Journal of Korean Association of Crystal Growth
Vol. 8, No. 3 (1998) 498-502

Sintering phenomena and grain growth of ultra-fine spinel ($MgAl_2O_4$); (II)

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순수 스피넬($MgAl_2O_4$)의 입성장 및 소결현상

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Abstract Sintering phenomena at refractory temperature ranges, from 1400°C to 1700°C, of the pure spinel ($MgAl_2O_4$) are analysed and compared to the experimental data from other researchers in terms of grain size (G), density(ρ), and activation energy (Q). The grain size and relative density relationships for the spinels present very similar trends. They exhibit two distinct regions, an intermediate sintering stage to about the 85~90 % density level and what appears to be the final stage sintering region above that transition-density level. The activation energy in terms of the grain size (G) and density (ρ) is determined to be 670±48 (kJ/mol) in this spinel and about 590 kJ/mol for the overall temperature range in other's spinel. These values are close to other published data, 360 to 580 kJ/mol.

요 약 순수 스피넬($MgAl_2O_4$)에 대하여 1400℃에서 1700℃까지에 내화온도 범위에서 입자크기(G), 밀도(ρ), 활성에너지(Q)를 구하고 다른 실험값과 비교 분석하였다. 스피넬에 대한 입자크기와 상대밀도는 매우 유사한 경향을 나타내었다. 이들은 두개의 뚜렷한 영역을 나타내었는데 상대밀도가 약 85~90 %까지의 중간소결단계와 전이-밀도 수준 이상의 마지막 단계, 소결영역으로 나타난다. 입자크기(G)와 밀도(ρ)의 관계에서 활성화에너지 값은 670-48 kJ/mol이었으며 다른 스피넬에서는 넓은 온도 범위에서 약 590 kJ/mol이었다. 이 값은 기존의 360~580 kJ/mol의 값은 근접하였다.

1. Introduction and review of sintering spinel ($MgAl_2O_4$)

Direct studies on the different variables affecting sintering process in ceramic materials demonstrate that it is not a simple and ideal process which occurs by a single mechanism over the full range of the variables, time, temperature, stress and microstructure, etc.

In the case of pure spinel ($MgAl_2O_4$) powder, nonideal sintering behavior in spinel powder has been reported by Clare and Bratton [1,2]. That behavior is particularly evident for powders calcined at temperatures lower than the optimum [3], in that a low limiting density usually occurred. Bratton has suggested that the activation energy (494 kJ/mol) for the intermediate stage sintering of $MgAl_2O_4$ is nearly identical to that for the initial stage sintering (about 482 kJ/mol). He concluded that a volume diffusion mechanism must be rate controlling during both stages of densification and that it was reasonable for two sintering models to have an order of magnitude difference in volume diffusivities with the grain growth exponent of two for normal grain growth and three for grain growth affected by porosity.

In other spinel studies, Hamano and Kanzaki [4] have reported that the volume diffusion of oxygen ions is the rate-controlling process for the initial stage of sintering. Ikegami et al. [5] have investigated the relationship between relative density vs. average grain size between 1300℃ and 1700℃ and have proved that the interactions between the grain boundaries and the pores are of great importance to the intermediate and final stages of sintering [6,7]. Kinoshita et al. [8] have also suggested that the relationship between porosity and grain size, as well as that between relative density and grain size between 1100℃ and 1700℃, could be expressed as two straight lines separating the intermediate and final stages of sintering at about 92 % relative density. These latter researchers did not complete an activation analysis.

In the present study, the significant features of the sintering process in terms of grain size (G), density (ρ), and activation energy (Q) at high temperature ranges, from 1400℃ to 1700℃, were analysed with the experimental data by Kinoshita et al., and compared to the other published data for the purpose of controlling the variables, which can lead to the fabrication of the better ceramic materials.

