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Activation Enthalpies for Plastic Deformation

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Activation energies for plastic deformation calculated from traditional phenomenological equations have been criticized frequently since the values are different by authors, and also by experimental conditions. The reasons of different activation enthalpies are clarified in this study. Our method for calculating activation enthalpies based on the authors' theory of plastic deformation was presented and discussed. The method was applied to various cases of alloys, the calculated activation enthalpies are listed and compared with the activation energies obtained by the traditional methods in order to show the reasonableness of our method. The physical meaning of the actiaation enthalpies which we found was clarified.

1. Introduction

Many theories for plastic deformation have been proposed. The representative ones are those proposed by Nabarro,[1] Gifkins *et al.*,[2] Herring,[3] and Coble.[4] According to these authors, the strain rate is expressed as a linear function of stress and as an iverse function of grain size raised to the power of one to three. In actual cases, however, these theories are in agreement with experiments only in a limited region of stress, so the flow equation is expressed phenomenologically as the following:[5]

$$\dot{s}=\frac{ADGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{f}{G}\right)^{n} \tag{1}$$

where A is a dimensionless constant, D is the appropriate diffusion coefficient, G is the shear modulus, b is the Burger's vector, k is Boltzman's constant, T is absolute temperature, d is the grain size, f is stress, and n and p are the stress and grain size index, respectively. Equation (1) can be transformed into the following at constant stress and grain size:

$$\dot{s}=\frac{A'}{G^{n-1}T}\exp\left(-\frac{Q}{RT}\right) \tag{2}$$

and

$$A'=AD_0b^{p+1}f^n/kd^p \tag{3}$$

where A' represents a temperature-independent constant,

$D=D_0$ exp $(-Q/RT)$, and Q represents activation energy for plastic flow.

According to this phenomenological flow equation, the activation energies for plastic deformation can be obtained from the plot of ln G^{n-1} $T\dot{s}$ *vs.* $1/T$, where the slope is $-Q/R$. Another method for obtaining the activation energies is to calculate the slope of the straight line from the Arrhenius type plot of log $\dot{s}$ *vs.* $1/T$. This method corresponds to the case where A'/G^{n-1} T in Eq. (2) is regarded as a temperature independent constant.

The activation energies (Q) calculated by the methods as described above showed in general that $Q_{\rm I}=Q_l$ at high stress level (region I), $Q_{\rm II}=Q_{gb}$ at intermediate stress level (region II), and $Q_{\rm III}=Q_l$ at low stress level (region III), where $Q_{\rm I}$, $Q_{\rm II}$ and $Q_{\rm III}$ represent the activation energies in the stress regions represented by the subscripts, and Q_l and Q_{gb} represent the activation energies for lattice diffusion and grain boundary diffusion, respectively.[6]

According to the experimental results, the values of n in Eq. (1) varies from $n=1$ to $n=7$ according to the applied stresses and generally they are not integers.[7] This fact suggests to us that plastic deformation does not occur by only one kind of flow process, but occur by many kinds of complicated flow processes occurring simultaneously at a given stress, thus the n value varies according to the stress levels due to the different degree of contribution of each process at different stresses. So it can be said that Eq. (1) is not a true flow equation, but an equation describing plastic deformation phenomenologically in a given narrow stress region. Referring to Eq. (3), A' can not be considered as a temperature independent constant, because n varies depending on stress and temperature. So the activation energies calculated by using Eq. (2) can be expected to have different values depending on stress and also not to be the true values of activation energies. Especially in region III of low stress levels, the activation energies are calculated nearly equal to that for lattice diffusion,[7] this does not agree with microstructural observations according to which grain boundary movement was observed predominantly at low stress level.[8]

According to Kim-Ree's theory,[9] plastic deformation occurs mainly by the flow groups of dislocation movement in region I (high stress level), in region III (low stress level) by those of grain boundary movement, and in region II (intermediate stress level) by the two compounded mechanisms mentioned above. Some materials do not show plastic deformation by dislocation flow groups. For these cases, only flow groups of grain boundary movement are effective in plastic deformation over the whole range of stresses of region I, II and III. And flow groups of grain boundary movement are generally composed of two kinds of flow groups $g1$ and $g2$ (g signifies grain boundary movement). The authors calculated activation enthalpies for $g1$ and $g2$ flow groups by applying Kim-Ree's theory to many plastic deformations. The purpose of this study is to show clearly why the activation energies for plastic flow were calculated differently in the past, and to show that the true activation energy should be calculated by our method which will be described below.

