

## 고상반응에 의한 표면 및 체적확산 계수측정

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### Diffusion in and on Solid Oxides

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#### Abstract

Electron microprobe analysis was used to measure the distribution profile of nickel ion in and on the spinel layer during the spinel formation reaction from nickel oxide and alumina single crystals in the temperature range from 1260° to 1470°C. The volume and surface diffusion coefficients of nickel ion ( $D_v$ ,  $D_s$ ) obtained are:

$$D_v = 8.54 \times 10^{-4} \exp\left(-\frac{48.6 \pm 5.8 \text{ Kcal/mol}}{RT}\right) \text{ cm}^2/\text{sec},$$

$$D_s = 2.7 \times 10^{-1} \exp\left(-\frac{20.5 \pm 1.2 \text{ Kcal/mol}}{RT}\right) \text{ cm}^2/\text{sec}.$$

A confits model was proposed for measurement of surface diffusion coefficient under free sintering of powder and the application was carried out for free sintering data of zinc oxide.

#### 1. Introduction

Studies of diffusion on and in solid oxides are important for the understanding of rate processes such as grain growth, sintering and solid state reactions.

In the solid state reaction, Jander's model <sup>1)</sup> has been used for the analysis of kinetic data. Jander's model neglected the topochemical character of the reaction. However, Jander's and the similar equations can describe the kinetic data from the initial stage of the reaction. The discrepancy between Jander's and Komatsu's model <sup>2,3)</sup> may be dissolved if the

surface diffusion is very faster than the volume diffusion and the particles of the minor component are quickly covered with the other component making a spherical shell as was proposed by Jander. However, no study has been made for the concurrent measurement of surface and volume diffusion coefficients in the reaction.

In the past decade considerable interest has been paid for the measurement of surface self-diffusion in metal oxides. Most of the studies have used mass transfer techniques-e. g. observing the variation with time of (a) the rate of growth of grain boundary grooves <sup>4)</sup>, (b) the rate of decay of single or multiple

scratches<sup>5)</sup> and (c) the rate of shrinkage of compacts in the combined sintering<sup>6)</sup>.

In general, volume diffusion coefficients obtained have been shown to be consistent with each other. However, surface diffusion coefficients obtained are widely different and no decisive result has been obtained. Especially, in the thermal grooving method, different observers using nominally similar experimental procedures have produced widely different results. This seems to be due to the difficulty in preparing a sample. The initial sintering technique was ambiguous in determining the pre-exponential term.

The object of the present paper is two-fold the first the determination of internal surface and volume diffusion coefficients in the spinel formation reaction from nickel oxide and alumina and second is the determination of activation energy for surface self-diffusion from the BET surface area change of zinc oxide during the initial sintering.

## 2. Experimental Procedure

Alumina single crystals (99.9% Al, 10 mm in diameter and 1 mm in thick, with  $\langle 001 \rangle$  face, supplied by Shinkosha K.K.) and nickel oxide single crystals (99.9% Ni, 10 mm in diameter and 1 mm in thick, with  $\langle 100 \rangle$  face, supplied by Nakazumi Crystal Co.) were used as diffusion couples in this experiment. The experimental setup of the diffusion couple is shown in Fig. 1. Nickel oxide single crystal was shaped by diamond cutter in 1 mm square with a length 10 mm. After polishing the surface with the polishing paper and alumina powder ( $0.3\mu\text{m}$ ), the alumina-nickel oxide diffusion couple was annealed in a SiC resistance furnace. The fluctuation of temperature was about  $\pm 5^\circ\text{C}$ . The diffusion couple was placed in Pt crucible and annealed for the desired length of time in an atmosphere.

Two Pt-PtRh thermocouples were attached to the crucible. One thermocouple was connected to an automatic controller and the other was used for recording the temperature. After annealing, the couples for measuring  $D_v$  was bisected with the diamond cutter parallel to the x-axis at the origin and the bisected surface was polished by a standard method, and for

$D_s$  the alumina plate was cleaned ultrasonically without polishing for the subsequent electron microprobe analysis. The electron microprobe x-ray analyzer (Shimazu model ARL) was used in this study. The excitation conditions of the excitation potential = 15 KV and the beam current =  $0.01\mu\text{A}$  were chosen for minimizing the analysis time. An adequate count was obtained during this time (10 sec). The spot size was  $3\mu\text{m}$  under this condition and the spot moving velocity was  $96\mu\text{m}/\text{sec}$  for obtaining surface diffusion profiles and the  $8\mu\text{m}/\text{sec}$  for volume diffusion profiles. The data output from the electron probe was converted to concentration by using the calibration curve.

