

Computer calculation for interstitial-undersized-solute complexes in an FCC metal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 4527

(<http://iopscience.iop.org/0953-8984/1/28/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:26

Please note that [terms and conditions apply](#).

Computer calculation for interstitial–undersized-solute complexes in an FCC metal

S Takamura[†], T Aruga[†], M Kobiyama[‡] and K Nakata[§]

[†] Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki, Japan

[‡] Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki, Japan

[§] Hitachi Research Laboratory, Hitachi Ltd, Hitachi, Ibaraki, Japan

Received 20 January 1988, in final form 30 November 1988

Abstract. The configurations and binding energies of interstitial–solute complexes with undersized solutes are calculated using the molecular dynamic technique. The mixed dumb-bell is most stable for a single interstitial–solute complex. The migration of a solute in the mixed dumb-bell is discussed. When the absolute value of misfit factor of a solute is very large, a substitutional solute is dissociated to a solute interstitial and a vacancy because of being energetically favourable. The appearance is similar to the diffusion mechanisms of the small-sized solute in Pb.

1. Introduction

The radiation-induced segregation of solutes and phase transformation are related to preferential migration of solutes with interstitials and vacancies. When a solute is undersized compared with a host atom, the stable mixed dumb-bell is created by interaction of an interstitial with a solute. The mixed dumb-bell can move by cage motion but a solute does not migrate to long range by this motion. On the contrary, the dissociation and rotational jumps of the mixed dumb-bell can give rise to the long-range diffusion of solutes and induce solute segregation (Robrock 1983, Wiedersich and Lam 1983). The calculations for the configuration and migration of the mixed dumb-bell have been given by Dederichs *et al* (1978) and Lam *et al* (1980, 1981, 1983). Dederichs *et al* (1978) have estimated the binding energies of complexes as a function of the atomic size difference between a host atom and a solute using a simple model; the calculation was performed without relaxation of the lattice. Lam *et al* (1980, 1981, 1983) calculated the stable configurations and binding energies of interstitial–solute complexes in Al alloys using the molecular dynamics technique. Various stable configurations of complexes with an undersized solute have been obtained from the calculation.

When the ratio of the atomic size of a solute to that of a host atom is very small such as a noble metal in Pb, the diffusivity of the solute may be many orders of magnitude greater than that of the host atom. The diffusion of a noble atom in Pb is referred to as fast diffusion where the mixed dumb-bell is called a diplon, and the long-range migration of solutes has been explained by reorientation of the diplon and the jumping of the solute from one nearest-neighbour host atom to an adjoining atom (Warburton and Turnbull 1975, Le Claire 1978). In contrast with the fast diffusion, the diffusivity of Cd and Hg in

Table 1. Binding energies in a mixed dumb-bell with undersized solutes of misfit factor $r_0/R_0 = -0.007, -0.021$ and -0.07 where R_0 is the equilibrium nearest-neighbour separation distance and r_0 the atomic size difference between a host atom and a solute.

Misfit factor	Binding energy (eV)
-0.007	0.10
-0.021	0.36
-0.07	1.4

Pb is well below those of the noble metal but is still one to two orders of magnitude above the self-diffusivity of Pb. To explain the high diffusivities, the interstitial–vacancy pair mechanism has been suggested by Miller (1969) and Miller and Edelstein (1969). The atomic sizes of solutes seem to be fundamental parameters in the diffusivity of solutes.

In the present work, the configurations and binding energies of interstitial–solute complexes are calculated and then the migration of a solute interstitial is studied from the potential map for the migration of a solute. The long-range migration of solutes is discussed in relation to the fast diffusion and interstitial–vacancy pair mechanisms.

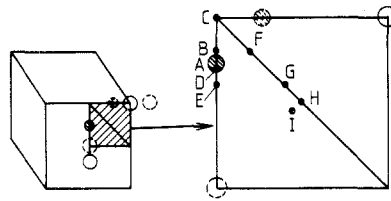
2. Computational procedure

The computational method has been described in a previous paper (Takamura *et al* 1989). The interaction potential used between host atoms was the Morse potential of Al derived by Cotterill and Doyama (1967). The interaction potential between a host atom and a solute was obtained by shifting the host atom potential by an amount equal to the atomic size difference towards smaller inter-ionic distances for undersized solutes. The elastic boundary condition was used (Gibson *et al* 1960). An interstitial–solute complex was initially set near the centre of the model crystal of $6a \times 6a \times 6a$ where a is the lattice constant. The position and velocity of atoms in the crystal were determined from numerical solution of the classical equations of motion. The crystal was relaxed towards equilibrium. When the total kinetic energy of the crystal reached a maximum value, the velocities of all the atoms were set to zero in order to attain an equilibrium configuration as fast as possible. Thermal vibrations were not taken into account for the calculations.

