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

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초미분 spinel($MgAl_2O_4$)의 입성장 및 소결현상(I)

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Abstract In the paper, Significant sintering phenomena at refractory temperature ranges, from 1400℃ to 1700℃, of the pure spinel ($MgAl_2O_4$) and the experimental data from other researchers are analysed and compared in terms of density (ρ), grain growth exponent (n), and activation energy (Q). Similar to the density rewsults, the grain growth results above 1600℃ appear similar for the spinel, but for temperatures lower than about 1600℃ results are distinctly differently grouped. However, the grain growth exponents are different, six for the spinel (below 1600℃), and five at high temperatures (above 1600℃), with the activation energy of 474±38 kJ/mol below 1600℃, which is very close to the published values, 360~580 kJ/mol.

요 약 순수 스피넬($MgAl_2O_4$)에 대하여 내화온도 범위인 1400℃에서 1700℃까지의 온도에서 주요 소결현상인 밀도(ρ), 입성장지수(n), 활성화에너지(Q)를 구하고 다른 실험 data와 비교 분석하였다. 1600℃ 이하의 온도에서 입성장은 밀도와 마찬가지로 스피넬과 비슷하였으나 1600℃ 이하의 온도에서는 아주 다르게 나타났다. 그러나 입성장지수는 1600℃ 이하에서는 스피넬에 대하여 6이었고 1600℃ 이상의 높은 온도에서는 5이었다. 활성화 에너지는 1600℃ 이하의 온도에서는 474.38 kJ/mol로 종래의 값인 360~580 kJ/mol에 매우 근접하였다.

1. Introduction of spinel ($MgAl_2O_4$) sintering

Interest has increased in spinel ($MgAl_2O_4$) as a refractory material for high temperature structural applications. Although spinel has a tendency for ductile behavior at high temperature [1], its structural performance is highly related with the same microstructural variables which affect other ceramic materials, such as porosity and grain size. The desire to control porosity and grain size has led to the current concern in its sintering phenomena for fabricating ceramic material.

According to Coble [2], the intermediate stage of sintering exists when grain growth initiates. The initial pore shape changes to approximate a continuous channel of pores coincident with three-grain edges throughout the matrix. Sintering then amounts to the shrinkage of these pores by a diffusion process untill they are squeezed off and eliminated.

Bratton [3] has studied diffusion in $MgAl_2O_4$ by examining published data for the kinetics of another diffusion-dependent process, namely that of the formation of spinel. The reaction between MgO and Al_2O_3 occurs by the counterdiffusion of cations through an interfacial spinel reaction layer. Oxygen ions are not believed to move appreciable during this process, thus the reaction rate is controlled by either the Mg^{+2} or the Al^{+3} diffusion. Comparison of the activation energy for sintering (486 kJ/mol) with that for spinel formation (419 to 448 kJ/mol) and the inference that the activation energy required for Mg^{+2} diffusion in $MgAl_2O_4$ is about 390 kJ/mol suggests that perhaps it is the Al^{+3} ions which control the rate of the initial stage of sintering of $MgAl_2O_4$.

Navias [4] has reacted Al_2O_3 single crytals with MgO vapor in the temperature range 1500°C to 1900°C and estimated the activation energy for the formation of $MgAl_2O_4$ to be about 420 kJ/mol. Hlavac [5] reacted 25 m spheres of α-Al_2O_3 with MgO powders in the temperature range 1100°C to 1334°C and determined the activation energy to be 418 kJ/mol.

In these papers in series, significant sintering phenomena at refractory temperature ranges, from 1400°C to 1700°C, of the pure spinel ($MgAl_2O_4$) and the experimental data from other researchers (Kinoshita et al.) were analysed in terms of density (ρ), grain size (G), grain growth exponent (n), and activation energy (Q).

2. Experimental procedures

2.1. *Raw materials and sample preparation*

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. Figure 1 presents the SEM picture of raw spinel ($MgAl_2O_4$) powder with a grain size of smaller than 1 m (×5000).

