Journal of the Korean Association of Crystal Growth
Vol. 11, No. 2 (2001) 78-84

Sintering and grain growth in binary forsterite(Mg_2SiO_4)/spinel($MgAl_2O_4$) system

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(Received February 13, 2001)

Abstract The binary forsterite(Mg_2SiO_4)/spinel ($MgAl_2O_4$) system, a possible refractory for industrial applications, is investigated for their density and grain growth the same firing conditions as the each component material between 1400°C and 1700°C (1650°C). The forsterite grain growth exponent is established to be equal to 5 for all compositions within this binary system. Generally, the spinel addition to forsterite inhibited the forsterite grain growth. The activation energies for the forsterite grain growth of the eight compositions(weight ratio of forsterite/spinel) within the binary system are determined to be; 952±79 (95/5), 363±37 (90/10), 219±21 (80/20), 220±44 (70/30), 112±16 (50/50), 112±23 (30/70), 198±26 (10/90), and 121±12 (5/95) KJ/mol. The more forsterite is contained within the binary system, the higher value the activation energy for forsterite grain growth. It is considered that the forsterite grain growth at the higher forsterite compositions are more inhibited by spinel than that of the lower forsterite compositions.

1. Introduction

There is considerable merit to develop the microstructure being with stable two phases for refractory applications. Doloma, which is a combination of CaO and MgO phases, is one of these two-phase refractory systems [1]. The CaO-MgO system has a simple binary eutectic phase diagram [2]. A similarly interesting case exists for forsterite(Mg_2SiO_4)-spinel($MgAl_2O_4$) system which also possess a simple binary eutectic phase diagram, that is free of liquid to temperatures near 1700°C.

By developing a dominantly forsterite microstructure with additions of a spinel second phase to produce a stable two phase microstructure, an attractive refractory for industrial applications may result. This spinel-addition concept is directly related to forsterite formation during the firing of naturally occurring olivines, $(Mg,Fe)_2SiO_4$. Those minerals often contain several R_2O_3 oxides, including Fe_2O_3, Al_2O_3 and Cr_2O_3. These oxides may be expected to react with the magnesia component during firing to yield spinel ($MgO \cdot R_2O_3$) phases dispersed within the forsterite grains of the fired microstructure.

For that reason, high purity, synthetic raw materials provide a complementary course of investigation that is equally valuable to gain a fundamental understanding of potential commercial refractory materials. Implementation of that technical approach requires preparation and investigation of the refractory compound in a high purity form, one which is produced from synthetic components [3, 4]. This experimental approach is a highly desirable one for it circumvents the complications which are caused by the natural, impurity-induced secondary phases that are common to most mineral-derived commercial refractory materials. Once the fundamentals of microstructural evolution have been established from the kinetic analysis of the development of a high purity synthetic structure, then the extension to minerals is often a direct process. This type of technical approach has been previously applied to the development of mullite ($3Al_2O_3 \cdot 2SiO_2$) refractories from either kyanite, andalusite or sillimanite combined with bauxite or other high alumina content minerals.

The model binary system yields a two phase microstructure that is of interest for the fundamental kinetic analysis of grain growth during forsterite microstructural development. As no studies have been completed for binary (Mg_2SiO_4)/($MgAl_2O_4$) ceramics, the development of their microstructures is not known. The results are interpreted in terms of the classical kinetic analyses of grain growth [5].

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2. Experimental Procedures

2.1. Raw materials

A pure forsterite was synthesized [6], and then milled and sieved through a 400 mesh screen to yield a fine forsterite powder suitable for the sintering and grain growth studies. The spinel powder was a commercial product from TAM Ceramics, Inc., New York. 'TAM Cernel 125' powder being used in this experiment. was -325 mesh particle size with 110~140 m^2/g surface area and 3.54 g/cm^3 density.

