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Normal grain growth in porous and dense compacts

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A rate equation of grain growth and a distribution function of grain radii were derived from the statistical viewpoint. The derived equation and function were successfully applied to the analysis of both the grain growth and grain radius distribution data in Cr-doped MgO. The diffusion coefficients of this sample were 10^3 times larger than the oxygen self-diffusion coefficients in pure MgO.

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1. Introduction

When a powder compact is heated, not only densification but also grain growth occurs. Many densification studies [1, 2] have been made by taking care of only the mass transfer from the interfacial area to the neck surface. The necessity of finding a new densification model, however, has been emphasized by several workers [3, 4] for describing the sintering of fine powder compacts. Recently, direct observation of the sintering processes [5] gave important evidence that the densification of fine particles is influenced by grain growth, that is, by the mass transfer across grain boundaries.

Burke [6], Feltham [7], and Hillert [8] have qualitatively derived the rate equations of a parabolic growth law for average grain size. Oel [9], and Tomandl [10] proposed a statistical approach to this problem, in which the theoretical treatment is mathematically equivalent to the theory of the Ostwald ripening of Wagner [11]. In contrast to these papers, the present study was made to characterize factors influencing grain growth of a single-oxide ceramic.

2. Diffusion paths

Fig. 1 shows a schematic arrangement of grains, in which a topological requirement may make a curved grain boundary between two grains with different sizes [6]. If grain growth takes place, the diffusion through paths 1 and 2 may be enhanced by that through path V because of the deviating local configuration at the intersection of two neck surfaces and the grain boundary from an equilibrium state. If the enhanced mass is so large that the mass through paths 3 and 4 can be negligible, the rate of densification [12] depends on that of grain growth.

3. Derivation of equations

3.1. A rate equation of grain growth

We make the following assumptions:

(1) Grain growth is rate-determined by the migration of grain boundaries.

(2) The normalized spatial distribution of grain radii $Z/Z_\mathrm{m} = f(r/r_\mathrm{m})$ is unchangeable during grain growth, where Z is the number of grains having a radius r and r_m is the radius in which Z has the maximum value Z_m.

From the Gibbs–Thompson relation [13], the difference in chemical potential $\Delta\mu$ between the adjacent interfaces of grains with radii r_1 and r_i may be given by

$$\Delta\mu = \Omega\gamma_{\mathrm{I}1i}\left(\frac{a_{1i}}{r_1} - \frac{b_{1i}}{r_i}\right), \tag{1}$$

where a_{1i} and b_{1i} are constants dependent on the topological situation around the grain r_1, $\gamma_{\mathrm{I}1i}$ is the interfacial energy and Ω is the atomic/ionic volume, respectively. The flux density j of atoms/

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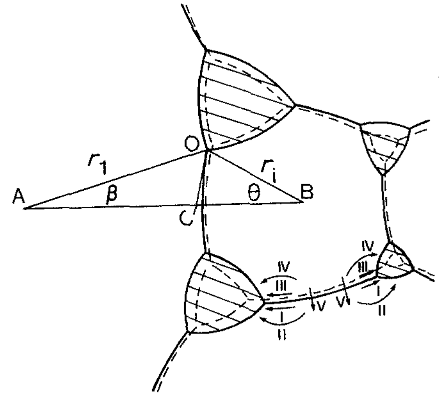

Figure 1 A model of the grain growth process in a porous body.

ions is calculated from Equation 1 and Fick's first law [14] is

$$j = \frac{\Omega D_{\mathrm{I}1i}\gamma_{\mathrm{I}1i}}{kTW_{\mathrm{I}1i}}\left(\frac{b_{1i}}{r_i} - \frac{a_{1i}}{r_1}\right), \qquad (2)$$

where $D_{\mathrm{I}1i}$ is the self-diffusion coefficient, k is Boltzmann's constant, T is the absolute temperature and $W_{\mathrm{I}1i}$ is the thickness of the grain boundary layer, respectively. If the interfacial area between these grains is given by $k_{\mathrm{I}1i}r_1^2$, the rate of volume change, $\mathrm{d}v_1/\mathrm{d}t$, in the grain r_1 is calculated as

$$\frac{\mathrm{d}v_1}{\mathrm{d}t} = \frac{\Omega}{kT}\int_0^\infty \sum_{i=1}^{N_1} \frac{\gamma_{\mathrm{I}1i}D_{\mathrm{I}1i}k_{\mathrm{I}1i}}{W_{\mathrm{I}1i}}\left(\frac{b_{1i}r_1^2}{r_i} - a_{1i}r_1\right) \times f\left(\frac{r_i}{r_\mathrm{m}}\right)\mathrm{d}r_i \bigg/ \int_0^\infty f\left(\frac{r}{r_\mathrm{m}}\right)\mathrm{d}r, \qquad (3)$$

where $k_{\mathrm{I}1i}$ is a constant dependent on the topological situation around the grain r_1, and N_1 is the contact number of the grain r_1. The sum of $\mathrm{d}v_1/\mathrm{d}t$ in growing grains $\mathrm{d}V/\mathrm{d}t$ is equal to

