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On Short Range Order Hardening

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Abstract

Phenomenological calculation which can introduce the concentration dependence into pair interaction energies is employed to estimate the Short Range Order Hardening for Cu-Au system at 720 K. Also, computer simulation technique is developed to analyze the effect of subsequent dislocations on the SROH. Finally, the deficiencies of the theoretical treatments developed for the SROH are pointed out.

1. Introduction

The basic theory for the Short Range Order Hardening (hereafter SROH) was first proposed by Fisher.[1] This theory claims that the increment of internal energy due to the destruction of atomic bond at thermal equilibrium state caused by a dislocation motion contributes to the hardening of an alloy. Flinn[2] calculated the hardening effect for an fcc solid solution by taking the 1st nearest neighbor (n. n.) pair interaction energy into the theory of Fisher.

Mohri et al.[3]estimated the magnitude of hardening based not only on the 1 st n. n. but also the 2 nd n. n. pair interaction energies, and the result was discussed in connection with a phase diagram[4] which is obtained in the same framework of an employed model.

We made use of the phenomenological calculation[5] which could introduce the realistic value into the pair interaction energies and attempted more realistic calculation of SROH for Cu-Au alloy. Also we employed the computer simulation teqhnique to estimate the SROH for slip of multiple dislocations. In this report, a brief review of the theoretical investigation advanced for the SROH is provided. The main emphasis is placed on our calculations based on phenomenological method and computer simulation.

2. Basic Theory

When a dislocation moves across the slip plane, the state of short range order is partially destroyed and a random configuration which has higher internal energy is produced. The energy increment γ per unit area of a slip plane can be related to the resolved shear stress τ in the following way[1]

$$\tau=\frac{\gamma}{b} \quad , \tag{1}$$

where b is the burgers vector.

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Flinn[2] calculated the energy increment γ for an fcc solid solution by taking the 1 st n. n. pair interaction energy into account. For an atom at position A in Figure 1, among the twelve nearest neighbors of the A atom, six atoms lie in the (111) plane where A is located, three atoms lie in the plane above and the other three atoms in the plane below. During the glide of a dislocation with Burgers vector $b=\frac{1}{2}a[10\bar{1}]$ where a is the lattice constant, out of the three nearest neighbors across a slip plane, one will be replaced by a 2 nd n. n. pair, another one by a different 1 st n. n. and the other by a 3 rd n. n. pair. The change of internal energy per atom, ΔE, is obtained in the following expression, provided that atomic correlations larger than 1 st n. n. vanishes.

$$\Delta E=2\cdot X_A X_B v_1 \alpha_1 \quad , \tag{2}$$

where X_A, X_B are, respectively, the atomic fraction of A and B atom, and v_1 and α_1 are, respectively, the effective pair interaction energy and Warren-Cowley short range order parameter for the 1 st n. n. pair. By dividing ΔE by the area occupied by one atom in the slip plane, the energy increment γ is obtained as :

$$\gamma=\frac{4.0}{a^2\sqrt{3}}\Delta E \quad . \tag{3}$$

Substitution of eq. (3) into eq. (1) yields the shear stress :

$$\tau=\frac{\gamma}{b}$$

$$=4.0\sqrt{\frac{2}{3}}\frac{\Delta E}{a^3} \quad . \tag{4}$$

In order to introduce further distant pair interactions and correlations, Mohri et al.[3] employed the Tetrahedron-Octahedron approximation[4] of the Cluster Variation Method[6] which takes pair correlations up to 2 nd n. n. pair into account. They derived[3] the following expression for ΔE,

$$\Delta E_M=\frac{1}{2}(2\,\xi_1-\xi_2-\xi_0^2)\,v_1+\frac{1}{2}(-\xi_1+3\,\xi_2-2\,\xi_0^2)\,v_2 \quad , \tag{5}$$

where ξ_i is the correlation function for an atomic cluster i. One of the advantages of Mohri et al. 's calculation is they discussed the SROH based on a phase diagram which is derived by the same framework of the thermodynamic model, ie. T-O CVM. However the common shortcomings shared by Flinn's and Mohri et al. 's calculations are that constancy of pair interaction energies are assumed, which is by far acceptable for a real alloy system. In order to introduce a concentration dependency into a pair interaction energy, we developed the following phenomenological scheme.