2. Experimental procedures

The spinel ($MgAl_2O_4$) powder was a commercial product from TAM Ceramics, Inc., New York. The TAM Cernel 125 was -325 mesh, 30 lb/ft^3 of bulk density, 110~140 m^2/g of surface area and had a specific gravity of 3.54 g/cm^3.

The spinel powder was pressed uniaxially at 100 MPa to yield specimen discs that were approximately 1 cm in diameter and 3~4 mm in thickness. The specimens of the spinel were fired in air at temperatures of 1400℃, 1489℃, 1589℃, and 1700℃ by heating from room temperature to the desired firing temperature at a rate of 7℃/m. Specimens were fired for a matrix of four different times: 0.5, 1, 2, and 4 hrs. at the four different temperatures, yielding a total 16 specimens for each of the spinel. The sintered densities were calculated from the dimensions and the weights of the sintered discs after firing. More details is in Part I.

3. Discusssion and results

3.1. *The G versus ρ relationship for spinel*

3.1.1. *The G versus ρ relationship of the pure spinel ($MgAl_2O_4$)*

The grain size (G) versus density (ρ) diagram for the $MgAl_2O_4$ spinel in this research illustrates a similar trend to that previously observed for the other pure material, as in the case of Han's synthetic forsterite [9], as shown in Fig. 1. It also reveals two distinct regions, probably with different mechanisms. The first is indicative of the intermediate sintering stage region and extends from about 53 % to just above the 85 % density level. What appears to be the final stage sintering region exists just above that transition density level. The slope of the grain size versus density plot for $MgAl_2O_4$ in the low density region is 0.01 cm^4/g. This value is much lower than that observed for the synthetic forsterite (0.25 cm^4/g), and the slopes reported by Gupta [10] in his review.

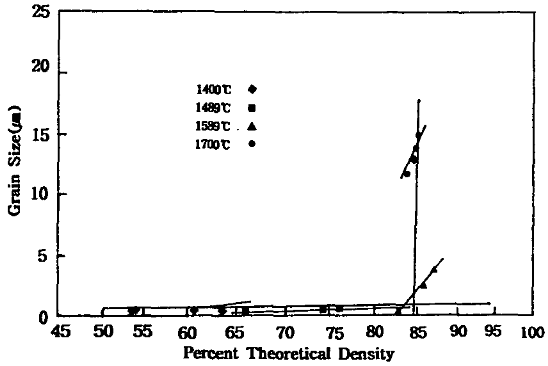

Fig. 1. The grain size vs. density diagram in the spinel.

The break, or knee in the spinel (G) vs. (ρ) plot occurs around the 85 % level in relative density, about 5 % lower than the 90 % level suggested for the synthetic forsterite. It is apparent that there are two distinct (G) vs. (ρ) regions, probably with different mechanisms for the spinel. The synthetic forsterite and this spinel exhibit the same trends. The grain size to density ratio has slopes of 0.01, 0.01, 0.89 and 3.14 (cm^4/g). These are similar with the trends of the synthetic forsterite. The overall slope of the (grain size) versus (density) plot for the 53~85 % density region is about 3.80 cm^4/g. It is much larger than the value observed of the synthetic forsterite, 0.25 cm^4/g.

$$Q_g \neq (Q_g - Q_\rho) = Q_{(dG/d\rho)} \quad (1)$$

and,

$$\frac{dG}{d\rho} = A\exp\left(-\frac{Q}{RT}\right) \quad (2)$$

From Equations (1) and (2) [9], the log (dG/dρ) versus (1/T) results can also be plotted with two

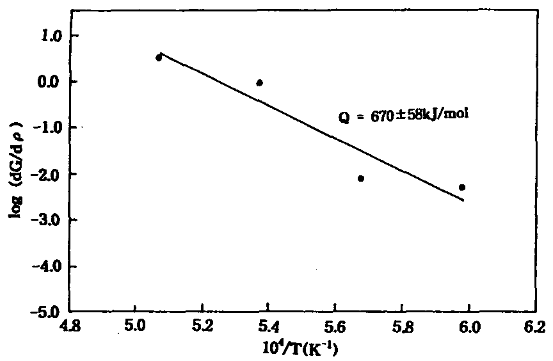

Fig. 2. Arrhenius plot for the log (dG/dρ) vs. (1/T) of the pure spinel.

slopes as shown in Fig. 2. The activation energy from the slope of log (dG/dρ) versus (1/T) is determined to be 670±48 (kJ/mol). This value is somewhat larger than other published data, 360 to 570 kJ/mol.

