

## 소성변형의 분자론 (제2보). 응용

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### Molecular Theory of Plastic Deformation (II). Applications

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**요 약.** 소성변형에 대한 저자들의 이론(제 1 보)<sup>1</sup>을 요업재료, 금속, 합금 및 단결정들에 적용하였다. 그 결과 다중 결정에서는 dislocation 운동과 grain boundary 운동이 실험조건에 따라 함께 또는 분리되어 나타나는 반면 단결정에서는 dislocation 운동만 나타났다. 유동식에 나타나는 파라미터 ( $\alpha_{d1}$ ,  $1/\beta_{d1}$ )와 ( $\alpha_{gj}/X_{gj}$ ,  $1/\beta_{gj}$ ) ( $j=1$  혹은  $2$ ) 및 활성화엔탈피  $\Delta H_{ik}^{\ddagger}$  ( $k=d$  혹은  $g$ )를 구하여 예측한 소성변형은 실험과 잘 일치함을 보았다. 여기서 첨자  $d1$ 는 첫번째의 dislocation 유동단위,  $gj$ 는  $j$  번째 grain boundary 유동단위를 나타낸다. 활성화엔탈피에 대하여  $\Delta H_{d1}^{\ddagger}$ 는 bulk의 자체확산에 대한 활성화엔탈피와 일치하고  $\Delta H_{g1}^{\ddagger}$ 는 grain boundary 자체확산에 대한 활성화엔탈피와 일치하였다. 이 사실은 저자들의 이론의 정당성을 보이고 있다.

**ABSTRACT.** The authors' theory developed in the preceding Paper 1<sup>1</sup> was applied to plastic deformation of ceramics, metals, alloys and single crystals. For polycrystalline substances, the flow mechanisms due to dislocation movement and grain boundary movement appear together or separately according to the experimental conditions whereas for single crystals, only the mechanism of dislocation movement appears. The parameters appearing in the flow equations ( $\alpha_{d1}$ ,  $1/\beta_{d1}$ ) and ( $\alpha_{gj}/X_{gj}$ ,  $1/\beta_{gj}$ ) ( $j=1$  or  $2$ ), and the activation enthalpies  $\Delta H_{ik}^{\ddagger}$  ( $k=d$  or  $g$ ) were determined and tabulated. Here, the subscript  $d1$  indicates the first kind of dislocation flow units and  $gj$  expresses the  $j$ th kind of grain boundary flow units.

The predictions of the theory were compared with experiment with good agreement. Concerning the activation enthalpies, it was found that  $\Delta H_{d1}^{\ddagger} > \Delta H_{g1}^{\ddagger}$  and that the former agrees with the activation enthalpy for bulk self-diffusion whereas the latter agrees with the activation enthalpy for grain boundary self-diffusion. These facts support the adequacy of the authors' theory which is considered as a generalized theory of plastic deformation.

#### INTRODUCTION

In the preceding Paper I,<sup>1</sup> we derived general equations for total stress  $f$  and shear rate  $\dot{s}$ ,

$$\begin{aligned} f &= f_d = \sum_i X_{di} f_{di} \\ &= f_g = \sum_j X_{gj} f_{gj} \end{aligned} \quad (1)$$

$$\dot{s} = \frac{1}{\beta_{di}} \sinh\left(\frac{\alpha_{di}}{X_{di}} X_{di} f_{di}\right) + \frac{1}{\beta_{gj}} \sinh\left(\frac{\alpha_{gj}}{X_{gj}} X_{gj} f_{gj}\right) \quad (2)$$

where  $f_d$  and  $f_g$  are the stress on a dislocation shear plane and on a grain boundary shear plane, respectively;  $f_{kn}$  is the stress acting on flow units of kind  $n$  ( $i$  or  $j$ ) of flow type  $k$  ( $d$  or  $g$ );  $X_{kn}$  is the fraction of area on a shear surface occupied by flow units of kind  $n$  of type  $k$ ;  $\alpha_{kn} = (\lambda\lambda_2\lambda_3)_{kn}/(2kT)$ ;  $\beta_{kn} = 1/[(\lambda/\lambda_1)2k']$ ;  $k'$  is the rate constant for the flow process when there is no stress applied;  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ , and  $\lambda$  are the molecular parameters in Eyring's viscosity formula;<sup>2</sup> and the subscript  $kn$  outside the parentheses indicates that the inside quantities belong to flow units  $kn$  ( $kn = di$  or  $gj$ ). By various combination of flow units  $kn$ , many kinds of plastic deformation patterns would be produced from Eqs. (1) and (2). In Paper 1, the four cases which are important in practice were considered. In this paper, the flow equations developed in Paper 1 will be applied to experimental deformation data, and the results will be discussed.

### SYNOPSIS OF THE THEORY

It is appropriate in the beginning to make a brief review on the results in Paper 1.

The simplest case is Case 1, where a single kind of flow units is acting. The creep equations for dislocation movement are

$$f = f_d = X_{d1} f_{d1} = f_{d1},$$

$$\dot{s} = \frac{1}{\beta_{d1}} \sinh\left(\frac{\alpha_{d1}}{X_{d1}} X_{d1} f_{d1}\right) = \frac{1}{\beta_{d1}} \sinh(\alpha_{d1} f) \quad (3a)$$

And similar equations hold for grain boundary movement:

$$f = f_g = X_{g1} f_{g1} = f_{g1},$$

$$\dot{s} = \frac{1}{\beta_{g1}} \sinh\left(\frac{\alpha_{g1}}{X_{g1}} X_{g1} f_{g1}\right) = \frac{1}{\beta_{g1}} \sinh(\alpha_{g1} f) \quad (3b)$$

The next case of interest is Case 2 where all the flow units of a given type are connected in parallel. The corresponding flow equations for dislocation movement are

$$f = \sum_i^n X_{di} f_{di} \quad (4a)$$

$$\dot{s} = \frac{1}{\beta_{di}} \sinh\left(\frac{\alpha_{di}}{X_{di}} X_{di} f_{di}\right)$$

and for grain boundary movement, the equations are

$$f = \sum_j^m X_{gj} f_{gj} \quad (4b)$$

$$\dot{s} = \frac{1}{\beta_{gj}} \sinh\left(\frac{\alpha_{gj}}{X_{gj}} X_{gj} f_{gj}\right)$$

When  $m=2$ , the total stress  $f$  is calculated by

$$f = \frac{X_{k1}}{\alpha_{k1}} \sinh^{-1}(\beta_{k1} \dot{s}) + \frac{X_{k2}}{\alpha_{k2}} \sinh^{-1}(\beta_{k2} \dot{s}) \quad (4c)$$

which is derived from Eqs. (4a) and (4b),  $k$  being equal to  $d$  or  $g$ .

Case 3 deals with the case where a single kind of dislocation flow units and a single kind of grain boundary flow units are connected in series. The flow equations are

$$f = f_d = X_{d1} f_{d1} = f_{d1} = f_g = X_{g1} f_{g1} = f_{g1} \quad (5)$$

and

$$\dot{s} = \frac{1}{\beta_{d1}} \sinh(\alpha_{d1} f) + \frac{1}{\beta_{g1}} \sinh(\alpha_{g1} f) \quad (6)$$

The most complicated case is Case 4 where a single kind of dislocation flow units is connected with a system in which two kinds of grain boundary flow units are connected in parallel. The corresponding creep equations are

$$f = f_d = X_{d1} f_{d1} = f_{d1} = f_g = X_{g1} f_{g1} + X_{g2} f_{g2} \quad (7)$$

and

$$\dot{s} = \frac{1}{\beta_{d1}} \sinh(\alpha_{d1} f) + \frac{1}{\beta_{g2}} \sinh\left(\frac{\alpha_{g2}}{X_{g2}} X_{g2} f_{g2}\right) \quad (8)$$

where  $X_{g2}f_{g2}$  can be calculated from the relation

$$\frac{\sinh\left[\frac{\alpha_{g1}}{X_{g1}}(f - X_{g2}f_{g2})\right]}{\sinh\left(\frac{\alpha_{g2}}{X_{g2}}X_{g2}f_{g2}\right)} = \frac{\beta_{g1}}{\beta_{g2}} \equiv C \quad (9)$$

In order to test our theory, it will be necessary to determine the parameters appearing in Eqs. (3), (4), (6) and (8), and to calculate  $\dot{s}$  from these equations. The predicted  $\dot{s}$  will be compared with experiment, the good agreement being the justification for our theory. In the present paper, all the parameters were determined by using the method described in Paper 1.

