Theory of Plasticity II : Critical Shear Stress of Binary Alloys

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Critical Shear Stress of Binary Alloys

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Synopsis

The critical shear stresses of binary alloys were calculated by means of two relations which have been derived in the previous paper. The curves of critical shear stress protted against the concentration of binary alloys take various forms for different values of X and Y, where $X=\frac{RT}{H}$, $Y=\frac{\Phi_1}{H}$ and $H=(F^i_a-F^r_a)-(F^i_b-F^r_b)$. F^i_a, F^r_a, F^i_b and F^r_b are the Helmholtz's free energy of pure crystal composed of atoms A or B in the real or in the imaginary crystal phase respectively, Φ_1, being the so-called ordering energy of the alloy. The quantity H hardly depends on temperature at sufficiently high temperatures. As $\frac{Y}{X}=\frac{\Phi_1}{RT}$ becomes smaller, the critical stress curve protted against the concentration approaches to a symmetric form. But it is very unsymetric for small values of X and the central part of curve becomes flat for large Y. The comparison with observations reveals good agreement in the cases of Au-Ag, Cu-Ni and Cu-Zn alloys.

I. Introduction

The resistance against motion of dislocation has been discussed under the mutual interference between the elastic strain in long range and the strain field in circumference of the dislocation(1) in crystals. But even if no elastic strain in long range were found in the crystal, the dislocation could not proceed freely owing to the structural imperfectness of dislocation centre in the cases when there are vacant lattice sites or other species of atoms in its centre as in alloys. In the previous paper(2) we have described a general method to calculate the resistance against motion of dislacation: namely the following two relations have been derived from a detailed consideration on the structure of dislocation centre.

I. It can be considered that the displacement of dislocation along the slip plane is produced through the repeated process of imaginary lattice transformation.

Let ΔG be the free energy difference per mole dissipated in the process of such lattice transformation, f the resistance to gliding per unit area and V the molar volume of crystal, then the following relation is satisfied,

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* The 555th Report from the Research Institute for Iron, Steel and Other Metals, Tôhoku University.

(1) G. I. Taylor; Proc. Roy. Soc. A. 145 (1934) 362. F. Seitz and Read; J. Appl. Phys. 12 (1941) 100; 170; 470; 538. Koehler; Phys. Rev. 60 (1941), 397.

(2) S. Takeuchi and H. Suzuki; Sci. Rep. RITU. 2 (1950), 50.

$$\left.\begin{aligned} \Delta G &= V\cdot f\cdot \Delta L\,, \\ \Delta L &= 0.306\,, \end{aligned}\right\} \qquad (1)$$

where

ΔL is the amount of deformation accompanied by the lattice transformation.

II. The quantity ΔG is given by the difference between Gibbs' free energies G^r and G^i of the states just before and after the imaginary transformation,

$$\left.\begin{aligned} G^r &= F^r + V\cdot a\cdot X\cdot \delta L\,, \\ G^i &= F^i - V\cdot X\cdot(\Delta L-\delta L)\,, \end{aligned}\right\} \qquad (2)$$

where F^r and F^r are the Helmholz's free energies of real and imaginary state free from stresses respectively, ΔL is a limiting value of reversible deformation in the real state state under a stress X and a a numerical constant $(1>a\geq 1/2.)$ The stress X is regulated so that G^r and G^i satisfy the condition of lattice transformation.

As the imaginary phase we take the lattice system which is attained by a relative displacement of neighbouring atomic planes parallel to the slip plane toward the glide direction in crystal in consideration. When the face centred cubic crystal is in question, for example, we take the body centred cubic latitce as the imaginarily transformed state and in the case of body centred crystal the face centred lattice is taken.

Using these two relations and the condition of lattice transformation, which has been already given by one of the authers[3], the amount of resistance against motion of dislocation can be calculated.

In order to carry out the calculation of resistance against gliding in metals and alloys, we must have a knowledge concerning the free energy of them. It is the most simple case when the crystal in consideration consists of the complete solid solution and there is no strain in it. First of all, as a simple application of this theory we will try to calculate the critical shear stresses of binary alloys.