## 3. Mathematical Analysis

### 3-1 Internal volume and surface diffusion in solid state reaction with line source

A diffusion couple consisting of nickel oxide and alumina single crystals was used for measuring the internal volume and surface diffusion coefficients in the solid state reaction. A schematic model of the couple is shown in Fig. 1. In Fig. 1, 2a is the width of a line source of nickel oxide,  $\delta$  is the thickness of the surface layer,  $x$  and  $z$  are coordinates as are given in Fig. 1. When a material balance is setup

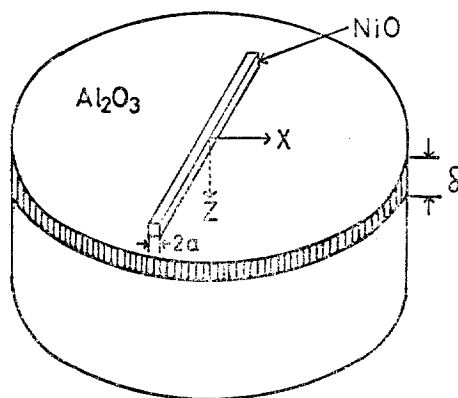


Fig. 1 Schematic geometry of diffusion couple setup with NiO line source

in a volume element of the surface layer, the differential equation describing the concentration change of nickel ion in this layer<sup>7)</sup> is

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} - \frac{1}{\delta} D_v \left( \frac{\partial C_v}{\partial Z} \right)_{z=0} \quad (1)$$

and

$$\frac{\partial C_v}{\partial t} = D_v \frac{\partial^2 C_v}{\partial Z^2} \quad (2)$$

Assuming that the concentration distribution of nickel ion on the surface layer is quasi-stationary after annealing for time,  $t_f$ , we obtain

$$C_s(x, t) = C_s(x, t_f) \quad (3)$$

Combination of Eqs. (1), (2) and (3) and solution of the resulting differential equation gives the concentration of nickel ion in alumina as follows,

$$\begin{aligned} C_v(x, Z, t_f) &= \frac{C_s(x, t_f)}{\sqrt{\pi D_v t_f}} \int_0^\infty \exp(-Z^2/4 D_v t_f) dZ \\ &= C_s(x, t_f) \operatorname{erfc}\left(\frac{Z}{2\sqrt{D_v t_f}}\right) \end{aligned} \quad (4)$$

From Eq. (4),  $\left(\frac{\partial C_v}{\partial Z}\right)_{z=0}$  in Eq. (1) is given by

$$\left(\frac{\partial C_v}{\partial Z}\right)_{z=0} = \frac{C_s(x, t_f)}{\sqrt{\pi D_v t_f}} \quad (5)$$

Combining Eqs. (1) and (5) and assuming a quasi-stationary state, we obtain

$$\frac{\partial C_s}{\partial t_f} = D_s \frac{\partial^2 C_s}{\partial x^2} - \frac{D_v C_s}{\delta \sqrt{\pi D_v t_f}} = 0 \quad (6)$$

The solution of Eq. (6) is

$$C_s(x, t_f) = A e^{-\alpha x} + B e^{\alpha x} \quad (7)$$

Upon inserting the boundary conditions of  $C_s(\infty, t_f) = 0$  and  $C_s(0, t_f) = C_0$  into Eq. (7), the result is

$$C_s(x, t_f) = C_0 e^{-\alpha x} \quad (8)$$

where  $\alpha = \sqrt{\frac{D_v}{D_s \delta \sqrt{\pi D_v t_f}}}$  and  $D_v$  and  $D_s$  are the

volume and surface diffusion coefficients of nickel ion, respectively. Eq. (8) describes the concentration of nickel ion in the surface layer at time  $t_f$ .

### 3-2 Free sintering at surface

As one of the methods for measuring the surface diffusion coefficient, we have studied the free sintering of oxide powder in which the surface diffusion is thought to be dominant<sup>8)</sup>.