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\Omega Z_\mathrm{m} r_\mathrm{m}^2}{kT}\int_{u_0}^\infty (B_1u_1^2 - A_1u_1)f(u_1)\,\mathrm{d}u_1, \qquad (4)$$

where r_1/r_m is replaced by u_1, A_1 is equal to

$$\left[\int_0^\infty \left(\sum_{i=1}^{N_1}\gamma_{\mathrm{I}1i}D_{\mathrm{I}1i}k_{\mathrm{I}1i}a_{1i}f(u_i)/W_{\mathrm{I}1i}\right)\mathrm{d}u_i\right] \times \left[\int_0^\infty f(u)\,\mathrm{d}u\right]^{-1},$$

B_1 is equal to

$$\left[\int_0^\infty \left(\sum_{i=1}^{N_1}\gamma_{\mathrm{I}1i}D_{\mathrm{I}1i}k_{\mathrm{I}1i}b_{1i}f(u_i)/u_iW_{\mathrm{I}1i}\right)\mathrm{d}u_i\right] \times \left[\int_0^\infty f(u)\,\mathrm{d}u\right]^{-1}$$

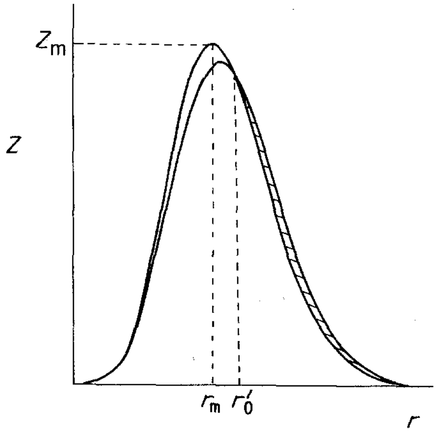

Figure 2 Variation of statistical distribution curves of grain radii over a short time interval.

and u_0 is the value of r_1/r_m in which $\mathrm{d}v_1/\mathrm{d}t$ is equal to zero, respectively.

An average radius of grains R is given by

$$R = r_\mathrm{m}\left[\int_0^\infty uf(u)\,\mathrm{d}u\right]\left[\int_0^\infty f(u)\,\mathrm{d}u\right]^{-1}. \qquad (5)$$

From assumption 2, the integrated terms in Equation 5 should be constants irrespective of r_m, and replacing $\int_0^\infty uf(u)\,\mathrm{d}u/\int_0^\infty f(u)\,\mathrm{d}u$ by k_1, $R = k_1r_\mathrm{m}$. The total volume of grains V_0 in the compact is equal to $Z_\mathrm{m}r_\mathrm{m}^4\int_0^\infty k_\mathrm{v}u^3f(u)\,\mathrm{d}u$, where k_v is the shape factor related to the volume characteristics of a grain. Replacing $\int_0^\infty k_\mathrm{v}u^3f(u)\,\mathrm{d}u$ by k_2, we obtain

$$Z = \frac{V_0}{k_2r_\mathrm{m}^4}f\left(\frac{r}{r_\mathrm{m}}\right). \qquad (6)$$

The value of r calculated from $\mathrm{d}Z/\mathrm{d}R = 0$ is equal to the radius r_0', in which Z is unchangeable with a slight increase in $\mathrm{d}R$. The $\mathrm{d}V$ value should be equal to the total volume of grains in the shaded region shown in Fig. 2, and

$$\frac{\mathrm{d}V}{\mathrm{d}R} = \frac{V_0}{k_2R}\int_{u_0'}^\infty k_\mathrm{v}u^3\left[-4f(u) - u\frac{\mathrm{d}f(u)}{\mathrm{d}u}\right]\mathrm{d}u \qquad (7)$$

is obtained, where u_0' is equal to r_0'/r_m. From Equations 4 and 7, one can derive the rate equation of grain growth

$$R\,\mathrm{d}R = \frac{\Omega k_1^2\int_u^\infty (Bu^2 - Au)f(u)\,\mathrm{d}u\,\mathrm{d}t}{kT\int_{u_0'}^\infty k_\mathrm{v}u^3\left[-4f(u) - u\dfrac{\mathrm{d}f(u)}{\mathrm{d}u}\right]\mathrm{d}u}. \qquad (8)$$