2. Theory

Kim-Ree's theory[9] is summarized in the following, especially the part necessary in this study, that is, the theory of plastic deformation occurring by grain boundary movement. According to the theory, there are j kinds of flow groups (*i.e.*, $j=1, 2, \cdots\cdots j$) on a grain boundary shear surface, and these flow groups can be represented by a generalized Maxwell model. In other words each kind of flow groups can be represented by a Maxwell model which has the activation enthalpy ΔH_{gj}^{*} for flow and is connected in parallel to the others. Therefore, the following relationships are held between stress f and strain rate $\dot{s}$:

$$f=\sum_j X_{gj}f_{gj}=\sum_j \frac{X_{gj}}{\alpha_{gj}}\sinh^{-1}\beta_{gj}\dot{s} \tag{4}$$

and

$$\dot{s}=\dot{s}_{gj}=\frac{1}{\beta_{gj}}\sinh \alpha_{gj}f_{gj} \tag{5}$$

Here X represents the fractional area occupied by gj flow groups of grain boundary movement, α_{gj}^{-1} and β_{gj}^{-1} represent the intrinsic shear stress and the intrinsic shear rate of flow group gj, respectively.[10] For binary alloys, the number of flow groups was appeared to be two, so Eq. (4) can be expressed as the following:

$$f=\frac{X_{g1}}{\alpha_{g1}}\sinh^{-1}\beta_{g1}\dot{s}+\frac{X_{g2}}{\alpha_{g2}}\sinh^{-1}\beta_{g2}\dot{s} \tag{6}$$

and

$$\dot{s}=\dot{s}_{g1}=\dot{s}_{g2}=\frac{1}{\beta_{g1}}\sinh \alpha_{g1}f_{g1}=\frac{1}{\beta_{g2}}\sinh \alpha_{g2}f_{g2} \tag{7}$$

The stress on each flow group depends on the total shear stress.

Erom Eq. (4) the ratio of stresses on the two flow groups is given by the following equation:

$$\frac{X_{g1}f_{g1}}{X_{g2}f_{g2}}=\frac{\frac{X_{g1}}{\alpha_{g1}}\sinh^{-1}\beta_{g1}\dot{s}}{\frac{X_{g2}}{\alpha_{g2}}\mathrm{sing}^{-1}\beta_{g2}\dot{s}}\equiv R \tag{8}$$

If we assume that in Eq. (8) $X_{g1}/\alpha_{g1}\simeq X_{g2}/\alpha_{g2}$, $\beta_{g2}\dot{s}<<1$, and $\beta_{g2}>>\beta_{g1}$ (in other words at low $\dot{s}$ or low stress), the following is obtained by approximate calculations:

$$\frac{X_{g1}f_{g1}}{X_{g2}f_{g2}}\simeq\frac{\beta_{g1}}{\beta_{g2}}\equiv R_l<<1 \tag{9}$$

That is, the stress contribution by flow group $g2$ is so large that the contribution by flow group $g1$ is negligible in the low stress region. On the other hand, if we apply the assumption $\beta_{gj}\dot{s}>>1$ at high stress level to Eq. (8), the stress ratio R can be approximated as the following:

$$\frac{X_{g1}f_{g1}}{X_{g2}f_{g2}}\simeq\frac{\ln 2\beta_{g1}\dot{s}}{\ln 2\beta_{g2}\dot{s}}\equiv R_h \tag{10}$$