## APPLICATIONS

1. **Magnesia.** Hensler *et al.*<sup>3</sup> studied the compressive creep behaviour of cylindrical MgO polycrystals (10 mm diameter, 25 mm length, 13 to 68 $\mu$  grain size). The experimental data of  $f$  vs.  $-\ln \dot{s}$  are shown in Fig. 1.

Our analysis showed that the pattern of the curve at 1400°C in Fig. 1 belongs to Case 3

which is the series connection of disln. 1 and GB1, where disln. 1 and GB1 denote dislocation flow unit 1 and grain boundary flow unit 1, respectively. The parameters  $\alpha_{k1}$  and  $1/\beta_{k1}$  ( $k=d$  or  $g$ ) determined by the method stated in Paper 1 are tabulated in Table 1.

The theoretical curves were calculated from Eq. (6) by using the parameters in Table 1. It is worthy of note that the theoretical curves for 1300°C and 1500°C in Fig. 1 were obtained from the parameters of  $\alpha_{k1}$  and  $1/\beta_{k1}$  in Table 1 at 1400°C and from  $\Delta H_{k1}^*$  ( $k=d$  or  $g$ ) in Table 5. The value of  $\Delta H_{k1}^*$  was determined by using the method detailed in Paper 1. The experimental data are in good agreement with the theoretical curves. This fact indicates the adequacy of the Hahn-Ree-Eyring theory.<sup>4</sup>

Hensler *et al.*<sup>3</sup> observed no structural change and no increase in porosity with the creep deformation, and noted especially that the grains did not change measurably in the length-to-width ratio with overall compressive deformation of the specimen as large as 40%. Thus

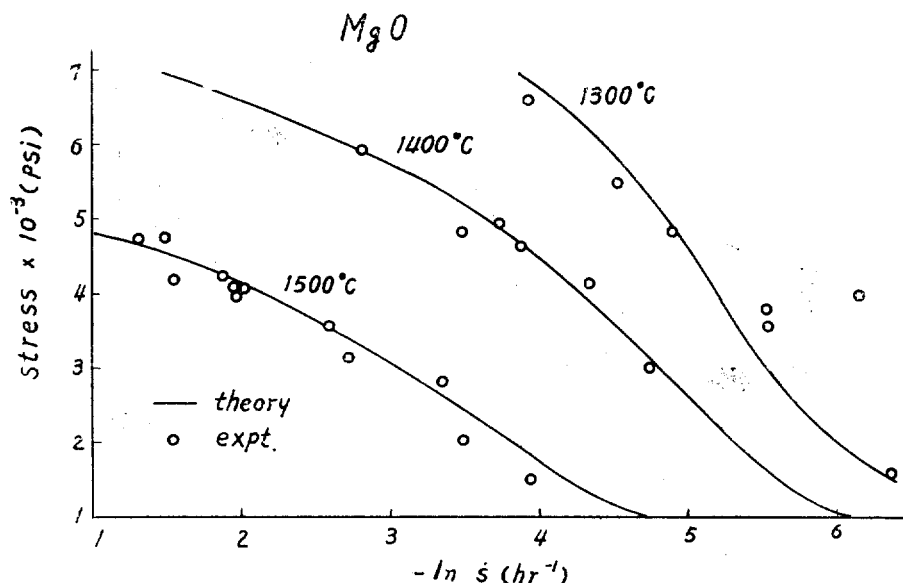


Fig. 1. Creep curves for MgO polycrystals. Curves for 1300°C and 1500°C were obtained from the flow parameters at 1400°C (Table 1) and  $\Delta H_{k1}^*$  ( $k=d$  or  $g$ ) (Table 5).

Table 1. Flow parameters for polycrystals of ceramics.

Sample	$\alpha_{g1}^{-1}$ (psi) <sup>-1</sup>	$\alpha_{g1}^{-1}$ (psi) <sup>-1</sup>	$1/\beta_{d1}$	$1/\beta_{g1}$	Temp. (°C)	Figure
MgO (13~68 $\mu$ )	$1.4 \times 10^{-3}$	$1.75 \times 10^{-4}$	$3.88 \times 10^{-4} \text{ hr}^{-1a}$	$2.06 \times 10^{-2} \text{ hr}^{-1a}$	1500	Fig. 1
MgO (13~68 $\mu$ )	$1.4 \times 10^{-3}$	$1.75 \times 10^{-4}$	$2.53 \times 10^{-5} \text{ hr}^{-1}$	$1.26 \times 10^{-2} \text{ hr}^{-1}$	1400	Fig. 1
MgO (13~68 $\mu$ )	$1.4 \times 10^{-3}$	$1.7 \times 10^{-4}$	$1.17 \times 10^{-6} \text{ hr}^{-1a}$	$6.95 \times 10^{-3} \text{ hr}^{-1a}$	1300	Fig. 1
YSZ (17 $\mu$ )	$8.47 \times 10^{-4}$	$3.79 \times 10^{-4}$	$2.64 \times 10^{-6} \text{ hr}^{-1}$	$5.56 \times 10^{-5} \text{ hr}^{-1}$	1485	Fig. 2
SSZ (1 $\mu$ )		$\left\{ \begin{array}{l} 2.21 \times 10^{-4b} \\ 1.64 \times 10^{-3c} \end{array} \right.$		$\left\{ \begin{array}{l} 3.18 \times 10^{-1} \text{ hr}^{-1} \\ 4.76 \times 10^{-3} \text{ hr}^{-1d} \end{array} \right.$	1378	Fig. 2
Al <sub>2</sub> O <sub>3</sub> (50 $\mu$ )	$4.95 \times 10^{-2}$	$\left\{ \begin{array}{l} 3.44 \times 10^{-3b} \\ 1.19 \times 10^{-2c} \end{array} \right.$	$1.49 \times 10^{-29} \text{ hr}^{-1}$	$\left\{ \begin{array}{l} 1.00 \times 10^{-2} \text{ hr}^{-1} \\ 6.02 \times 10^{-7} \text{ hr}^{-1d} \end{array} \right.$	1800	Fig. 3
Al <sub>2</sub> O <sub>3</sub> (34 $\mu$ )		$3.15 \times 10^{-4}$		$1.37 \times 10^{14} \text{ hr}^{-1d}$	1800	Fig. 3'
Al <sub>2</sub> O <sub>3</sub> (7 $\mu$ )	$6.00 \times 10^{-4}$	$4.20 \times 10^{-5}$	$2.72 \times 10^{-11} \text{ min}^{-1}$	$1.01 \times 10^{-3} \text{ min}^{-1}$	1500	Fig. 3
Al <sub>2</sub> O <sub>3</sub> (7 $\mu$ )	$6.00 \times 10^{-4}$	$4.20 \times 10^{-5}$	$3.07 \times 10^{-1} \text{ min}^{-1a}$	$5.67 \times 10^{-3} \text{ min}^{-1a}$	1600	Fig. 3

<sup>a</sup>Values obtained by substituting  $\Delta H_{ii}^{\ddagger}$  ( $k=d$  or  $g$ ) (Table 5) to Eqs. (15a) and (15b) of reference 1. <sup>b</sup>This value represents  $\alpha_{g1}/X_{g1}$ . <sup>c</sup>This value represents  $\alpha_{g2}/X_{g2}$ . <sup>d</sup>This value represents  $1/\beta_{g2}$ . <sup>e</sup>Parameters obtained from the curve  $f$  vs.  $-\ln Z$  where  $Z = \dot{\epsilon} \exp(\Delta H^{\ddagger}/RT)$ .