3.2. A distribution function of grain sizes

A distribution function of grain sizes is obtained from the solution of the continuity equation [14]

$$\frac{\partial Z_m f(r/r_m)}{\partial t} = -\frac{\partial [Z_m f(r/r_m) \times \dot{r}]}{\partial r}. \quad (9)$$

The function $f(r/r_m)$ has, by assumption 2, only one variable r/r_m, and so $\partial Z_m f(r/r_m)/\partial t = -(V_0/k_2 r_m^5)(\mathrm{d}r_m/\mathrm{d}t)\,[4f(r/r_m) + (r/r_m)\,\mathrm{d}f(r/r_m)/\mathrm{d}(r/r_m)]$, and $\partial[Z_m f(r/r_m) \times \dot{r}]/\partial r = (V_0/k_2 r_m^5)\,[\dot{r}\,\mathrm{d}f(r/r_m)/\mathrm{d}(r/r_m) + r_m f(r/r_m)\,\partial\dot{r}/\partial r]$. Using these relations and Equations 3 ($\mathrm{d}v = 3k_v r^2\,\mathrm{d}r$), 8 and 9, one can derive

$$\left(Cu - \frac{B}{3k_v} + \frac{A}{3k_v u}\right)\frac{\mathrm{d}f(u)}{\mathrm{d}u} = \left(\frac{\partial}{\partial u}\left(\frac{B}{3k_v}\right) - \frac{\partial}{\partial u}\left(\frac{A}{3k_v u}\right) - 4C\right) f(u), \quad (10)$$

where C is equal to $[\int_u^\infty (Bu^2 - Au) f(u)\,\mathrm{d}u]\,[\int_{u_0'}^\infty k_v u^3(-4f(u) - u\,\mathrm{d}f(u)/\mathrm{d}u)\,\mathrm{d}u]^{-1}$. By the condition $\mathrm{d}f(u)/\mathrm{d}u = 0$ at $u = 1$, $4C$ is equal to

$$\left[\frac{\partial}{\partial u}\left(\frac{B}{3k_v}\right)\right]_{u=1} - \left[\frac{\partial}{\partial u}\left(\frac{A}{3k_v u}\right)\right]_{u=1}.$$

If A/k_v and B/k_v are independent of r (assumption 4), the integration of Equation 10 by replacing B/A with K_R results in

$$f(u) = \frac{C_0 u}{(u^2 - 4K_R u + 4)^{5/2}} \times \exp\left[\frac{3K_R}{\sqrt{(1 - K_R^2)}} \tan^{-1}\frac{(u - 2K_R)}{2\sqrt{(1 - K_R^2)}}\right], \quad (11)$$

where C_0 is a constant.

4. Experimental details

Pure magnesium chips (99.99%)* were dissolved in a high purity HCl† aqueous solution, to which a high purity NH_4OH‡ aqueous solution was added to obtain magnesium hydroxide as a precipitate. The resulting precipitate was thoroughly wet-mixed with 4 mol% reagent grade $Cr(NO_3)_3 \cdot 9H_2O$ and dried at 70° C. The dried cakes were crushed lightly, calcined at 900° C for 16 h in flowing O_2 gas, hydrostatically pressed at 5000 kg cm^{-2}, and fired at 1500 and 1600° C for a given period in vacuum. The fired compacts were ground on successively finer grades of SiC powder, lapped on a high-speed wheel for 15 min using a 1 μm diamond slurry, and thermally etched at 1400° C for 2 h in flowing O_2 gas. Scanning electron microscopy was used to determine grain sizes.

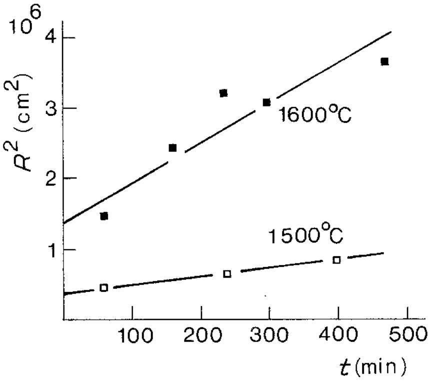

Figure 3 Grain growth of Cr-doped MgO as a function of time.