In the free sintering, the sintering rate was estimated by measuring the decrease of the BET area of powder (not compact) as a function of time. However, no effort has been made for deriving the kinetic equation of the free sintering.

In this study, the kinetic equation was derived on the following assumptions;

- (1) The shape of powder particle is a confits form.
- (2) The surface of the confits is smoothed by the diffusion and no neck growth occurs between the particles.
- (3) The surface diffusion is predominant in the very initial stage of the sintering.
- (4) The surface diffusion coefficient and the surface free energy are independent of the crystallographic orientation.

The model used for deriving the kinetic equation was shown in Fig. 2. In the model (Fig. 2), the decrease of the surface area is calculated on the assumption

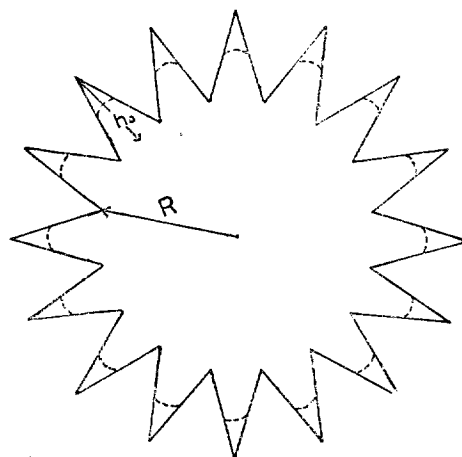


Fig. 2-a Model of confit-surfaced spherical particle

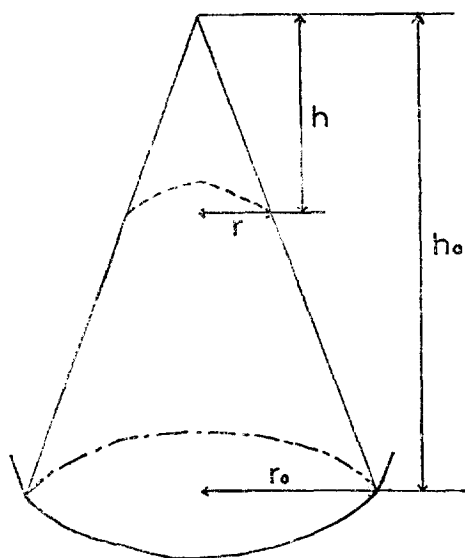


Fig. 2-b Schematic illustration of the thermal smoothing of the cone

—————; original cone  
 - - - - -; after annealing

tion that the pointed head of a cone is blunted by the diffusion from the top to the bottom of cones. The surface area decrease,  $\Delta S$  is given by

$$\Delta S = \pi r \sqrt{r^2 + h^2} - c\pi r^2 \quad (9)$$

where the term  $c\pi r^2$  is the correction term for the curved head. Assuming the following relation among  $h_0$ ,  $h$ ,  $r_0$  and  $r$

$$\frac{h}{h_0} = \frac{r}{r_0} \quad (10)$$

and combining Eqs. (9) and (10), we obtain

$$\frac{\Delta S}{S_0} = \left[ 1 - \frac{C}{\sqrt{1 + \left(\frac{h_0}{r_0}\right)^2}} \right] \left( \frac{r}{r_0} \right)^2 \quad (11)$$

where  $S_0$  is the surface area of a cone at time equal to zero. Next, assuming

$$h_0 > r_0, \quad r_0 \cong r \quad (12)$$

we obtain

$$\begin{aligned} \frac{\Delta S}{S_0} &\cong \frac{\pi r_0 h - C\pi r^2}{\pi r_0 h_0} \\ &\cong \frac{h}{h_0} = \frac{r}{r_0} \end{aligned} \quad (13)$$

We assume that surface diffusion is the only process operating and gradients of chemical potential along the surface will be associated with gradients of curvature on the surface of conifits. Such gradient will produce a drift of surface atoms with an average velocity ( $\bar{v}$ ) given by the Nernst-Einstein relation<sup>9)</sup>

$$\bar{v} = -\frac{D_s \gamma \Omega}{kT} \Delta_s K \quad (14)$$

and the surface flux of atoms  $J_s$  is the product of  $\bar{v}$  by the number of atoms per unit area  $\nu$ .

$$J_s = \bar{v}\nu = -\frac{D_s \gamma \Omega \nu}{kT} \nabla_s K \quad (15)$$

where

$J_s$ ; the surface flux of atoms (atoms/cm sec)