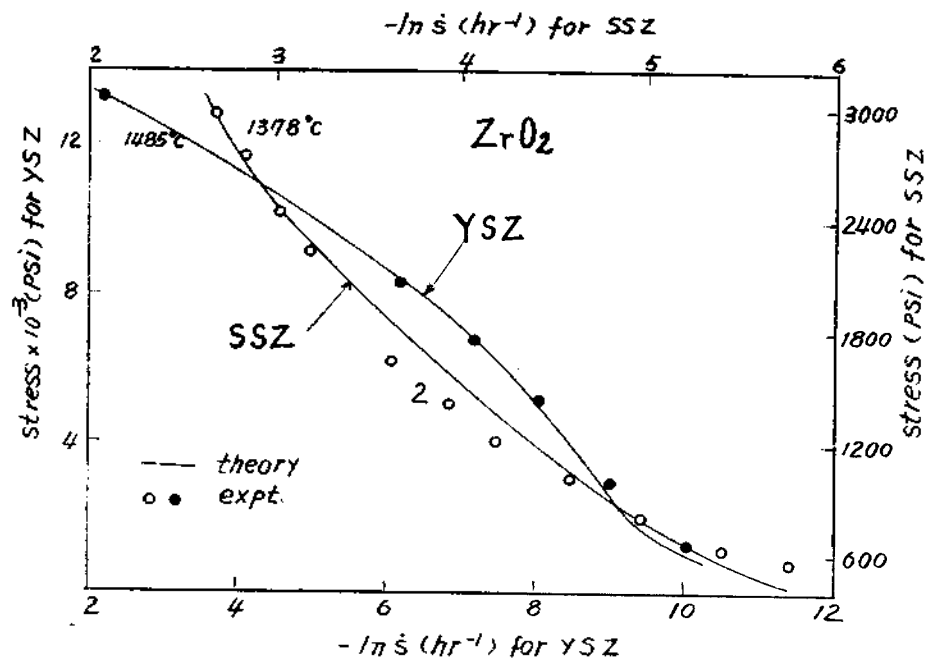


Fig. 2. Creep curves for ZrO<sub>2</sub> polycrystals: Curve 1, yttria stabilized zirconia (YSZ). Curve 2, scandia stabilized zirconia (SSZ).

Hensler concluded that creep in MgO appears to occur by extensive grain boundary sliding. According to our result, however, the creep deformation occurs not only by the grain boundary movement, but also by the dislocation

movement.

**2. Zirconia.** Evans *et al.*<sup>5</sup> observed the compressive creep of scandia-stabilized zirconia (SSZ) and yttria-stabilized zirconia (YSZ). The specimens were cylinders (0.2" diameter, 0.4"

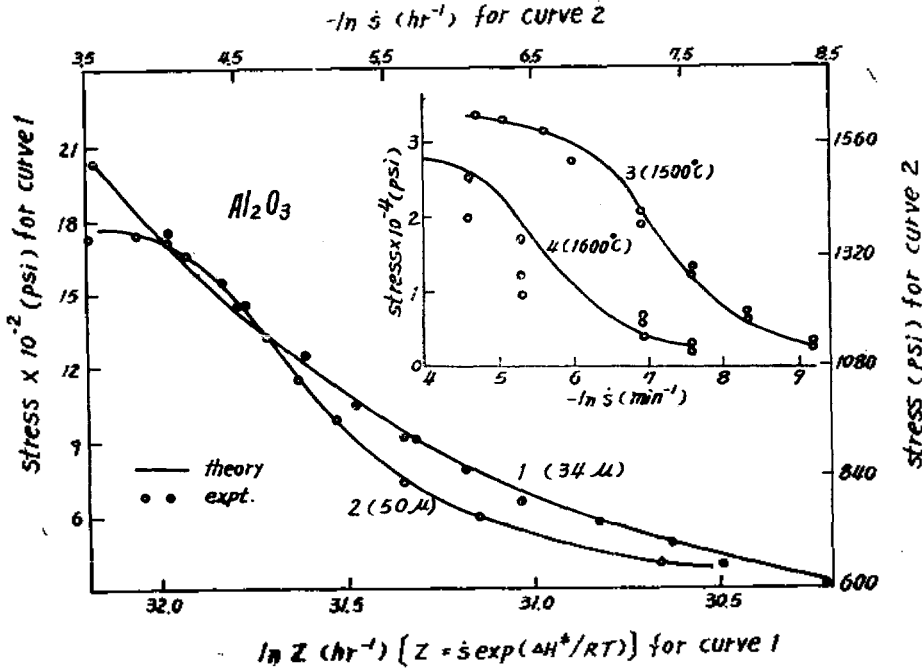


Fig. 3. Creep curves for  $Al_2O_3$  polycrystals of different grain sizes and temperatures. Curve 1, grain size  $34\mu$ , at  $1800^\circ C$ . Curve 2,  $50\mu$ , at  $1800^\circ C$ . Curve 3,  $7\mu$ , at  $1500^\circ C$ . Curve 4,  $7\mu$ , at  $1600^\circ C$ . Curve 4 ( $1600^\circ C$ ) was obtained from the flow parameters at  $1500^\circ C$  (Table 1) and  $\Delta H_{ij}^*$  ( $k=d$  or  $g$ ) (Table 5).

length), and SSZ was  $1\mu$  in grain size containing 6 mole %  $Sc_2O_3$ , and YSZ was  $17\mu$  in grain size containing 6 mole %  $Y_2O_3$ .

The creep data for these specimens (Fig. 2) were analysed, and the necessary parameters were obtained by the method described in Paper 1, and are shown in Table 1. In Fig. 2, YSZ showed the deformation belonging to Case 3 (the series-connection of GB1 and disln. 1 flow units). The theoretical curve of  $f$  vs.  $-\ln \dot{s}$  was obtained by introducing  $\alpha_{k1}$  and  $1/\beta_{k1}$  ( $k=d$  or  $g$ ) in Table 1 to Eq. (6). One notes that the experimental data well agree with the theoretical curve. On the other hand, the SSZ showed the deformation belonging to Case 2 (the parallel connection of GB1 and GB2 flow units). The deformation of SSZ appeared in the low stress region, where YSZ deforms predominantly by the grain boundary movement. Because of the low stress region, SSZ showed only the defor-

mation due to the grain boundary flow units. The theoretical curve for SSZ was calculated from Eq. (4c) by using  $\alpha_{kj}/X_{kj}$  and  $1/\beta_{kj}$  ( $j=1$  or  $2$ ) in Table 1.

Microstructural observation showed that no change in grain size occurred before and after creep deformation, and that the pores on boundaries moved toward the stress axis for both YSZ and SSZ.<sup>5</sup>

**3. Alumina.** Warshaw and Norton<sup>6</sup> examined the steady-state creep behavior of polycrystalline  $Al_2O_3$  at  $1800^\circ C$  over a range of stress from 100 to 2000 psi using the four-point transverse bending method. The specimen was a bar one face of which was  $3/64'' \times 1''$ . Curve 2 in Fig. 3 is for polycrystalline  $Al_2O_3$  (above  $50\mu$  in grain size), and corresponds to Case 4. The theoretical curve 2 was obtained by introducing the parameters  $\alpha_{d1}$ ,  $1/\beta_{d1}$ ,  $\alpha_{g2}/X_{g2}$ ,  $1/\beta_{g2}$  (Table 1) and  $X_{g2}f_{g2}$  [calculated from Eq.