II. The formula for the critical shear stress of binary alloys

When the lattice transformation occurs from the real phase with the concentration x_1 to the imaginary phase of the same x_1, the real phase must be in a state of excessive free energy compared with the imaginary phase by a certain amount. This amount is given by the free energy difference between both states when a tangent drawn for the free energy *vs.* concentration curve of the imaginary state at the concentration x_1 in consideration comes to the common tangent for the both free energy curves. Consequently we have on the common tangent,

$$\left(\frac{\partial G^i}{\partial x}\right)_{x_1} = \left(\frac{\partial G^r}{\partial x}\right)_{x_2} = \frac{G^i_{x_1} - G^r_{x_2}}{x_1 - x_2}\,, \qquad (3)$$

where x_2 is another concentration at which the curve of real phase is in contact with the

(3) S. Takeuchi; Sci. Rep. RITU. A 1 (1949), 43. N.K.G. 6 (1942), 361.

common tangent. Using (2) and (3), ΔG, the free energy difference to be dissipated in the process of transformation, is expressed as follows,

$$\Delta G=G^r_{x_1}-G^i_{x_2}=F^r_{x_1}-F^r_{x_2}-(x_1-x_2)\left(\frac{\partial F^r}{\partial x}\right)_{x_2}, \tag{4}$$

because the quantities $\alpha\cdot X\cdot\delta L$ and $X\cdot\Delta L$ in (2) are functions of x_1, but are independed on any other concentration and the change in the molar volume V due to variation of concentration is negligible small. And we have approximately

$$\left(\frac{\partial F^i}{\partial x}\right)_{x_1}=\left(\frac{\partial F^r}{\partial x}\right)_{x_2}. \tag{5}$$

When we substitute from (5) into (4), the resistance to gliding, f, can be calculated by means of (1).

An approximate formula of free energy for binary alloys is given by

$$F=(1-x)F_a+xF_b+RT\{(1-x)\log(1-x)+x\log x\}+x(1-x)\Phi_1,$$

where x is the concentration of species B of constituent atoms, F_a and F_b are the free energies of pure metals composed of atoms A and B respectively, and

$$\Phi_1=2E_{ab}-E_a-E_b,$$

Φ_1 is the so-called ordering energy. $2E_{ab}/Nz$, $2E_a/Nz$ and $2E_b/Nz$ are energies of mutual interaction of a pair of nearest neighbours AB, AA and BB respectively, z is the number of nearest neighbours around an atom and N is the Avogadoro's number. Then, if the following relation is allowed approximately

$$\Phi^r_1=\Phi^i_1=\Phi_1$$

we have

$$\begin{aligned}\Delta G&=G^r_{x_1}-G^i_{x_1}\\&=RT\left\{\log\frac{1-x_1}{1-x_2}+x_1\log\frac{x_1(1-x_2)}{x_2(1-x_1)}\right\}+(x_1-x_2)^2\Phi_1\end{aligned} \tag{6}$$

and

$$-H+RT\log\frac{x_1(1-x_2)}{x_2(1-x_1)}+2(x_1-x_2)\Phi_1=0, \tag{7}$$

where

$$H=(F^i_a-F^r_a)-(F^i_b-F^r_b),$$

and this quantity hardly depends on temperature at sufficiently high temperatures. Putting

$$\frac{RT}{H}=X,\quad \frac{\Phi_1}{H}=Y,\quad \frac{\Delta G}{H}=Z, \tag{8}$$

we obtain

$$Z=X\log\frac{1-x_1}{1-x_2}+x_1-(x_1-x_2)Y, \tag{6'}$$

and

$$X \log \frac{x_1(1-x_2)}{x_2(1-x_1)} = 1-2(x_1-x_2)Y\,. \qquad (7')$$

Substituting from (7′) into (6′) Z is expressed as a function of x_1, the concentration of the alloy. The curves Z *vs.* concentration take various forms for different values of X and Y. For example, curves were drawn for $Y=0.01$ and $X=0.1$, 0.4 and 1.0 in Fig. 1