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°C, 1489°C. 1589°C, and 1700°C by heating from room temperature to the desired firing temperature at a rate of 7°C/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. Ths sintered densities were calculated from the dimensions and the weights of the sintered discs after firing.

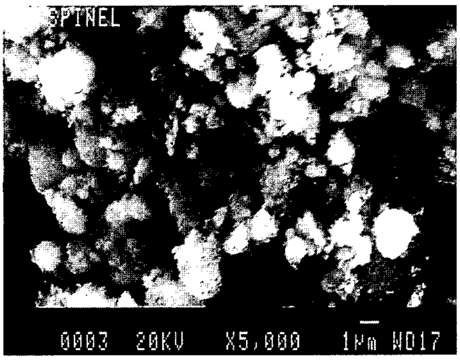

Fig. 1. SEM micrograph (×5,000) of the spinel powder.

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 alpha alumina abrasive powder. Etching was with dilute hydrofluoric acid (10 %) for times that varied from a few seconds to 30 min [6]. For the SEM examinations the polished samples were gold coated prior to observation.

2.2. *Analysis of grain sizes*

Grain sizes were determined directly from photomicrographs of the polished and etched specimens by applying the liner intercept technique described by Mendelson [7]. 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:

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

where L is the average grain boundary intercept length of a series of random lines drawn across the photomicrographs. 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.

2.3. *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:

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

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

$$G^n = K_o\, t \exp\left(-\frac{Q}{RT}\right). \qquad (3)$$

The logarithmic form of Equation (3) is:

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

This form of Equation (4) is readily applied to a (log 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. Discussion and results

3.1. Densities after firing

3.1.1. Densities after firing of the pure spinel ($MgAl_2O_4$)

Fired densities of the pure spinel ($MgAl_2O_4$) bodies are shown in Fig. 2 for the different sintering times and temperatures. When compared to the theoretical density of spinel (3.58 g/cm^3), these fired densities range from only 53.1 % to 86.6 % of the theoretical value. Only the two higher firing temperatures consistently yielded densities at 85 % of the theoretical level. For firing at 1400℃ and 1489℃, the spinel specimens only achieved densities of about 53 % and 75 %. As these densities are much lower than those which were observed for the pure forsterite, this spinel may be considered to still be in the initial stages of sintering. These will be discussed in combination with the results previously reported by Kinoshita et al. [8].

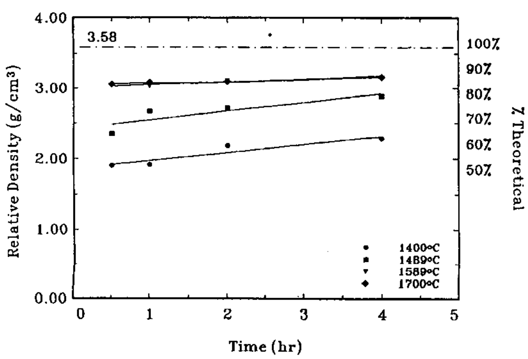

Fig. 2. Fired densities for the pure spinel.

3.1.2. Densities after firing of spinel ($MgAl_2O_4$) as reported by kinoshita et al.

Kinoshita et al. [8] have suggested that the relative density of spinel usually does not exceed 80 % for firing at temperatures below about 1600℃. The spinel in this study only achieved about 87 % of density even at 1700℃. Lower densities, only about 80 % or slightly greater, were obtained for the spinel specimens fired above 1489℃. The reason for this may be that in the $MgAl_2O_4$ spinel, the rate of transport by lattice diffusion is comparable to that by evaporation-condensation. Hence, in this spinel, evaporation-condensation is counterproductive to the densification processes by lattice diffusion. When a mechanism that does not contribute to densification and shrinkage directly competes with a mechanism that does, the driving force available for densification will usually be decreased. Because the activation energies for the respective processes may be different, the temperature dependence

