Configurations of interstitial-oversized-solute complexes in an FCC metal

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Abstract. The internal friction peak at 10–12 K of Al–Pb, Al–Sn and Al–Ge alloys is observed for a stress in the $\langle 100 \rangle$ direction and the peak at 55–60 K for a stress in the $\langle 111 \rangle$ direction. To interpret the results in dilute Al alloys, the configurations and binding energies of single interstitial–solute complexes with oversized solutes are calculated by using the molecular dynamics technique. The two internal friction peaks are considered to be due to the stress-induced ordering of the tilted dumb-bell.

1. Introduction

There have been several studies of the computer calculation for the configuration and symmetry of interstitial–solute complexes. Dederichs *et al* (1978) have estimated the configurations and binding energies of the complexes as functions of the atomic size difference between a solute and a host atom, and they reported that a mixed dumb-bell was formed for an undersized solute and the most stable configuration for a complex with an oversized solute was the type *b* first-neighbour complex which could reorient on equivalent nearest-neighbour positions around a solute. The interaction potential between a host atom and a solute has been obtained by shifting the host atom potential by the atomic size differences between a host atom and a solute on the inter-atomic distance. These calculations were 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 have been obtained. For example, for Al–Ca and Al–K alloys having oversized solutes, the type *b* first-neighbour complex was most stable. In Al–Mg alloy, the self-interstitial occupied a second-neighbour position of the solute. No complexes possessing a $\langle 111 \rangle$ symmetry axis in alloys with oversized solutes have been found from the above-mentioned computer calculation. The main peak of internal friction in Al–Mg alloy has a nearly trigonal symmetry from experiments (Takamura and Kobiyama 1984). In alloys with oversized solutes such as Ge, Sn and Pb, the internal friction peaks at 10–12 K and 55–60 K have been observed for a stress in the $\langle 100 \rangle$ direction and the $\langle 111 \rangle$ direction, respectively after electron irradiation (Kobiyama *et al* 1988). These peaks were annihilated by annealing at 120–130 K (Takamura and Kobiyama 1985). Thus a few results in the internal friction measurement are inconsistent with that of the above-mentioned computer calculations.

In this work, to interpret the results of internal friction experiments after electron and neutron irradiation, the configurations of interstitial–solute complexes with oversized solutes are calculated using a simplified shift potential, which is obtained by shifting the host atom potential by the atomic size difference between a host atom and a solute.

2. Calculational procedure

In the present investigation, a computer code GRAPE was used for the molecular dynamics calculation. A cubic crystal of edge length six lattice constants (i.e. $6a$ where a was the lattice constant) bounded by {100} planes was used in the calculation. The crystal contained 1099 atoms. The solute and interstitial were set near the centre of the crystal. Several different types of inter-atomic potential were used. The calculation was first carried out using the Morse potential of Al derived by Cotterill and Doyama (1967) as follows:

$$\varphi = 0.119306\{\exp[-2 \times 2.353643(r - 2.864944)]$$
$$- 2\exp[-2.353643(r - 2.864944)]\}.$$

However, the existence of interstitial–solute complexes with trigonal symmetry which appeared in the internal friction measurements could not be shown. Another potential for Al was tried but similarly a reasonable result could not be obtained. Therefore, another type of potential, the Johnson potential of Cu (Johnson and Wilson 1972), was tried. The Johnson potential of Cu was represented as follows:

$$\varphi = 0.14481872r^6 - 4.6748698r^5 + 48.165321r^4 - 236.39382r^3 + 613.65431r^2$$
$$- 818.49496r + 444.08761$$
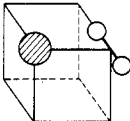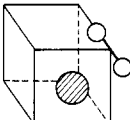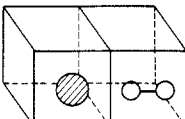
where r is in ångströms.

The interaction between a host atom and a solute consists of two terms—elastic and electronic—and the interaction between an interstitial and a solute seems to depend mainly on the atomic size difference. The long-range term of the interaction potential is important in the interaction between substitutional atoms. However, in the present calculations the interaction potential between a host atom and a solute was obtained by shifting the host atom potential by the atomic size difference towards larger inter-ionic distances for oversized solutes. The elastic boundary condition was used (Gibson *et al* 1960). The positions and velocities of atoms in the crystal were determined by the numerical solution of the classical equations of motion. The time step used in the calculation was $t = 3 \times 10^{-16}$ s during 100 time steps from the beginning of calculation and $t = 3 \times 10^{-15}$ s subsequently. Since the equilibrium configuration and potential energy of the system were saturated nearly after about 300 time steps, 600 or 400 time steps were used in the calculations. Thermal vibrations of atoms were not taken into account in the calculations. When the total kinetic energy of crystal reached a maximum value, the velocities of all the atoms were set to zero, i.e. quenching occurred, in order to attain an equilibrium configuration as quickly as possible.