3.1.2. The G versus ρ relationship of for the spinel of kinoshita et al.

The grain size versus density diagram for the $MgAl_2O_4$ spinel studied by Kinoshita et al. reveals a similar trend to that observed for the spinel of this study. It is shown in Fig. 3. and exhibits two distinct regions. The first is indicative of the intermediate sintering stage region and extends from about 83% to just above the 90% density level. What appears to be descriptive of final stage sintering exists just above that transition density level. The slope of the grain size versus density plot for Kinoshita's $MgAl_2O_4$ in the low density region is 0.23 cm^4/g. This value is similar to that reported by Gupta [10] for the other oxides.

The break, or knee in the spinel plot occurs around the 93% level in relative density. It is apparent that there are two distinct regions with different mechanisms for Kinoshita's spinel. From Equation 2, the log (dG/dρ) versus (1/T) results can also be plotted with two slopes as shown in Fig. 4. The grain size to density ratio for the lower temperatures has a slope of 0.23 (cm^4/g), but similar grain size to density ratios exists for the high temperature region, with the slopes of 5.45, 4.66, 6.45 and 5.55. This is different from the trends of the synthetic forsterite. It also reveals that grain growth is affected by the densification at 1700℃ similar to the spinel in this research. The overall slope of the (grain size) versus (density) plot in the high temperature region (the 93~95% density range) is about 12 cm^4/g. It is the much smaller than the value for the synthetic forsterite, 43 cm^4/g.

The slopes yield activation energies of 1799±169 kJ/mol for the low temperatures and 29±5 kJ/mol for the high temperatures. The activation energy for the overall temperature range has a value of 593 (kJ/mol), also as shown in Fig. 4. It is very comparable with other published values about 380~570 kJ/mol. These activation energy is very close, compared with previous ones and other published data. In the case of Al^{+3} as the diffusing element in $MgAl_2O_4$, 439 kJ/mol has been reported [11]. In the case of Mg^{+2}, 361 kJ/mol [12] and in the case of oxygen, values of about 380~570 kJ/mol [13-15] have also been reported. Even though the activation energies not comparable with other data, it is obvious that there exist different mechanisms in the two different temperature regions.

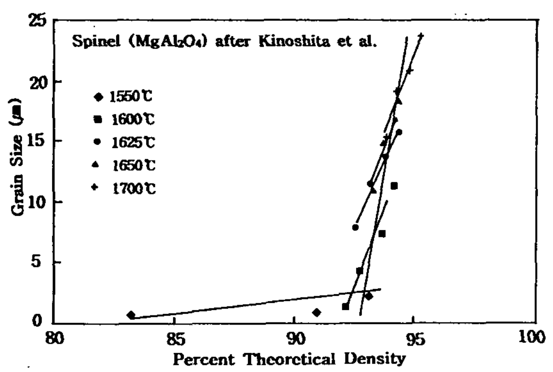

Fig. 3. The grain size vs. density diagram in the spinel after Kinoshita et al.