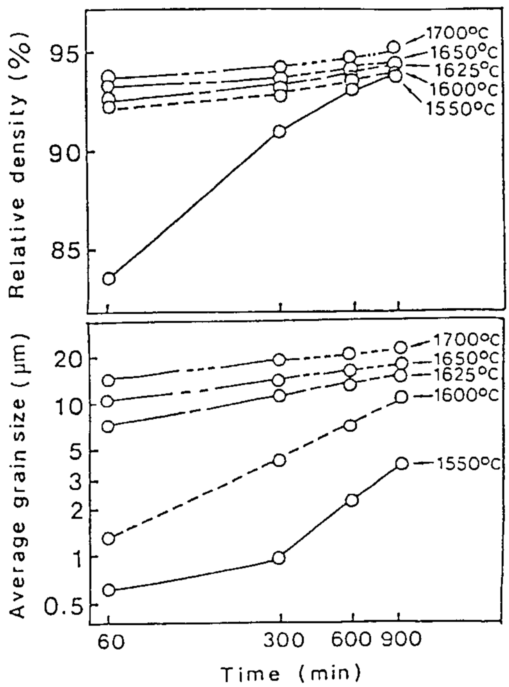

Fig. 3. Changes in relative density and grain size, fired for 1, 5, 10, 15 hrs at 1550℃, 1600℃, 1625℃ and 1700℃ after Kinoshita et al.

observed during firing may be different from that for the transport mechanism giving rise to densification. Figure 3 presents changes in relative density sintered at 1550℃, 1600℃, 1625℃, 1650℃, 1650℃ and 1700℃ for 1, 5, 10, 15 hrs, from the study by Kinoshita et al.

3.2. Grain growth of the spinel

3.2.1. Grain growth of the pure spinel ($MgAl_2O_4$)

Figure 4 illustrates microstructures of the fractured surfaces of the $MgAl_2O_4$ sintered at 1400℃, 1489℃, 1589℃ and 1700℃ for 2 hours. These clearly represent characteristics of the initial and intermediate stages of sintering at 1400℃ and 1489℃ as the grain size is only about 0.3 μm. The final stage of sintering occurs at 1589℃ for the grain size of about 1~9 μm and at 1700℃ with the grain size of about 12 μm.

Figure 5 presents the results of the isothermal grain growth studies of the spinel at 1400℃, 1489℃, 1589℃ and 1700℃ for 0.5, 1, 2, and 4 hours. It is presented in the logarithmic form of Equation (4) as log (G) versus log (t). The average spinel grain size increases with increasing firing temperature at all of the temperatures, as expected from Equation (4). The slopes of the three lines for the firing temperatures of 1400℃, 1489℃ and at 1700℃ in Fig. 5 are similar. For the three firing temperatures the slopes of the log (G) versus lot (t) plot are

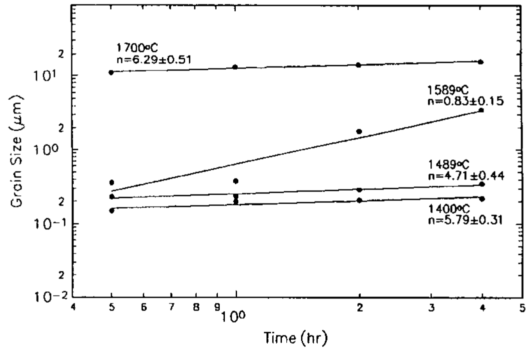

Fig. 5. Isothermal grain growth of the pure spinel at 1400℃, 1489℃, 1589℃ and 1700℃ for 1/2, 1, 2, and 4 hrs.

approximately equal to one sixth, one fifth and one sixth. The inverse values of these slopes are the grain growth exponents: 5.79±0.18, 4.71±0.44, 6.29±0.51, respectively. The nearest integers are six, five, and six, an average grain growth exponent of about six.

