Sintering is an extremely old technology, which has been used since prehistory. However, it is so complicated that a quantitative study just began to start in the 1950's. A theory for sintering in a simple model was separately derived by Frenkel, Kuczynski, Kingery, and Coble. They elucidated the mechanism of material transport in sintering by the rate of interface growth and distance between the centers of two spherical particles. The equation derived was successfully applied to the shrinkage data of powder compacts. Since then, these so-called log-log plots of data have been widely used by many researchers in order to elucidate the mechanisms of the sintering shrinkage.

In such a situation, Moriyoshi and Komatsu pointed out that the log-log plot method was not necessarily suitable because of the effect of many factors such as the combined mechanisms of sintering, the size distribution of particles, particle shape, and so on. They reported this in a series of papers (Kinetics of Initial Sintering with Grain Growth, J. Am. Ceram. Soc., 53, No. 12, 621–675 (1970); Analysis of Initial Combined Sintering, Yogyo-Kyokai-Shi, 81[3], 102–107 (1973); Initial Sintering of Glass, ibid., 82[8], 426–429 (1974); A Method for Obtaining Surface Diffusion Coefficients from Initial Sintering Data, ibid., 86[2], 130–136 (1978)), in which they suggested that various processes such as surface and volume diffusion, grain boundary and volume diffusion, and other processes proceeded concurrently during sintering. The above paper was the first one in the series, in which a different method was used to evaluate and to define a sintering mechanism. The paper also served as an important trial encouraging other sintering studies of ceramics.

Moriyoshi and Komatsu pointed out that the method of log-log plots was not necessarily reliable and that the decision of a mechanism at the initial stage of sintering should be carried out by the comparison of activation energies obtained from sintering data with those obtained from the tracer diffusion of ions. From these viewpoints, they derived theoretically an equation to obtain activation energies from shrinkage data at a constant rate of heating. As a result, it was shown that activation energies of sintering shrinkage can be simply obtained with precision by using the equation derived. Then, they indicated that the activation energies obtained in the shrinkage data of ZnO, NiO, and Fe₂O₃ compacts were in good agreement with the values obtained from tracer measurements. Based on these results, they discussed the rate determining steps in the sintering process.

This paper not only provides fundamental information to understand sintering processes such as sintering shrinkage, grain growth, and others, but also stimulates the studies concerning solid state reactions, erosion and corrosion of ceramics, creeps associated with ion diffusion, and so on. The study also gave basic information to fabricate ceramic materials.
1. Introduction
Kinetic studies with the method of a constant rate of heating have been made by many investigators and proved to be very simple and useful for getting the information of the mechanism of sintering. Data describing thermoluminescence were correlated with exponential relations describing first order reactions. Similar expressions were developed for ionic thermoelectricity. Ingraham and Marier successfully applied the method to chemical reaction. The similar application of the method to the solid state reaction has also been made by Kubo and Shirasaki.

Recently, Cutler has combined the method with the kinetic equation of sintering proposed by Frenkel and successfully obtained an analytical expression for the initial sintering of compacts of glass powder. Johnson has applied the method to the cooperative sintering of silver and obtained an analytical expression by retaining only the first term of the infinite series of the integral form obtained by combining kinetic equation and a rate of heating. However, no investigation has been made on the extension of this method to the kinetic study of diffusion sintering.

The purpose of this paper is to develop a simple analytical equation for the initial stage of diffusion sintering at constant rate of heating without neglecting the higher terms of the infinite series.

2. Experimental
2.1 Specimens and Experimental Method.
2.1.1 ZnO Reagent grade basic zinc carbonate was decomposed in vacuum at 300°C for 30 hrs. The resulting zinc oxide was fired at 500°C for 15 hrs in air. The powder was then ground with an agate mortar for five minutes. The electron microscopy revealed that the particle size of the powder was less than 0.2 μ and the particle shape is nearly spherical.