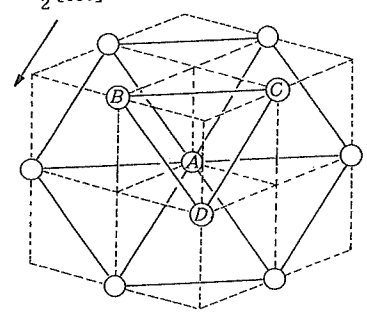

Fig. 1 Perspective view of an fcc lattice. Atom A is located below the slip plane and atoms B, C, D are above the slip plane.

3. Phenomenological calculation

Phenomenological calculation of a phase diagram was first devised by Sanchez et al.[5] to calculate γ/γ' phase boundary for Ni-Al system. They adopted Lennard-Jones potential[5] to describe atomic interactions separated by a distance r :

$$e_{ij}=e_{ij}^{0}\left\{\left(\frac{r_{ij}}{r}\right)^{8}-2\left(\frac{r_{ij}}{r}\right)^{4}\right\} \quad , \tag{6}$$

where i and j stand for atomic species (A or B). Six unknown coefficient terms for a binary system, e_{ij}^{0} and r_{ij} can be estimated from experimental values of cohesive energies of constituents metals, heats of formation of an intermetallic compound and the lattice constants in the following manner.[5]

The internal energy is generally given by

$$E=\frac{1}{2}\omega N\sum_{ij}\mathrm{e}_{ij}(r)\,y_{ij} \quad , \tag{7}$$

where ω is the coordination number of 1 st n. n., N is the total number of lattice points and y_{ij} is the pair probability of finding i-j pair at 1 st n. n. For a pure metal A,

$$y_{\mathrm{AA}}=1 \quad , \tag{8}$$

and

$$y_{\mathrm{AB}}=y_{\mathrm{BB}}=0 \quad . \tag{9}$$

Similary for pure metal B,

$$y_{\mathrm{BB}}=1 \quad , \tag{10}$$

and

$$y_{\mathrm{AA}}=y_{\mathrm{AB}}=0 \quad , \tag{11}$$

then the internal energies for pure metals A and B are, respectively, given by

$$E_{\mathrm{A}}=\frac{1}{2}\omega N e_{\mathrm{AA}}(r) \quad , \tag{12}$$

and

$$E_{\mathrm{B}}=\frac{1}{2}\omega N e_{\mathrm{BB}}(r) \quad . \tag{13}$$

For a completely ordered intermetallic compound A_3B with L 1_2 structure, on the other hand, y_{ij}'s are given as

$$y_{\mathrm{AA}}=\frac{1}{2} \quad , \tag{14}$$

$$y_{\mathrm{AB}}=\frac{1}{2} \quad , \tag{15}$$

and

$$y_{BB}=0 \quad . \tag{16}$$

Then, the internal energy is described as

$$E_{A_3B}=\frac{1}{2}\omega N\left(e_{AA}(r)+e_{AB}(r)\right)\times\frac{1}{2} \quad . \tag{17}$$

Those energies, eqs. (12), (13) and (17), should have a minimum at an equilibrium lattice constant r^* ;

$$\left\{\frac{d}{dr}\left(\sum_{ij}e_{ij}y_{ij}\right)\right\}_{r=r^*}=0 \quad . \tag{18}$$

Together with experimental heats of formation and lattice constant, substitution of the eqs. (12), (13) and (17) into (18) determines unknown Lennard-Jones parameters uniquely.

