photographs were developed at a magnification that gave an average intercept length of between 5 and 10  $\mu\text{m}$ . An average of 500 measurements of intercepts were taken from each photograph.

*Electron-probe examination.* Pellets that had been sintered for 8 h at each temperature were mounted together with a reference sample of monticellite, since this contains equal molar proportions of Ca, Mg, and Si. The mount was polished and given a thin carbon coating. Point counts in the centre of the periclase grains were made of Mg, Ca, and Si, and compared with the counts taken from the reference sample to give a quantitative estimate of  $\text{Ca}^{2+}$  and  $\text{Si}^{4+}$  present. Scans across the periclase grains showed that no change in the point counts occurred, inferring that the phases present had reached equilibrium.

### Results

*Sintered densities and volumes.* The shrinkage of the sintered mixtures is presented here as a volume shrinkage parameter  $F_V$  for a given firing temperature:

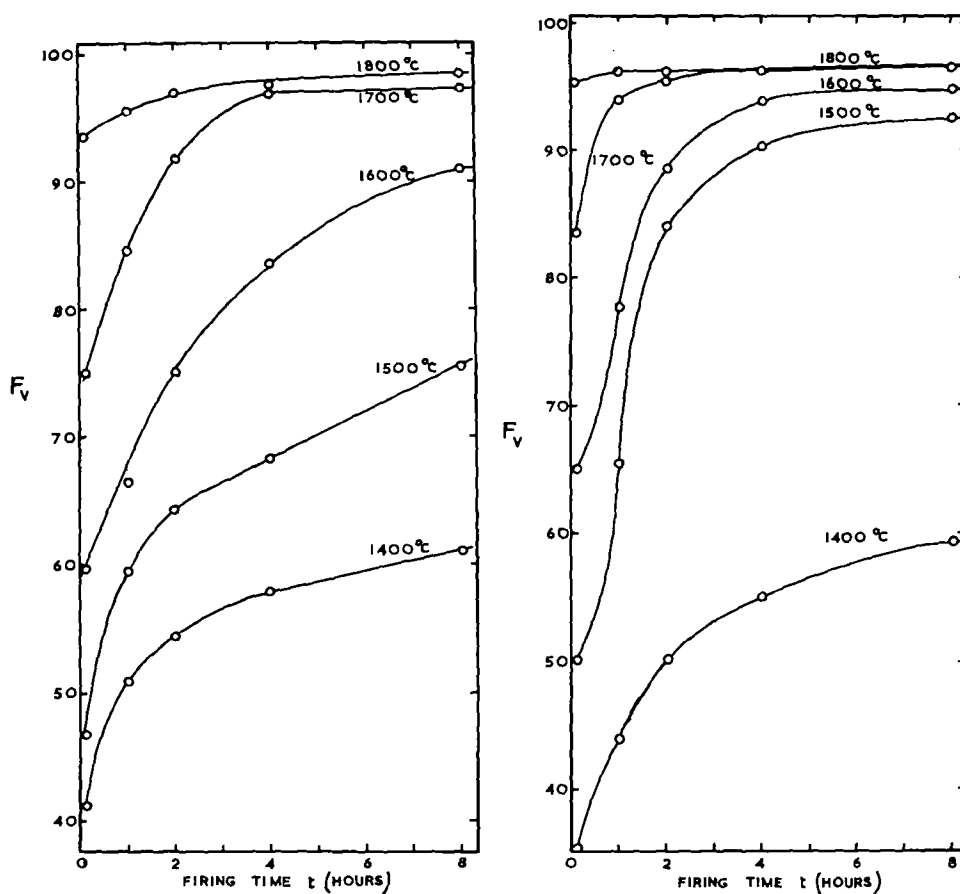
$$F_V = 100 (\text{vol. change of mixture})/(\text{max. vol. change possible}) \\ = 100 (\text{pressed bulk vol.} - \text{fired bulk vol.})/(\text{pressed bulk vol.} - \text{specific vol.}).$$

The values of  $F_V$  against time at sintering temperature for pure magnesia are shown graphically in fig. 1. Similar values for the mixture of magnesia and 0.5 mole % forsterite are plotted in fig. 2, and a corresponding set of values for the mixture of magnesia and 0.5 mole % lime are plotted in fig. 3.

A comparison between the effects of both levels of 0.5 and 1.0 mole % of addition on the sintering of the magnesia mixtures at each temperature with that of pure

magnesia is given in table I, where  $F_V$  values after 4 h of sintering have been chosen as a time comparable with commercial sintering practice.