It is significant that the slopes of the three lines at the firing temperatures of 1400℃, 1489℃ and 1700℃ are distinctly different from that at the temperature 1589℃. The results for the grain growth at 1400℃, 1489℃ and 1700℃ appear to be similar, while those for 1589℃ are significantly displaced. The inverse value of the grain size/time slope at 1589℃ yields grain growth exponent of only 0.83±0.15. For this firing temperature, the slope of the

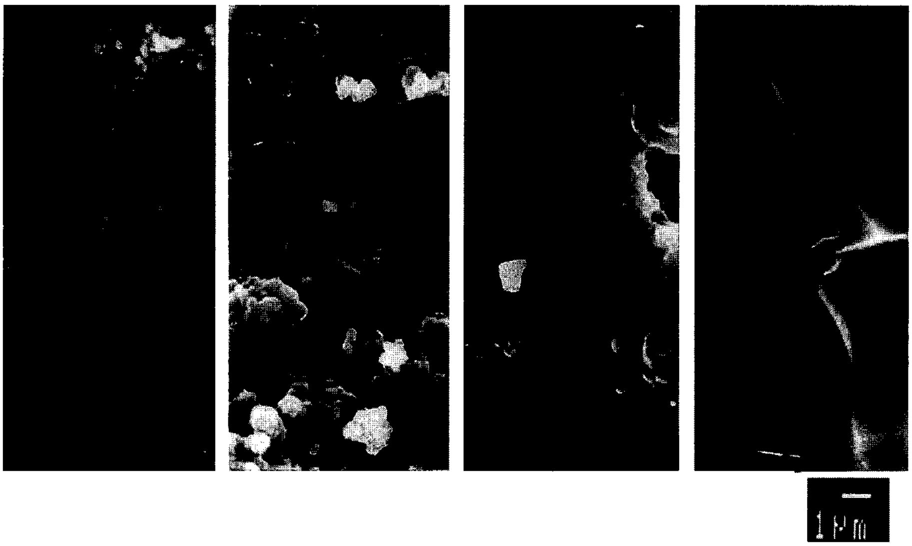

Fig. 4. Microstructures of the fractured surfaces of the $MgAl_2O_4$ fired for 2 hrs at 1400℃, 1489℃, 1589℃ and 1700℃.

log (G) versus log (t) plot is less than one half. However, it must be at least two, so these results will be analyzed with a grain growth exponent equal to two.

The grain growth of this $MgAl_2O_4$ during sintering at low temperatures can then be expressed as:

$$G^5 - G_0^5 = K_o\, t \exp\left(-\frac{Q}{RT}\right) \tag{5}$$

Since the growing grains of $MgAl_2O_4$ in their embryonic stage are only about 0.2 μm in diameter, and the final grain sizes approach 15 μm, it is possible to discount the G_o term in Equation (5) during further analysis of the results as expressed at low temperatures:

$$G^5 = K_o\, t \exp\left(-\frac{Q}{RT}\right). \tag{6}$$

This can be rewritten for the low temperatures as:

$$(G^5/t) = K_o \exp\left(-\frac{Q}{RT}\right) \tag{7}$$

From the slope of a plot of log (G^5/t) versus (1/T), the apparent activation energy for the spinel grain growth process can be determined.

Figure 6 illustrates the Arrhenius plot for the grain growth of the pure spinel. The apparent activation energy for the grain growth of this spinel, $MgAl_2O_4$, at the low temperatures, as calculated from the slope of the line in Fig. 6 is 474±38 kJ/mol, which is very close to the published values for the activation energies for spinels, 360~580 kJ/mol [9-14]. However, the activation energy at the high temperatures could not be determined because of transition of sintering mechanisms during 1589℃ firing as shown in Fig. 6.