(9)] to Eq. (8). The agreement between experiment and theory is very good. Curve 1 is the result for the polycrystalline  $\text{Al}_2\text{O}_3$  ( $34\mu$  grain size) over a low stress region, and it exhibits a pattern of deformation different from the alumina sample mentioned above. Curve 1 corresponds to Case 1 (a single type of grain boundary flow units); the theoretical curve was obtained by introducing the parameters  $\alpha_{g1}$  and  $1/\beta_{g1}$  in Table 1 into Eq. (3b).

Microstructural observation showed that the grain structure for coarse-grained alumina ( $50\mu$  to  $100\mu$ ) was not so well defined as in the case of the fine-grained structure, i. e., there were regions of abnormal grain growth in the structure, and the grains were columnar rather than quasi-spherical. But no change was observed in grain shape and grain size before and after creep deformation for the coarse grain alumina as well as for all the finely-grained alumina (3, 7, 13,  $34\mu$ ).<sup>6</sup> Curves 1 and 2 in Fig. 3 are quite different in the deformation patterns although the experiments were conducted at about same stress levels. The different pattern is considered to be due to the large difference in the grain structures between coarse- and fine-grained alumina.

Folweiler<sup>7</sup> also examined the steady-state creep behavior of the pore-free, fine-grained alumina of various grain size prepared in the same way as in Warshaw's method.<sup>6</sup> This author studied at temperatures from 1500 to 1800°C over a range of stresses from 1000 to 33,000 psi by using three-point transverse bending method. The specimen size was approximately  $0.1'' \times 0.15'' \times 2''$ . The experimental data are plotted in Fig. 3 (see curves 3 and 4), and the parameters  $\alpha_{k1}$  and  $1/\beta_{k1}$  ( $k=d$  or  $g$ ) obtained from these data are shown in Table 1. This case belongs to Case 3 (series connection of disln. 1 and GB1 flow units). The theoret-

ical curves 3 and 4 in Fig. 3 is obtained by introducing the parameters in Table 1 to Eq. (6) describing Case 3. Previously, we found that curve 1 in Fig. 3, which was obtained for polycrystalline  $\text{Al}_2\text{O}_3$  ( $34\mu$  grain size), belonged to Case 1 (a single kind of GB1 flow units) whereas the curves 3 and 4, which was obtained for polycrystalline  $\text{Al}_2\text{O}_3$  ( $7\mu$  grain size), belong to Case 3. The main reason for this difference is in the stress levels since the experimental data of curve 3 and 4 in Fig. 3 were obtained under stresses ranging from low to high levels. Thus, the data of curve 3 and 4 showed the movements due to dislocation flow units as well as the grain boundary flow units whereas curve 1 showed only the grain boundary movement since it was obtained at such low stress levels at which only grain boundary movement is possible.

The theoretical curve 4 (1600°C) in Fig. 3 was obtained from the parameters  $\alpha_{k1}$ ,  $1/\beta_{k1}$  ( $k=d$  or  $g$ ) at 1500°C (Table 1) and  $\Delta H_k^\ddagger$  ( $k=d$  or  $g$ ) (Table 5). Considering the large relative error of the experimental data of 1600°C, the theory seems to be in satisfactory agreement with experiment.

Microstructural observations<sup>7</sup> showed that there was a strong tendency for voids to occur on boundaries perpendicular to the principal tensile stress, and that the small voids grew up to larger ones along the grain boundaries. Grain rotation and grain boundary sliding was also observed.

**4. Commercial 7075 Aluminum.** Commercial 7075 aluminum is an Al-Zn-Mg-Cu alloy the composition of which is: Al(base), Zn(5.84%), Mg(2.61%), Cu(1.6%), trace of Si, Fe, Mn, Ti, Cr, Ni and Zr. Embury *et al.*<sup>8</sup> studied the tensile deformation behavior of this alloy at various temperatures. The authors confirmed by observing the microstructures that at 100°C and

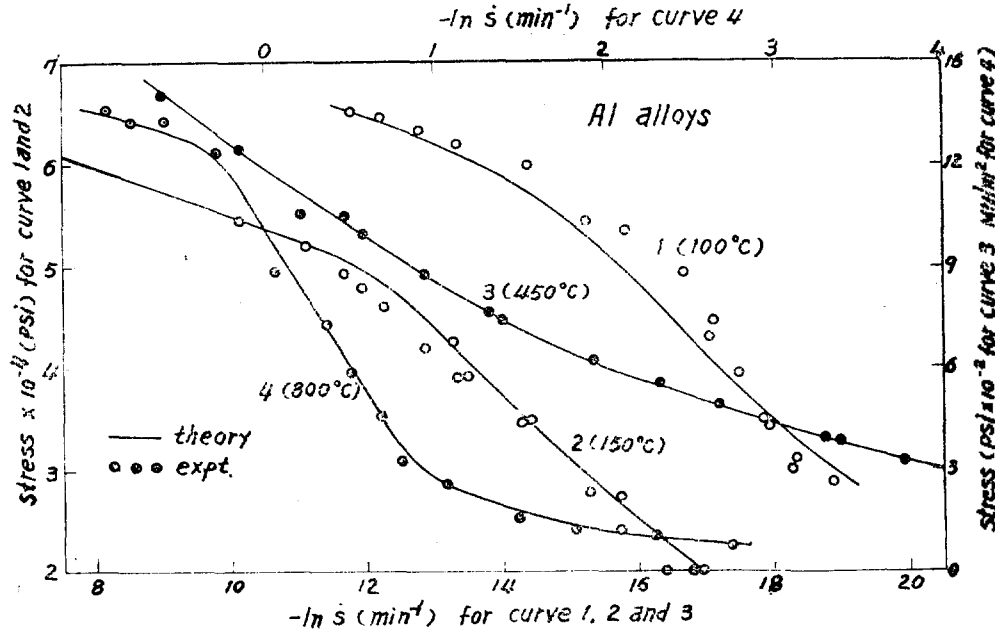


Fig. 4. Creep curves for Al-alloys. Curve 1, 2 and 3 are for commercial 7075 aluminum at different temperatures, and curve 4 for Al-bronze at 800°C. Curve 1 (100°C) was obtained from the flow parameters at 150°C (Table 2) and  $\Delta H_k^{\ddagger}$  ( $k=d$  or  $g$ ) (Table 5).

Table 2. Flow parameters for the polycrystals of metals and alloys.