Eight binary compositions, in addition to the two pure compositions, were chosen for investigation : 95/5, 90/10, 80/20, 70/30, 50/50, 30/70, 10/90 and 5/95 (wt. ratio of forsterite/spinel).

2.2. Sintering specimens

The forsterite/spinel binary composition specimens were also heated from room temperature to the desired firing temperatures at a rate of 7°C/min. However, the series of these specimens were fired at 1400°C, 1489°C, 1589°C and 1700°C for the four different times of 0.5, 1, 2, and 4 hrs. The three forsterite rich compositions, 100 %, 95 % and 90 % were sintered at 1650°C instead of 1700°C. Thus each forsterite/spinel composition also had 16 time-temperature combinations. The sintered densities were calculated from the dimensions and the weights of the sintered discs after firing.

2.3. Microstructure examination

For microstructural examination, the sintered disc specimens were cut into halves by diamond sawing and then mounted in an acrylic resin. Mounted samples were initially wet ground with successively finer SiC papers from 320 through 600 grit sizes. Ultrasonic cleaning of the samples was performed after each individual polishing step. Final polishing was completed with an automatic vibratory polishing machine using a 0.3 μm Al_2O_3 abrasive powder. Etching of polished specimens was done by immersing in dilute hydrofluoric acid (10 %) for times that varied from a few seconds to 30 min [7].

2.4. Grain size analysis

Grain sizes were determined directly from photomicrograph of the polished and etched specimens by applying the linear intercept technique described by Mendelson [8]. The average grain size is related to the average intercept length by a proportionality constant equal to 1.56. The average grain size, G, is expressed as:

$$G = 1.56\bar{L} \tag{1}$$

where, $\bar{L}$ is the average grain boundary intercept length of a series of random lines drawn across the photomicrograph. For the two phases microstructures, the forsterite appears dark and the spinel appears light in reflected light. It is necessary to individually measure each phase on the random lines and consider the average intercept length for each phase independently.

2.5. Analysis of grain growth parameters

The grain growth results were then analyzed for each individual phase in terms of the phenomenological kinetic grain growth expression:

$$G^n - G_0^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

If it is assumed that the initial average grain size, G_0, is relatively small compared to the final average grain size, G, after sintering for a time t, ($G \gg G_0$), then $G^n \gg G_0^n$ and Equation (2) can be reduced to:

$$G^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

The logarithmic form of Equation (3) is:

$$n \log G = \left(\log K_0 - 0.434\frac{Q}{RT}\right) + \log t \tag{4}$$

This form of Equation (4) is readily applied to a (log

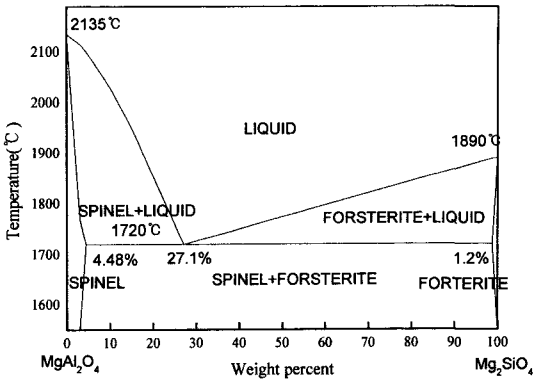

Fig. 1. The phase diagram for the binary forsterite (Mg_2SiO_4)/spinel($MgAl_2O_4$) system.

G) versus (log t) plot to estimate the experimental kinetic grain growth exponent, the n-value. The exponent, or n-value is the inverse of the slope of the line (log G) versus (log t).