2.1.2 NiO Reagent grade nickel nitrate was decomposed at low temperature on a sand bath and the resulting oxide (black) was further fired at 600°C for 3 hrs. The nickel oxide obtained was greenish gray. The oxide was doped in the following: To the solution of known quantity of reagent grade lithium nitrate, the oxide was added. The suspension was stirred for 30 min and was evaporated to dryness with an infrared lamp. The mixture was lightly ground and fired at 650°C for 3 hrs in air. Amount of dopants was 1.0 atm%. Pure nickel oxide as a reference was also treated with nickel nitrate solution and fired at 650°C for 3 hrs. Pure nickel oxide, lithium doped oxide (NiO (Li)), and aluminum doped oxide (NiO(Al)) were greenish grey, gray and green, respectively. The electron microscopy revealed that the particle size of the powder was from 0.1 to 1.0 μ. The particle shape of NiO(Li) was nearly spherical and that of NiO and NiO(Al) were angular, respectively.

2.1.3 Fe₂O₃ The powder was prepared by the decomposition of reagent grade ferrous sulfate, purchased from Rico Corporation. Electron microscopy indicated that the particle size of the powder was 0.4 ~ 0.7 μ. The particle shape was nearly spherical.

The powders were pressed at 1 t/cm² into compacts (10 mm in diameter and 4 mm in thick) without binder. The density of compacts before sintering was about 50% of the theoretical density. Electron microscopic observation on various ZnO and Fe₂O₃ compacts was made as the same method reported previously. However, electron microscopy of NiO compacts gave only an ambiguous result, therefore, Scanning Type Electron Microscope (Type JSM-U3) was used for observing the fracture surface.

3. Theoretical
By considering simple geometrical models, early workers theoretically derived the relation between shrinkage and time at a given constant rate of heating. However, no investigation has been made on the extension of this method to the kinetic study of diffusion sintering.
temperature. They obtained Eq. (1) for describing the shrinkage data of a compact of spherical particles on diffusion sintering.

$$\frac{dL}{L_0} = K_t a^D \exp\left(-\frac{E}{RT}\right)$$

where the parameters, m and p, are determined by the mechanism of material transport, k_v = numerical constant, r = surface free energy, a^3 = vacancy volume, D = self-diffusion coefficient, k_b = the Boltzmann constant, T = absolute temperature, r = particle radius, t = time.

The self-diffusion coefficient, D, can be described by the exponential relation,

$$D = D_0 \exp\left(-\frac{E}{RT}\right)$$

where D_0 is a preexponential term, E activation energy, R the gas constant, and T absolute temperature, and temperature is given as a linear function of time according to the expression,

$$T = A + Bt$$

where A is an initial temperature and B is a constant describing the rate of heating. Combining Eqs. (1), (2), and (3) gives,

$$\frac{dL}{L_0} = K_t a^D \exp\left(-\frac{E}{RT}\right)$$

where K_t is k_v a^D k_b r^p.

Shrinkage data at constant rates of heating can be correlated with Eq. (4). However, this differential equation requires obtaining slopes describing the differential of shrinkage with respect to time at various temperatures. Slight fluctuations in length with time make data gathering difficult. Consequently, it is convenient to integrate Eq. (4). Integration of Eq. (4) with the initial condition of $dL/L_0 = 0$ at $t = 0$ gives,

$$\frac{dL}{L_0} = K_t a^D \exp\left(-\frac{E}{RT}\right)$$

In the previous report 13), we have discussed the role of grain growth in the initial sintering kinetics. However, for simplicity of mathematical treatment, Eq. (5) was integrated by assuming that no grain growth occurred in the initial stage and that m and p were independent of temperature. The resulting equation was an infinite series and was not suitable for practical use. Therefore, the integration was done by using the mean value theorem of definite integral. According to the theorem, the integration term of Eq. (5) was transformed into

$$\int_0^t \exp\left(-\frac{E}{R(A+BT)}\right) d\tau = \exp\left(-\frac{E}{R(A+BT)}\right)$$

where $\xi$ is a value of $t$ which exists between zero and $t$. Introducing a parameter, $K_t$, Eq. (6) is transformed into

$$\exp\left(-\frac{E}{R(A+BT)}\right)$$

where $K_t = \frac{1}{R(A+BT)} \int_0^t \exp\left(-\frac{E}{R(A+BT)}\right) d\tau$$

Combination of Eqs. (5), (6) and (7) gives

$$\int_0^t \exp\left(-\frac{E}{R(A+BT)}\right) d\tau = \exp\left(-\frac{E}{R(A+BT)}\right)$$

where $K_t$ is the mean value of (1/B).