Comparing Eq. (9) with Eq. (10), it can easily be proved $R_h > R_l$, and the ratio R increases continuously from R_l to R_h (which is still <1) with increasing total stress from low to high levels. Combining Eq. (6) with Eq. (8), the ratio of the stress on each flow group to the total stress can be expressed as in the following:

$$\frac{X_{g2}f_{g2}}{f}=\frac{1}{1+R} \tag{11}$$

and

$$\frac{X_{g1}f_{g1}}{f}=\frac{R}{1+R} \tag{12}$$

Referring to Eq. (11), the stress contribution of flow group $g2$ is predominant at low stress, because R is small in this stress region. And since R increases with an increase of stress, the contribution of $g2$ flow group decreases, while that of flow group $g1$ increases in accordance with Eq. (12).

As explained above, the degree of contribution of many flow mechanisms are different depending on stress levels. So it would be obvious that the values $\Delta H^{\ddagger}$ calculated by the traditional methods are different depending on stress levels, and that the physical meaning of the values are ambiguous.

Now the method of calculating $\Delta H^{\ddagger}$ values according to Kim-Ree's theory is discussed in the following. An experimental flow curve is decomposed into two component curves by a method described earlier. Figure 1 shows the schematic representation of the result in the plot of f *vs.* -ln$\dot{s}$. Curve $g1$ and $g2$ represent the contributions due to flow groups $g1$ and $g2$ to the total stress, respectively. The full curve, $g1+g2$, is obtained by synthesizing curve $g1$ and $g2$ (*i.e.* by adding the stresses of $g1$ and $g2$ at a given $\dot{s}$), and represents schematically the experimental flow curve. Figure 1 shows that the stress contribution of flow group $g2$ is predominant at low stress level in agreement with Eq. (11).

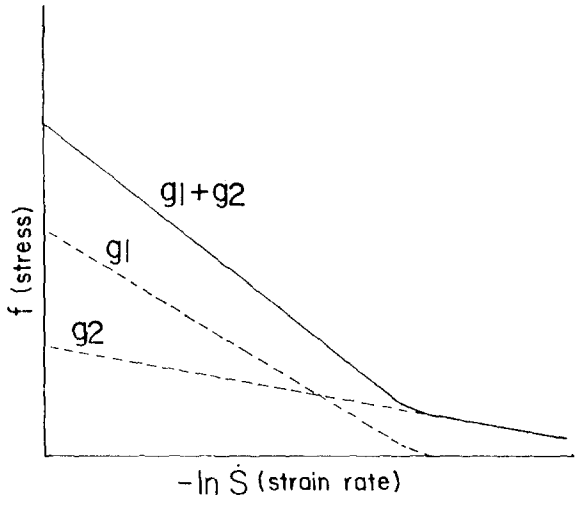

Figure 1. Schematic representation of flow curves in plots of f *vs.* –ln s. The dotted curves represent the stresses on the two kinds of flow groups ($g1$ and $g2$) on grain boundary; the full curve is obtained by adding the stresses on $g1$ and $g2$ at a given $\dot{s}$, and represents schematically the experimental curve.

So the flow parameters X_{g2}/α_{g2} and β_{g2} can be obtained from the experimental flow curve at low stress region III. Now the flow curve due to flow group $g1$ can easily be obtained in the middle stress region (region II) by subtracting the stress due to flow goup $g2$ from the total stress at a given shear rate $\dot{s}$. The flow curve of $g1$ flow group being obtained, the flow parameters of this flow group X_{g1}/α_{g1} and β_{g1} can be calculated by a similar method to that used for flow group $g2$. Next, activation enthalpies can be obtained from the calculated flow paramerte β_{gj} in the following way. According to Eyring,[11] β_{gj}^{-1} is obtained as:

$$\beta_{gj}^{-1}=\left(\frac{\lambda}{\lambda_1}\right)_{gj}\frac{2kT}{h}\exp\left(\frac{\Delta S_{gj}^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_{gj}^{\ddagger}}{RT}\right) \tag{13}$$