3. Results

The potential energy is reduced when a solute and an interstitial are brought together to form a complex from a large separation. The reduced energy corresponds to the binding energy of a complex. A mixed dumb-bell is the most stable configuration when a solute is undersized. The potential and binding energies in the mixed dumb-bell are shown against the misfit factor of a solute in table 1. The misfit factor is represented by r_0/R_0 , where R_0 is the equilibrium nearest-neighbour separation distance and r_0 is the atomic size difference between a host atom and a solute. The binding energy between an interstitial and a solute increases with decreasing atomic size of a solute. A solute interstitial is situated at the octahedral site for the mixed dumb-bell with a solute having the absolute value of misfit factor above 0.07.

Table 2. Energy required for migration of a solute from the most stable position. One atom (solute) of the mixed dumb-bell is fixed in the positions shown in the diagram and the other atoms are allowed to relax. Site H is the saddle point for the long-range migration.



Position in solute	Potential energy difference (eV) for the following misfit factors				
	-0.021	-0.07	-0.18	-0.25	-0.35
A	0				
B	0.04	0.04	0.19		
C	0.09	0	0	0	0
D		0.08			
E	0.88	0.17	0.68		
F	0.04	0.09	0.36		
G		0.43			
H	0.32	0.51	0.93	0.93	0.45
I		0.71			

An energy map for migration of an interstitial is shown in table 2. The values indicate the energy difference from the potential energy at the most stable position. The calculation is carried out by fixing the solute interstitial of a mixed dumb-bell and allowing other atoms to relax. The long-range migration of a solute proceeds along the line FGH in table 2. With decreasing atomic size of a solute, the energy required for the migration of a solute along the path FGH through the site H increases. When the absolute value of misfit factor is above 0.25, the migration energy inversely decreases.

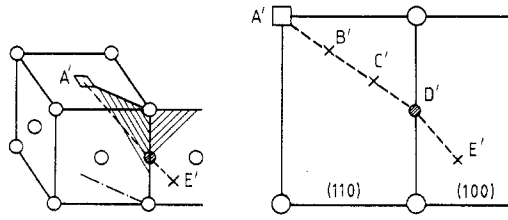
An energy map for formation of a solute interstitial and a vacancy in the crystal involving a substitutional solute is shown in table 3. When the absolute value of the misfit factor of a solute is -0.021 and -0.07 , the formation energy is very large. When the absolute value of the misfit factor of a solute is larger than about 0.18, the position of a solute deviates from the normal substitutional site towards the $\langle 111 \rangle$ direction and is situated at the site B' shown in table 3 when the misfit factor of a solute is -0.18 .

4. Discussion

4.1. Mixed dumb-bell

When a solute is undersized compared with a host atom, the solute in a mixed dumb-bell occupies the off-centre octahedral site. The solute is situated increasingly closer to the octahedral site with decreasing atomic size of a solute. The solute rearranges to the equivalent sites around the octahedral site under the applied stress at a low temperature. This is the cage motion of a mixed dumb-bell. Internal friction peaks arising from the cage motion were observed in irradiated Al-Fe and Al-Mn alloys (Robrock 1987,

Table 3. Energy required for dissociation of a solute interstitial and a vacancy. The value shows the potential energy difference from the potential energy in the most stable configuration where a solute is situated at site A'.



Position in solute	Potential energy difference (eV) for the following misfit factors				
	-0.021	-0.07	-0.18	-0.25	-0.35
A'	0	0	0		
B'			0	0.11	0.22
C'					0.27
D'	3.7	2.6	0.57	0	0
E'				0.93	0.45

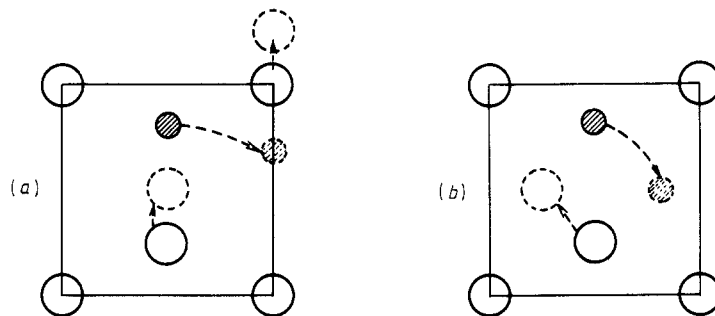


Figure 1. Schematic jump processes for long-range migration of a solute interstitial in a mixed dumb-bell (relaxations of atoms are not shown): (a) jumping without rotation of a solute interstitial which is two-dimensional migration; (b) rotation without jumping. The solute interstitial is represented by a small shaded circle.