$\gamma$ ; the surface energy (erg/cm<sup>2</sup>)

$\Omega$ ; the volume of the diffusion species (cm<sup>3</sup>/atom)

$\nu$ ; atoms per unit area

$s$ ; the arc length along the profile

$K$ ; curvature of the surface

$k$ ; Boltzmann constant

The assumed diffusion path  $\gamma$  then

$$K \cong \frac{1}{r_s}$$

$$\nabla_s K \cong \frac{\partial k}{\partial r} = -\frac{1}{r^2} \quad (16)$$

The rate of volume change is

$$\frac{dV}{dt} = 3C'\pi r^2 \frac{dr}{dt} \quad (17)$$

Upon combining Eqs. (15), (16) and (17) and rearranging, the result is

$$3C'\pi r^2 \frac{dr}{dt} = -2\pi r \Omega J_s$$

$$= 2\pi r \frac{D_s \Omega^2 \gamma \nu}{r^2 k T} \quad (18)$$

Integration of Eq. (18) gives

$$r^4 = 6C'Bt$$

where

$$B = \frac{D_s \Omega^2 \gamma \nu}{k T} \quad (19)$$

Combining Eqs. (11), (113) and (19), we obtain

$$\frac{\Delta S}{S_0} = \left[ 1 - \frac{C}{\sqrt{1 + \left( \frac{h_0}{r_0} \right)^2}} \right] \left( \frac{1}{r_0^2} \right) (6C'Bt)^{\frac{1}{2}} \quad (20-a)$$

$$\frac{\Delta S}{S_0} = \frac{1}{r_0} (6C'Bt)^{\frac{1}{4}} \quad (20-b)$$

or  $\left( \frac{\Delta S}{S_0} \right)^4 = Ht : (h_0 > r_0)$

## 4. Results and Discussion

### 4-1 Volume and surface diffusion coefficients of Ni ion in $\text{NiAl}_2\text{O}_4$

-Volume diffusion-

Typical volume and surface diffusion profiles of nickel ion are displayed in Fig. 3-a, and 3-b. Volume diffusion coefficient was obtained by Eq. (4).  $\text{Erf}^{-1} \left( 1 - \frac{C_z}{C_0} \right)$  were plotted versus the volume diffusion depth  $Z$  in Fig. (4). From the least-squares-fits of the slope of these straight line, the volume diffusion coefficient  $D_v$  can be estimated.  $\log D_v$  were plotted versus the reciprocal absolute temperature in Fig. 5.

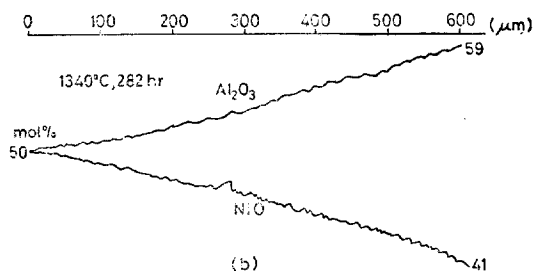
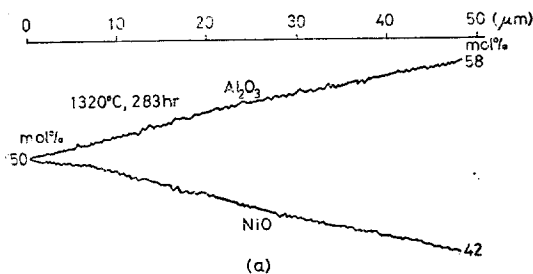


Fig. 3 Typical EPMA diagrams showing concentration gradient in (a) and on (b) the spinel layers