3. Results and Discussion

The phase diagram for the binary forsterite(Mg_2SiO_4)-spinel($MgAl_2O_4$) system is presented in Fig. 1 [9]. The

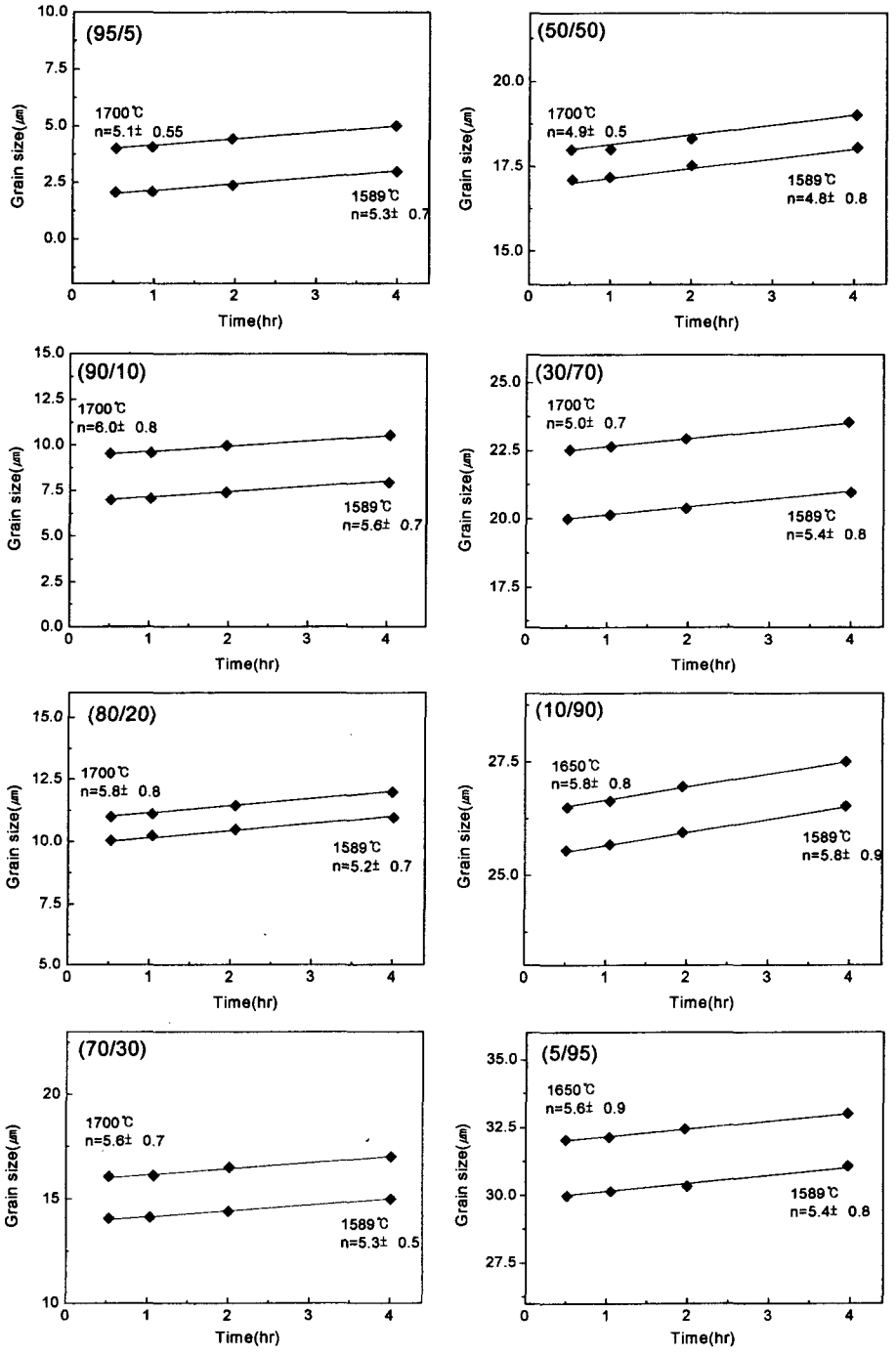

Fig. 2. Isothermal grain growth of the forsterite phase in the binary compositions at 1589℃ and 1700℃ for 1/2, 1, 2 and 4 hrs.

maximum solid solubility of spinel in forsterite is only about 1.2 wt%, even at 1720°C (the temperature of the binary eutectic). Only about 4.5 wt% forsterite is soluble in the spinel crystal structure at that temperature.