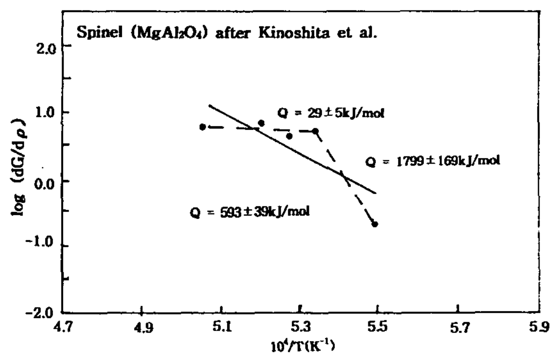

Fig. 4. Arrhenius plot for the log (dG/dρ) vs. (1/T) of the pure spinel after Kinoshita et al. at two distinct temperature regions and overall temperature ranges.

A close relationship between the grain size and the relative density of powdered compacts during sintering has been reported in several sintering studies. This is especially so during the intermediate stage of sintering [16]. It may be assumed that during sintering all of the particles/grains in a compact build a homogeneously distributed network structure.

$$\log\left\{\frac{\rho(1-\rho_o)}{\rho_o(1-\rho)}\right\} = K_I \log\left(\frac{G}{G_o}\right) \quad (3)$$

Here K_I is a constant. Equation (3) is valid for the case when all of the grains form a network structure. Actually, however, a few networked microregions are broken and some pores may grow heterogeneously during sintering. Other grains are not surrounded by pores. Finer grains in this region may be primarily consumed for grain growth rather than densification. Therefore, a K_{II} must be introduced into Equation (3) for utilization over a heterogeneous compact, yielding:

$$\log\left\{\frac{\rho(1-\rho_o)}{\rho_o(1-\rho)}\right\} = K_{II} \log\left(\frac{G}{G_o}\right) \quad (4)$$

Consequently, Equation (3) will be valid for the initial sintering stage of porous microregions, and Equation (4) will be valid for the intermediate and final stages of sintering. Therefore in the normal sintering process, the relationship between porosity and grain size, as well as that between relative density and grain size, can be expressed by two straight lines. The $dG/d\rho$ slopes are expected to be different depending on the stages of sintering, lower at during the initial stage and much higher for the intermediate and final stages, as has already been demonstrated in the study of $MgAl_2O_4$ by Kinoshita.

Figure 5 illustrates the logarithmic plots of log ($\rho(100-\rho_o)/\rho_o(100-\rho)$) vs. log (G/Go). It reveals that the mechanisms may change where the relative density of the spinel exceeds about 91 % and 85 % from Kinoshita's spinel and the spinel of this research, respectively. In terms of Kinoshita's data, $\rho \leq 92$ % or $P_o \geq 8$ % ($\rho = 100 - P_o$) at the initial stage, and $\rho \geq 92$ % or P_o 8 % at the intermediate and final stages. The former case suggests that the average grain size increases only gradually, irregardless of the rapid decrease in the porosity, an increase in

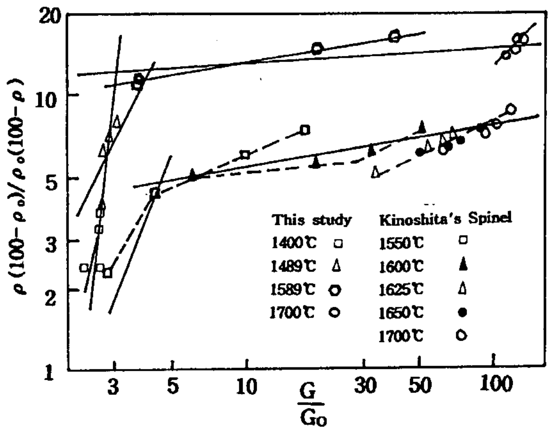

Fig. 5. Comparison of the logarithmic plots of ρ ($100-\rho_o)/\rho_o(100-\rho)$ vs. log (G/G_o) between the different pure spinels.

the density. Grain boundary migration is restricted by the pores. The latter presents the case that densification has practically stopped with the pores entrapped within the grains. Therefore, Equations (3) and (4) can also represent the relationship of Equation (1) concerning the activation energies for grain growth and densification.