Before use of Eq. (8), an approximate integral form of Eq. (4), we must check the internal consistency of Eqs. (4) and (8). This was done by examining the values of the ratio of the differential to the integral form of Eq. (8). The differential form of Eq. (8) is

$$\frac{dL}{L_0} = K_t a^D \exp\left(-\frac{E}{R(A+BT)}\right)$$

where $f(t)$ is a value of $t$ which exists between zero and $t$. The values of $f(t)$ calculated for the given values of $A = 298 K$ and $B = 2.0^\circ/\min$, and $E = 50$ and 70 kcal/mole are recorded in Table 1. Table 1 shows

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<th>Temperature (°C)</th>
<th>Values of $f(t)$</th>
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<td>1123 (1050)</td>
<td>28.5</td>
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</table>

The values of $f(t)$ calculated for the given values of $A = 298 K$ and $B = 2.0^\circ/\min$, and $E = 50$ and 70 kcal/mole are recorded in Table 1. Table 1 shows
that the value of $f(t)$ gradually increases with increasing time or temperature and that the rate of increase of the values has relation to the value of given activation energy. However, the change of the value in the experimental temperature range is not so large. Therefore, the value of $f(t)$ is assumed to be constant in our experiments. On this assumption, Eq. (8) is used to describe the experimental data.

Taking logarithms of Eq. (8) and rearranging the resulting equation, we obtained Eq. (11).

$$\log \left( \frac{L}{L_0} \right) = -\frac{E}{R(A+B)} - \frac{A}{A+B} \log(A+B)$$

where the value of $m$ was determined from the slope of the log-log plots of isothermal run.

4. Results and Discussion

According to Eq. (11), a straight line should be obtained when $\log(\frac{L}{L_0}) = -\log(A+B)/A$ is plotted vs. $1/(A+B)$ and the activation energy should be calculated from the slope of the plot. The value of $m$ was found to be 0.40 (volume diffusion) for NiO and Fe$_2$O$_3$ as shown in Fig. 1 and 2, and that for ZnO 0.31 (grain-boundary diffusion) in the previous report$^{13})$.

4.1 ZnO

Fractional shrinkage vs. temperature relationship obtained for zinc oxide compact is given in Fig. 3. The curve represents that the compact begins to shrink at about 547°C after an initial thermal expansion. Grain growth during the sintering was not observed up to about 830°C as revealed by the electron micrographs in Fig. 4. Therefore, the consideration of grain growth during sintering is not necessary for the analysis of the data up to about 830°C. In the present, the authors can not explain the fact that grain growth did occur in the isothermal sintering$^{13}$ and does not at constant rate of heating. Further study on this problem will be carried out. The data from Fig. 3 were plotted according to Eq. (11) in Fig. 5. The plot satisfactorily gave a straight line and the activation energy obtained from the slope was 76.8 kcal/mole. The value agreed with 71.1 kcal/mole obtained in previous work$^{13}$ taking account of grain growth in isothermal sintering. These two values are in good agreement with those (70-76 kcal/mole) of volume diffusion of Zn in ZnO from direct tracer measurements$^{14,15})$. This shows that the technique at constant rate of heating described here is reasonable for analysis of sintering mechanism and is evidently a quick and simple method in obtaining an apparent activation energy of sintering. However, as Johnson$^{7}$ and Rockland$^{19}$ have reported, in the case of the combined sintering in which more than one mechanism of diffusion were operating, the apparent activation energy increased to the higher values than that expected from grain boundary diffusion. Therefore, the agreement of apparent activation energy obtained in our experiment with that from the tracer measurements may be only an artifact result from the effect of surface diffusion. No conclusion on the mechanism of the sintering could deduced from the sintering of such small particles as used in our experiment.

