研究

Initial Sintering and Grain Growth Kinetics of Magnesium Oxide (MgO) Prepared by Alkoxy-Method

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The kinetics of the initial sintering and grain growth of magnesium oxide (MgO) prepared by the alkoxy-method were investigated by means of dilatometry, electron microscopy and the measurement of isothermal shrinkage. The obtained results are summarized as follows.

(1) The initial sintering kinetics of MgO were determined from 1000 to 1200°C. The sintering process was governed by the volume diffusion of oxygen ions which was represented by $D=2.54 \times 10^{-5} \exp(-64,000/RT) \text{ cm}^2/\text{sec}$.

(2) The grain growth of MgO was represented by the expression of $G^2 - G_0^2 = kt$, and the temperature dependence of k was given by $k=3.3 \times 10^{-3} \exp(-77,000/RT) \text{ cm}^2/\text{sec}$.

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I Introduction

It has previously been reported¹⁾ that the magnesium oxide (MgO) powders prepared by the alkoxy-method were highly sinterable. This reason was explained as follows. The alcoholic hydrocarbon occluded in powders or free carbon produced by its decomposition may react with oxygen of MgO at the surface, resulting in the evolution of CO and/or CO₂ and H₂O. As a result, many oxygen vacancies in non-equilibrium would be produced in the vicinity of grain boundary, and the sintering of MgO could be accelerated remarkably. The present investigation deals with the kinetics of the initial sintering and grain growth of MgO prepared from alkoxy.

II Experimental Procedure

II-1 Material

The starting material was synthesized by heating magnesium foil of 99.9% purity in an excess isoamyl alcohol containing a small amount of ethyl bromide as catalyst at 130°C for 7 h¹⁾⁻³⁾. The obtained magnesium isoamyloxide was hydrolyzed by pouring slowly into water at 90°C. X-Ray diffraction patterns showed that the resulting product was Mg(OH)₂. Thermal analysis of the powder at the heating rate of 10°C/min showed that the dehydration was completed at 440°C. Gradual weight loss of 3.45% was observed between 440 and 930°C. This would be attributed to the liberation of alcoholic residue occluded in the derived powder. Loose Mg(OH)₂ powders were calcined at 800°C for 2 h. The average particle size determined from electron microscopic observation was 700 Å.

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II-2 Isothermal Shrinkage

Compacts of 10 mm in diameter and about 1.5 mm in thickness were prepared at 3 ton/cm² with distilled water as a binder. The pressed compacts were pre-heated at 200°C for 1 h to remove the binder. The density of the compacts was about 55% of the theoretical density.⁴⁾ Linear shrinkage measurement of the compact was carried out from room temperature to 1200°C in air at heating rate 200°C/h prior to that of isothermal shrinkage. The shrinkage proceeded gradually from about 880°C and rapidly from 930°C. On the basis of this result, isothermal shrinkage measurement was carried out in the temperature range between 1000 and 1200°C in air. It required about 30 seconds for the furnace to reach at a definite temperature. The furnace was controlled within $\pm 5^\circ\text{C}$ by a program controller.

II-3 Microscopic Observation

The fractured surfaces of sintered compacts were prepared in order to examine grain growth. The average grain size, D , was calculated by the following equation,⁵⁾

$$\bar{D} = 1.56 \frac{C}{MN} \quad (1)$$

where C is the total length of test line used, N the number of intercepts, and M the magnification of the photomicrograph. The constant, 1.56, is a correction factor which was derived by Mendelson.⁶⁾

III Results and Discussion

III-1 Initial Sintering Mechanism

The diffusion shrinkage equation⁷⁾⁻⁹⁾ for the initial sintering of the compact is:

$$\left[\frac{\Delta L}{L_0} \right] = \left[\frac{K\gamma a^3 D}{kT r^p} \right]^m t^m \quad (2)$$

where $\Delta L/L_0$ =shrinkage rate, k =the Boltzmann constant, T =absolute temperature, r =particle radius, γ =surface energy, a^3 =vacancy volume, D =diffusion coefficient for the rate controlling species, t =time, and K , m and p are constants depending on mechanism.

According to Wermuch et al.¹⁰⁾ oxygen ions in grain-boundary diffusion are the rate controlling species for the initial sintering (814–1060°C) of MgO and the value of the activation energy is 60.2 kcal/mol. On the other hand, Matuda et al.¹¹⁾ have reported that the initial sintering process for obtaining the transparent MgO compact is governed by volume diffusion of oxygen ions and the activation energy is 55.8 kcal/mol.

The results of isothermal shrinkage are plotted by the $\log(\Delta L/L_0) - \log t$ in Fig. 1. The data showed straight lines with a slope of 0.49–0.50. Therefore, the results suggest that the initial sintering process is governed by volume diffusion mechanism which can be represented by the following Coble's model.⁹⁾

$$\left[\frac{\Delta L}{L_0} \right] = \left[\frac{2\gamma a^3 D}{kT r^3} \right]^{0.5} t^{0.5} \quad (3)$$

Figure 2 shows the diffusion coefficients calculated from Eq. (3) by assuming that the diffusion of the oxygen ion vacancy ($a^3 = 1.86 \times 10^{-23}$) controls the rate. The values of r and γ used are 350 Å and 1000 erg/cm²,⁹⁾ respectively. Consequently, the following equation was derived:

$$D = 2.54 \times 10^{-5} \exp(-64,000/RT) \text{ cm}^2/\text{sec} \quad (4)$$

Fig. 1 Isothermal shrinkage of MgO.