Takamura and Kobiyama 1985). The peak height of internal friction in Al-Be and Al-Cu alloys was very small. This seems to be because the migration distance of the cage motion is very small and the solute is nearly situated at the octahedral site.

The cage motion of a mixed dumb-bell does not lead to long-range migration of a solute. Long-range migration requires mechanisms such as rotation without jumping or jump without rotation as shown in figure 1 (Lucasson *et al* 1983, Maury 1984). The present calculation shows that the energies for the two mechanisms are the same since a solute migrates along the $\langle 110 \rangle$ direction through the lowest-energy route passing through FGH in table 2. The long-range migration energy of a solute through site H increases with increasing absolute value of the misfit factor of a solute at first but starts to decrease when the absolute value of misfit factor is larger than 0.25 as shown in table 2. The maximum energy of migration occurs at a misfit factor between -0.18 and -0.25 .

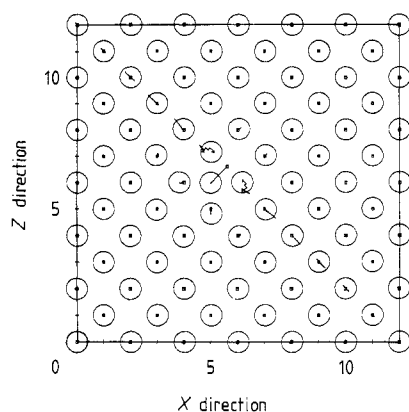


Figure 2. Migration of a mixed dumb-bell when an energy of 0.3 eV is given to a solute in a mixed dumb-bell. The misfit factor of the solute is -0.07 . The solute in a mixed dumb-bell was initially at site G in table 2 and finally migrated to the octahedral site.

When an initial energy of 0.3 eV is given to a solute having a misfit factor of -0.07 in a mixed dumb-bell, the migration of a mixed dumb-bell is observed as shown in figure 2, where a solute is initially situated at point G in table 2 and the initial energy is in the direction GH. For a misfit factor of -0.021 , either two-dimensional migration of a solute which is described in figure 1(a), i.e. jump without rotation, or rotation without jumping shown in figure 1(b) occurs when an initial energy of 0.1 eV is given in a direction slightly tilted from the direction GH. Thus the activation energy for two-dimensional migration and that for rotation of a mixed dumb-bell are the same. The diffusion of a solute is controlled by the height of the energy barrier at site H.

4.2. Diffusion of small-sized solutes

When the misfit factor of a solute is -0.18 , the solute is situated at a site of distance $(0.16a, 0.16a, 0.16a)$ from the substitutional site in the perfect crystal where a is the lattice constant. When the absolute value of the misfit factor of a solute is above 0.25, a substitutional solute dissociates to a vacancy and a solute interstitial situated at the octahedral site. The solute interstitial can migrate to the next octahedral sites through an energy barrier E' in table 3 where the height of the barrier at E' is the same as the potential energy at site H in table 2. The amount of potential energy required for migration of a solute interstitial along the path $B'C'D'E'$ is shown in figure 3. The energy required for migration through site E' decreases with increasing absolute value of the misfit factor above 0.25. With decreasing absolute value of the misfit factor below 0.25, the energy for dissociation of an octahedral interstitial and a vacancy increases abruptly, as shown in table 3.

The diffusivities of the small-sized solutes in Pb are many orders of magnitude greater than those of the host atom. For example, the diffusivity of Au in Pb at 175 °C is 10 times greater than the self-diffusivity of Pb. This diffusion is called fast diffusion (Warburton and Turnbull 1975, Le Claire 1978). When the misfit factors are -0.25 and -0.35 , shown in figures 3(b) and 3(c), respectively, this corresponds to fast diffusion since solute interstitial formation is energetically favourable. In contrast with the fast diffusion of a noble metal in Pb, the diffusivity of Cd and Hg in Pb is well below that of the noble metal but is still one to two orders of magnitude above the self-diffusivity of Pb. It is said that this diffusion occurs by an interstitial-vacancy pair mechanism. The case in figure 3(a) corresponds to this diffusion. Experiments for solute diffusion in Pb showed that there