5. Results

It is very difficult to polish a porous compact, which is hardly beneficial for the quantitative examination of the present theory. All the fired samples have relative densities larger than 98% of the theoretical. Fig. 3 shows the isothermal grain growth in the form R^2 against time for Cr-doped MgO. As can be seen, grain-growth data follow the square kinetics $R^2 - R_0^2 = Kt$ and the rate constants K were equal to 1.9×10^{-11} cm^2 sec^{-1} at 1500° C and 9.8×10^{-11} cm^2 sec^{-1} at 1600° C.

Fig. 4 shows two examples of the normalized planar distribution of grain radii. The respective data closely fit the experimental equation (the dotted line) proposed by Aboav and Langdon [15]

$$Z = Z_m \exp\{-\alpha^2[(r/r_m)^{1/2} - 1]^2\}, \quad (12)$$

especially in the range $r/r_m > 1$, and α was equal to 3.8 independent of the extent of grain growth.

6. Discussion

The experimental determination of the function $f(r/r_m)$ is very laborious, but the planar ones $\phi(r/r_m)$ were reliable [15–17]. Kendall and Moran [18] gave the important relation between those functions for a polycrystalline body having spherical grains

$$\phi\left(\frac{r}{r_m}\right) = \frac{r}{R}\int_r^\infty \frac{f(x/r_m)\,\mathrm{d}x}{\sqrt{(x^2 - r^2)}}. \quad (13)$$

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†Fe < 0.05, Zn, Hg < 0.02, Pb, Cr, Mn, Co < 0.01 (ppm); Wako Pure Chemical Industry Ltd, Osaka, Japan.

‡Na < 0.5, Ca, Mg, Fe < 0.1, Ni, Cu < 0.04 (ppm); Wako Pure Chemical Industry Ltd, Osaka, Japan.

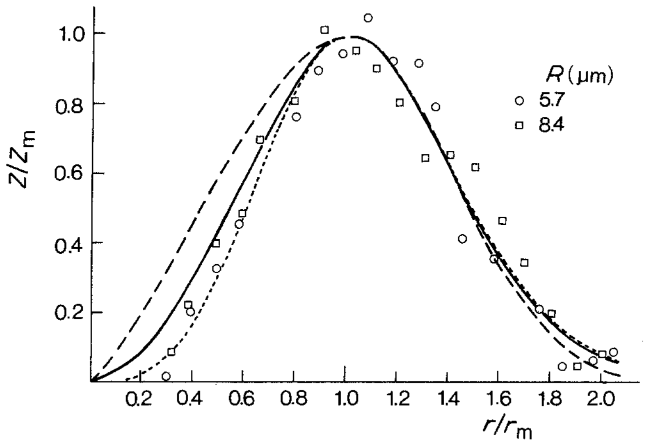

Figure 4 Variation of Z/Z_m with r/r_m. The broken line was obtained from Equation 14, the dotted one from Equation 12 and the solid one from Equation 15.

Since a sintered body, however, consists of grains having various polygonal shapes, the calculated value of $\phi(r/r_m)$ in the region $r < r_m$ should be very over estimated as shown in Fig. 5. We conveniently assume that all grains have the same shape as shown in Fig. 5, and that the probability of a plane cutting a grain with radius x is proportional to ∠DOF/∠DOE in the range $0 < r < x/2$. A more reasonable $\phi(r/r_m)$ is given by

$$\phi\left(\frac{r}{r_m}\right) = \frac{r}{R}\int_r^{2r} \frac{f(x/r_m)\,\mathrm{d}x}{\sqrt{(x^2-r^2)}} + \frac{\cot^{-1}[(x/r)-\tan 30]}{30} \times \frac{r}{R}\int_{2r}^{\infty} \frac{f(x/r_m)\,\mathrm{d}x}{\sqrt{(x^2-r^2)}}. \tag{14}$$