*Porosities.* The comparative effects of the additions on the densification of the mixtures, when compared with the pure magnesia, can be demonstrated by considering the



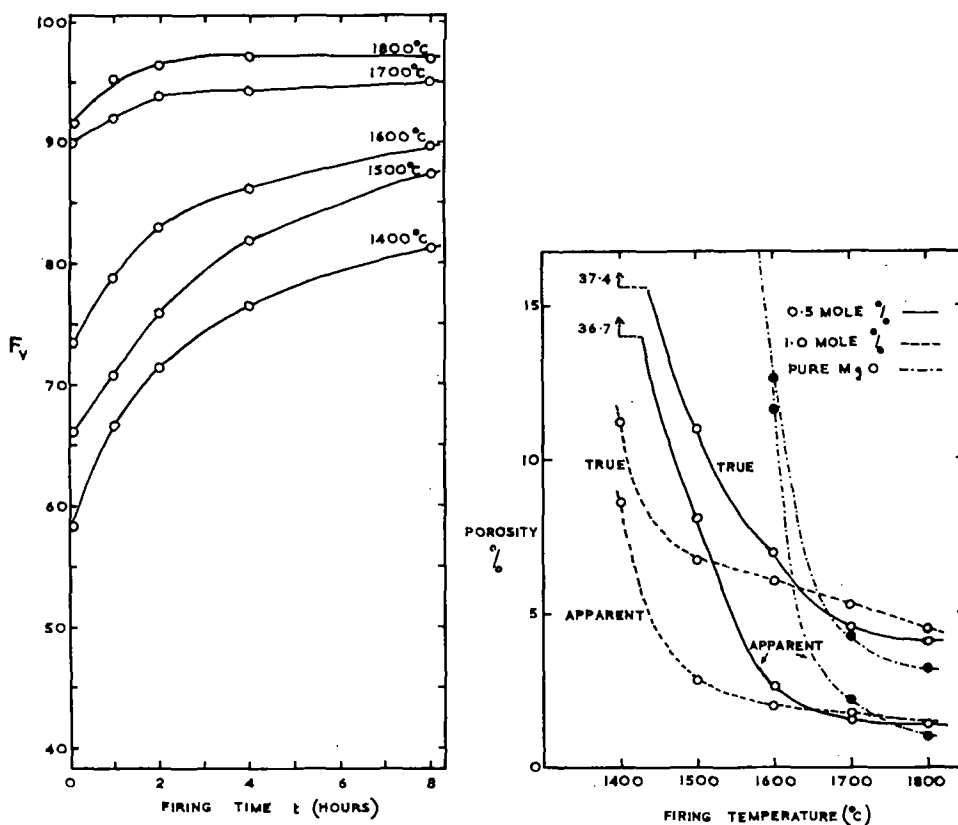
FIGS. 1 and 2: Fig. 1 (left). Shrinkage of pure magnesia: plots of shrinkage parameter  $F_V$  % against time at temperature. Fig. 2 (right). Shrinkage of mixtures of magnesia containing 0.5 mole % of forsterite: plots of shrinkage parameter  $F_V$  % against time at temperature.

porosities of the sintered pellets after 4 h. Fig. 4 compares the effect of 0.5 and 1.0 mole % forsterite additions to pure magnesia on the true and apparent porosities when plotted against sintering temperature. A similar series of graphs compares the effects of the same levels of addition of lime to pure magnesia in fig. 5.

*Grain sizes.* The grain sizes of pure magnesia compared with those of mixtures containing 0.5 mol % additions are plotted against time at the sintering temperature in

fig. 6. The effects of 0.5 and 1.0 mole % additions on the grain size of the mixtures are shown in comparison with pure magnesia in fig. 7, where the grain sizes after 4 h are plotted against sintering temperature.