Fig. 2 Self-diffusion of ions in MgO and the diffusion coefficients from initial sintering of MgO.

The self diffusion data for $\text{MgO}^{(12),(13)}$ are also shown in Fig. 2. The activation energy in the present study is in good agreement with that (62.4 kcal/mol¹³⁾ for oxygen self diffusion in MgO in the extrinsic range. Therefore, this activation energy may refer to oxygen ion mobility.¹³⁾ From this fact, it was found that the initial sintering process of MgO prepared by the present method is governed by the volume diffusion of oxygen ions. However, oxygen diffusion coefficients are about one order of magnitude greater than those for oxygen self diffusion in MgO. This seems because many oxygen vacancies in non-equilibrium produced in the vicinity of grain boundary as described earlier¹⁾ promote the migration of oxygen ions. Therefore, so long as oxygen ions are the rate controlling species, the sintering of MgO could be accelerated.

III-2 Grain Growth

The MgO powder was prepared under the same condition as that in isothermal shrinkage. The pressed compacts were sintered between 1200 and 1400°C. The relative density of the sintered compacts was in the range of 95.4 to 97.8%. The densification at low temperatures in this way resulted in the sintered compacts consisting of fine grains. Photograph 1 shows the fracture surfaces of the compacts sintered at 1200, 1300 and 1400°C for 3 h. The rate of grain growth is represented by the following equation,

$$G - G_0 = k' t^{1/n} \quad (5)$$

Photo. 1 Electron micrographs of the fractured surface of MgO sintered at various temperatures for 3 h.

Fig. 3 Isothermal grain growth of MgO.

Fig. 4 Temperature dependences of the rate constants for the grain growth of MgO.

A: Present study, B: Spriggs et al.
C: Daniels et al., D: Gupta

where G is the grain size of the sintered compacts, G_0 the initial grain size, t the time, k' the rate constant, and n is usually $2^{14)}$ or $3^{15)}$ for the sintering of oxides in the absence of a liquid phase. To determine the relation of the grain size vs time, the measured grain size was plotted as a function of both the square root and the cubic root of time. The plot as the function of the square root of time gave a favorable linear relation. Therefore, the grain growth for MgO is given by the relation of $n=2$ in Eq. (5) as follows,

$$G^2 - G_0^2 = kt \quad (6)$$

Figure 3 shows the plots of $\log(G^2 - G_0^2)$ against $\log t$. The value of G_0 used is $700 \text{ \AA}$. The rate constant for the grain growth was calculated at each temperature and the activation energy obtained from Arrhenius plot was the value of 77 kcal/mol (Fig. 4). The grain growth data gave the following expression for the temperature of k :

$$k = 3.3 \times 10^{-3} \exp(-77,000/RT) \text{ cm}^2/\text{sec} \quad (7)$$

The data for the grain growth reported by other investigators¹⁶⁾⁻¹⁸⁾ are also shown in Fig. 4. The relation of $n=2$ in Eq. (5) is applied to all the reports. The activation energy (77 kcal/mol) in the present study was nearly identical to that ($81 \text{ kcal/mol}^{16)}$, $75.5 \text{ kcal/mol}^{17)}$) obtained by Spriggs et al.¹⁶⁾ and Gupta.¹⁷⁾ However, the value of k was about three orders of magnitude smaller than that of other data.

References

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本会記事

第115回理事会議事録

日 時：昭和52年 5月17日(火) 10時30分～11時30分
 会 場：神田学士会館
 出席者：鹿取会長他 21名, 委任状 7名 計 29名
 議 事：

1. 昭和51年度事業報告, 収支決算報告の件 (承認)
2. 会計監査報告の件 (承認)
3. 昭和52年度事業計画, 収支予算案の件 (承認)
4. 協会賞受賞候補者推薦委員選出の件 (承認)
5. 創立20周年記念事業の件 (承認)
6. その他諸報告
 - 1) 第9回粉末冶金入門講座開催の報告
 - 2) 第7回フェライト夏季セミナー開催の件
 - 3) 第15回粉体に関する討論会共催の件
 - 4) 第16回窯業基礎討論会共催の件
 - 5) 日本工学会 創立100周年記念 事業準備委員推薦依頼の件
 - 6) 第3回国際フェライト会議の件
 - 7) 特別会員脱会の件
 - 8) 金属研究連絡委員会及び金属関係10学協会連絡委員会報告

第23回評議員会議事録

日 時：昭和52年 5月17日(火) 11時30～11時45分
 会 場：神田学士会館
 出席者：70名 (うち委任状 57名)
 議 事：

1. 昭和51年度事業報告, 収支決算報告の件 (承認)
2. 会計監査報告の件 (承認)
3. 昭和52年度事業計画, 収支予算案の件 (承認)
4. 昭和51年度協会賞受賞者報告の件 (承認)
5. 名誉会員推薦提案の件 (承認)

第23回総会議事録

日 時：昭和52年 5月17日(火) 11時45分より
 会 場：神田学士会館
 出席者：246名 (うち委任状 213名)
 議 事：

1. 昭和51年度事業報告, 収支決算報告の件 (承認)
2. 会計監査報告の件 (承認)
3. 昭和52年度事業計画, 収支予算案の件 (承認)
4. 昭和51年度協会賞受賞者報告の件 (承認)
5. 小藤甫, 武井武, 内藤逸策の各氏を
 名誉会員に推薦する件 (決定)