Sample	$\alpha_{d1}$	$\alpha_{g1}$	$1/\beta_{d1}$	$1/\beta_{g1}$	Temp (°C)	Figure
7075 Al						
(Al-Zn-Mg-Cu)	$4.69 \times 10^{-4} (\text{psi})^{-1}$	$1.54 \times 10^{-4} (\text{psi})^{-1}$	$5.19 \times 10^{-19} \text{min}^{-1}$	$1.19 \times 10^{-10} \text{min}^{-1}$	100	Fig. 4
(Al-Zn-Mg-Cu)	$4.69 \times 10^{-4} (\text{psi})^{-1}$	$1.5 \times 10^{-4} (\text{psi})^{-1}$	$3.59 \times 10^{-16} \text{min}^{-1}$	$4.65 \times 10^{-9} \text{min}^{-1}$	150	Fig. 4
(Al-Zn-Mg-Cu)		$\{1.33 \times 10^{-2} (\text{psi})^{-1b}$ $1.67 \times 10^{-2} (\text{psi})^{-1c}$		$\{8.77 \times 10^{-7} \text{min}^{-1}$ $1.81 \times 10^{-11} \text{min}^{-1d}$	450	Fig. 4
Al-bronze						
(Cu base-Al-Fe)	$2.00 (\text{MN}/\text{m}^2)^{-1}$	$\{3.49 \times 10^{-1} (\text{MN}/\text{m}^2)^{-1}$ $4.51 \times 10^0 (\text{MN}/\text{m}^2)^{-1}$	$1.84 \times 10^{-13} \text{min}^{-1}$	$\{1.65 \times 10^{-1} \text{min}^{-1}$ $7.40 \times 10^{-5} \text{min}^{-1d}$	800	Fig. 4
Zr (50 $\mu$ )	$2.50 \times 10^{-3} (\text{psi})^{-1}$	$4.61 \times 10^{-4} (\text{psi})^{-1}$	$2.36 \times 10^{-6} \text{hr}^{-1}$	$1.22 \times 10^{-4} \text{hr}^{-1}$	567	Fig. 5
Zircaloy-2 (10 $\mu$ )	$9.00 \times 10^{-4} (\text{psi})^{-1}$	$2.79 \times 10^{-5} (\text{psi})^{-1}$	$2.53 \times 10^{-6} \text{hr}^{-1}$	$8.57 \times 10^{-4} \text{hr}^{-1}$	551	Fig. 5

<sup>a</sup>Values obtained by introducing  $\Delta H_k^{\ddagger}$  ( $k=d$  or  $g$ ) (Table 5) to Eqs. (15a) and (15b) in reference 1; <sup>b</sup>This value represents  $\alpha_{g1}/X_{g1}$ ; <sup>c</sup>This value represents  $\alpha_{g2}/X_{g2}$ ; <sup>d</sup>This value represents  $1/\beta_{g2}$ .

150°C, the deformation occurs by both dislocation and grain boundary movement and that simple nets of dislocations have developed within the original subgrains. They also found that at 450°C, the contribution of grain boundary sliding was predominant.

The experimental data ( $f$  and  $-\ln \dot{s}$ ) are plotted in Fig. 4 (see curve 1, 2 and 3). The parameters for this alloy are given in Table 2, from which theoretical curves 1 (100°C), 2 (150°C), and 3 (450°C) were calculated, and shown in Fig. 4. According to Fig. 4, curve 1

(100°C) and 2 (150°C) belong to Case 3, but curve 3 (450°C) belongs to Case 2. Here curve 1 (100°C) is a predicted one from the parameters at 150°C and  $\Delta H_h^\ddagger$  ( $k=d$  or  $g$ ) in Table 5, and one notes that the agreement with experiment is satisfactory. The reason that the creep behavior of curve 3 (450°C) is different from that of curve 1 and 2 is considered to be responsible to the phase transformation of the GP zone to the  $\eta$  phase which occurs at 450°C, and also to the low stress level where the experiment was performed. The theoretical curve 3 (450°C) was calculated from Eq. (4c) by using the parameters  $\alpha_{gj}/X_{gj}$  and  $1/\beta_{gj}$  ( $j=1$  or  $2$ ) on Table 2.

5. **Al-Bronze.** Dunlop *et al.*<sup>9</sup> investigated the microstructure of micrograins of Al-bronze (CDA alloy 619, Cu base, Al 9.5%, Fe 4.0%) after deformation over various range of strain rates at 800°C. The results showed that in the low strain rate range, clumps of grains slide together as units on sliding interface. After deformation in this low strain-rate range there was no evidence for dislocation motion within the grains. With increasing strain-rate, however, evidence for dislocation motion steadily increased whereas the tendency for grain sliding diminished.

The experimental data are shown in Fig. 4 (curve 4). The pattern of curve 4 belongs to Case 4. Curve 4 is the theoretical curve obtained by introducing the parameters of  $\alpha_{d1}$ ,  $1/\beta_{d1}$ ,  $\alpha_{g2}/X_{g2}$ ,  $1/\beta_{g2}$  and  $X_{g2}f_{g2}$  [calculated from Eq. (9)] into Eq. (8). From the result of analysis we know that the system deforms with three kinds of flow units, two are grain boundary flow units connected in parallel with each other and the other is the dislocational flow units connected in series with the former system. Al-bronze is known as a superplastic material at 800°C.

6. **Zirconium and Zircaloy-2.** Bernstein<sup>10</sup> studied the creep behavior for pure zirconium and zircaloy-2 (Zr base, Sn 1.42%, Fe 0.14%, Cr 0.1%, other metals in trace). The size of the flat specimens was  $1 \times 0.25 \times 0.02$  in., and the grain size was about  $50\mu$  for zirconium and about  $10\mu$  for zircaloy-2. The experimental results showed that two mechanisms are rate controlling, one is predominant in the low-stress region where the rate-controlling process is characterized by a grain boundary diffusion creep, and the other is predominant in the higher-stress region where the rate-controlling process is characterized by dislocation movement.

The plot of  $f$  vs.  $-\ln \dot{\epsilon}$  of experimental data obtained by Bernstein<sup>10</sup> are shown in Fig. 5. The theoretical curves in the figure were obtained by introducing the parameters of zirconium and zircaloy-2 in Table 2 into Eq. (6) for Case 3 where a single kind of dislocation flow units and a single kind of grain boundary flow units are connected in series.

7. **Single Crystals.** Since no grain boundaries are present in the interior of single crystals, the creep deformation due to grain boundary flow units will not occur in this case. Thus the creep deformation of single crystals is due to dislocation flow units only. But there will be two cases, in one of which only a single kind of dislocation flow units appears in the deformation whereas in the other a parallel connection of two or more kinds of flow units appear. Creep behavior of single crystals of metals, alloys, ceramics and ionic compounds are considered in the following.

Single crystals of metals, such as Al,<sup>11</sup> Zn,<sup>12</sup> Pb,<sup>13</sup> Ni,<sup>14</sup> all showed the plastic deformation where a single kind of dislocation flow units is acting (Case 1). The theoretical curves of  $f$  vs.  $-\ln \dot{\epsilon}$  for these metals are obtained from



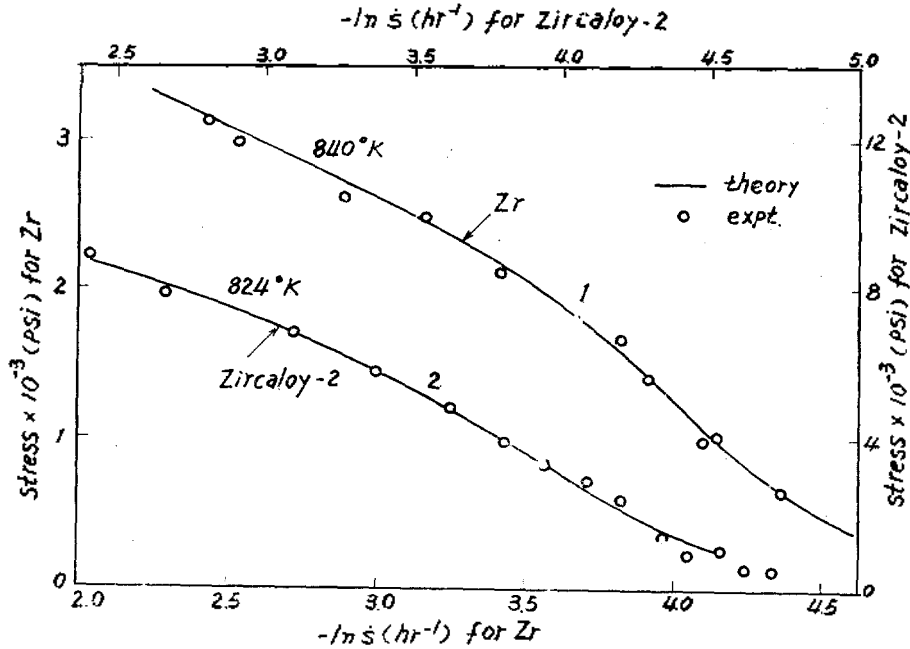


Fig. 5. Creep curves for zirconium of  $50\mu$  grain size (curve 1) and zircaloy-2 of about  $10\mu$  grain size (curve 2).