3.2.2. Grain growth of spinel ($MgAl_2O_4$) as reported by kinoshita et al.

Figure 7 presents the results of the isothermal grain growth studies of a pure $MgAl_2O_4$ spinel by Kinoshita et al. at 1550℃, 1600℃, 1625℃, 1650℃ and 1700℃ for 1, 5, 10 and 15 hours. It is presented in the logarithmic form of Equation (4) as log (G) versus log (t). The average grain size increases with increasing firing temperature as well as for the longer firing times, as expected from Equation (4). The grain growth processes at 1625℃, 1650℃ and 1700℃ appear to be similar, while the results for the two lower temperatures, 1550℃ and 1600℃ are significantly displaced.

The slopes for the three lines describing grain growth at the higher temperatures, 1625℃, 1650℃ and 1700℃ in Fig. 7 are similar. For the three highest firing temperatures the slopes of the log (G) versus log (t) plot are approximately equal to one fourth, one fifth and one seventh. The inverse values of these slopes are the grain growth exponents: 4.02±0.38, 5.31±0.48, 6.76±0.54, respectively. The nearest integers are four, five, and seven, which yield an average grain growth exponent of about five. The value of five for Kinoshita's data and the six observed in this study are very similar.

It is significant that the slopes of the lines for the two lower temperatures, 1550℃ and 1600℃, are distinctly different from those at three higher temperatures. However, the two are similar. The inverse

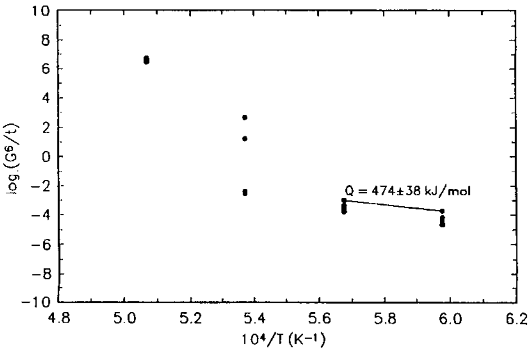

Fig. 6. Arrhenius plot for the grain growth of the pure spinel.

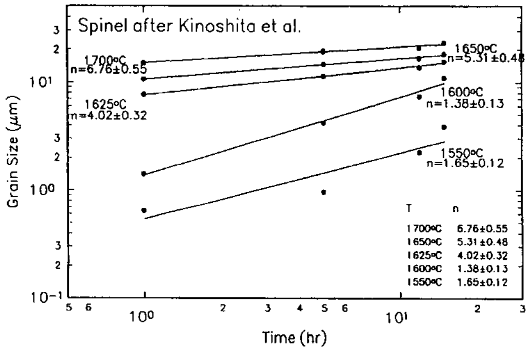

Fig. 7. Isothermal grain growth of the pure spinel after Kinoshita et al. at 1550℃, 1600℃, 1625℃, 1650℃ and 1700℃ for 1, 5, 10 and 15 hrs.

values of the low temperature slopes yield grain growth exponents of only 1.65±0.11 and 1.38±0.14. For the two lower firing temperatures, the slopes of the log (G) versus log (t) plot are less than one half. However, it must be at least two, so these results will be analyzed with a grain growth exponent equal to two. The tendency at tha firing temperature range between 1550℃ and 1600℃ of the Kinoshita study is very close to that at 1589℃ in this research. This confirms that some distinct microstructural change occurs at about 1600℃ during the firing of spinel.

The grain growth of the Kinoshita $MgAl_2O_4$ during sintering at high temperatures can then be expressed for temperatures above 1600℃ as:

$$G^5 - G_0^5 = K_o\, t \exp\left(-\frac{Q}{RT}\right) \quad (8)$$

Below 1600℃, it can be expressed as:

$$G^2 - G_0^2 = K_o\, t \exp\left(-\frac{Q}{RT}\right) \quad (9)$$

Since the initial grain size of the $MgAl_2O_4$ was about 0.2 μm and the final grain sized are about 20 μm, it is possible to neglect the G_o^n term in Equation (9). However, it is desirable to consider the initial grain size for the two lower temperatures with a grain growth exponent only equal to two.