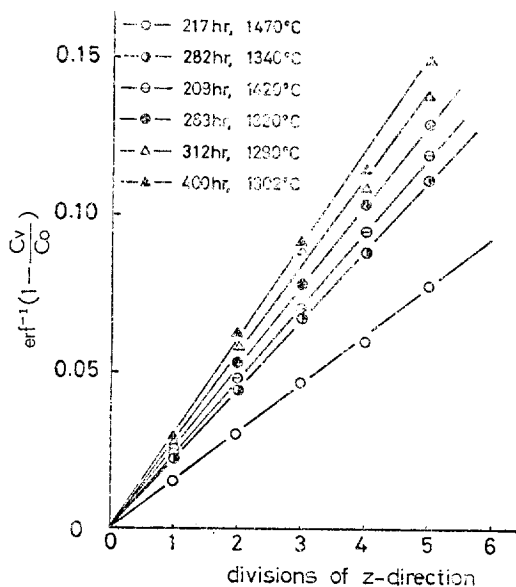


Fig. 4 The plot of  $\text{Erf}^{-1} \left( 1 - \frac{C_z}{C_0} \right)$  vs.  $Z$  (1 div. =  $8 \mu\text{m}$ )

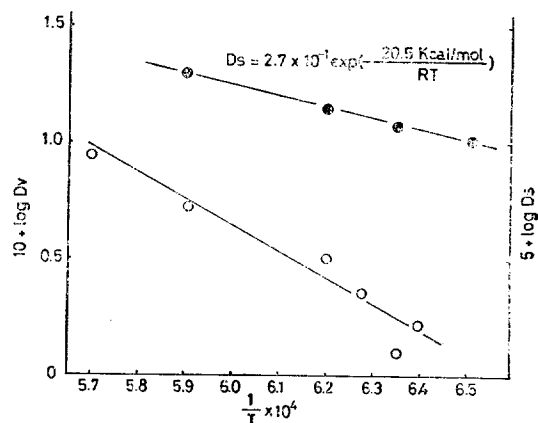


Fig. 5 Arrhenius plots of the volume diffusion  $D_v$  and surface  $D_s$  diffusion coefficient. The left-hand scale applies to  $D_v$ , the right-hand scale to  $D_s$ .

$1/T$  gives the activation energy of  $48.6 \pm 5.8$  Kcal/mol and pre-exponential value  $D_0 = 8.54 \times 10^{-4}$  cm<sup>2</sup>/sec for the volume diffusion of nickel ion in  $\text{NiAl}_2\text{O}_4$  and

$$D_v = 8.54 \times 10^{-4} \exp\left(-\frac{48.6 \pm 5.8 \text{ Kcal/mol}}{RT}\right)$$

This activation energy 48.6 Kcal/mol for volume diffusion of nickel ion in  $\text{NiAl}_2\text{O}_4$  is in good agreement with that of 40.2 Kcal/mol obtained by initial sintering method<sup>(6)</sup> and 52 Kcal/mol by tracer method<sup>(10)</sup> within experimental error.

Surface diffusion coefficient

In the calculation of surface diffusion coefficient by Eq. (8), logarithmic concentrations normalized with  $C_s(0, t_f)$  were plotted versus the surface diffusion length  $x$ , in Fig. 6. By measuring the slope of  $\log \frac{C_s}{C_0}$  vs.  $x$  at different temperature (Eq. (8)), the surface diffusion coefficients can be calculated as a function of temperature. A plot of  $\log D_s$  vs.  $\frac{1}{T}$  (Fig. 5) gives the activation energy ( $E_s = 20.5 \pm 1.2$  Kcal/mol) and frequency factor ( $D_{s0} = 2.7 \times 10^{-1}$  cm<sup>2</sup>/sec).

The surface diffusion coefficient as function of temperature is presented in

Fig. 5 and given by  $D_s = 2.7 \times 10^{-1} \exp\left(-\frac{20.5 \pm 1.2}{RT}\right)$

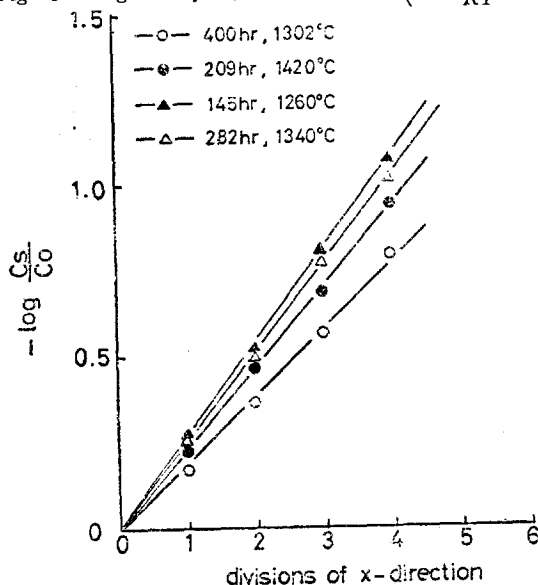


Fig. 6 The plot of  $\log\left(\frac{C_s}{C_0}\right)$  vs.  $x$  (1 div. = 96  $\mu\text{m}$ )

Kcal/mol). The surface activation energy 20.5 Kcal/mol is slightly different from that of the free sintering data of 29.6 Kcal/mol,<sup>(8)</sup> however, this activation energy 20.5 Kcal/mol agrees fairly good with that of sintering data 20.8 Kcal/mol<sup>(5)</sup>.