*Grain growth kinetics.* At each temperature  $T$  °K the grain growth of pure magnesia and its mixtures was assumed to be a simple function of time  $t$ , as given by Turnbull



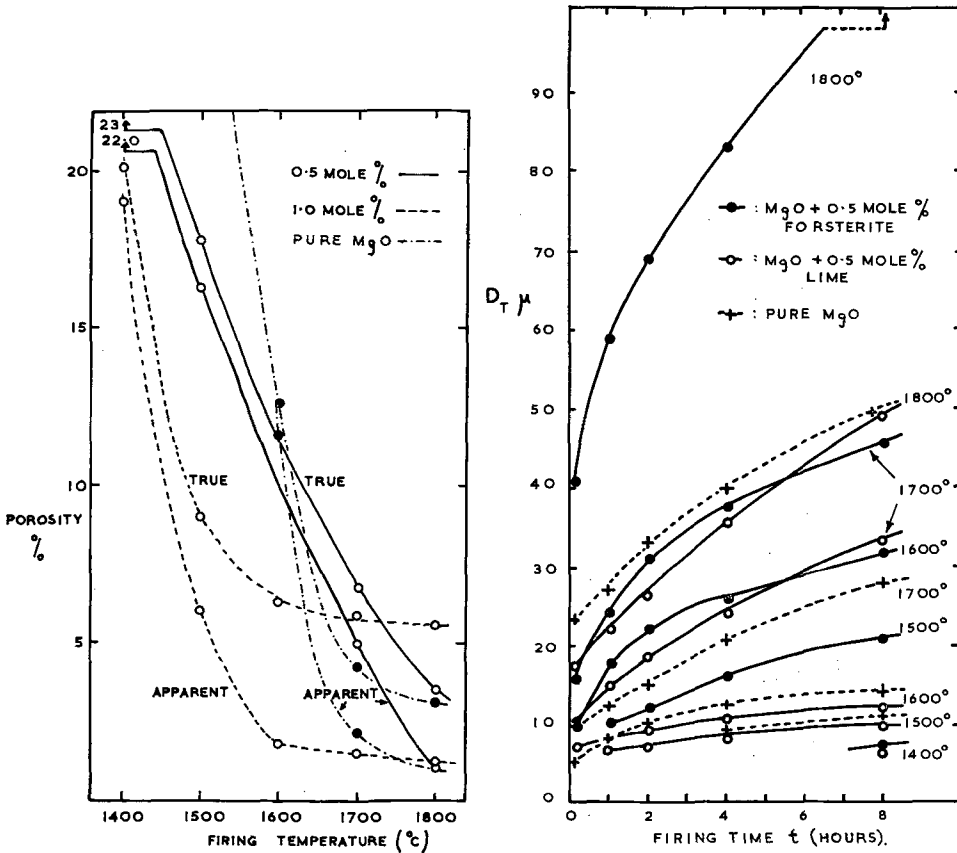
Figs. 3 and 4: Fig. 3 (left). Shrinkage of mixtures of magnesia containing 0.5 mole % of lime: plots of shrinkage parameter  $F_V$  % against time at temperature. Fig. 4 (right). Comparison of porosities (after 4 h at temperature) of pure magnesia with mixtures containing 0.5 and 1.0 mole % forsterite additions.

(1965):  $Kt = D_T^n$ , where  $K$  is the rate constant for grain growth at the given temperature. This becomes  $K(t-t_0) = D_T^n - D_0^n = (k\gamma V)(t-t_0)$ , where  $t_0$  is some arbitrary zero time and  $D_0$  the grain size at that moment,  $t$  a later time when the grain size is  $D_T$ ,  $k$  is related to  $K$ ,  $\gamma$  is the interfacial energy and  $V$  is the gram-atomic volume of the material. We took  $t_0 = 0.1$  h and the value of  $D_0$  at that time and applied the above equation to the grain size measurements obtained.

Examination of plots of  $\log(t-t_0)$  versus  $\log(D_T^n - D_0^n)$  showed that when  $n = 2$