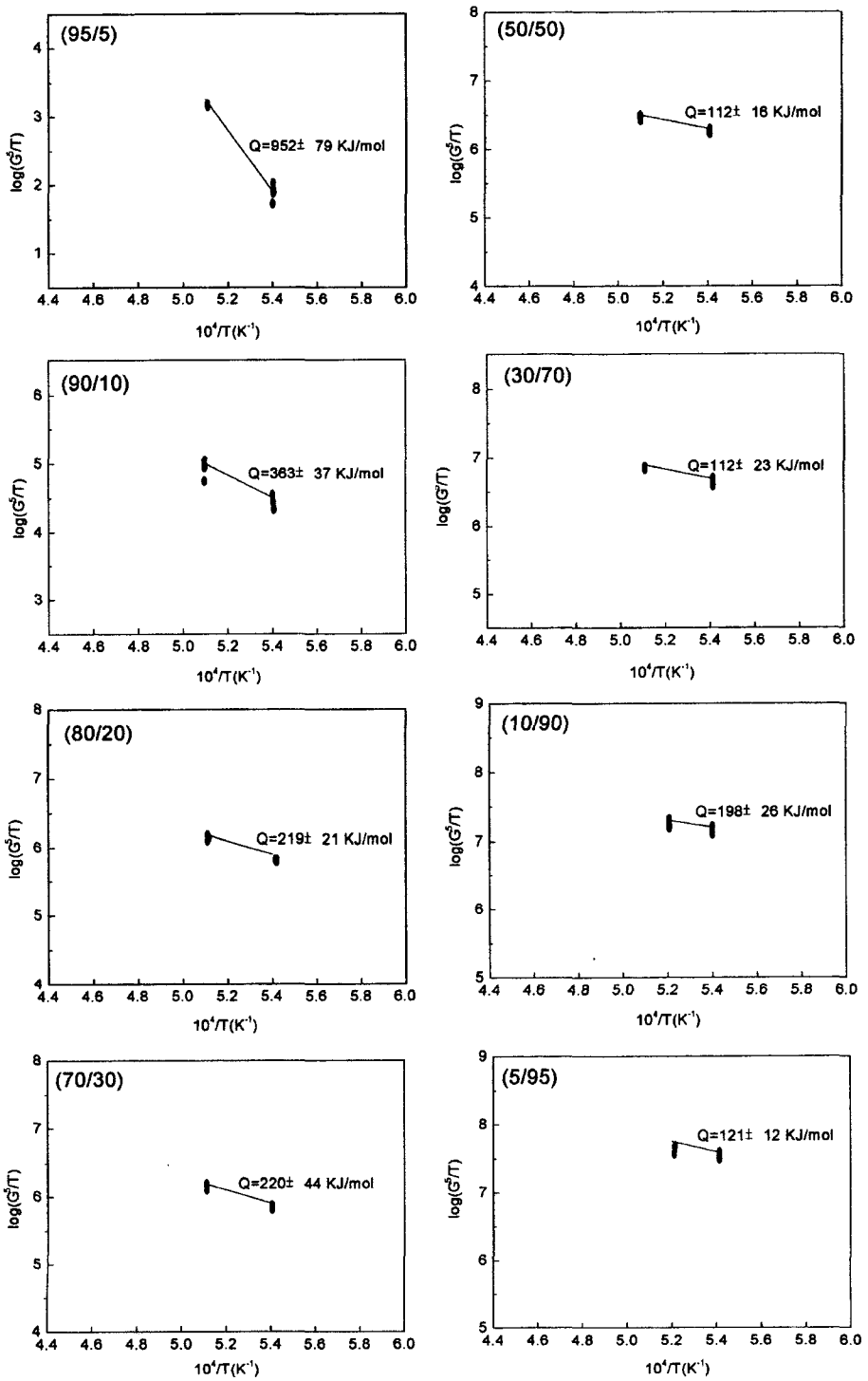

Fig. 3. Arrhenius plots for the grain growth of the binary system.