3. Results and discussion

Table 1 shows the binding energies calculated using the Morse potential of Al for several stable complexes of a single interstitial–solute with an oversized solute, where the misfit

factor is r_0/R_0, 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 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 the complexes. If a rigid boundary where the atoms on the boundary are fixed to the initial position throughout the calculation is used, the binding energies of the complexes agree within 5% with that for an elastic boundary; for example, the value for the type b first-neighbour configuration, S2, in the elastic boundary is 0.38 eV, and that in the rigid boundary is 0.36 eV. Hereafter, in the calculations, an elastic boundary will be used. A mixed dumb-bell with an oversized solute is unstable or has a low binding energy compared with that in other stable complexes. Therefore, it is assumed that a mixed dumb-bell is not created in alloys with an oversized solute.

Table 1. Binding energies of stable single interstitial–solute complexes with oversized solutes of misfit factor $r_0/R_0 = 0.021$ and 0.07. The Morse potential is used. The minus indicates repulsion.

No.	Configurations	Binding energy (eV) for the following misfit factors	
		0.021	0.07
S1		−0.003	0.04
S2		0.09	0.38
S3		0.04	0.15

Since the internal friction peaks were observed on Al–Pb, Al–Sn and Al–Ge alloys (containing a concentration of complexes of only several parts per million) irradiated with 3 MeV electrons, a single interstitial–solute complex is probably responsible for the main internal friction peak in dilute Al alloys.

Figure 1 shows the orientation dependence of internal friction peaks in electron-irradiated Al–Pb alloy where the Seitz radius of the Pb atom is 23.20% larger than that of the Al atom and where the Pb atom is considered to be an oversized solute as shown previously (Takamura and Kobiyama 1985). Similar results were obtained by internal
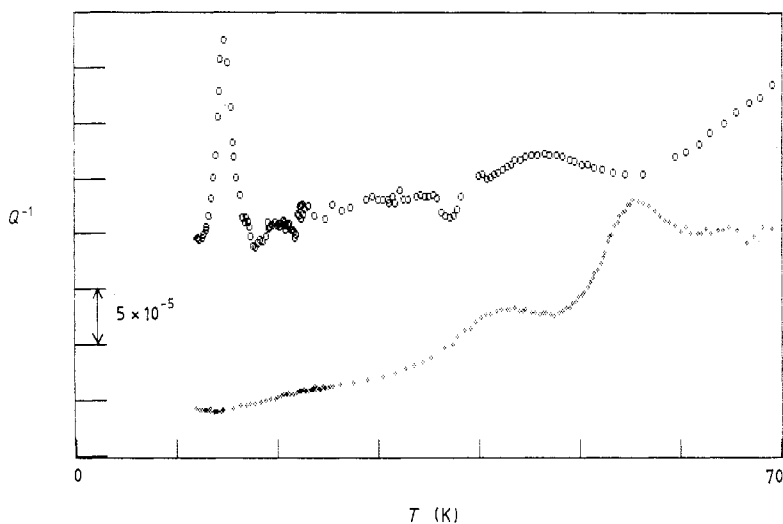
Figure 1. The internal friction peaks in electron-irradiated Al–Pb alloy of single crystals with a $\langle 100 \rangle$ direction (○) and with a $\langle 111 \rangle$ direction (+). The Pb content is about 0.03 at.%.

friction experiments on Al–Sn and Al–Ge single crystals where the Seitz radii of Sn and Ge atoms are 17.70% and 10.94%, respectively, larger than that of the Al atom (Kobiyama *et al* 1988). There are some resemblances between the spectra of the internal friction peaks in these alloys as follows.

(i) The peaks at 10–12 and 55–60 K are annihilated at nearly the same temperature, 120–130 K.

(ii) The internal friction peak at 10–12 K is observed only for a stress in the $\langle 100 \rangle$ direction and not for a stress in the $\langle 111 \rangle$ direction.