The broken line in Fig. 4 is of $\phi(r/r_m)$ calculated from Equation 14 with Equation 11 and $K_R = 0.93$. Fig. 6 shows the distribution curves obtained from reported data [15, 16]. The calculated distribution curves fit the experimental data well in the range $u > 1$, but are appreciably larger than those for $u < 1$. This means that the reducing speed of smaller grains in size is very much higher than those calculated from Equation 3 based on the generally accepted assumption 4 [9] in practice. Estimated from Equation 10 by the method of trial and error,

$$\left(Cu - \frac{B}{3k_v} + \frac{A}{3k_v u}\right)\frac{\mathrm{d}f(u)}{\mathrm{d}u} = \left(\frac{4A}{3k_v u^2} - \frac{3B}{3k_v u} - 4C\right) f(u)$$

is integrated as

$$f(u) = \frac{C_0 u^4}{(\{u - [2K_R/(4-3K_R)]^2 + [4(4-3K_R+K_R^2)/(4-3K_R)^2]\})^4} \times \exp\left[-\frac{6K_R}{\sqrt{(4-3K_R-K_R^2)}}\tan^{-1}\frac{(4-3K_R)u-2K_R}{2\sqrt{(4-3K_R-K_R^2)}}\right]. \tag{15}$$

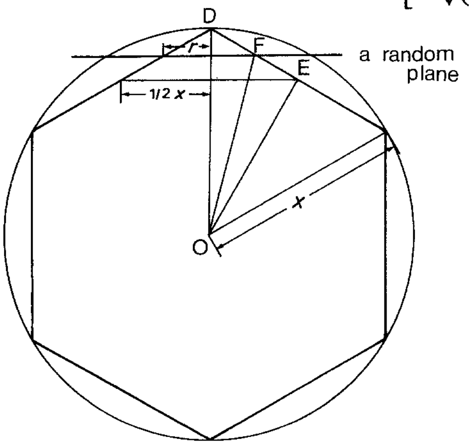

Figure 5 The geometry involved in the intersection of a grain by a random plane.

The solid lines in Figs 4 and 6 prove the successful result of the foregoing calculation with Equation 15 and $K_R = 0.85$ or $= 0.6$, respectively.

The spread of the distribution curves concerned increases with decreasing K_R, the value of which depends on the properties of grain boundaries (factors a_{1i}, b_{1i}, k_{11i}, γ_{11i}, D_{11i} and W_{11i}). If pores and/or impurities have statistically a slight influence on the development of a geometrical structure, K_R should be constant during isothermal growth. These discussions may be supported by Aboav and Langdon's data [15, 16] (the constant α and the empirical linear relation $R = k_c(n-2)$ between R and the number of sides n with a suitable constant k_c).

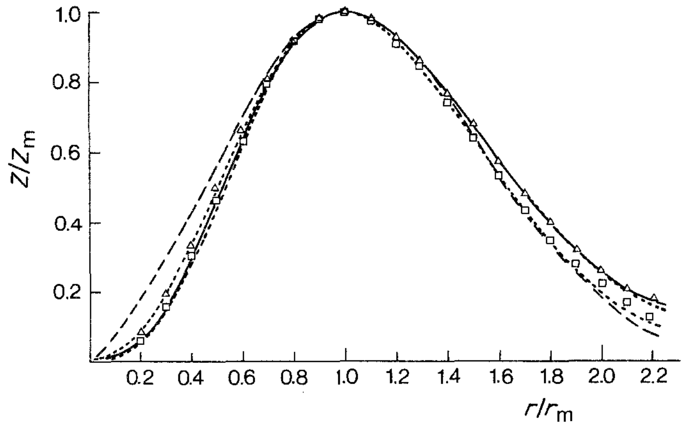

Figure 6 Variation of the functions $\phi(r/r_m)$, which are drawn to have the same maximum value. The broken line was obtained from Equation 14, the dotted one from Equation 12 and the solid one from Equation 15. △ - - - $\alpha = 2.8$ [15], □ - - - $\alpha = 3.1$ [16].