The grain growth equation for Kinoshita's spinel at high temperatures can then be expressed as:

$$G^5 = K_o\, t \exp\left(-\frac{Q}{RT}\right) \quad (10)$$

$$G^2 = K_o\, t \exp\left(-\frac{Q}{RT}\right) \quad (11)$$

while at the two lower temperatures it can be expressed as; These can be rewritten as:

$$(G^5/t) = K_o \exp\left(-\frac{Q}{RT}\right) \quad (12)$$

and:

$$(G^2/t) = K_o \exp\left(-\frac{Q}{RT}\right) \quad (13)$$

From the slopes of a plot of log (G^5/t) versus (1/T) and log (G^2/t) versus 1/T, the apparent activation energies for the spinel grain growth process can be estimated.

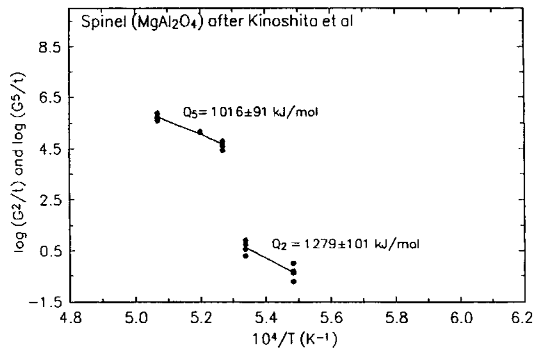

Fig. 8. Arrhenius plot for the grain growth of the pure spinel after Kinoshita et al.

Figure 8 illustrates the Arrhenius plots for the grain growth of the pure spinel studied by Kinoshita et al. There exists a distinct separation of the (G^5/t) values for the three higher temperatures from the (G^2/t) values from the two lower temperatures. These two results exhibit linear relationships on the log (G^5/t) and log (G^2/t) versus (1/T) plot. This implies that the rate controlling mechanism for grain growth, or grain boundary migration is different for the microstructures which develop over these two temperature ranges. The apparent activation energy for the grain growth of this spinel, $MgAl_2O_4$, at the high temperatures, as calculated from the slope of the line is 1016±91 kJ/mol and, 1279±101 at the two lower temperatures, in Fig. 8.

The activation energies for this spinel appear to be too much high when they are compared to other published values for spinel [9-13]. It is very difficult to compare these high activation energies determined in terms of the data by Kinoshita et al. to the values in other published papers. However, the two activation energies determined from the slopes of a plot of log (G^5/t) versus (1/T) and log (G^2/t) versus (1/T) are similar and close value between these two mechanisms. This suggests that there are occurring two distinct mechanisms during the sintering process with the grain growth exponents of two below 1600℃ and five at higher temperatures between 1600℃ and 1700℃.

4. Conclusions

Several comparisons can be made between the pure spinel of this study and Kinoshita's spinel. For these pure spinels the relative densities increases with temperature, reaching only 87 % of the theoretical density in this study, although 96 % for Kinoshita's spinel study. The latter was sintered for 15 hrs at 1700℃, almost four times longer in time, but only 50℃ higher in sintering temperature.

Similar to the density results, the grain growth results above 1600℃ appear similar for these spinels, but for temperatures lower than about 1600℃ results are distinctly differently grouped. However, the grain growth exponents are different, six for the spinel (below 1600℃), and five at high temperatures (above 1600℃), and only two at low temperatures (below 1600℃) for the Kinoshita's spinel.

The activation energy for the grain growth of this spinel, $MgAl_2O_4$, at the low temperatures, with an grain growth exponent of five is 474±38 kJ/mol, which is very close to the published values, 360~580 kJ/mol. The activation energies with five at high temperatures and two at low temperatures in Kinoshita's spinel are determined about 1000 and 1300 kJ/mol. Those activation energies appear to be almost twice as high as the published values of 360~580 kJ/mol. In spite of the different activation energies, the microstructural evolution mechanism was observed to be similar between the two temperature ranges in these two materials.

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