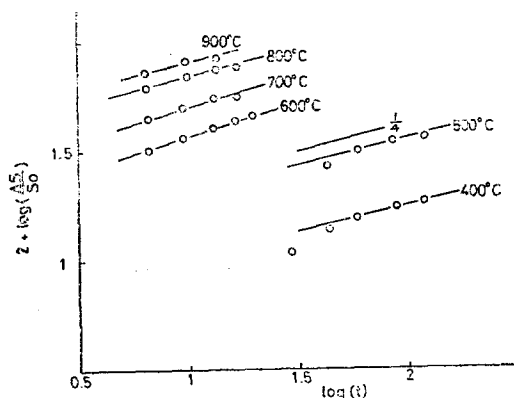


Fig. 7 Log plots of the relative surface area change for free sintering of ZnO at 25 torr  $\text{O}_2$

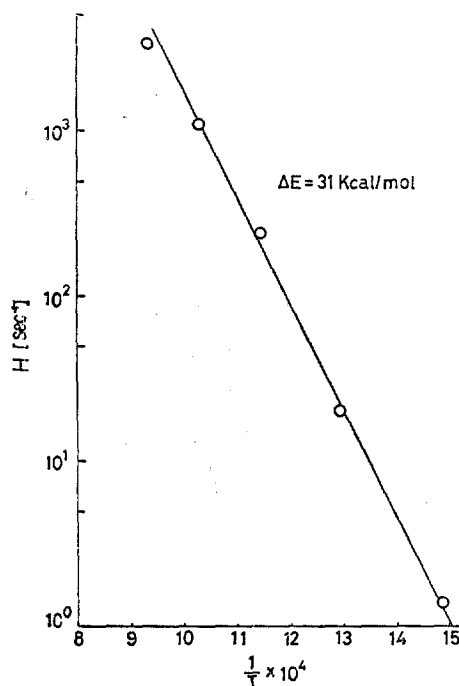


Fig. 8  $\log H$  vs.  $\frac{1}{T}$  for ZnO

#### 4-2 Application of confits model

Assuming the surface diffusion is predominant

throughout in the free sintering process of the powder particle, we can calculate the activation energy for the surface-self diffusion by measuring the change of BET surface area of powder particles as a function of free sintering time. A plot of  $\log\left(\frac{\Delta S}{S_0}\right)$  vs.  $\log t$  for  $\text{ZnO}^{(11)}$  is shown in Fig. 7. The activation energy for surface diffusion of ZnO can be estimated by Eq. (20-b).  $\log H$  was plotted vs.  $\frac{1}{T}$  in Fig. 8. The activation energy for surface diffusion of ZnO could not be shown in reference. However, the ratio of  $E_s/E_v$  ( $E_v=79$  Kcal/mol)<sup>(12)</sup> obtained in this study was reported equal to  $\frac{2}{5}$ . As a consequence, the activation energy 31 Kcal/mol for ZnO might be a reasonable value.

## 5. Conclusions

(1) During the spinel formation reaction in temperature range from 1260° to 1470°C, the volume and surface diffusion coefficients of nickel ion ( $D_v$ ,  $D_s$ ) obtained are:

$$D_v = 8.54 \times 10^{-4} \exp\left(-\frac{48.6 \pm 5.8 \text{ Kcal/mol}}{RT}\right)$$

$$D_s = 2.7 \times 10^{-1} \exp\left(-\frac{20.5 \pm 1.2 \text{ Kcal/mol}}{RT}\right) \text{ cm}^2/\text{sec}$$

(2) Assuming the surface diffusion is predominant

throughout in the free sintering process, the activation energy 31 Kcal/mol is obtained by measuring the change of BET surface area of zinc oxide powder particles.

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