If the variation of γ_I, D_I or W_I is negligible during grain growth, and if a geometrical arrangement can be expressed as shown in Fig. 1 ($\angle AOC = \angle BOC$), one can calculate a rough D_I value from Equation 8 by using estimated (k_{I1i}, γ_I, W_I), measured (t, T, K_R) and known (k, Ω) values. $\Sigma_{i=1}^{N_1} k_{I1i}$ is nearly equal to $3k_v$. From the relation $\angle AOC = \angle BOC$, $a (= 4/b)$ is calculated as $(2 \cos \beta/2)/(\cos \theta/2)$, which is virtually a constant $(= 2)$ for any pair of grains. Since Cr-doped MgO should be single-phase for the high solubility of Cr in MgO [19], the W_I value was estimated as 0.5 nm. The reported ratios of interfacial energy to surface energy [20, 21] are 0.2–0.5 for oxide ceramics, in general. The surface energy of MgO is evaluated as $1000\,\text{erg cm}^{-2}$ [22], and we roughly estimated the γ_I value of the present sample as $300\,\text{erg cm}^{-2}$. The ratio of the integrated terms in Equation 8 was calculated from the relations $C = A(4 - 3K_R)/12k_v$ and $A = 6D_I\gamma_I k_v/W_I$ instead of integration of those terms. Fig. 7 shows the calculated D_I values together with oxygen self-diffusion coefficients in pure MgO [23]. The ratio ($\approx 10^3$) between those values is nearly equal to that between the rate constants of the present and undoped ($4 \times 10^{-15}\,\text{cm}^2\,\text{sec}^{-1}$ at 1500° C) MgO [24].

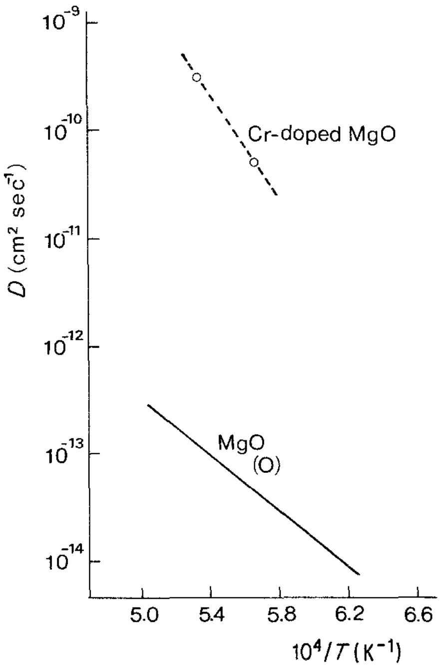

Figure 7 Comparison of the calculated diffusion coefficients with the oxygen self-diffusion coefficients in MgO.

Fig. 8 shows reported data [4] on grain growth of a relatively porous BeO (a value of relative density ρ varied from 57% to 94% of theoretical). The drawn curve was obtained from Equation 8 with the suitable rate constant and relations $\log \rho(1-\rho_0)/\rho_0(1-\rho) = k_e \log (R/R_0)$ and $\Sigma_{i=1}^{N_1} k_{I1i} = 4k_p(1-\rho)$ [12], where ρ_0 and R_0 are the initial values of ρ and R, and k_e and k_p are experimentally obtained constants, respectively. The slope of the drawn curve in the low-porosity region is close to $\frac{1}{2}$, which is in accordance with the present as well as reported [25, 26] grain-growth data. These results mean that pores have an unnoticeable effect on grain growth, which is the opposite to other data (slopes $< \frac{1}{3}$) reported by several workers, notably Kingery and François [27], and Gupta [28]. For these different results, no explanation has yet been given.

7. Conclusions

A rate equation of grain growth has been derived statistically for oxide ceramics with various relative densities, and the diffusion coefficients of Cr-doped MgO calculated from this equation were 10^3 times larger than the oxygen self-diffusion coefficients in pure MgO.

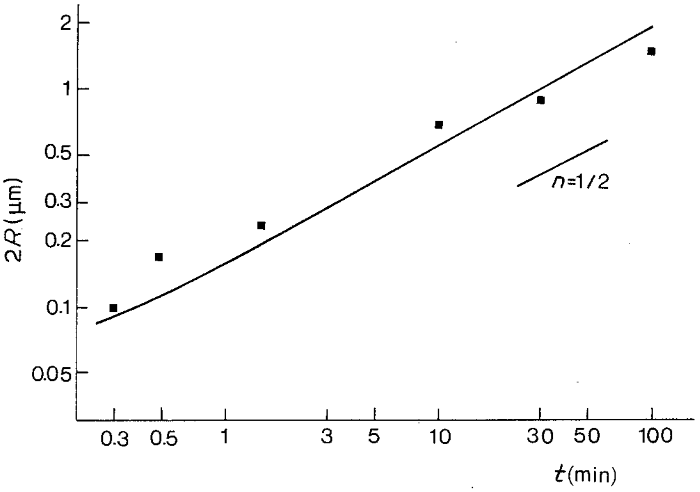

Figure 8 Grain growth of relatively porous BeO.

The spatial and planar distribution functions of grain radii were derived from the continuity equation. The spread of the size distribution depends on the properties of grain boundaries.

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