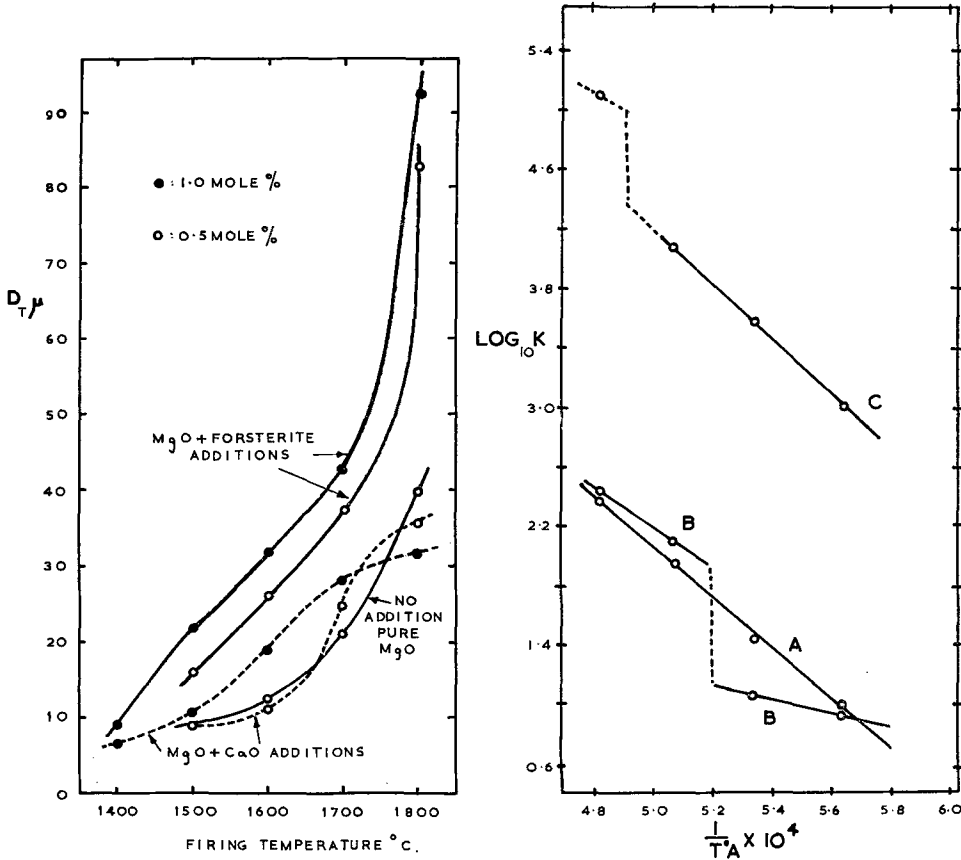
TABLE I. Shrinkage parameter:  $F_V$  % values. Comparison of the effect of 0.5 and 1.0 mole % additions of forsterite and lime

Material	Addition mole %	Sintering for 4 h at temperatures of:				
		1400 °C	1500 °C	1600 °C	1700 °C	1800 °C
MgO	—	58.1	68.2	83.6	96.9	97.5
MgO+M <sub>2</sub> S	0.5	55.1	90.2	93.9	96.2	96.5
MgO+M <sub>2</sub> S	1.0	89.9	94.3	94.8	95.6	96.1
MgO+CaO	0.5	76.6	82.0	86.2	94.4	97.1
MgO+CaO	1.0	80.0	92.1	94.9	94.9	95.1



FIGS. 5 and 6: Fig. 5 (left) Comparison of porosities (after 4 h at temperature) of pure magnesia with mixtures containing 0.5 and 1.0 mole % lime additions. Fig. 6 (right). Grain growth of pure magnesia, compared with the grain growth of mixtures of magnesia containing 0.5 mole % forsterite and lime additions: plots of average grain size  $D_T$  (micrometres) against time at temperature.

the data for pure magnesia and mixtures of magnesia with lime addition were linear plots with slopes approaching unity, whereas a linear plot with a slope approaching unity only occurred for  $n = 3$  with data for the mixtures of magnesia containing additions of forsterite.



Figs. 7 and 8: Fig. 7 (left). Comparison of average grain size  $D_T$  (after 4 h at temperature) of pure magnesia with mixtures containing 0.5 and 1.0 mole % forsterite and lime additions. Fig. 8 (right). Plots of  $\log_{10} K$  against  $1/T$   $^{\circ}\text{K}$  to determine activation energies of grain growth. Systems obeying the relationship:  $K(t-t_0) = D_T^n - D_0^n$ : A: Pure magnesia,  $n = 2$ . B: Magnesia with 0.5 mole % lime,  $n = 2$ . C: Magnesia with 0.5 mole % forsterite,  $n = 3$ .

Table II gives the values of  $n/2$  or  $n/3$ , which should be 1.00 if the equations are true quadratic or cubic respectively. These values indicate how closely the equation is followed. This table also presents the values of  $K$  determined from the logarithm plots, and Fig. 8 shows the  $\log K$  versus  $1/T$  plots for pure magnesia and mixtures containing 0.5 mole % additions.

