GRAIN GROWTH 
IN 
SINTERED MAGNESITES
GRAIN GROWTH IN SINTERED MAGNESITE

8.1 INTRODUCTION :

The process of sintering in ceramic materials generally results in grain growth along with densification. Grain growth in polycrystalline materials generally proceeds by the motion of grain boundaries. It is generally accepted that the driving force for grain growth is derived from the free energy decrease due to reduction in surface area of the resultant larger grains over the original smaller grains [1].

In the final stage of microstructural development of polycrystalline materials, grain boundaries are curved for which a pressure difference generally exists across the boundary and atoms diffuse from high pressure side (concave) to the low pressure side (convex). These curved boundaries move towards their respective centres of curvature as a result of which the grains with small radius of curvature and high surface free energy diminish in size and eventually disappear. This gives rise to a matrix of large grains formed from a coalescence of the small grains through material transfer at contact points called necks. The lowered surface energy of such a process is the major cause for grain growth [1,2].

Grain boundary motion is also influenced by the presence of a wetting liquid secondary phase in the presence of impurities in natural materials. This phenomenon may sometimes be coupled with reaction resulting in a transport mechanism of reaction induced grain growth impediment which controls the grain growth mechanism.
8.2 GRAIN GROWTH IN SALEM AND ALMORA MAGNESITE:

The average grain sizes obtained for the various fired magnesia compacts are tabulated in TABLE 8.1. These grain sizes were measured on samples fired between 1500° and 1700°C with two hour soaking at maximum temperature, at 50° intervals, using the lineal intercept method described in Chapter 3.0. In case of Salem magnesite, at 1500°C, initial grain size without titania addition was found to be 17 μm which ultimately reached about 41 μm at 1700°C. With 0.5% titania addition the initial grain size increased to about 34 μm at 1500°C and became 123 μm at 1700°C. On the other hand, in Almora, the initial grain size without any addition was found to be 34 μm. The maximum increase in grain size in this magnesite was observed at around 1600°-1650°C. With 0.5% titania added Almora samples, maximum grain size reached to 80 μm at 1700°C. An indication of the influence of titania on the grain growth of magnesia is described schematically in Figure 8.1 where the average grain size in Salem and Almora magnesites have been plotted as a function of the TiO₂ content for compacts sintered at 1700°C with two hour soaking at the maximum temperature. The results for the two types of magnesites detailed in TABLE 8.1. In case of Salem magnesite, the addition of 0.05% TiO₂ was significant with respect to periclase grain growth which increased from 41 μm to 64 μm at 1700°C.

TABLE 8.1
AVERAGE GRAIN DIAMETER OF SINTERED MAGNESIA COMPACTS WITH AND WITHOUT TITANIA ADDITION:

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>1/T×10⁻⁴</th>
<th>AVERAGE GRAIN DIAMETER (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO</td>
<td>S1</td>
</tr>
<tr>
<td>1500</td>
<td>5.60</td>
<td>17</td>
</tr>
<tr>
<td>1550</td>
<td>5.48</td>
<td>20</td>
</tr>
<tr>
<td>1600</td>
<td>5.33</td>
<td>24</td>
</tr>
<tr>
<td>1650</td>
<td>5.20</td>
<td>31</td>
</tr>
<tr>
<td>1700</td>
<td>5.06</td>
<td>41</td>
</tr>
</tbody>
</table>

* for sample code see TABLE 3.1A in CHAPTER 3.0
The concentration of titania refers to the original magnesite. Upon increasing titania concentration, the maximum grain size reached was about 123 \( \mu m \) at 1700\(^\circ\)C as shown in Figure 8.1 and seems to level off exponentially indicating a certain limit of solubility for titania in magnesia and compares well with the observed behaviour of titania in alumina and magnesia (3-5). On the other hand, in the case of Almora magnesite, rate of increase in grain size was enhanced to a lesser extent by the addition of \( TiO_2 \) when compared with the Salem variety though the initial grain size was large as observed from Figure 8.1 and this appears to be due to other accessory impurities and grain distribution in the original magnesites.

8.3 Grain Growth in Silica Bioleached Sintered Magnesite

In general, the crystal size of periclase in the untreated silica rich and treated silica bioleached magnesite increased with temperature of sintering at a more or less uniform rate. In treated magnesite, the rate of growth became rapid in the lower temperature range, i.e. 1450\(^\circ\) to 1550\(^\circ\)C, which tended to slow down at high temperature. In titania added treated magnesite, the grain size increased to a great extent between 1500\(^\circ\) and 1600\(^\circ\)C and again slowed down at higher temperatures. The grain sizes obtained for the fired magnesia compacts plotted as a function of titania concentration are given in Figure 8.2. These grain sizes were measured on samples fired at 1700\(^\circ\)C for two hours. Titania addition in treated magnesite showed a marked increase in grain diameter in the range of 0.2 wt % \( TiO_2 \) addition. The maximum grain size reached was about 80 \( \mu m \) which finally seemed to level off exponentially for further addition indicating again that a certain limit exists for the solubility for titania in cryptocrystalline magnesia.