where λ and λ_1 are the molecular parameters in Eyring's theory of flow,[11] and $\Delta S_{gj}^{\ddagger}$ and $\Delta H_{gj}^{\ddagger}$ are the activation entropy and activation enthalpy for flow group gj ($j=1$ or 2), respectively. The logarithm of β_{gj}^{-1} is given below:

$$\ln\beta_{gj}^{-1}=\ln A_{gj}+\left(-\frac{\Delta H_{gj}^{\ddagger}}{R}\right)\frac{1}{T} \tag{14}$$

where

$$A_{gj}=\left(\frac{\lambda}{\lambda_1}\right)_{gj}\frac{2kT}{h}\exp\left(\frac{\Delta S_{gj}^{\ddagger}}{R}\right) \tag{15}$$

the factor A_{gj} is regarded as a temperature independent constant in the following treatment. Equation (14) shows that the plots of ln β_{gj}^{-1} *vs.* $1/T$ give a straight line whose slope is $-\Delta H_{gj}^{\ddagger}/R$. Thus the activation enthalpies can be calculated from the value of this slope.

3. Results and Discussions

In a previous paper,[9] we have reported the parametric values of X_{gj}/α_{gj} and β_{gj} ($j=1$, 2) obtained by applying the above-mentioned method to various cases. By using the β_{gj} values, the activation enthalpy $\Delta H_{gj}^{\ddagger}$ was obtained from the plot of ln β_{gj}^{-1} *vs.* $1/T$. The $\Delta H_{gj}^{\ddagger}$ values ($j=1$ or 2) thus obtained for each sample are tabulated in Tables 1 to 4, and are compared with the literature values which were obtained by the conventional methods mentioned previously.

(1) Zn-Al Eutectoids. The $\Delta H_{gj}^{\ddagger}$ values for Zn-Al eutectoid samples are tabulated in Table 1. For the sample of grain size 0.55μ the activation enthalpies are $\Delta H_{g1}^{\ddagger}=2.16$ and $\Delta H_{g2}^{\ddagger}=1.17$ kcal/g·atom which were calculated by using Eq. (14). On the other hand Naziri *et al.*[12] calculated activation energy Q from the plot of ln $\dot{s}$ *vs.* $1/T$ by using Eq. (2), where A'/G^{n-1} T was assumed to be constant, and these values showed different activation energies depending on stress levels as shown in Table 1. That is, $Q=20$ at $f=4.8$ MN/m^2, $Q=18.5$ at $f=6.9$ MN/m^2, $Q=16.3$ at $f=13.8$ MN/m^2, and $Q=13.0$ kcal/ g·atom at $f=27.6$ MN/m^2. (note: $Q=\Delta H^{\ddagger}+R\simeq\Delta H^{\ddagger}$). Moreover, these values are much highter than $Q=11$ kcal/g·atom for pure Al bicrystal[13] and $Q=4.7$ kcal/g.atom for pure Zn bicrystal[14] as shown in Table 1. And taking into account the fact that the activation energy for pure Al bicrystal is twice as large as that

TABLE 1: $H_{gj}^{\neq}$ **ΔValues for Zu–Al Eutectoids**[a]

Samples	Grain size	$\Delta H_{gj}^{\neq}$ (kcal/g·atom)	A_{gj} in Eq. (15)	Ref.
Zn–Al eutectoid	0.55 μ	2.16 [$\Delta H_{g1}^{\neq}$ (Al)]	3.21	This work [exp. data: ref. (12)]
		1.17 [$\Delta H_{g2}^{\neq}$ (Zn)]	-5.23	
		20 (4.8 MN/m^2)[b]		Naziri[12]
		18.5 (6.9 MN/m^2)[b]		
		16.3 (13.8 MN/m^2)[b]		
		13.0 (27.6 MN/m^2)[b]		
	2.5 μ	10.8 [$\Delta H_{g1}^{\neq}$ (Al)]	9.02	This work [exp. data: ref. (15)]
		4.6 [$\Delta H_{g2}^{\neq}$ (zn)]	-7.24	
	4.4 μ	*ca.* 25 (low stress)		Mohamed[17]
		ca. 16 (internediate stness)		
Pure A	Bicrystal	11		Rhines[13]
Pure Zn	Bicrystal	4.7		Turner[14]

[a] $\Delta H_{g1}^{\neq}$ and $\Delta H_{g2}^{\neq}$ represent the activation enthalpies for flow groups $g1$ and $g2$, respectively. The expected diffusing atoms are given in parentheses. [b] The values in parentheses represent applied constant stresses of the experiment.