Table 3. Flow parameters for single crystals of metals and alloys.

Samples	$\alpha_{d1}$	$1/\beta_{d1}$	Temp. ( $^{\circ}$ K)	Figure
Al	$2.5 \times 10^{-4} (\text{psi})^{-1}$	$9.97 \times 10^8 \text{ sec}^{-1}$	10 to 70	Fig. 6
Ni	$2.33 (\text{kg}/\text{mm}^2)^{-1}$	$3.97 \times 10^{-5} \text{ sec}^{-1}$	295	Fig. 6
Zn	$3.36 (\text{g}/\text{mm}^2)^{-1}$	$1.46 \times 10^{-15} \text{ sec}^{-1}$	546	Fig. 6
Pb	$1.02 \times 10^{-2} (\text{psi})^{-1}$	$1.82 \times 10^{-3} \text{ hr}^{-1}$	rm. temp.	Fig. 6
Ni-Cr (21.5%)	$2.32 (\text{kg}/\text{mm}^2)^{-1}$	$4.42 \times 10^{-14} \text{ sec}^{-1}$	295	Fig. 7
Ni-Cr (4.36%)	$1.61 (\text{kg}/\text{mm}^2)^{-1}$	$1.07 \times 10^{-5} \text{ sec}^{-1}$	295	Fig. 7
Ni-Cr (21.5%)	$1.45 (\text{kg}/\text{mm}^2)^{-1}$	$6.45 \times 10^{-8} \text{ sec}^{-1}$	550	Fig. 7

Eq. (3a) by using the parameters given in Table 3. The results are shown in Fig. 6, the agreement between theory and experiment is very good.

The results for single crystals of Ni-Cr alloys<sup>14</sup> (Ni base, Cr 4.36% or 21.6%) are shown in Fig. 7, all showed plastic deformation due to a single kind of flow units (Case 1). The theoretical curves calculated from Eq. (3a) by using the parameters shown in Table 3 are

compared with experiment in Fig. 7.

Chang<sup>15</sup> examined the creep behavior of single crystals of  $\text{Al}_2\text{O}_3$  (ruby and sapphire) at  $1823^{\circ}$ K. Chang explained the experimental result by assuming the mechanism of dislocational climbing-up. But our theoretical curves were obtained by introducing the parameters in Table 4 into Eq. (3a) (Case 1), they are in good agreement with experiment as shown in Fig. 8.

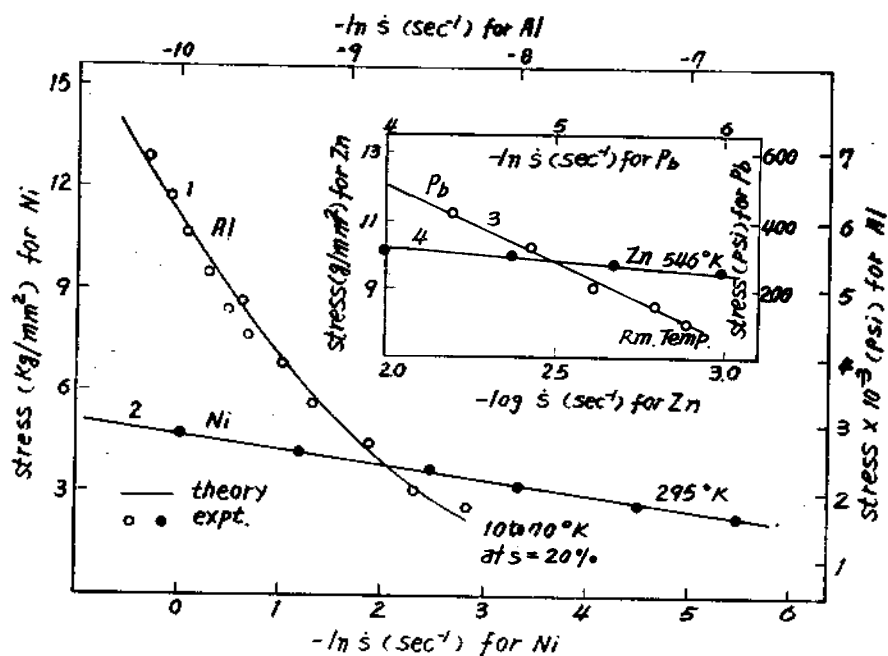


Fig. 6. Creep curves for single crystals of metals. Curve 1, Al; curve 2, Ni; curve 3, Pb; curve 4, Zn.

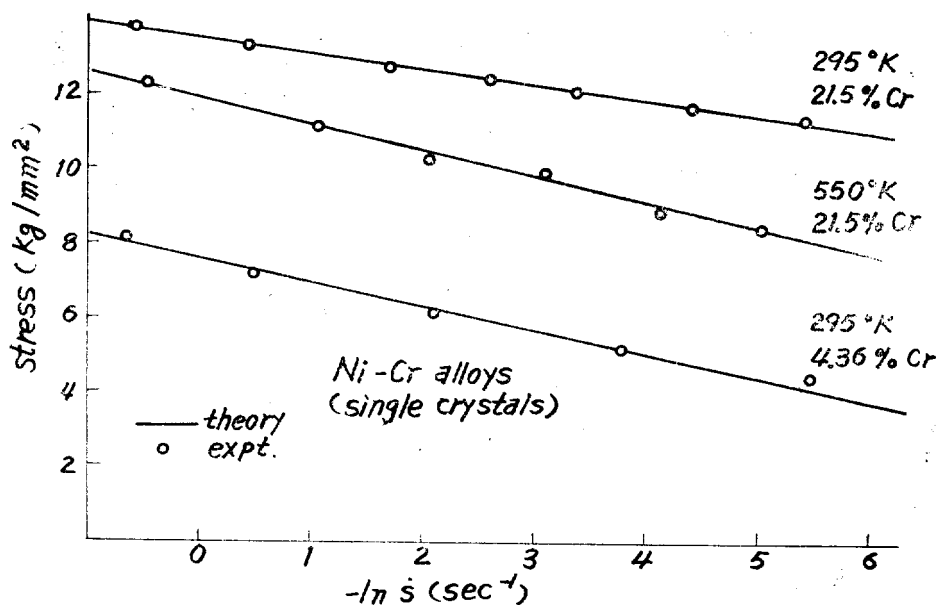


Fig. 7. Creep curves for single crystals of Ni-Cr alloys.

Table 4. Flow parameters for single crystals of oxides and ionic compounds.