These solid solubilities seem to be rather limited for structures that are so similar. At the eutectic point of 27.1 % forsterite, spinel and forsterite crystalline solid solutions and a liquid phase coexist.

When compared to the theoretical densities(3.27 (100 % forsterite), 3.29 (95/5), 3.30 (90/10), 3.35 (80/20), 3.42 (70/30), 3.50 (50/50), 3.51 (30/70), 3.55 (10/90), 3.56 (5/95) and 3.58 (100 % spinel)) estimated by the rule of mixtures [6]. these sintered densities range from about 70 % to 90 % of the theoretical values.

Figure 2 illustrates the results of the isothermal grain growth of the forsterite phase in the binary compositions at 1589°C and 1700°C (1650°C) for 1/2, 1, 2, 4 hours. For each of the two firing temperatures at 1589°C and 1700°C (1650°C) for the eight compositions the slope of the log (G) vs. log (t) plot is approximately one fifth for forsterite as shown in Fig. 2. The grain growth exponent is thus established to be equal to five for the binary system, yielding the grain growth equation:

$$G^5 - G_0^5 = K_0 t \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

However, since the initial forsterite grains in their embryonic stage are only 0.5 μm in diameter and the final grain sizes are nearly 40 μm, it is possible to ignore the G_0^n term relative to the first term in Equation (5).

It is difficult to identify the two individual phases except at the two high temperatures when they are clearly revealed by optical microscopy. For the 1489°C temperature firing, some larger grains start to form in the forsterite rich compositions (90 % forsterite).

Equation (5) for the forsterite phase can be written in the logarithmic form as:

$$\log\left(\frac{G^5}{t}\right) = \log K_0 - 0.434\left(\frac{Q}{RT}\right) \quad (6)$$