TABLE 2: $\Delta H_{gj}^{\neq}$ **Values for Al–Cu Eutectics**[a]

Samples	Grain size	$\Delta H_{gj}^{\neq}$ (kcal/g·atom)	A_{gj} in Eq. (15)	Ref.
Al–Cu eutectic	1.7 to 2.7 μ	10.2 [$\Delta H_{g1}^{\neq}$ (Al)]	2.13	This work [exp. data: ref. (18)]
		14.2 [$\Delta H_{g2}^{\neq}$ (Cu)]	-0.64	
		40		Holt[18]
Al–17 wt. % Cu	10 μ	7.28 [$\Delta H_{g1}^{\neq}$ (Al)]	-1.35	this work [exp. data: ref. (19)]
		8.09 [$\Delta H_{g2}^{\neq}$ (Cu)]	-6.26	
		10 (f-f_0 = 1 or 2 N/mm^2)[b]		Cahoon[19]
		32 (f-f_0 =12 N/mm^2)[b]		

[b] $\Delta H_{g1}^{\neq}$ and $\Delta H_{g2}^{\neq}$ represent the activation enthalpies for flow groups $g1$ and $g2$, respectively. The expected diffusing atoms are given in parentheses. [b] f_0 represents the threshold stress of Ashby *et al.*[20]

TABLE 3: $\Delta H_{gj}^{\neq}$ **Values for Some Alloys**[a]

Samples	Grain size	$\Delta H_{gj}^{\neq}$ (kcal/g·atom)	A_{gj} in Eq. (15)	Ref.
Mg–Al eutectic	2.2 μ	11.2 [$\Delta H_{g1}^{\neq}$ (Al)]	9.27	This work [exp. data: ref. (21)]
		13.2 [$\Delta H_{g2}^{\neq}$ (Mg)]	-0.614	
Al Polycrystal	10.6 μ	19.2[b]		D. Lee[21]
Zn–0.10Ni–0.04Mg	1.9 μ	9.63 [$\Delta H_{g1}^{\neq}$]	7.95	This work [exp. data: ref. (22)]
		8.09 [$\Delta H_{g2}^{\neq}$]	0.456	
		13.1 (low stress)		J. D. Lee[22]
		15.2 (3 kg/mm^2)[c]		

[a] $\Delta H_{g1}^{\neq}$ and and $\Delta H_{g2}^{\neq}$ represent the activation enthalpies for flow groups $g1$ and $g2$, respectively. The expected diffusing atoms are given in parentheses. [b] This value was obtained by a tracer experiment. [c] The value in the parenthesis represents constant stress o the experiment.

for pure Zn bicrystal, our values $\Delta H_{g1}^{\neq}$=2.16 and $\Delta H_{g2}^{\neq}$=1.17 kcal/g·atom may be assigned to the activation enthalpies for self-diffusion of Al and Zn, respectively. For the sample of grain size 2.5 μ, we calculated the activation enthalpies by using Mohamed *et al.*'s experimental data;[15] the values are $\Delta H_{g1}^{\neq}$=10.8 and $\Delta H_{g2}^{\neq}$= 4.6 kcal/g.atom. These values are in good agreement with bicrystal data of Al[13] and Zn[15] as cited above. By comparing these bicrystal data with authors' values, our $\Delta H_{g1}^{\neq}$ may be inferred to the activation enthalpy for self-diffusion of Al on grain boundaries, and $\Delta H_{g2}^{\neq}$ to that of Zn. It has been also reported that generally activation enthalpies increase with the increase of grain size.[16] For the sample of grain size 4.4 μ, Mohamed *et al.*[17] obtained a crude estimate of activation enthalpies as *ca.* 25 kcal/g·atom at a low stress level and *ca.* 16 kcal/g·atom at an intermediate stress level by using the traditional method. But our method was not applied to Mohamed *et al.*,s data,[17] since the experiments had not so far been conducted systematically.