Samples	$\alpha_{d1}$	$1/\beta_{d1}$	Temp. ( $^{\circ}\text{C}$ )	Figure
Ruby	$2.74 \times 10^{-8} \text{ (dynes/cm}^2\text{)}^{-1}$	$7.35 \times 10^{-9} \text{ sec}^{-1}$	1550	Fig. 8
Sapphire	$6.11 \times 10^{-8} \text{ (dynes/cm}^2\text{)}^{-1}$	$1.46 \times 10^{-8} \text{ sec}^{-1}$	1550	Fig. 8
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$7.61 \times 10^{-9} \text{ sec}^{-1b}$	1454	Fig. 9
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$2.63 \times 10^{-8} \text{ sec}^{-1b}$	1503	Fig. 9
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$8.28 \times 10^{-8} \text{ sec}^{-1b}$	1551	Fig. 9
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$2.81 \times 10^{-7} \text{ sec}^{-1}$	1605	Fig. 9
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$8.37 \times 10^{-7} \text{ sec}^{-1b}$	1656	Fig. 9
MgO <sup>a</sup>	$2.78 \times 10^{-3} \text{ g}^{-1}$	$2.22 \times 10^{-6} \text{ sec}^{-1b}$	1704	Fig. 9
NaCl	$1.18 \times 10^{-1} \text{ (g/mm}^2\text{)}^{-1}$	$2.17 \times 10^{-3} \text{ sec}^{-1}$	780	Fig. 10
KCl	$1.24 \text{ (g/mm}^2\text{)}^{-1}$	$5.77 \times 10^{-18} \text{ sec}^{-1}$	780	Fig. 10
LiCl	$\{3.45 \times 10^{-2} \text{ (g/mm}^2\text{)}^{-1}$ $\{5.91 \times 10^{-2} \text{ (g/mm}^2\text{)}^{-1}$	$\{2.22 \times 10^{-5} \text{ sec}^{-1}$ $\{2.52 \times 10^{-6} \text{ sec}^{-1}$	780	Fig. 10

<sup>a</sup>The unit of the stress was expressed in grams and dimension of the sample was not specified in the original;

<sup>b</sup>Values obtained by introducing  $\Delta H_{d1}^{\ddagger}$  (Table 5) to Eq. (15a) in reference 1; <sup>c</sup>This value represents  $\alpha_{d1}/X_{d1}$ ;

<sup>d</sup>This value represents  $\alpha_{d2}/X_{d2}$ ; <sup>e</sup>This value represents  $1/\beta_{d2}$ .

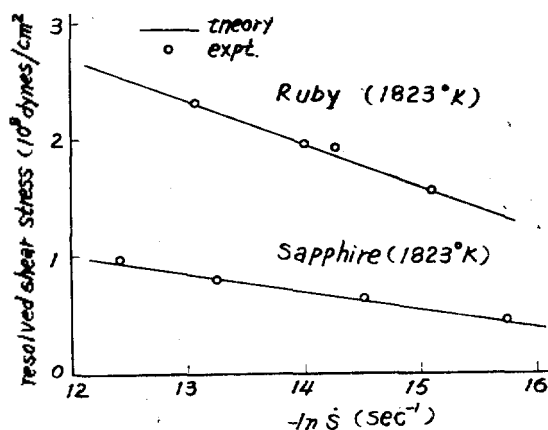


Fig. 8. Creep curves for alumina single crystals (ruby and sapphire).

Cummerow<sup>16</sup> investigated the creep behavior of single crystals of MgO in the temperature range from 1400 $^{\circ}\text{C}$  to 1700 $^{\circ}\text{C}$ . The MgO single crystals also showed the deformation by a single kind of flow units (Case 1) as shown in Fig. 9. The parameters are given in Table 4, and the theoretical curves are obtained by using these parameters from Eq. (3a). All the parametric values of  $1/\beta_{d1}$  at various temperatures,

which were used for calculating the theoretical curves, are the predicted values from the  $1/\beta_{d1}$  at 1605 $^{\circ}\text{C}$  and  $\Delta H_{d1}^{\ddagger}$  (Table 5).

The single crystals of ionic compounds such as NaCl, KCl, LiCl<sup>17</sup> showed the plastic deformation by the dislocation movement as shown in Fig. 10. NaCl and KCl showed the flow behavior of Case 1 caused by a single kind of flow units. On the other hand, LiCl single crystals showed the deformation of Case 2, where two kinds of dislocation flow units connected in parallel with each other. The theoretical curves for NaCl and KCl were obtained from Eq. (3a), and the curve for LiCl was obtained from Eq. (4c), in which  $k$  is replaced by  $d$ , by using the parameters  $\alpha_{di}/X_{di}$  and  $1/\beta_{di}$  ( $i=1$  or  $2$ ) in Table 4.

## DISCUSSIONS

**Activation Enthalpies for Flow Mechanisms.** We have assumed that, in plastic deformation of solids, the self-diffusion of the neighboring atoms around bad sites on the slip

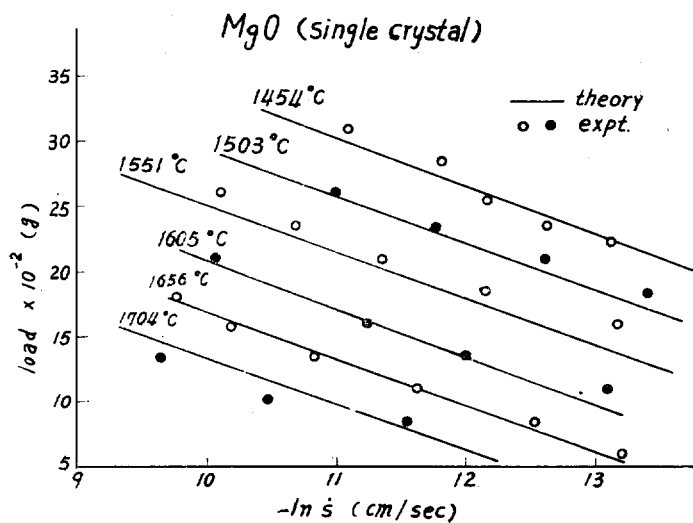


Fig. 9. Creep curves for single crystals of MgO at different temperatures. All the curves except for 1605°C were obtained from the flow parameters at 1605°C (Table 4) and  $\Delta H_{gr}^{\ddagger}$  (Table 5).

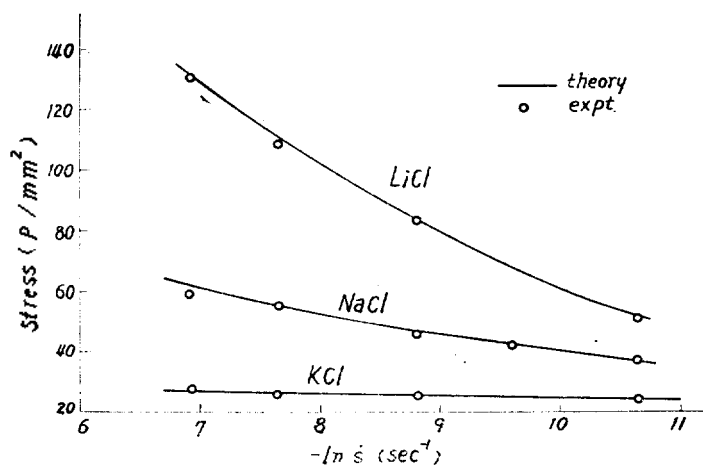


Fig. 10. Creep curves for single crystals of LiCl, NaCl, and KCl.

planes is the rate determining step. Thus the activation enthalpy for plastic deformation may be expected to be equal to that for self diffusion. Since the grain boundary is a region where atoms are distributed randomly with many vacancies, it is also expected that the activation enthalpy ( $\Delta H_{gr}^{\ddagger}$ ) for grain boundary movement

would be smaller than that ( $\Delta H_{dl}^{\ddagger}$ ) for dislocation movement. The quantities,  $\Delta H_{dl}^{\ddagger}$  and  $\Delta H_{gr}^{\ddagger}$ , which were calculated by using the method described in Paper 1 [cf. Eq. (16) of the latter], are presented in Table 5, and are compared with the experimental values in the literature. In Table 5, the values of  $\Delta H_{dl}^{\ddagger}$  which were indirectly obtained by using Eq. (17) of Paper 1, are also presented; the parenthesized  $\Delta H_{dl}^{\ddagger}$  data in Table 5 are the values obtained indirectly.