$$e^0_{AA}=-\frac{2}{\omega}E_A \quad , \tag{19}$$

$$r_{AA}=\frac{a_A}{\sqrt{2}} \quad , \tag{20}$$

$$e^0_{BB}=-\frac{2}{\omega}E_B \quad , \tag{21}$$

$$r_{BB}=\frac{a_B}{\sqrt{2}} \quad , \tag{22}$$

$$e^0_{AB}=\frac{2}{\omega}\frac{\left[E_A\times\Delta^4-2\times E_{A_3B}\right]^2}{E_A\times\Delta^8-2\times E_{A_3B}} \tag{23}$$

and

$$r_{AB}=\frac{a_{A_3B}}{\sqrt{2}}\times\left(\frac{E_A\times\Delta^8-2\times E_{A_3B}}{E_A\times\Delta^4-2\times E_{A_3B}}\right)^{\frac{1}{4}} \quad , \tag{24}$$

where E_A, E_B, are cohesive energies for A and B, E_{A_3B} is the heats of formation of A_3B, a_A, a_B, a_{A_3B} are the lattice constants and Δ is a_A/a_{A_3B}.

By combining this Lennard-Jones type pair potential with Tetrahedron approximation of the CVM, grand potential of a system is calculated. The minimization of the grand potential is carried out with respect to both the volume (equivalently lattice constant r) and cluster probabilities x_i (point), y_{ij} (pair), w_{ijkl} (tetrahedron), under a constraint $\sum_{ijkl} w_{ijkl}=1$. This operation provides the equilibrium lattice constant and cluster concentrations (configuration). By substituting the pair interaction energy and calculated short range order parameters (cluster probabilities) into eq. (2) , SROH is evaluated.

In this study SROH was calculated for Cu-Au system at 720 K. In order to determine the coefficent terms of above equation, cohesive energies of Cu and Au, heats of formation of Cu_3Au, and lattice constants of these substances are cited from Hultgren[7] and Pearson[8]. The calculated values of these coefficent terms as well as the employed energies are tabulated in the Table 1, and the resulting Lennard-Jones potential are shown in Fig. 2. One can see that the bottom of the pair potential for Cu-Au is deeper than those for Cu-Cu and Au-Au, which indicates the ordering tendency of this system.

Shown in Fig. 3 are the concentration dependency of calculated SROH and short range

Table 1 The employed energies and the calculated values of coefficent terms which determine Lennard-Jones potential.

	lattice constant (Å)	cohesive energy (kcal/mol)	heat of formation (kcal/mol)
Cu	3.6147	−80.860	
Au	4.0785	−87.300	
Cu_3Au	3.7426		−1.710

	e°_{ij} (kcal/mol)	r_{ij} (Å)
Cu−Cu	13.48	2.5560
Cu−Au	14.94	2.7061
Au−Au	14.55	2.8839

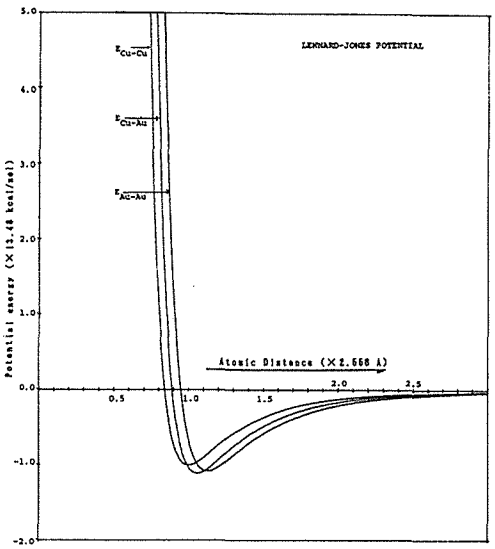

Fig. 2 Lennard-Jones Potential for Cu-Au system. The parameters employed are given in Table 1.

order parameter at 720 K, and the cross marks are measured critical resolved shear stresses by Nosova al[9]. As compared with these values, the calculated SROH are glossly overestimated. This discrepancy may be explained in the following way. In the present model, these pairs are arranged on a lattice which deforms without allowing local lattice distortion. Then, both Au-Au pairs and Cu-Cu pairs are forced to have equivalent atomic distance which is larger than the equilibrium lattice constant of pure Cu and shorter than that of pure Au. Therefore, the internal energies are

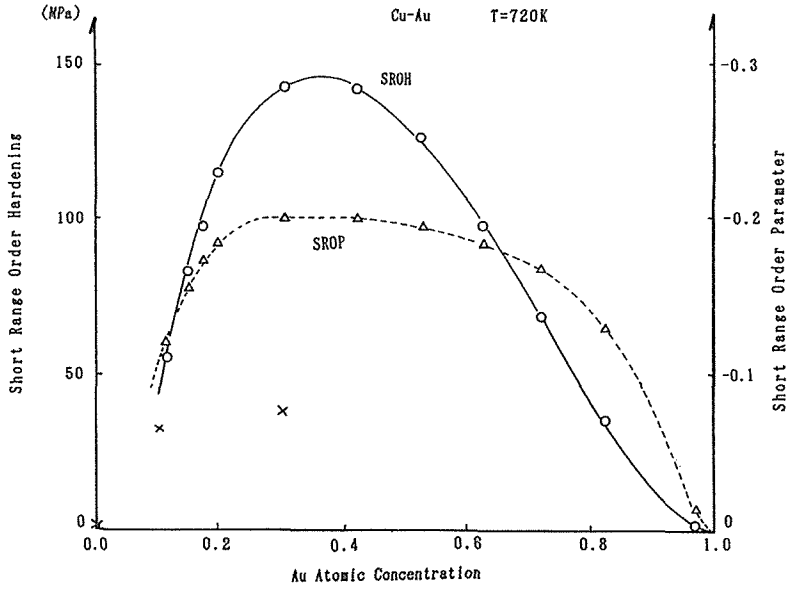

Fig. 3 Concentration dependency of SROH and Short Range Order parameter at 720K. Full line and dotted line represent SROH and Short Range Order parameter, respectively.

overestimated. Due to the dislocation motion, the equilibrium short range order is destroyed and a more random configuration is created. This suggests that the number of unlike pairs (short range order) is decreased while that of like pairs is increased with reference to the state before dislocation motion. Then, the energy difference between like atom pairs and unlike atom pairs contributes to ΔE. In order to resolve this defficiency and to consider multiple dislocations motion, we employed the following computer simulation.

4. Computer Simulation

The computer simulation technique is a powerful means which is free from a framework imposed by a theory. The present simulation program was originaly developed by Williams[10] to simulate an atomic configuration for a set of experimentally obtained Warren-Cowley short range order parameters $\{\alpha_i\}$. The program was then modified by us so that dislocations slip can be incorporated in the following manner.

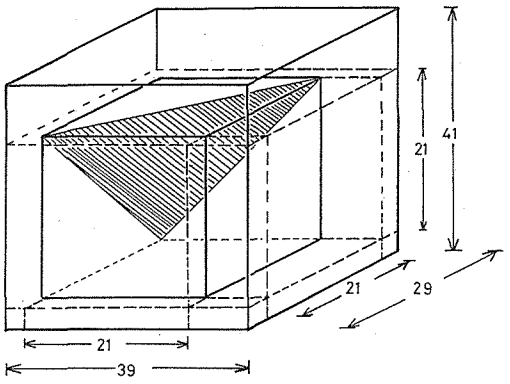

Fig. 4 The model fcc crystal employed in this study.
The hached area indicates the {111} slip plane. [15]

The model crystal, as is shown in Fig. 4[15], contains $29\times39\times41$ lattice points. Since no periodic boundary condition is introduced the effective size of a slip plane is limited to $21\times21\times21$ lattice points. For this size of a crystal the upper limit of the number of passed dislocations is six.

In order to create an initial equilibrium atomic configulation, a set of Warren-Cowley short range order parameter $\{\alpha_i\}$, which are sited from ref.11, are input. Then the energy increasement due to a slip of a dislocation is calculated by directly counting change of the atomic bonds between the initial and final configulation from the following equations :

$$E=\sum_i v_i\xi_i \quad , \tag{25}$$

and

$$\Delta E=E^{aft}-E^{bfr}$$

$$=\sum_i v_i\Delta\xi_i \quad , \tag{26}$$

where v_i is the effective interaction energies for i-th distant pair which are cited from ref.12 and $\Delta\xi$ is the change of correlations before and after the slip.

5. Results and Discussions

Prior to the SROH calculation, the perfectly ordered system was simulated in order to examine the validity of this study. Fig. 5[15] is the changes of the Warren-Cowley short-range

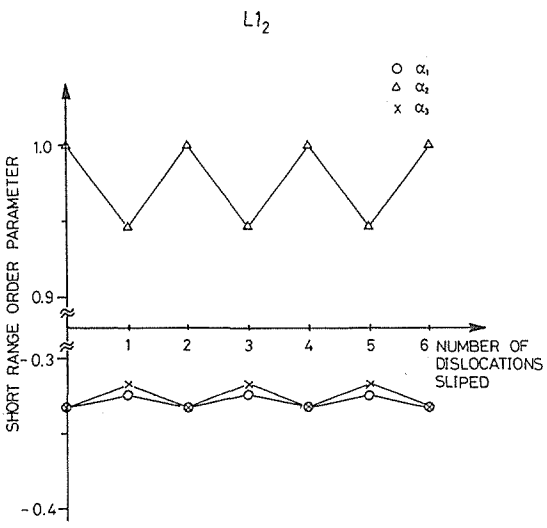

Fig. 5 The change of Warren-Cowley short range order parameter with the passage of six dislocations for $L1_2$ ordered phase. Each line, from top to bottom, corresponds to the short range order parameter for the 2nd, 3rd and 1st nearest neighbor pair, respectively. [15]

order parameters for L 1_2 phase, with the motion of dislocations. One can clearly see that the changes are exactly cyclic and the ordered state is perfectly recovered after a passage of a pair of dislocations. This has been certainly observed in an ordered alloy as a formation of a superdislocation, which rationalizes the present simulation.

In order to compromise the accuracy of the calculated result with the economy of computer time, pair interaction energies up to sixth distant pair are taken into account. In fact, up to sixth n. n. pair interaction, one can reproduce the 98% of measured heats of formation as is shown in Fig. 6[15].

Fig. 7[15] shows the SROH by passage of dislocations for Cu-25 at%Au at 678 K. Each line corresponds to the different initial configurations. The biggest value which is in the range of 15 MPa to 30 MPa is caused by the leading dislocation. The negative values for the 2 nd dislocation suggest the recovery of the states of order. The fact that the absolute values of SROH for the subsequent dislocations approch zero indicates that a plastic deformation destroys the state of order and randomizes a crystal.

The experimental Critical Resolved Shear Stress for this alloy is reported to be ~40 MPa.[13] The SROH obtained by phenomenlogical calculation 50 MPa to 150 MPa were above this value, while 15 MPa to 30 MPa obtained from the present simulation are below this level. However, Buttner et al.[14]concluded that the SROH for Cu-10 at%Au is negligibly small based on their experiment. Since more frequent reconstruction of atomic bonds takes place in a concentrated alloy the SROH is expected to be bigger for higher concentrations. In fact, our preliminary study of the concentration dependency of SROH, in which $\Delta\xi_i$ in eq. (26) due to the passage of a leading dislocation was calculated, indicates that the SROH for 50 at%Au at 700 K is about 2.1 times higher than that for 25 at%Au at 678 K, provided that v_i does not have significant concentration dependency.

The above mechanism, however, does not explain the discrepancies satisfactorily. We believe that the major reason for overestimated SROH can be ascribed to the following theoretical shortcomings in this study as well as in previous analytical studies. In the calculations, a one to one correspondence of atoms across the slip plane has been assumed. Hence, all atoms on one side of the slip plane are subject to a uniform displacement relative to those on the other side of the slip plane. This is virtually a perfect crystal. It has been

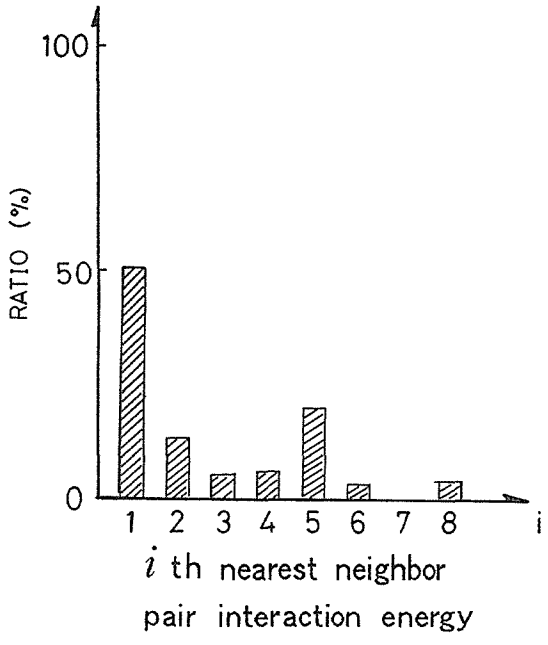

Fig. 6 The contribution of i-th pair interaction energy to the measured [7] heats of formation for Cu-25at. %Au at 678K. Note that each pair interaction energy is given [12] by $\frac{1}{2}N \cdot X_A \cdot X_B \cdot Z_i (1-\alpha_i) \cdot v_i$, and the sum up to $i=6$ provides 98% of the experimental value. [15]

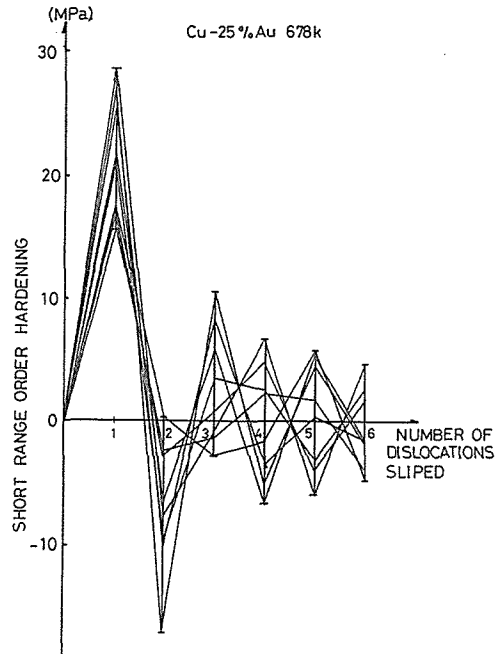

Fig. 7 The change of SROH with the slip of six dislocations for Cu-25at. %Au at 678K. Each line corresponds to the different initial configuration. [15]

well known that an introduction of a dislocation perturbes the one to one atomic correspondence, and part of the energies demanded by atoms climbing up the potential field which is formed by atoms on the opposite side of a slip plane are compensated by other atoms going down the potential field. This is, in fact, a dislocation motion in a Peierls potential field, and we believe that the net SROH would be reduced to a certain extent with this mechanism.

Furthermore, in the estimation of the SROH, the change of the internal energy, that is eqs. (2) and (26), is evaluated before and after the slip ie. ΔE per $|b|$. Although this provides the first approximated solution more rigorous treatment would demand the energy profile as a function of atomic displacement from original position to $|b|$. The maximum inclination of the energy profile could provide a refined SROH value. These points, however, are beyond the scope of the present simulation. We will discuss the detail of this mechanism in a separate issue.

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