(2) Al–Cu Eutectics. The activation enthalpies for Al–Cu eutectics are tabulated in Table 2. The activation enthalpies calculated from Holt *et al.*'s experimental data[18] for the sample of grain size 1.7 to 2.7 μ are $\Delta H_{g1}^{\neq}$=10.2 and $\Delta H_{g2}^{\neq}$=14.2 kcal/g.atom, and $\Delta H_{g2}^{\neq}$=10.2 kcal/g·atom is nearly in agreement with $\Delta H_{g1}^{\neq}$=10.8 kcal/g·atom of Zn–Al eutectoid of grain size 2.5 μ, which was the activation enthalpy for self-diffusion of Al (refer to Table I). Thus the values $\Delta H_{g1}^{\neq}$ and $\Delta H_{g2}^{\neq}$ for Al–Cu eutectic are inferred to the values for self-diffusion of Al and Cu, respectively. On the other hand Holt *et al.*[18] calculated the activation enthalpy as 40 kcal/g·atom from Arrhenius type plot of ln $\dot{s}$ *vs.* $1/T$. This value is too large, so Holt interpreted it as the activation enthalpy for self-diffusion of Cu in hard Al_2Cu phase.

TABLE 4: ΔH_{gj}^{*} Values for Pb–Sn Entectics[a]

Samples	Grain size	ΔH_{gj}^{*} (kcal/g·atom)	A_{gj} in Eq. (15)	Ref.
Pb–Sn eutectic	5.8 μ	3.68 [ΔH_{g1}^{*} (Sn)]	−2.14	This work [exp. data: ref. (5)]
		4.71 [ΔH_{g2}^{*} (Pb)]	−7.95	
		13.7 (1.38 MN/m^2)[b]		Mohamed[5]
		19.6 (6.9×10^{-2} MN/m^2)[b]		
Pure Pb	Bicrystal	4.7[c]		Stark[23]
	ca. 1 mm	15.8[c]		Okkerse[24]
Pure Sn	*ca.* 0.5 mm	9.56[c]		Lange[25]

[a] ΔH_{g1}^{*} and ΔH_{g2}^{*} represent the activation enthalpies for flow groups $g1$ and $g2$, respectively. The expected diffusing atoms are given in parentheses. [b] The values in parentheses represent applied constant stress of the experiment. [c] These values were obtained by tracer experiment.

The results of the authors' analysis for Cahoon's experimental data[19] for the sample of Al–17 wt.% Cu were $\Delta H_{g1}^{*}=7.28$ and $\Delta_{g2}^{*}=8.09$ kcal/ g·.atom (see Table II). This sample was consisted of two phases which were Al–4.5 wt.% Cu matrix and Al_2Cu phase, and the grain size of the matrix was 27μ and was changed to 10 μ after heat–treatment at 520 °C. Cahoon[19] analysed the flow data according to Ashby *et al.*'s method[20] and calculated activation energies as $Q=$ 10 kcal/g·atom at low stress, $Q=32$ kcal/g·atom at high stress as shown in Table 2. Cahoon explained $Q=10$ kcal/g.atom as the activation energy for grain boundary diffusion and $Q=32$ kcal g·atom as that for volume diffusion at Al–rich solid solution or θ phase.[21] One notes that Cahoon's Q(=32 kcal/g·atom) value is unreasonably large compared with our values ($\Delta H_{g1}^{*}=7.28$ and ΔH_{g2}^{*} 8.09 kcal/g·atom) obtained by using the same experimental data. Comparing these ΔH_{gj}^{*} values of ours with those obtained for the sample of grain size of 1.7 to 2.7 μ (Table 2), one may conclude that our ΔH_{gj}^{*} values for the sample (Al–17 wt.% Cu) are reasonable although the composition and metallurgical structure are different from those of the sample of Al–Cu eutectic.