*Grain growth and sintering temperature.* Using the data for pure magnesia, a plot of  $\log K$  versus  $1/T$  is linear. This indicates that an Arrhenius relationship holds

TABLE II. Summary of the effect of additions on the kinetics of the grain growth of magnesia

Addition to Magnesia in mole %	$n^*$	Slope of plot $\log_{10} t$ vs.		Rate constant $K$				Temperature range of change in mechanism	Apparent activation energy			
		1500 °C	1600 °C	1700 °C	1800 °C	1500 °C	1600 °C		1700 °C	1800 °C	Low temp. kcal	High temp. kcal
No addition	2	—	0.93	1.03	0.94	10.0	26.0	89.0	247	No change	78 ± 2	—
0.5 Forsterite	3	0.94	0.95	0.95	1.01	1060	3810	12300	$1.28 \times 10^5$	1700–1800 °C	85 ± 2	—
0.5 Calcium oxide	2	0.93	0.94	1.00	1.03	8.40	11.5	128	276	1600–1700 °C	22 ± 4	62 ± 4

\* Integer  $n$  in the relation  $Kt = D^n$ .



$K = \text{constant} \cdot e^{-E/RT}$ , where  $E$  cal/mole is a phenomenological 'activation energy' for the grain growth process. A similar analysis was carried out for the mixtures containing the 0.5 mol % additions, and it was found that a break in the Arrhenius plots occurred in the temperature range 1700–1800 °C for the magnesia–forsterite mixtures, and within the range 1600–1700 °C for the magnesia–lime mixtures. The 'activation energies' for the temperature ranges on each side of these breaks are given in table II.

*Electron-probe information.* The percentages of CaO found in solid solution in the periclase of a sintered mixture containing 0.5 mole % (0.69 wt %) CaO after 8 h sintering were: sintered at 1400 °C, nil; at 1500 °C, 0.52 %, at 1600, 1700, and at 1800 °C, 0.69 %; for a mixture containing 1.0 mole % (1.38 wt %) CaO, the corresponding figures were: 1500 °C, 0.72 %, 1600 °C, 0.91 %, 1800 °C, 1.38 %. Allowing for corrections for background counts, these results are considered to be accurate to  $\pm 0.02$  wt %. No appreciable amounts of  $\text{Si}^{4+}$  ions were found in the periclase grains.

#### *Discussion of results*

The controlling property that can explain the results obtained appears to be the average grain size  $D_T$  of the materials. This can be related to porosity (and therefore shrinkage) and according to Turnbull (1965) it is related to time by the above equation.

Further, Burke (1957) has suggested that  $D_T$  is a function of the average pore size  $d$  and the total porosity  $P$ . Pores can be considered as a second phase that inhibits continuous grain growth and Smith (1948) says that this growth will stop when  $D_T = d/P$ . Considering the equation for grain growth, it is possible to suggest suitable mechanisms that will explain the grain growth behaviour of the magnesia with additions of forsterite and lime. These additions can be shown to have different effects on the interfacial energy of the periclase phase of the mixtures, which alters the  $D_T$  values. These in turn affect the values of porosity, and hence density and shrinkage values, which are related as Burke suggests.

#### *Magnesia*

*Grain growth.* The  $D_T \sim t^{1/2}$  relationship is expected for the grain growth of normal crystalline solids where the grain boundaries move towards their centre of curvature and the pores, if present, do not drastically affect the growth rate. The grain growth behaviour described here for our pure magnesia has been found by other researchers. Spriggs, Brissette, and Vasilos (1963) examined the grain growth of fully dense magnesia having an impurity content of 200 ppm. They found that the  $D_T \sim t^{1/2}$  relationship held for their material and determined an activation energy of 81 kcal/mole. Our value of  $78 \pm 2$  kcal/mole agrees favourably with this considering that our level of impurity is different. However, Daniels, Lowrie, Gibby, and Cutler (1962) examined a very impure magnesia and found the same grain growth behaviour. They determined an activation energy of 60 kcal/mole, which is nearer to the value determined for our magnesia and lime mixture with 0.69 wt % CaO,  $62 \pm 4$  kcal/mole.

#### *Mixtures of magnesia and forsterite*

*Grain growth.* Fig. 6 shows that the presence of 0.5 mole % forsterite in the magnesia mixtures gives a greatly increased grain size when compared with pure magnesia, for