Bratton [17], Yamaguchi et al. [18], and Hamano et al. [19] have all recently reported that it is the volume diffusion of oxygen ions in $MgAl_2O_4$ that is the rate-controlling process for the initial stage of sintering. The activation energy is about 460 kJ/mol. Kinoshita et al. [20] have also presented results which confirm that the logarithmic relationship between shrinkage and time exhibits a straight line with a slope of 0.40, similar to the results of the above researchers. They reported that the changes in relative density are strongly affected by the microstructure, that is the grain size and shape. At only 1100℃, their spinel grains appeared to be spherical, approximately 0.2 μm in diameter. At 1300℃ and 1500℃, the grains still retain their spherical shapes, but are larger than those at 1100℃. At 1700℃, the grains increase from 5 to 10 μm and are arranged in a close packed array. Some pores become trapped within the individual grains.

In the pure spinel studied here, the microstructural evolution follows the same trends as those of Kinoshita et al. However, the grains do not appear to be arranged in close packing at 1700℃, which is different from the observations of Kinoshita et al. This may be the result of shorter sintering times than those employed by Kinoshita.

The microstructural evolution of spinel ($MgAl_2O_4$) during sintering has been discussed by Kinoshita et al. They suggest that the interparticle neck growth, which corresponds to the initial stage of sintering, continues through about 1500℃. The mechanism is suggested to be that of evaporation-condensation. They concluded this because of the slow rate of change in the grain-size distribution at that temperature. Kinoshita et al. have also suggested that above 1625℃, the sintering of the grains proceeds in the intermediate stage, leaving the neck growth between original grains. The $MgAl_2O_4$ grain size increased to about 20 μm after 15 hrs at 1700℃. Bratton has discussed this distinctive sintering behavior of $MgAl_2O_4$ between 1400℃ and 1600℃. He has suggested that the probable cause of the situation is the poor packing characteristics of the finely divided $MgAl_2O_4$ powder rather than a mechanism change. Figure 5 does not support Bratton's suggestion. These two pure spinels present very close aspect with increasing trend in the logarithmic plots of log $(\rho(100-\rho_o)/\rho_o(100-\rho))$ vs. log (G/G_o) in Fig. 5. At between 1400℃ and 1489℃ in the pure spinel of this study the interparticle neck growth is considered to proceed, which corresponds to the initial stage of sintering with the slow rate of change in the grain-size distribution at that temperature. At 1589℃, the sintering of the grains proceeds in the intermediate stage in the pure spinel of this study. The $MgAl_2O_4$ grain size increased to about 10 to 14 μm after 4 hrs at 1700℃.

4. Conclusions for the spinels

The grain size and relative density relationships for the spinels present very similar trends. They exhibit two distinct regions, an intermediate sintering stage to about the 85~90 % density level and what appears to be the final stage sintering region above that transition-density level. The slopes of the (grain size) versus (density) plots for the intermediate sintering regions of these spinels are 0.01 and 0.23 cm^4/g. The vertical slopes above the transition-density level are 0.01, 0.01, 0.89 and 3.14 for this spinel, and 5.45, 4.66, 6.45 and 5.55 (cm^4/g) with three increased temperature ranges and show decreasing or steady values for the spinels at 1700℃. The value of the overall slopes of the (grain size) versus (density) plot at the temperature regions below 1600℃ is about 3.8 in this spinel and for the three temperature regions above 1600℃ is about 12 cm^4/g in Kinoshita's spinel.

The activation energy from the slope of log (dG/dρ) versus (1/T) is determined to be 670±48 (kJ/mol) in this spinel. This value is somewhat larger than other published data, 360 to 580 kJ/mol. The slopes yield activation energies of the activation energies by the slopes of log (dG/dρ) versus (1/T), 1799 kJ/mol at a low temperature region and 29±5 kJ/mol at a high temperature region in Kinoshita's spinel. The activation energy for the overall temperature range has a value of about 590 kJ/mol.

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