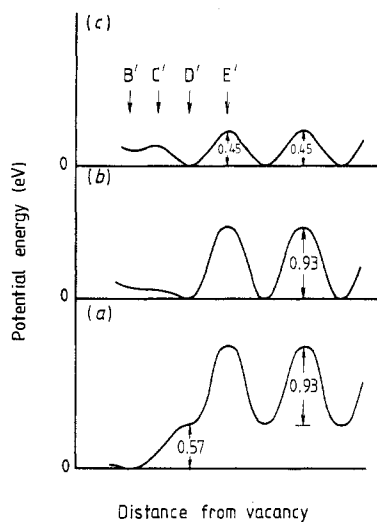


Figure 3. Illustrating map of the potential energy for migration of a solute. B', C', D' and E' correspond to the sites in table 3. (a) The energy for forming a solute interstitial-vacancy pair where the solute is situated at site D' is 0.57 eV for a solute with misfit factor of -0.18 . (b), (c) The substitutional solute dissociates to an octahedral interstitial and a vacancy for a solute with misfit factors of (b) -0.25 and (c) -0.35 . The energy required for migration to the next octahedral site through an energy barrier is 0.93 eV and 0.45 eV for (b) and (c), respectively.

is a striking correlation between the atomic size and solute diffusion (Hood 1978, 1981). The misfit factor of Au and Ag in Pb is -0.087 and that of Cd and Hg in Pb is -0.05 (Hood 1981). Although there is disagreement between the misfit factor obtained from the atomic volume of the elements given by Hood and the values used in the present work for fast diffusion and interstitial-vacancy pair mechanisms, there seems to be correlation between the diffusivity of solutes and their misfit factors.

5. Summary and conclusions

Molecular dynamic calculations are performed to obtain the configurations and binding energies of interstitial-solute complexes with undersized solutes. The interaction potential between a solute and a host atom is obtained by shifting the host atom potential by a certain amount towards shorter inter-atomic distances. The following results are obtained.

(i) The mixed dumb-bell configuration is most stable for single interstitial-solute complexes. With increasing absolute value of the misfit factor of a solute, the site of a solute in the mixed dumb-bell moves closer to the octahedral site.

(ii) The energy for jumping of a solute around the octahedral site is very small. The rearrangement of a solute to the equivalent site around the octahedral site under the applied stress induces the relaxation peak. The internal friction peaks in Al-Fe and Al-Mn alloys occur as a result of the cage motion which takes place owing to this jumping.

(iii) The long-range migration of a solute arises by passage along the lowest-energy route FGH shown in table 2.

(iv) The substitutional solute is dissociated to a solute interstitial and a vacancy when the absolute value of the misfit factor of solute is above 0.25. The diffusion of a solute is controlled by the potential height at site H shown in table 2. This appearance is similar to the fast diffusion mechanism of small-sized solutes in Pb. With decreasing absolute value of the misfit factor below 0.25, the energy required for dissociation of a solute interstitial and a vacancy increases abruptly. Therefore, when the absolute value of the

misfit factor is slightly smaller than 0.25, the interstitial–vacancy pair mechanism seems to arise.

References

- Cotterill R M J and Doyama M 1967 *Lattice Defects and their Interactions* ed. R R Hasiguti (New York: Gordon and Breach) p 1
- Dederichs P H, Lehmann C L, Schober H R, Scholz A and Zeller R 1978 *J. Nucl. Mater.* **69–70** 176
- Gibson J B, Goland A N, Milgram M and Vineyard G H 1960 *Phys. Rev.* **120** 1229
- Hood G M 1978 *J. Phys. F: Met. Phys.* **8** 1677
- 1981 *Phys. Rev. B* **23** 4253
- Lam N Q, Dagens L and Doan N V 1983 *J. Phys. F: Met. Phys.* **13** 1369
- Lam N Q, Doan N V and Adda Y 1980 *J. Phys. F: Met. Phys.* **10** 2359
- Lam N Q, Doan N V, Dagens L and Adda Y 1981 *J. Phys. F: Met. Phys.* **11** 2231
- Le Claire A D 1978 *J. Nucl. Mater.* **69–70** 70
- Lucasson P, Maury F and Lucasson A 1983 *Radiat. Eff. Lett.* **86** 7
- Maury F 1984 *J. Phys. F: Met. Phys.* **14** 1395
- Miller J W 1969 *Phys. Rev.* **181** 1095
- Miller J W and Edelstein W A 1969 *Phys. Rev.* **188** 1081
- Robrock K H 1983 *Phase Transformations During Irradiation* ed. F V Nolfi Jr (London: Applied Science) p 115
- 1987 *Mater. Sci. Forum* **15–18** 537
- Takamura S, Aruga T, Kobiyama M and Nakata K 1989 *J. Phys. Condens. Matter* **1** 4519
- Takamura S and Kobiyama M 1985 *Radiat. Eff.* **91** 21
- Warburton W K and Turnbull D 1975 *Diffusion in Solids* (New York: Academic) p 171
- Wiedersich H and Lam N Q 1983 *Phase Transformations During Irradiation* ed. F V Nolfi Jr (London: Applied Science) p 1