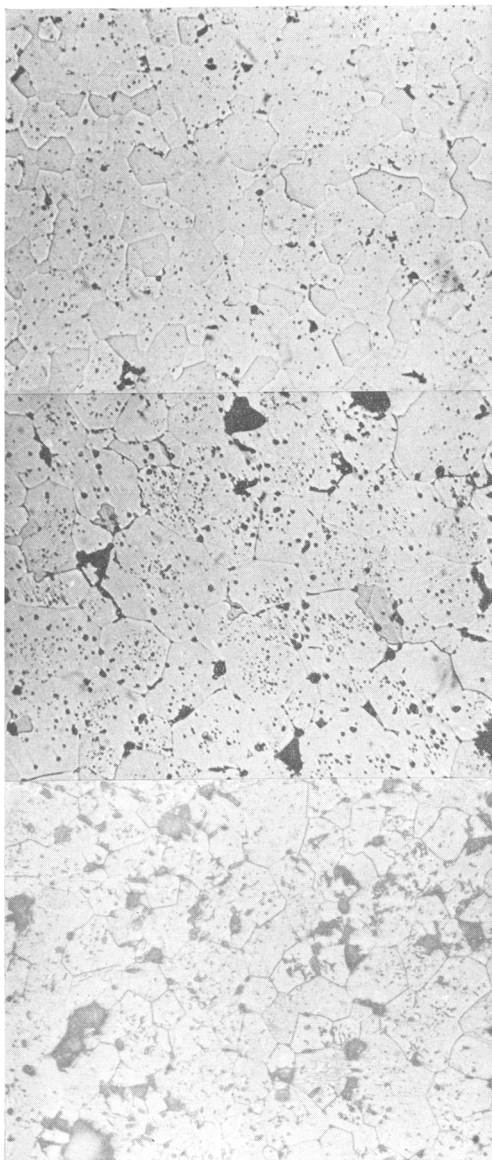


FIG. 9. Examples of microstructures of materials after sintering for 8 h at 1800 °C: *a* (top), pure magnesia; unetched as polished. Notice the angular grains and the small pores.  $\times 100$ . *b* (centre), magnesia with 1.0 mole % forsterite addition; etched with sulphuric acid. Notice the rounding of the grain boundaries at grain boundary junctions, also the large rounded pores (black) in the centre of the grains. The grain boundaries appear to have swept up pores during the grain growth, pores appear at grain boundary junctions. The dark grey phase is forsterite.  $\times 100$ . *c* (bottom), magnesia with 1.0 mole % lime addition: etched with sulphuric acid. Notice the smaller angular grains and the small pores.  $\times 200$ .

sintering temperatures up to 1700 °C. This effect increases with the concentration of forsterite from 0.5 to 1.0 mole % (fig. 7). Up to 1700 °C, the grain growth of the mixtures obeys the growth equation for a value of  $n = 3$ . This is unusual, since we consider that the MgO and 2MgO.SiO<sub>2</sub> phases are solid in this temperature range. The MgO-SiO<sub>2</sub> phase diagram (Levin *et al.*, 1964) shows that a liquid phase only occurs for temperatures above 1850 °C. The equation has been found by Spencer and Coleman (1969*a*) to be obeyed for silicates in the CaO-MgO-SiO<sub>2</sub> system that are liquid at the sintering temperature and in contact with a periclase phase. However, Kingery and Francois (1965) present evidence for UO<sub>2</sub> showing that a single solid phase can sinter in such a way that the grain size is proportional to  $t^{\frac{1}{3}}$  provided that the pores migrate along with grain boundaries during normal grain growth. Examination of the microstructure of these sintered mixtures shows that pores do concentrate on grain boundaries, particularly at grain boundary junctions, as shown in the typical microstructure given in fig. 9*b*.

Electron-probe analyses searching for the presence of silicon in the periclase phase of mixtures sintered from 1400 to 1800 °C showed that there was no measurable solution of Si<sup>4+</sup> ions retained in the periclase lattice. This has also been shown by Henney and

Jones (1969), who examined by X-ray diffraction mixtures quenched from 1750°C, and were unable to detect lattice parameter changes that would indicate the presence of Si<sup>4+</sup> ions in the periclase phase. It is therefore concluded that during sintering the forsterite diffuses around the grains, along grain boundaries, so that the interfacial energy of the grains is changed. Since this change allows increased grain growth compared with pure magnesia, it can be assumed that the presence of the forsterite causes a reduction in the interfacial energy  $\gamma$  with a resultant change in the growth rate constant  $K$  (cf. table II). The grain growth rate for the mixtures has a greater temperature dependence than the growth rate for magnesia, as shown by the higher activation energy of 85 kcal/mole for the magnesia-forsterite mixtures, compared with 78 kcal/mole for pure magnesia (table II).