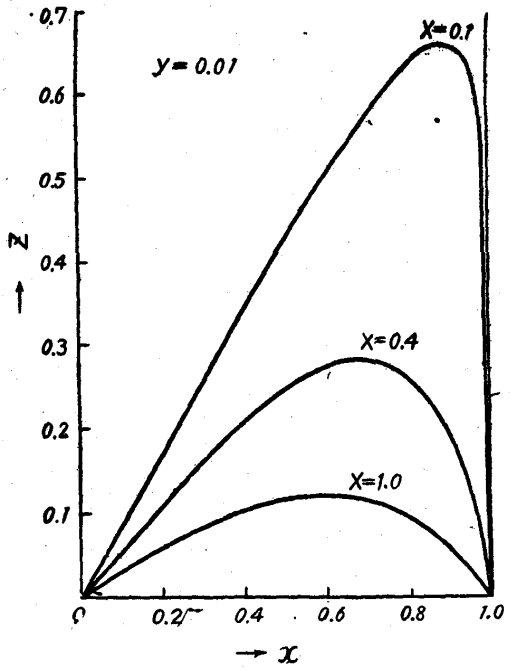

Fig. 1. Curve of Z *vs.* x for $Y=0.01$

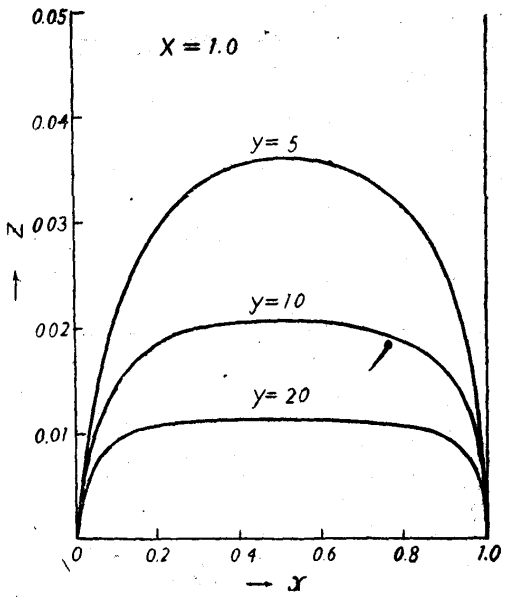

Fig. 2. Curve of Z *vs.* x for $X=1.0$

and for $X=1.0$ and $Y=5$, 10 and 20 in Fig. 2. As easily seen in these figures when the quantity $\frac{Y}{X}=\frac{\Phi_1}{RT}$ becomes smaller, Z approaches to a form, $Z=Cx(1-x)$, where C is a constant. But the curves are of very unsymmetric form for small values of X and the central part of the figure becomes flat for large values of Y.

III. Comparison with experimental data

If the values of constants H and Φ_1 were known, one could by means of the formula (1), (8), (6′) and (7′) compute values of the critical shear stress f for various concentrations and temperatures, and compare the values calculated with experimental data. But as the theory does not predict the values of H and Φ_1 a priori, we must examine whether these constants can be so chosen as to fit the experimental data for f, and examine whether these constants so determined can be consistent with our knowledge of thermodynamical properties of alloys.

Since the curves of critical shear stress *vs.* concentration contain X and Y as independent parameters, it will be very difficult to determine the values of these quantities precisely by a vague comparison with experimental data. The following formula is very

useful for this purpose, that is

$$\frac{Z_{max}}{X}=\frac{Vf_{max}\Delta L}{RT}=\frac{1}{4XY+X^2}, \qquad (9)$$

where Z_{max} and f_{max} are the maximum value of Z and of critical shear stress, under a set of certain X and Y, respectively. Using the value of f_{max} we can easily select a groupe of curves Z *vs.* concentration which have only one parameter. The resultant determination of the values of X and Y is then carried out by the following procedure: that is to construct curves, as shown in Fig. 3, of Z plotted against concentrations for different values of the parameter—— X or Y ——and to examine whether any of these can be superposed on the experimental curve of $V\cdot f\cdot \Delta L/RT$ plotted against the concentration.

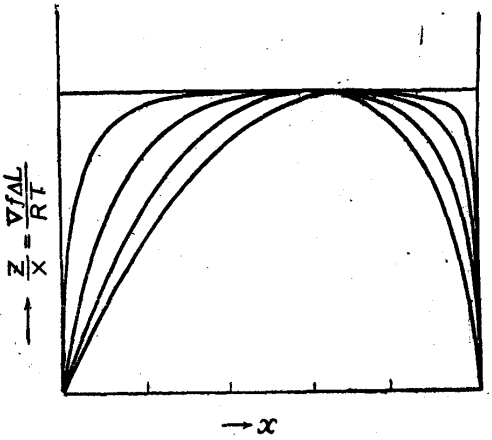

Fig. 3. A group of curves of Z *vs.* x for a given value of $\frac{Vf_{max}\Delta L}{RT}$

The formula (9) might be obtained by eliminating x_1 and x_2 from (6′), (7′) and the following condition:

$$\left(\frac{\partial Z}{\partial x}\right)_{X,Y}=0 \quad \text{for} \quad Z=Z_{max}.$$

But we have failed to prove (9) analytically, and we have been satisfied in finding that by numerical calculation it is always correct in the range of $0\leqq X\leqq 10$ and $0\leqq Y\leqq 20$.