From the slope of the plot of log (G^5/t) vs. (1/T), the

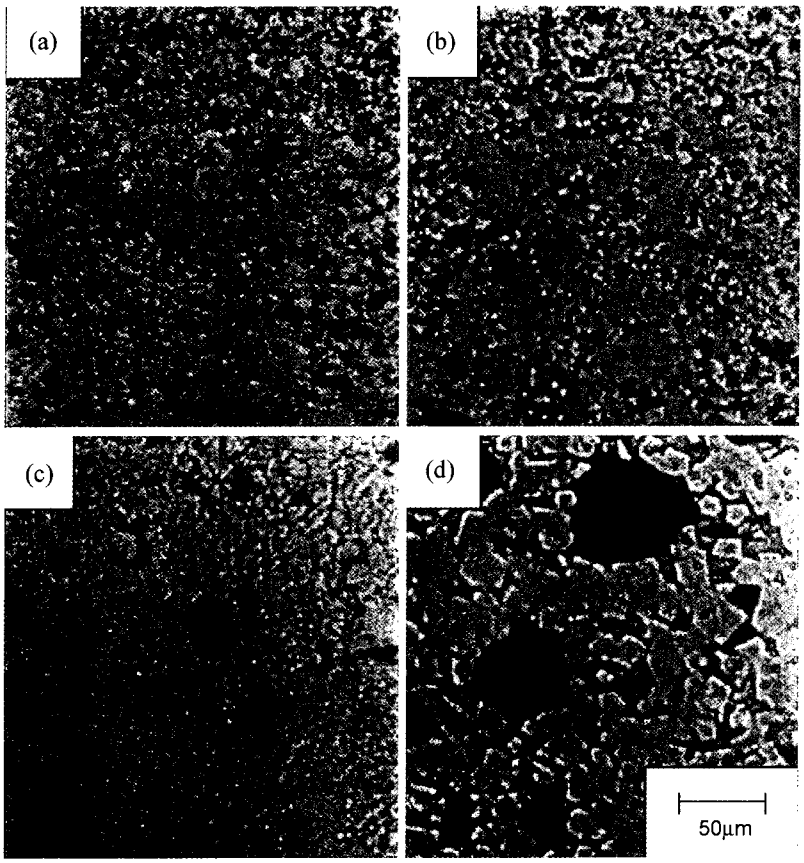

Fig. 4. The microstructures illustrating grain growth of the forsterite/spinel (50/50) composition at (a) 1400°C, (b) 1489°C, (c) 1589°C and (d) 1700°C for 4 hrs.

apparent activation energy for the grain growth process of forsterite can be determined. Figure 3 illustrates the Arrhenius plots for the grain growth of the binary system. The activation energies for the grain growth of the forsterite phase in the binary system are determined to be; 952±79 (95/5), 363±37 (90/10), 219±21 (80/20), 220±44 (70/30), 112±16 (50/50), 112±23 (30/70), 198±26 (10/90), and 121±12 (5/90) KJ/mol. The activation energy of forsterite grain growth for the compositions contained spinel have the lower values than that of forsterite without spinel (400~650 KJ/mol) [6, 11], except for the 95/5 composition. It may be the impurity effect in the starting powders. Thought this values are not good as a precision data, we can find out the relationship between composition and this activation energy value within this experiment. The more forsterite is contained within the binary system, the higher value the activation energy for forsterite grain growth have. It is considered that the forsterite grain growth at the higher forsterite compositions are more inhibited by spinel than that of the lower forsterite compositions.

The spinel phase could not be measured satisfactorily because they did not grow sufficiently to reach suitable grain sizes to be observed under optical microscopy. The forsterite phase at 1400°C and 1489°C could not be measured satisfactorily either. It is believed that the spinel phase hindered and inhibited the growth of the forsterite phase. Researchers [10, 12] have studied the grain growth inhibition in this binary system.

Figure 4 presents the microstructures of the isothermal grain growth of the 50/50 composition at 1400, 1489, 1589 and 1700°C for 4 hours. At the two lower temperatures, it is very hard to identify the two individual phases, but at the two high temperatures, the individual phases are clearly revealed by optical microscopy. In the forsterite/spinel binary system, which was sintered at 1400°C, the initial sintering stage phenomena prevailed for all of the compositions, with no obvious grain growth in the binary systems. For the 1489°C temperature firing, some larger grains (white : spinel, grey : forsterite) start to form in the forsterite rich composition (90 % forsterite). However, these compositions also revealed noticeable microcracks in the samples which were sintered for more than 2 hrs. In the 95 % forsterite composition, microcracks were detected after only 1 hour of sintering.

Two forsterite rich compositions (90 % and 95 %) were fired at 1489°C for 1 and 2 hrs. At 1589°C, the spinel rich compositions (> 90 %) are considered to still be experiencing initial sintering stage. However, the grain growth of the forsterite phase has already begun. At 1700°C (1650°C), the grain growth is observed with increasing time.

4. Conclusions

In the binary compositions with the forsterite(Mg_2SiO_4)-spinel($MgAl_2O_4$) system between 1400°C and 1700°C (1650°C), generally, the spinel addition to forsterite inhibited the forsterite grain growth.

The forsterite grain growth exponent was established to be equal to 5 for all compostions within this binary system. The activation energies for the grain growth of forsterite in the binary systems were determined to be; 952±79 (95/5), 363±37 (90/10), 219±21 (80/20), 220±44 (70/30), 112±16 (50/50), 112±23 (30/70), 198±26 (10/90), and 121±12 (5/90) KJ/mol (wt. ratio of forsterite/spinel). The more forsterite is contained within the binary system, the higher value the activation energy for forsterite grain growth have. It is considered that the forsterite grain growth at the higher forsterite compositions are more inhibited by spinel than that of the lower forsterite compositions.

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