4.2 NiO

The threshold temperature of shrinkage were 873°C, 843°C, and 903°C for NiO, NiO(Li), and NiO
The electron micrographs in Fig. 6 indicated that grain growth was not obvious up to about 780°C. The plots of Eq. (11) for pure and doped NiO were shown in Fig. 7. The plot for the compact NiO(Li) satisfactorily gave a straight line from the initial part, however, those for NiO and NiO(Al) a straight line with an initial curved portion. This discrepancy between the theory and the experiment for the compacts of NiO and NiO(Al) is thought to be due to the fact that these compacts consist of angular particles, as pointed out by Cutler and Cutler and Henrichsen. Therefore, electron microscopic observation of pure NiO particles was done. Electron micrographs of fracture surface (Fig. 8a) evidently revealed that compacts of pure NiO consist of angular particle. The powders were preheated for 20 hrs at 700°C in air. The pretreated powders became less angular than the original as shown by the micrograph in Fig. 8b. The plots for the pretreated NiO compact gave a straight line as shown in Fig. 9. The result suggests that the initial curvature in Fig. 7 for the NiO compacts is due to the angularity of NiO particles. The same discussion may also be possible for the NiO(Al) compacts.

As for the effect of dopants on the sintering, sinterability of NiO is promoted by doping of Li$_2$O and retarded by Al$_2$O$_3$ (Fig. 7). The results state that material transport in NiO does not depend on the concentration of nickel ion vacancies, but on the concentration of electron hole, trivalent nickel ion, which has smaller ionic radius than bivalent nickel ion. 

Fig. 4. Electron micrographs of fracture surface of ZnO during sintering at constant rate of heating (2°C/min). (×15,000)

Fig. 5. Data for ZnO compacts plotted according to Eq. (11).
Fig. 6. Electron micrographs of fracture surface of NiO compacts during sintering at constant rate of heating (2°C/min).

Fig. 7. Data for pure and doped NiO compacts plotted according to Eq. (11).

Fig. 8. Electron micrographs of fracture surface of NiO compact.

Fig. 9. Data for preheated NiO compact plotted according to Eq. (11).
The activation energies obtained from the slope of Fig. 7 were 48.0, 62.0, and 48.8 kcal/mole for NiO, NiO(Li), and NiO(Al), respectively. For the preheated NiO, the value was 46.2 kcal/mole (Fig. 9). Moore\(^1\) obtained an activation energy of 44.0 kcal/mole for the self-diffusion of nickel in NiO. The contribution of surface diffusion is estimated to be large in such fine particles as used in this experiment\(^1\). However, the agreement of activation energies between these values was fairly good except that for NiO(Li). This result may indicate that surface diffusion has little effect on an apparent activation energy in the volume diffusion sintering of NiO. The activation energy obtained for NiO(Li) was larger than that for NiO and NiO(Al). It is not clear whether the increase of activation energy is due to the decrease of lattice constant of NiO by doping with Li\(_2\)O\(^2\), or due to other reason.

For further examination of Eq. (11), it was applied to the sintering of Fe\(_2\)O\(_3\) compacts. The powder compact began to shrink at 700°C. The plots of Eq. (11) was shown in Fig. 10 and satisfactorily gave a straight line. The deviation from straight line at initial part was also considered as the effect of particle shape. The activation energy was 115 kcal/mole and was in fairly good agreement with that of 112 kcal/mole obtained by direct tracer measurement\(^1\). The result may suggest that the initial sintering of Fe\(_2\)O\(_3\) takes place by volume diffusion of Fe\(^{3+}\). However, the foregoing discussion on the effect of the combined sintering on an apparent activation energy is also possible.

As Cutler\(^5\) pointed out, the constant rate of heating method for gathering shrinkage data is more analogous to the usual sintering conditions than isothermal experiments. The method appears to be more simple than a series of isothermal run in obtaining activation energy. The activation energies obtained were in good agreement with the values from direct tracer measurements.

**References**

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昇温法による焼結の速度論的研究

守吉信介・小松和翼
（東京工業大学工学部）

従来、提出されている初期焼結の速度式から、一定速度で昇温した場合の速度式 (1) を理論的に導出した。

\[
\log \left( \frac{L}{L_0} \right)^m - \log \log \frac{A}{R^2} = \log K - \frac{E}{R(A+B)}
\]  (1)

この式の妥当性を検討するため、ZnO, NiO および Fe₂O₃ の焼結を昇温法で行なった。収縮の測定には差動電位計動器を用い、また焼結過程での焼き所面の状態を調べるために走査電子顕微鏡などを用いて観察した。この結果、各体の焼結の場合、実験データはきわめてよく式 (1) によってあらわされ、式 (1) のプロットからえられた見掛けの活性化エネルギーが文献値とよく一致することを示した。

(3/28/1971 受付)