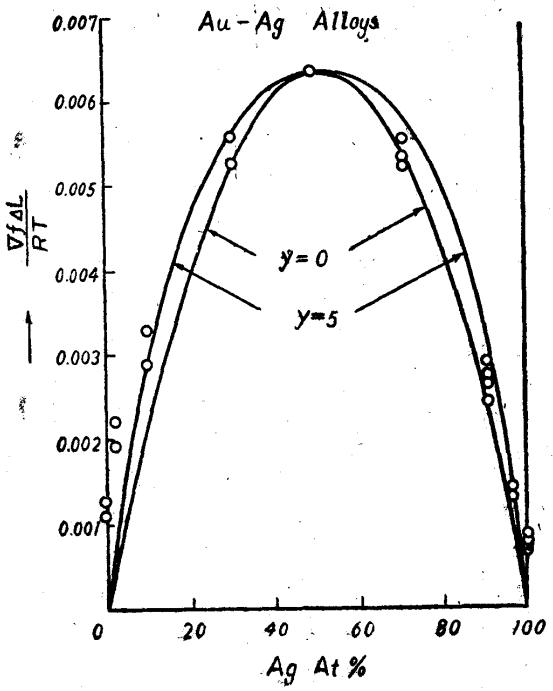

Fig 4. Critical shear stress of Au-Ag alloys (after G. Sachs and J. Weerts)

The experimental results for Au-Ag[4], Cu-Ni[5] and Cu-Zn[6] alloys are given in Figs. 4—6, where they are compared with theoretical curves for suitable values of X and Y. In the case of Au-Ag alloys the curves were calculated for $Y=0$ and $Y=5$. It will be seen that the observed values for very low and high concentrations deviate from those curves, and the accuracy of measure-

(4) G. Sachs u. J. Weerts; Zs. f. Phys. **62** (1930), 473.
(5) E. Osswald; Zs. f. Phys. **83** (1933), 55.
(6) V. Goeler u. G. Sachs; Zs. f. Phys. **55** (1929), 581.

ment does not yet permit an exact determination of Y. However, at any rate, it may be found that the curves for $0 \leqq Y \leqq 5$ are more suitable than that for the other values of Y. The deviation of the theoretical curves from the observed values for low and high concentrations seems to be caused by the fact that the effect of impurity is not negligible compared with that of the other kind of constituent atoms.

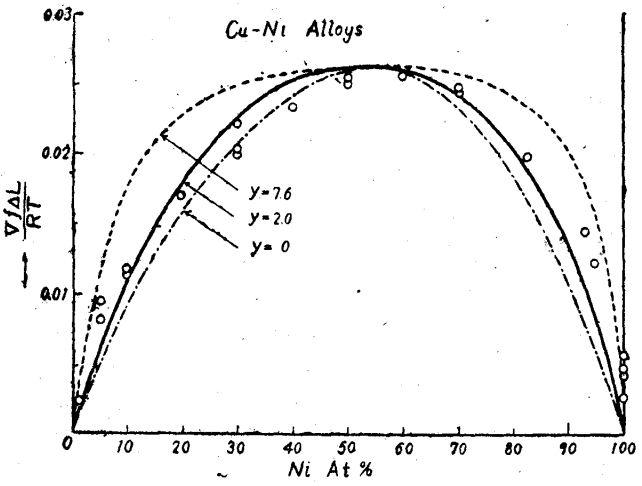

Fig. 5. Critical shear stress of Cu-Ni alloys (after E. Osswald)

In cases of Cu-Ni alloys the curve was drawn for a set of $X=1.74$ and $Y=-2$ as the most suitable value, but the unsymmetricity about the abscissa in the experimental curve is larger than in the theoretical curve. For reference, two calculated curves for $Y=7.6$ and 0 were drawn, but the discrepancy between the experimental data and these calculated curves becomes greater. It is of interest to notice that the curves of critical shear stress plotted against the concentration would take a more unsymmetric from about the abscissa, if the measurement would be carried out at a lower temperature such as that of liquid nitrogen.