It is evident from the above results that the grain growth of periclase with rise in temperature is mainly influenced...
Figure 8.1: Effect of titania addition on the periclase grain diameter in sintered magnesia compacts.

Figure 8.2: Effect of titania mineralizer on grain size of untreated (VO), treated (TO) Salem Magnesite.
by the nature and amount of the impurities present in the raw magnesite as well as the matrix minerals formed at high temperature. In the parent magnesite which is silica rich, monticellite and forsterite predominated over all other crystalline secondary matrix minerals and this appears to be the reason for favourable grain growth in these natural magnesites. In the treated magnesite, which is rich in CaO, compared to SiO₂ impurity, the rate of grain growth slowed down at higher temperature range but the final grain size was larger than the parent magnesite. CaO was present in the secondary matrix in the form of monticellite and dicalcium silicate. It is well known that the nature and amount of the secondary matrix mineral depends on the lime/silica ratio and the total fluxing oxide present.

In case of titania added natural and treated magnesite it is believed that the additive ion Ti³⁺ and Ti⁴⁺ would substitute Mg²⁺ at the grain interfaces and form one or two cation vacancies forming solid solution at the grain boundary. It is assumed that titania increases the flux creating a new transport mechanism - Flux Growth [3,4]. Again, the enveloping of periclase grain by liquid silicate indicates another transport mechanism, i.e. Ostwald Ripening, which would govern the grain growth behaviour in the final stage of sintering [4].

8.4 KINETICS OF GRAIN GROWTH :

Buist et al [6] have shown that kinetics of grain growth in a liquid phase can be expressed by a linear relationship between log diameter and log time. Greenwood [7] has predicted that a linear increase of $d^3$ with $t$ should occur in a dispersion of round particles (grains) in a liquid phase, in which they are appreciably soluble where $t$ is the time of soaking at the maximum temperature of firing.
For any one grain, the radius of curvature of a side is directly proportional to the grain diameter, so that driving force and therefore the rate of grain growth is inversely proportional to the grain size [11].

The kinetics of grain growth in these cases have usually been described by the traditional phenomenological rate equation [8-13]:

\[ G_{tf}^n - G_{to}^n = k(t_f - t_o) \]  \( (8.1) \)

where \( G_{tf} \) is the average grain size after soaking time \( t_f \), \( G_{to} \) is the initial average grain size at time \( t_o \), \( n \) is the grain growth kinetic exponent, \( k \) is a rate constant. As the grain size is very small in the embryonic stage for magnesia from magnesite, the grain size at zero time may be neglected. Then, \( G_0 \ll G_{tf} \) and \( G_0^n \ll G_{tf}^n \), when \( n \gg 2 \). Then, \( n - G_{tf}^n - G_0^n \approx G_{tf}^n \) \( (8.2) \)

At \( t_o = 0 \), equation (8.1) can be written as

\[ G_{tf}^n = k t_f \]  \( (8.3) \)

Here, the equation for increase in average grain diameter, \( G \), as a function of soaking time, \( t \), can also be written as

\[ G^n = k t \]  \( (8.4) \)

Taking logs on both sides,

\[ n \log G = \log k + \log t \]  \( (8.5) \)

\[ \log G = \frac{1}{n} \log k + \frac{1}{n} \log t \]  \( (8.6) \)

Grain growth in porous ceramic system such as \( \text{Al}_2\text{O}_3 \) [14], \( \text{MgO} \) [15], \( \text{UO}_2 \) [16] and \( \text{ZnO} \) [17] may be expressed by the equation

\[ G^3 - G_0^3 = k t \]  \( (8.7) \)

Thus the kinetic exponent \( n \) is given by the inverse slope, \( (1/m) \), of a straight line between \( \log G \) and \( \log t \).
TABLE 8.2
VALUES OF SLOPE, m AND KINETIC EXPONENT, n, FROM log-log PLOTS OF GRAIN SIZE VERSUS TIME FOR MAGNESIAS SINTERED AT VARIOUS TEMPERATURES:

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Slope, m at temp.(°C)</th>
<th>Kinetic exponent, n at temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SALEM</td>
<td>1500 1550 1600</td>
<td>1500 1550 1600</td>
</tr>
<tr>
<td>S0</td>
<td>0.31 0.29 0.29</td>
<td>3.22 3.44 3.44</td>
</tr>
<tr>
<td>S1</td>
<td>0.24 0.26 0.32</td>
<td>4.16 3.84 3.12</td>
</tr>
<tr>
<td>S2</td>
<td>0.21 0.21 0.27</td>
<td>4.76 4.76 3.70</td>
</tr>
<tr>
<td>S3</td>
<td>0.34 0.36 0.35</td>
<td>2.94 2.77 2.85</td>
</tr>
<tr>
<td>S4</td>
<td>0.29 0.31 0.34</td>
<td>3.44 3.22 2.94</td>
</tr>
<tr>
<td></td>
<td>AVERAGE n FOR SALEM = 3.70 3.60 3.21 ≈ 3.50</td>
<td></td>
</tr>
</tbody>
</table>

| ALMORA     | 1500 1550 1600        | 1500 1550 1600                   |
| A0         | 0.28 0.30 0.31         | 3.57 3.33 3.57                   |
| A1         | 0.24 0.22 0.22         | 4.16 4.54 4.54                   |
| A2         | 0.22 0.21 0.21         | 4.54 4.76 4.76                   |
| A3         | 0.25 0.28 0.26         | 4.00 3.57 3.44                   |
| A4         | 0.26 0.29 0.28         | 3.84 3.84 3.57                   |
|            | AVERAGE n FOR ALMORA = 4.02 4.00 3.97 ≈ 4.00 |