(3) Magnesium Alloys. For the sample of Mg–Al eutectic of 2.2 μ grain size, D. Lee's experimental data[21] were analysed by using our Eqs. (6), (7) and (14), and the results of calculation were obtained as ΔH_{g1}^{*} 11.2 and $\Delta H_{g2}^{*}=$ 13.2 kcal/g·atom (refer to Table 3). The value $\Delta H_{g1}^{*}=$ 11.2 kcal/g·atom is in good agreement with the value of ΔH_{g1}^{*} (=10.8 kcal/g·atom) for Zn–Al eutectoid of 2.5 μ grain size (refer to Table 1), so ΔH_{g1}^{*} for Mg–Al eutectic is considered as the activation enthalpy for self–diffusion of Al on grain boundaries, and ΔH_{g2}^{*} (=13.2 kcal/g·atom) as that for Mg self–diffusion. According to a tracer experiment for Al polycrystals of grain size 10.6 μ, D. Lee[21] reported that the activation energy for self–diffusion of Al on a grain boundary was 19.2 kcal/g·atom. Considering the grain size dependence of Q, this value is also in good agreement with our ΔH_{g1}^{*}(Al) of Mg–Al eutectic (=11.2 kcal/g.atom) of grain size 2.2 μ.

J. D. Lee *et al.*[22] obtained flow data by mechanical test at various temperatures for the dispersion strengthened Zn alloy (Zn–0.10Ni–0.04Mg) of 1.9 μ grain size, plotted the data of ln $\dot{s}$ *vs.* $1/T$, and calculated the activation energies from the slope of the least–square fitted straight line. The results were 13.1 kcal/g·atom at low stress, and 15.2 kcal/g.atom at high stress (refer to Table 3). But according to our analysis by Eq. (14), the activation enthalpies were $\Delta H_{g2}^{*}=9.63$ and $\Delta H_{g2}^{*}=8.09$ kcal/g·atom. It is difficult to assign the elements to which these activation enthalpies are attributed because of the lack of experimental data.

(4) Pb–Sn Eutectics. Mohamed *et al.*[5] tested mechanical properties of Pb–Sn eutectics of grain size 5.8 μ and calculated the activation energies by applying Eq.(2) to experimental data, where G was corrected for temperatures and for composition of alloys, and different values of n were used according to applied stresses. The results were 13.7 kcal/g·atom at stress 1.38 MN/m^2, and 19.6 kcal/g·atom at 6.9×10^{-2} MN/m^2 as shown in Table 4. The same data of Mohamed[5] were analysed by using Eqs. (6), (7) and (14), and we obtained the values of $\Delta H_{g1}^{*}=3.68$ and $\Delta H_{g2}^{*}=$ 4.71 kcal/g.atom. According to tracer experiment, the activation energy for diffusion of pure Pb–bicrystal is 4.7 kcal/g·atom,[23] while it is 15.8 kcal/g·atom for the sample of grain size of *ca.* 1 mm.[24] The value 4.7 kcal/g·atom is in good agreement with our $\Delta H_{g2}^{*}=4.71$ kcal/g.atom (refer to Table 4). So ΔH_{g2}^{*} (=4.71 kcal/g·atom) for Pb–Sn eutectics may be inferred to the activation enthalpy for self–diffusion of Pb on grain boundaries, and ΔH_{g1}^{*} (=3.68 kcal/g·atom) is inferred to the activation enthalpy for self–diffusion of Sn. We do not have self–diffusion data for Sn of grain size of 5.8 μ except for grain size of *ca.* 0.5 mm (Table 4), for which $Q=9.56$ kcal/g.atom has been reported.[25] Considering the grain size dependence of Q, the above reasoning seems to be not so absurd.

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