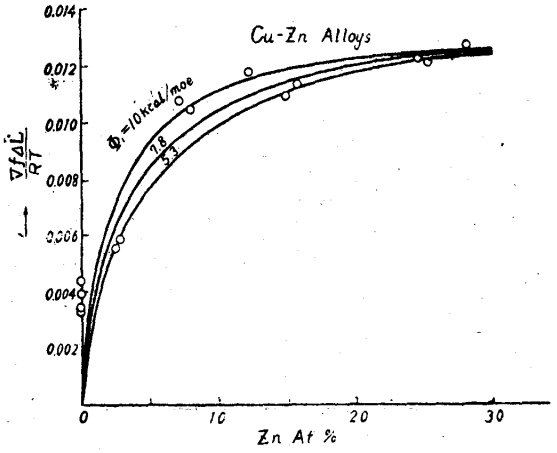

Fig. 6. Critical shear stress of Cu-Zn alloys (after V. Goeler and G. Sachs)

In cases of Cu-Zn alloys the observed values have a very wide flat part corresponding to higher concentration, as shown in Fig. 6. According to the general feature of the curves of Z *vs.* concentration, it may be expected that Φ_1 will take a very large value for these alloys. The curves in this figure are calculated for $\Phi_1=10$ Kcal, 7.8 Kcal and 5.3 Kcal respectively. It may be found that there is sufficient agreement between observed and theoretical values, if we consider the accuracy of measurement.

We will now examine whether the value of X and Y, determined by the above procedure, can be consistent with our knowledge of thermodynamic properties of these alloys. The numerical values of X and Y for each alloy are as follows.

Au-Ag alloys: $3.34<X<4.41$

$0<Y<5$

$134<H<179$ cal/mol

$0<\Phi_1<895$ cal/mol

$T_c<218°K$

Cu-Ni alloys: $X\sim1.74$

$Y\sim2.0$

$H\sim340$ cal/mol

$\Phi_1\sim680$ cal/mol

$T_c\sim167°K$

Cu-Zn alloys: $1<X<1.33$

$12<Y<17.3$

$445<H<592$ cal/mol

5.3 Kcal$<\Phi_1<10$ Kcal

$670°<T_c<1250°K$

where T_c is the critical temperature of superlattice formation estimated according to Bragg-William's approvimation.

Although we have no informations about H, it will be shown in the forthcoming paper that those values for H might be reasonable beause they are considerably smaller than $F_a^i-F_a^r$ or $F_b^i-F_b^r$. In cases of Cu-Ni and Au-Ag, T_c which is so determined as to fit the experimental data for f, is lower than room temperature, and this fact is consistent with the experimental result that no superlattice has been found in these alloys. But in the case of α-brass, theoretical T_c must be higher than $400°C$, while the superlattice Cu_3Zn has not yet been found(7). This discrepancy seems to be caused by the imperfection of theory of superlattice, because, according to the direct measurements of vapour pressure(8) or the electro-chemical measurements of activity(9) of Zn in these alloys, the value of Φ_1 falls into $5\sim8$ Kcal/mol, which is consistent with our results.

In the evaluation of free energy, used in this paper as well as elsewhere, the difference of atomic radius in alloys is not taken into account, but it seems to play a very important role in the resistance to gliding. In order to discuss the effect of difference in atomic radius, not only the precise evaluation of free energy but further consideration on the structure of dislocation should be required. We will try to carry out a detailed treatment on this subject in a forthcoming paper.

(7) Some authers report on anormallies at 220—450°C in this alloy, but it seems to require further investigations to conclude that the anormallies are caused by superlattice Cu_3Zn.

(8) R. Hargreaves; J. Inst. Metals, **64** (1939), 15.

(9) F. Weibke; Z. f. Metallk., **29** (1937), 79.

Summary

The critical shear stress of binary alloys are calculated by means of two relations which have been derived in the previous paper[2], considering the structure of the center of dislocation. The curves of critical shear stress plotted against the concentration of binary alloys take various forms for different values of X and Y, where $X=\frac{RT}{H}$, $Y=\frac{\Phi_1}{H}$, $H=(F_a^i-F_a^r)-(F_b^i-F_b^r)$, and F_a^i, F_a^r, F_b^i, and F_b^r are the Helmholtz's free energy of pure cvrystal composed of atoms A and B in the real and in the imaginary crystal phase respectively. The quantity H hardly depends on temperature at sufficiently high temperatures. As $\frac{Y}{X}=\frac{\Phi_1}{RT}$ becomes smaller, the critical shear stress f is nearer to the form, $f=Cx(1-x)$, where C is a constant and x is the concentration. But the curves take very unsymmetric forms for small values of X and the central part of the curve becomes flat for large Y.

The comparison with observations shows good agreement in the cases of Au-Ag. Cu-Ni and Cu-Zn alloys, in which two sorts of constituent atoms have almostly the same atomic radius. The difference of atomic radius between two kinds of constituent atoms seems to play an important role in the resistance against glidiñg and it is desirable to take this factor into acocunt.