Above 1700 °C, a change occurs in the slope of the graph given in fig. 8. This suggests the presence of a liquid phase, presumably formed from the impurities present in the silica used to make the forsterite phase, since the magnesia is very pure. Traces of this liquid phase were seen in the microstructures of mixtures sintered at 1800 °C, where some rounding of grain boundaries occurred. If this is so, a large change in the interfacial energy at the grain boundary would be expected and would give rise to this break in the grain growth behaviour.

*Shrinkage and porosity.* Kingery and Francois (1965) consider that for cases such as this, where the  $D_T \sim t^3$  relationship holds, the grain (and pore) growth is more rapid than other changes, so the pore-grain geometry remains about the same. Thus the pore size of the material remains nearly proportional to the grain size. These effects have a bearing on the shrinkage for these mixtures in the early stages of sintering, when the number of pores is high. Fig. 2 shows the marked difference in the values of  $F_V$  for the mixtures above 1400 °C compared with those values of  $F_V$  for pure magnesia after the same sintering time. The values at 1400 °C are about the same in figs. 1 and 2; this is attributed to the low diffusion rate of forsterite around the grains at this temperature for the lower level of addition of forsterite. At the higher level of addition this does not occur. At temperatures of 1700 and 1800 °C the amount of sealed porosity increases with forsterite content (cf. fig. 4), as would be expected and the over-all porosities are slightly higher than the comparable values for pure magnesia. In the later stage of sintering at these high temperatures, although the grain size is increasing more rapidly for the mixtures than for the pure magnesia (and the shrinkages correspondingly increased) the growing amount of sealed porosity is now controlling the final density and ultimate shrinkage. Then, for the same level of porosity, a high value of  $D_T$  means a large value of  $d$ , and therefore large diameter pores would be expected in magnesia mixtures containing forsterite after sintering for a long time at high temperatures, when the grain growth is slowing down. This is exactly what is seen on the examination of microstructures, such as the example in fig. 9b, where pores at grain boundaries are as large as those left in the centre of the grains by the receding grain boundary. Few pores are seen in the areas through which a grain boundary has moved; this again infers that the pores move with the grain boundary.

*Mixtures of magnesia and lime*

*Grain growth.* Electron probe data show that below 1600 °C the lime addition present at the grain boundaries is dissolving in the magnesia grains. Also, complete solution is achieved above this temperature, but only after long sintering times.

Below 1600 °C, the grain size of the mixtures, as shown in fig. 7, is dependent on the lime content. The more rapid increase in grain size of the 1.0 mole % mixtures over that of the pure magnesia could be explained by this solution of the  $\text{Ca}^{2+}$  ions in the periclase. Since there is a mismatch of ion radii given by Wells (1962) as:  $\text{Ca}^{2+}$  0.99 Å,  $\text{Mg}^{2+}$  0.65 Å, for every  $\text{Ca}^{2+}$  ion replacing a  $\text{Mg}^{2+}$  ion a distortion in the periclase is produced. X-ray analysis of these mixtures has been carried out by Mead (1969) and by Spencer, Beamond, and Coleman (1970), and the periclase lattice parameter was shown to expand with the presence of  $\text{Ca}^{2+}$  ions in proportion to the lime content of the mixture. If the lattice is distorted sufficiently, vacancies can be generated at the grain boundaries, as well as being adsorbed there, as Burke suggests. The resultant flow of vacancies to the grain boundary 'sinks' is altered, resulting in larger grains for the mixtures at temperatures below 1600 °C. This effect would be expected to be dependent more on the lime content at the grain boundaries than the sintering temperature. This would account for the low temperature-dependence of the grain growth at this stage, as shown by the very low activation energy of 22 kcal/mole.

Above 1600 °C, when the solution of  $\text{Ca}^{2+}$  ions in the periclase grains has been completed, the disturbing effect of vacancy generation at the grain boundary (which must affect the interfacial energy there) is removed. The grain growth reverts to a rate very similar to that for pure magnesia, as shown by the increase in activation energy from 22 to 62 kcal/mole. This indicates that the growth has become more temperature-dependent than below 1600 °C, which is more consistent with a diffusion process by vacancy flow than with a diffusion process by a vacancy flow involved also in solid solubility effect at the grain boundaries. For this reason, the grain sizes are very similar for pure magnesia and the mixtures at about 1700 °C as shown in fig. 7; but at 1800 °C the presence of lime in the periclase has an inhibiting effect on the grain growth and the porosity development has been different.