First, let us consider the result of MgO polycrystals. Referring to Table 5, our activation enthalpy for grain boundary movement ( $\Delta H_{gr}^{\ddagger}$ ) is 112 kcal/mole, and that for dislocation movement is 160 kcal/mole. The activation enthalpy for self-diffusion of oxygen in MgO single crystals was measured by Cummerow<sup>16</sup> to be 160 kcal/mole, which is in good agreement with our value of  $\Delta H_{dl}^{\ddagger}$ . Our result of grain boundary movement ( $\Delta H_{gr}^{\ddagger}=112$  kcal/mole) is also in good agreement with the 110 kcal/mole of Hensler.<sup>3</sup> We see here that  $\Delta H_{dl}^{\ddagger} > \Delta H_{gr}^{\ddagger}$  as was predicted previously.

Next, consider the case for ZrO<sub>2</sub>. Evans<sup>6</sup> obtained the activation enthalpies of deformation of YSZ at the stress of 4860 psi, the value was 86 kcal/mole. Referring to Fig. 2 the stress of 4860 psi is in the range where the deformation by grain boundary movement contributes predominantly. So on the assumption

Table 5.  $\Delta H_{\dot{\epsilon}}^{\ddagger}$  values for flow mechanisms.<sup>a</sup>

Samples	$\Delta H_{\dot{\epsilon}}^{\ddagger}$ (kcal/mole)	$\Delta H_{\dot{\epsilon}}^{\ddagger}$ (kcal/mole)	Reference
MgO (polycrystal)	160	112	This work
MgO (single crystal)	[160]		Cummerow <sup>16</sup>
MgO (polycrystal)		110	Hensler <sup>3</sup>
ZrO <sub>2</sub> : YSZ	(93)		This work
YSZ		86	Evans <sup>5</sup>
CSZ	[92.5]		Rhodes <sup>18</sup>
Al <sub>2</sub> O <sub>3</sub> (polycrystal)	160	114	This work
Al <sub>2</sub> O <sub>3</sub> (polycrystal)		130	Folweiler, <sup>7</sup> Warsaw <sup>6</sup>
Al <sub>2</sub> O <sub>3</sub> (polycrystal)		[110]	Oishi <sup>19</sup>
Al <sub>2</sub> O <sub>3</sub> (single crystal)	[152±5]		Oishi <sup>19</sup>
Al-Zn-Mg-Cu alloy (7075 aluminum)	41	23	This work
Zr metal	(36.1)		This work
Zr metal	~56	29.7	Bernstein <sup>10</sup>
Zr metal	[45.5]		Kidson <sup>20</sup>
Zircaloy-2	(52.1)		This work
Zircaloy-2	68.5	42.5	Bernstein <sup>10</sup>
Zircaloy-2	[~62]		Kidson <sup>20</sup>

<sup>a</sup>Parentesized data were indirectly obtained from the value of  $\Delta H_{\dot{\epsilon}}^{\ddagger}$ , and square bracketed ones from self-diffusion experiment.

that  $\Delta H_{\dot{\epsilon}}^{\ddagger}=86$  kcal/mole, the activation enthalpy for the dislocation movement is calculated to be  $\Delta H_{\dot{\epsilon}}^{\ddagger}=93$  kcal/mole by using the indirect method in Paper 1 (Table 5). Rhodes and Carter<sup>18</sup> measured the activation enthalpy for the diffusion of Zr<sup>4+</sup> in the calcia stabilized zirconia (CSZ), and the value was found to be 92.5 kcal/mole. This result is nearly equal to our value of  $\Delta H_{\dot{\epsilon}}^{\ddagger}$  (=93 kcal/mole), so the deformation by dislocation movement is considered to be controlled by the bulk diffusion of Zr<sup>4+</sup>.

Next, the case for Al<sub>2</sub>O<sub>3</sub> crystals is considered below. Referring to Table 5, our values are:  $\Delta H_{\dot{\epsilon}}^{\ddagger}=114$  and  $\Delta H_{\dot{\epsilon}}^{\ddagger}=160$  kcal/mole. The activation enthalpy found by Folweiler<sup>7</sup> and Warsaw and Norton<sup>6</sup> was  $\Delta H_{\dot{\epsilon}}^{\ddagger}=130$  kcal/mole, and the activation enthalpy of O<sup>18</sup> self-diffusion in polycrystalline alumina (20~30  $\mu$ ) was 110 kcal/mole (Oishi and Kingery<sup>19</sup>). These experimental values are in good agree-

ment with our value of  $\Delta H_{\dot{\epsilon}}^{\ddagger}=114$  kcal/mole. Oishi and Kingery<sup>19</sup> also experimented the O<sup>18</sup> self-diffusion in single crystals of alumina, and reported the activation enthalpy of 152±5 kcal/mole. This is also in good agreement with our value  $\Delta H_{\dot{\epsilon}}^{\ddagger}=160$  kcal/mole.

Now, let us turn to the case of metals and alloys. For the Al-Zn-Mg-Cu alloy, our values,  $\Delta H_{\dot{\epsilon}}^{\ddagger}=23$  and  $\Delta H_{\dot{\epsilon}}^{\ddagger}=41$  kcal/mole, are presented in Table 5. No values of  $\Delta H_{\dot{\epsilon}}^{\ddagger}$  and  $\Delta H_{\dot{\epsilon}}^{\ddagger}$  for this alloy have been published on the literature.

Bernstein *et al.*<sup>10</sup> measured the activation enthalpies of zirconium at the stress of 1500 psi, and obtained 29.7 kcal/mole, but at a high stress not specified, the  $\Delta H^{\ddagger}$  value was about 56 kcal/mole. On the assumption of  $\Delta H_{\dot{\epsilon}}^{\ddagger}=29.7$  kcal/mole, we calculated  $\Delta H_{\dot{\epsilon}}^{\ddagger}=36.1$  kcal/mole by applying the indirect method of Paper 1. Meanwhile the tracer experiment<sup>20</sup> showed  $\Delta H_{\dot{\epsilon}}^{\ddagger}=45.5$  kcal/mole. The consider-

able difference between the literature value of  $\Delta H_{\dot{\gamma}}^{\ddagger}$  and that of our theory (36.1 kcal/mole) may be due to some erroneous assumption on the value of  $\Delta H_{\dot{\gamma}}^{\ddagger}$  (=29.7 kcal/mole.) Referring to Fig. 5, the stress of 1500 psi, where  $\Delta H_{\dot{\gamma}}^{\ddagger}$  (=29.7 kcal/mole) was obtained, is in the middle range that two mechanisms act considerably mixed. So  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =29.7 kcal/mole obtained at this stress may have a considerable error.

For zircaloy-2, Bernstein<sup>10</sup> obtained  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =42.5 kcal/mole at the stress of 1815 psi and  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =68.5 kcal/mole at higher stresses. Our  $\Delta H_{\dot{\gamma}}^{\ddagger}$  value of 52.1 kcal/mole was calculated by using the indirect method under the assumption that  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =42.5 kcal/mole. According to the tracer experiment,<sup>20</sup>  $\Delta H_{\dot{\gamma}}^{\ddagger}$  is about 62 kcal/mole for Zr-1.3% Sn alloy. In Fig. 5, the stress of 1815 psi is in the range where the deformation by grain boundary movement is predominantly occurring, so the assumption that  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =42.5 kcal/mole is considered to be valid. Using this assumption, the value of  $\Delta H_{\dot{\gamma}}^{\ddagger}$ =52.1 kcal/mole was obtained by the indirect method. This value is much smaller than the experimental values of 62 and 68.5 kcal/mole. Taking into account of the approximation introduced in the determination of  $\Delta H_{\dot{\gamma}}^{\ddagger}$ , however, the result may be said to be satisfactory.

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