8.5 EFFECT OF SOAKING TIME ON GRAIN GROWTH:

Based on equation (8.6), the average grain diameter of the MgO with and without added titania has been plotted as a function of soaking time as shown in figure 8.3 a,b,c and figure 8.4 a,b,c, while assuming the initial diameter at zero time to be significantly small compared to final diameter. According to Kingery [11], the value of n usually lies between 2 to 10. These values have been related to the processes controlled by intrinsic grain boundary motion in the case of pure system at high temperature, by porosity or by solute drag effects on the grain boundary mobility and liquid phase controlled processes. In the present case, Almora and Salem compacts with and without titania additive show slopes to a close approximation of n=3 (Salem, n=
Figure 8.3: Plot of average grain diameter of Sample, with and without titania addition, as a function of time.
Figure 8.4: Plot of average grain diameter of Almora Magnesite, with and without titania addition, as a function of time.
According to previous work this exponent of three or more is indicative of slowing of grain growth due to the increasing accumulation of impurities at the grain boundaries as the grains grow larger \(15\). Data studied by Spriggs et al \(18\) and Daniels et al \(15\) for fully dense MgO and porous magnesia, appears to indicate normal grain growth kinetics for MgO. The study also indicates limiting of grain size \(\leq 100 \mu m\) as the soaking time approaches 2000 minutes or temperature increases. It should be realised that during the normal grain growth process, some grains grow larger and the smaller ones disappear, but the range of grain sizes continue to have a normal distribution as the average grain diameter increases with time. Since grain boundary migrate towards its centre of curvature, grains with less than six sides tend to grow smaller, and grains with more than six sides tend to grow larger \(11\).

Previous work has shown that an exponent of 3 or 4 is indicative of a retardation in the grain growth process due to segregation of impurities at the grain boundaries as the grains grow larger \(18\). Kinetic studies by Nicholson \(19\) proposed an exponent value of 4 for MgO with 1% Fe\(_2\)O\(_3\) addition. The values of kinetic exponent have been related to the processes controlled by intrinsic grain boundary motion in case of pure systems at high temperature, by porosity or by solute drag effects on the grain boundary mobility and liquid phase controlled processes.

Grain growth kinetic exponent greater than 4 has been reported for MgO in specially densified system and for the growth of crystallites less than 600 Å in size \(8\). Again the highest degree of MgO sintering was achieved with TiO\(_2\) doped samples. It is anticipated that additive atoms occupy low energy sites adjacent to the boundary. Due to boundary movement these atoms tend to stay in the high energy state as a result of which the energy of the system is raised. At this stage, the boundary is pinned at the location of the additive atoms. The restricted boundary
movement reduces the rate of grain growth. A possible rate limiting step for boundary movement under these conditions is the diffusion of additive atoms along with boundary rather than simply the jumping of host atoms across the boundary from the shrinking to the growing grains. If the impurity or additive has an aliovalent cation like Ti\(^{4+}\) or Si\(^{4+}\) in an oxide system, the outcome is defect solid solution with vacancies which can accelerate volume diffusion.

In the present case, titania generates a reactive secondary phase which usually situates at the multiple grain junctions and the dissolution reaction occur only from the secondary phase into the main phase i.e., transport of dissolving component from multiple grain junction to the bulk of the crystals, is assumed to proceed by fast grain boundary diffusion and slow bulk diffusion from the grain boundary to the centre of the crystals [4]. These new processes include diffusion of the matrix phase through the liquid phase due to dissolution and reprecipitation, vacancy creation, lower viscosity phase for enhanced mobility and so forth, which generally assists grain growth. If a small amount of a boundary liquid is formed it tends to slow grain growth since the driving force is reduced and the diffusion path is increased. Porosity appears to decrease not only the grain growth rate but also to limit the grain size and to decrease the time exponent [15]. When the pore and grain growth is more rapid than other changes, the pore-grain geometry remains about the same and thus the pore size remains nearly proportional to the grain size [20].

The action of the mineraliser towards sintering and grain growth of MgO is to decrease the grain wetting behaviour of the interface liquid formed at high temperature this permitting grain to grain contact.

Densification of magnesite is enhanced with distribution of secondary liquid phase over the entire surface. In presence of the dopants there is reaction in the secondary
B.6 REFERENCES:


