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journal or publication title	Materials Transactions
volume	42
number	3
page range	429-431
year	2001
URL	http://hdl.handle.net/10097/52196

Strain Dependence of Solute Atom Energy in Aluminum-Rich Alloys*

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The dependence of the solute atom energy on the homogeneous strain is derived by expanding the energy of the binary alloy to the second order in the solute concentration and the homogeneous strain components. The energy change is found to be proportional to the solute induced stress. An *ab-initio* method is then applied to calculate the solute induced stress for Cu, Fe, Li, Mg, Mn, Si, and Zn solute atoms in aluminum.

(Received October 31, 2000; Accepted January 10, 2001)

Keywords: aluminum, alloy, solution energy, strain

1. Introduction

A material is always subjected to some strain field imposed by its environment or the defects in the material itself. The strain field affects the energy of the solute atoms, and induces their migration resulting in a strain dependent distribution of solute atoms. An example of such effect is the segregation of solute atoms by the dislocation.¹⁾ Today computing resources allow us to perform parameter-free computation of the effect from the first principles. We derive the effect of the homogeneous strain on the solute atom energy by expanding the energy of the binary alloy to the second order in the concentration and the homogeneous strain, and then apply an *ab-initio* method to calculate the effect for Cu, Fe, Li, Mg, Mn, Si, and Zn solute atoms in aluminum.

2. Theory

The energy of an A-rich binary alloy, $A_{1-c}B_c$ can be written as a function of the concentration of B and the homogeneous strain. The reference strain state, *i.e.* the atomic positions in which the strain is said to be zero, is normally chosen as the state of lowest energy, however, as we are considering alloys with different concentrations, it is more convenient to take the equilibrium position of the host lattice as the reference for alloys of all concentrations. An alloy with a concentration c has a different equilibrium volume as the host lattice, therefore, using the chosen reference strain state, the equilibrium state of the alloy is spontaneously strained. It is also important to emphasize that the strain we are considering here is the homogeneous strain imposed on the alloy by an external factor, rather than the internal strain resulting from the atomic relaxation around the solute atoms.

For a dilute alloy and a small strain, the energy can be expanded around the concentration $c = 0$ and the strain $\bar{\epsilon} = 0$ in terms of the first derivative with respect to the concentration (the derivative with respect to the strain vanishes) and the second derivatives with respect to the concentration and strain as

$$E_a(c, \bar{\epsilon}) = E_a^0 + c \frac{\partial E_a}{\partial c} + \frac{1}{2} \left[c^2 \frac{\partial^2 E_a}{\partial c^2} + 2c \sum_{i,j} \epsilon_{ij} \frac{\partial^2 E_a}{\partial c \partial \epsilon_{ij}} + \sum_{i,j,k,l} \epsilon_{ij} \epsilon_{kl} \frac{\partial^2 E_a}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right], \quad (1)$$

where E_a is the alloy energy, E_a^0 is the energy of the strain free host lattice. The summations are taken over $i, j, k, l = x, y, z$, and all the partial derivatives are to be evaluated at $c = 0$ and $\bar{\epsilon} = 0$.

The partial derivatives with respect to the strain components in eq. (1) form two tensors, the derivative of the stress tensor, $V_0 \partial \sigma_{ij} / \partial c = -\partial^2 E_a / \partial c \partial \epsilon_{ij}$, and the elastic modulus tensor, $V_0 C_{ijkl} = \partial^2 E_a / \partial \epsilon_{ij} \partial \epsilon_{kl}$. The stress tensor is zero for the host lattice at the equilibrium; its derivative with respect to the concentration is, therefore, the stress due to adding the solute atom into the host lattice, and hence will be referred to as the solute induced stress.

The symmetry consideration reduces the number of the independent non-vanishing components of the two tensors. For a random substitutional binary alloy $A_{1-c}B_c$, the probability of finding an A atom at a lattice site, p_A , and that of a B atom, p_B , are the same at every lattice site, and therefore, the alloy has the same symmetry as the underlying lattice. An A-rich alloy has the same underlying lattice and, thus, the same symmetry as the pure A material. In the particular case of a cubic host material, like aluminum, its dilute random alloy will have the cubic symmetry also. As the quantities characterizing the alloy properties must remain unchanged under the alloy symmetry operations, the derivative of the stress tensor has only one independent non-vanishing component,²⁾ $\partial \sigma_{xx} / \partial c = \partial \sigma_{yy} / \partial c = \partial \sigma_{zz} / \partial c$.

The effect of the strain on the solute atom energy can be evaluated from the energy difference between two systems, both consisting of two subsystems, each containing the same number of atoms, N , but one subsystem has a solute concentration $c = 0$ and the other subsystem $c = c_0$. In system A, the subsystem with $c = 0$ is strain free and the subsystem with $c = c_0$ has a strain $\bar{\epsilon}_0$, while in system B, the subsystem with $c = 0$ has the strain $\bar{\epsilon}_0$ and the subsystem with $c = c_0$ is strain free. The only difference between the two systems is whether the solute atoms are in the strained or the strain free subsystems, and therefore, the energy difference between the two systems is the change of the energy of the solute atom,

*This Paper was Presented at the Autumn Meeting of the Japan Institute of Metals, held in Nagoya, on October 3, 2000.

E_s , due to the strain,

$$E_s(\bar{\varepsilon}_0) - E_s(0) = \frac{[E_a(0, 0) + E_a(c_0, \bar{\varepsilon})] - [E_a(0, \bar{\varepsilon}) + E_a(c_0, 0)]}{c_0 N}. \quad (2)$$

Substituting the expansion of the alloy energy, eq. (1), we obtain,

$$E_s(\bar{\varepsilon}) - E_s(0) = -\frac{V_0}{N} \sum_{ij} \varepsilon_{ij} \frac{\partial \sigma_{ij}}{\partial c}. \quad (3)$$

Equation (3) gives the change of the solute atom energy in term of the derivative of the stress tensor. Eshelby³⁾ has developed a continuum theory of lattice defects by describing a defect as an elastic inclusion with a particular equilibrium volume and elastic moduli in a hole in the host matrix with a different equilibrium volume and elastic moduli. In this work, however, we will use an *ab-initio* method to compute $\partial \sigma_{ij} / \partial c$ directly without introducing empirical parameters such as the solute-host volume difference and the solute elastic moduli.

As a cubic material has only one independent component of the stress tensor, $\partial \sigma_{xx} / \partial c$, its solute atom energy depends on the hydrostatic components of the strain only. Solute atoms that increase the equilibrium volume of the alloy will have a lower (higher) energy under expansive (compressive) strain, and the reverse is true for solute atoms that decrease the equilibrium volume of the alloy.

3. Calculation Method and Results

The pseudo-potential method is used to calculate the electronic structure of the alloy by Vienna *Ab-initio* Simulation Package.⁴⁾ The method is based on the local density approximation⁵⁾ of the density functional theory, and utilizes ultra-soft pseudo-potentials.^{6,7)} The Brillouin-zone integrations use Monkhorst-Pack⁸⁾ special k-points.

The calculations were done using supercells consisting of 8 atoms, Al_7X with X being one of Al, Cu, Fe, Li, Mg, Mn, Si, and Zn as shown in Fig. 1. The supercells translation vectors were in the same directions as the primitive translation vectors of the face-centered cubic lattice, with the length twice as long. The shortest distance between the solute atoms is equal to twice that of the aluminum atoms.

The energy of the aluminum supercell was calculated as a function of the cell size, and the result was fitted to Birch's equation of state.⁹⁾ The equilibrium lattice parameter was determined from the minimum of the energy with respect to the lattice parameter. The supercells of the alloys were set to have the same lattice parameter and the stress tensors were calculated.

The calculations were performed with constant cut-off energies for expanding the wave-functions and for the augmentation charges of 300 eV and 400 eV, respectively. Both cut-off energies were large enough for the ultra-soft pseudo-potentials used in the calculation. The reciprocal space integrations were performed on a $19 \times 19 \times 19$ k-point mesh in the first Brillouin zone of the supercell, which is equivalent to 54,872 k-points in the first Brillouin zone of the primitive cell of aluminum. To estimate the error due to the reciprocal space integrations, calculations were also performed for the Al_8 , Al_7Fe and Al_7Li cells with three additional meshes,

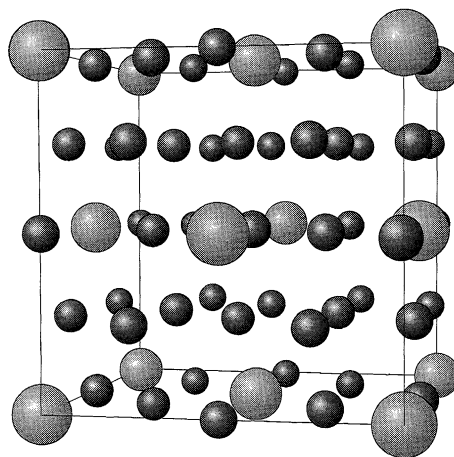


Fig. 1 Supercell of Al_7X used in the calculations with Al and X being represented by the black and the white spheres, respectively.

Table 1 Calculated stress (GPa) due to the solute atom and the solute atom energy change (kJ/mol) with respect to the hydrostatic strain, $\varepsilon \equiv \Delta V / V_0$.

Solute atom	$\partial \sigma_{xx} / \partial c$	$\Delta E_s / \varepsilon$
Cu	-32.9	-313
Fe	-73.1	-695
Li	-2.8	-26
Mg	22.8	216
Mn	-64.5	-613
Si	-12.1	-115
Zn	-10.0	-95

namely, $13 \times 13 \times 13$, $15 \times 15 \times 15$, and $17 \times 17 \times 17$ k-point meshes. The errors are estimated from the standard deviation of the stress tensors calculated with different k-point meshes, and the errors in $\partial \sigma_{xx} / \partial c$ are expected to be ± 0.07 and ± 0.25 GPa for Li and Fe, respectively.

Table 1 shows the calculated values of $\partial \sigma_{xx} / \partial c$ and the change in the solute atom energy per fractional volume change, $\varepsilon \equiv \Delta V / V_0$. The effect of the strain was found to be minimal for the Li solute atom. It was more pronounced for Zn, Si, Mg and Cu, respectively, and was particularly strong for the Mn and Fe solute atoms. All species, except Mg, were found to decrease the equilibrium volume of the alloy and to have a lower energy under compressive strain. Therefore, when a non-uniform strain field is imposed on the alloy, the concentration of these atoms will be enhanced in the area where the strain is compressive. The Mg solute atom will behave in the opposite way. The slip plane of an edge dislocation divides the areas where the strain field is compressive and where the strain field is expansive. According to the above result, Cu, Mn, Li, Si, and Zn will be attracted to one side of the slip plane while Mg will be attracted to the opposite side.

The solute energy change per atom can be compared to the thermal energy at a particular temperature. If the temperature is 300 K, the thermal energy is about 26 meV, whereas one percent volume reduction causes changes in the solution energy of 3, 10, 10 and 22 meV for Li, Si, Zn and Mg, respectively. Therefore, the effect of the strain will be smeared by the thermal fluctuation and a higher strain is needed to produce observable change in the concentration profile of these

atoms. The same strain may produce significant effect to the Cu, Mn and Fe solute atoms, whose energy changes are 30, 60 and 70 meV, respectively.

4. Conclusion

When the binary alloy energy is expanded to the second order in the solute concentration and the strain, the effect of the strain on the solute atom energy can be derived to be proportional to the solute induced stress. The symmetry consideration suggests that for a cubic material the hydrostatic component of the strain only affects the energy, and the energy change is proportional to the volume change due to the strain. Solute atoms that increase the equilibrium volume of the alloy will have a lower energy in the expansive strain, while the opposite is true for solute atoms that decrease the equilibrium volume of the alloy. According to the calculated solute induced stress, Cu, Fe, Li, Mn, Si and Zn atoms in aluminum will migrate towards compressed areas, whereas Mg atoms

will migrate towards dilatated areas. The energy change was found to be largest for the Mn and Fe solute atom, and has values of about 6 and 7 kJ/mol for a percent volume change, respectively. The effect is weaker for Li, Si, Zn and Mg, and it may be observable only under larger strain fields.

REFERENCES

- 1) C. L. Rohrer: *J. Mater. Res.* **10** (1995) 578–590.
- 2) See for example L. D. Landau and E. M. Lifshitz: *Course of Theoretical Physics*, Vol. 7, *Theory of Elasticity*, 3rd ed., chapter 10 (Pergamon Press, New York, 1986) pp. 32–35.
- 3) J. D. Eshelby: “The Continuum Theory of Lattice Defects” in *Solid State Physics: Advances in Research and Applications* Vol. 3, Ed. by F. Seitz and D. Turnbull (Academic Press, New York, 1956) pp. 79–144.
- 4) G. Kresse and J. Furthmüller: *Comp. Mat. Sci.* **6** (1996) 15–50.
- 5) J. P. Perdew and A. Zunger: *Phys. Rev. B* **23** (1981) 5048–5079.
- 6) D. Vanderbilt: *Phys. Rev. B* **41** (1990) 7892–7895.
- 7) G. Kresse and J. Hafner: *J. Phys.: Condens. Matt.* **6** (1994) 8245–8257.
- 8) H. J. Monkhorst and J. D. Pack: *Phys. Rev. B* **13** (1976) 5188–5192.
- 9) F. Birch: *J. Geophys. Res.* **83** (1978) 1257–1267.