*Shrinkage and porosity.* The enhancement of sintering at low temperatures caused by the addition of lime to magnesia has also been found by Degtyareva, Kainarski, and Prokopenko (1967), who found that magnesia with the addition of 0.45 wt % CaO had a greater shrinkage than pure magnesia in the sintering temperature range 800–1400 °C. The decrease in the grain growth behaviour shown in fig. 7, which occurs above 1600 °C for the magnesia and lime mixtures, helps to explain the porosity changes shown in fig. 5. The mixtures decrease in porosity more rapidly as the temperature increases than does the pure magnesia, and develop a sealed porosity, which appears to increase with the greater lime content of the mixture. However, the shrinkage values, although related to the porosities, tend to the same value at 1800 °C.

Below 1600 °C, the grain growth of the lime mixtures increases with lime content as does the shrinkage, but above this temperature, due to the inhibiting effect of lime now dissolved completely in the periclase, the retarded grain growth counteracts the

shrinkage. Therefore, the pure magnesia and the mixtures arrive at similar porosity and shrinkage values (cf. table I) by different processes of pore development and grain growth.

#### Conclusions

*Magnesia-forsterite mixtures.* The addition of up to 1.0 mole % forsterite to magnesia increases its grain growth within the temperature range 1400–1800 °C. This growth follows a relationship of (grain size)<sup>3</sup> proportional to time at temperature, since the pores move with the grain boundaries. The densification of these mixtures at temperatures below 1600 °C is initially increased during the high grain growth, but the final density of these mixtures at 1800 °C is lower than that for pure magnesia under the same conditions, since the presence of the insoluble forsterite phase causes an increase in the sealed porosity.

*Magnesia-lime mixtures.* The addition of 1.0 mole % lime to magnesia dissolves completely in the periclase above a sintering temperature of 1600 °C. Below 1600 °C, during the solution of lime, the grain growth of the mixtures is slightly increased and the grain growth process has a low activation energy. After complete solution of Ca<sup>2+</sup> ions in the periclase above 1600 °C, the grain growth is inhibited and reduced below comparable values for pure magnesia. The grain growth follows a relationship of (grain size)<sup>2</sup> proportional to time at temperature; the same relationship holds for pure magnesia. Although densification is initially increased while the grain growth is increased at temperatures below 1600 °C, the final densities at 1800 °C of these mixtures is also lower than for pure magnesia under the same conditions due to the increase in sealed porosity.

#### REFERENCES

- LEVIN (E. M.) *et al.*, 1964. *Phase Diagrams for Ceramists*, Amer. Ceram. Soc., Columbus, Ohio.
- SPENCER (D. R. F.) and COLEMAN (D. S.), 1969a. *Trans. Brit. Ceram. Soc.* **68** (3), 125.
- 1969b. *Science of Ceramics*, 5th edn, 23 April, Ronneby Brunn (Sweden).
- FULLMAN (R. L.), 1953. *Trans. A.I.M.E.* **197**, 81.
- TURNBULL (D.), 1965. *J. Metals*, **3**, *Trans. A.I.M.E.* **191** (8), 661.
- BURKE (J. E.), 1957. *J. Amer. Ceram. Soc.* **40** (3), 80.
- SMITH (C. S.), 1948. Grains, phases and interfaces: an interpretation of microstructure, *Metals Technol.* **15**, (4), *Trans. A.I.M.M.E.* **175**, 15.
- SPRIGGS (R. M.), BRISSETTE (L. A.), and VASILOS (T.), *J. Amer. Ceram. Soc.* **46** (10), 508.
- DANIELS (A. U.), LOWRIE (R. C.), GIBBY (R. L.), and CUTLER (I. B.), 1962. *Ibid.* **45** (6), 282.
- KINGERY (W. D.) and FRANCOIS (B.), 1965. *Ibid.* **48** (10), 546.
- HENNEY (J. W.) and JONES (J. W. S.), 1969. *Trans. Brit. Ceram. Soc.* **68** (4), 201.
- WELLS (A.), 1962. *Structural Inorganic Chemistry*, 3rd edn, Clarendon Press (Oxford).
- MEAD (G. F.), 1969. Unpublished research, dissertation, Department of Materials Technology, University of Technology, Loughborough.
- SPENCER (D. R. F.), BEAMOND (T. W.), and COLEMAN (D. S.) 1970, *Trans. Brit. Ceram. Soc.* (in press).
- DEGTYAREVA (E. V.), KAINARSKII (I. S.), and PROKOPENKO (M. I.), 1967. *Ogneupory*, (3), 41.