The peak at 55–60 K is observed for a stress in the $\langle 111 \rangle$ direction. The two peaks seem to be due to a 'frozen free-dumb-bell' configuration (Nowick and Berry 1972, Robrock 1982) in which a defect reorients by two different jump processes. Ultrasonic attenuation measurements on Al–Si and Al–Ag alloys (Granato *et al* 1982, Johnson and Granato 1987) demonstrated that there were two peaks with tetragonal and trigonal symmetry annealed out at nearly the same temperature. They explained the two peaks in terms of a tilted caged mixed dumb-bell. This model is suitable for alloys with solutes of relatively small atomic size. However, a different model is necessary in order to interpret the relaxation peaks in alloys with solutes of large atomic size such as Al–Sn, Al–Ge and Al–Pb alloys since a mixed dumb-bell is not considered to be the stable configuration for these alloys and experimentally to form from the results of channelling and perturbed angular correlation measurements in Al–In alloy (Swanson *et al* 1978, Swanson and Howe 1982, Wichert 1982, Sielemann *et al* 1982).

The energy map for migration of a dumb-bell interstitial is obtained by fixing one atom of a dumb-bell and allowing other atoms to relax (table 2). The energy necessary for jumping of the dumb-bell with configuration S2 to equivalent positions around a solute through site D, shown in table 2, is about 0.08 V in spite of the atomic size difference between a solute and a host atom. This value is nearly equal to the free migration energy of a dumb-bell in Al. If this jumping energy is equal to 0.02 eV (which is the activation energy for orientation in the 10–12 K peak), under the influence of a solute the reorientation of a dumb-bell would give rise to a relaxation peak at 10–12 K. However, the energy difference is too large.

Table 2. Potential energy map for migration of an interstitial using the Morse potential. One atom of a dumb-bell is fixed in the positions shown in the figure and the other atoms are allowed to relax. The value is taken as the difference from the potential energy at the position A where is the most stable position.
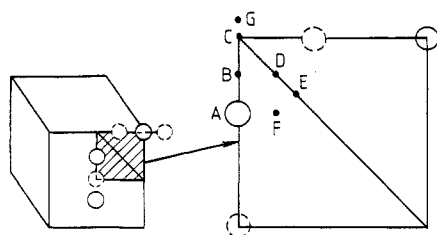
Position in solute	Potential energy difference (eV) for the following misfit factors		
	0	0.021	0.07
A	0	0	0
B			0.09
C	0.19		0.26
D	0.08	0.08	0.07
E			0.19
F			2.1
G			0.30

The internal friction peak at 55–60 K appears under a stress in the $\langle 111 \rangle$ direction in the measurements of Al alloys with oversized solutes such as Pb, Sn and Ge atoms. A complex with trigonal symmetry has not been found in the results of the computer calculations by Dederichs *et al* (1978) and Lam *et al* (1980, 1981, 1983) for alloys with an oversized solute. As long as the Morse potential is used in the calculation, the presence of a stable interstitial–solute complex with trigonal symmetry cannot be shown. Another potential for Al (Pettifor and Ward 1984) has been tried but reasonable results could not be obtained. So, the Johnson potential of Cu will next be used.

Three stable configurations of interstitial–solute complexes for a misfit factor r_0/R_0 of 0.07 are shown in figure 2. The interstitial is initially aligned in a position shown by the dot and the lattice is relaxed. The type *b* first-neighbour configuration (figure 2(*a*)) is most stable for a relatively large size of the solute. The potential energies of the complexes shown in figure 2 are plotted against r_0/R_0 in figure 3. The type *b* first-neighbour configuration is not necessarily the most stable, as shown in figure 3. The configuration in figure 2(*b*) has a lower potential energy when the misfit factor of a solute is relatively small. The configurations in figure 2(*c*), the octahedral configuration, are stable when the Johnson potential is used, although they are saddle points. For the tilted dumb-bell in figure 4(*a*) which corresponds to that in figure 2(*b*), there are three equivalent sites forming a triangle about a particular $\langle 111 \rangle$ axis which is connected between a solute and a centre of the cubic edge. The free energy levels of each tilted dumb-bell in the three equivalent sites are the same for a stress applied along a $\langle 111 \rangle$ direction at a low temperature where a translational jump is not permitted, but the free-energy levels are split for a stress along the $\langle 100 \rangle$ direction. The redistribution of the tilted dumb-bell to a new set of equilibrium values, from one site to another equivalent site in a triangle, is referred to as stress-induced ordering. An internal friction peak would appear in a specimen
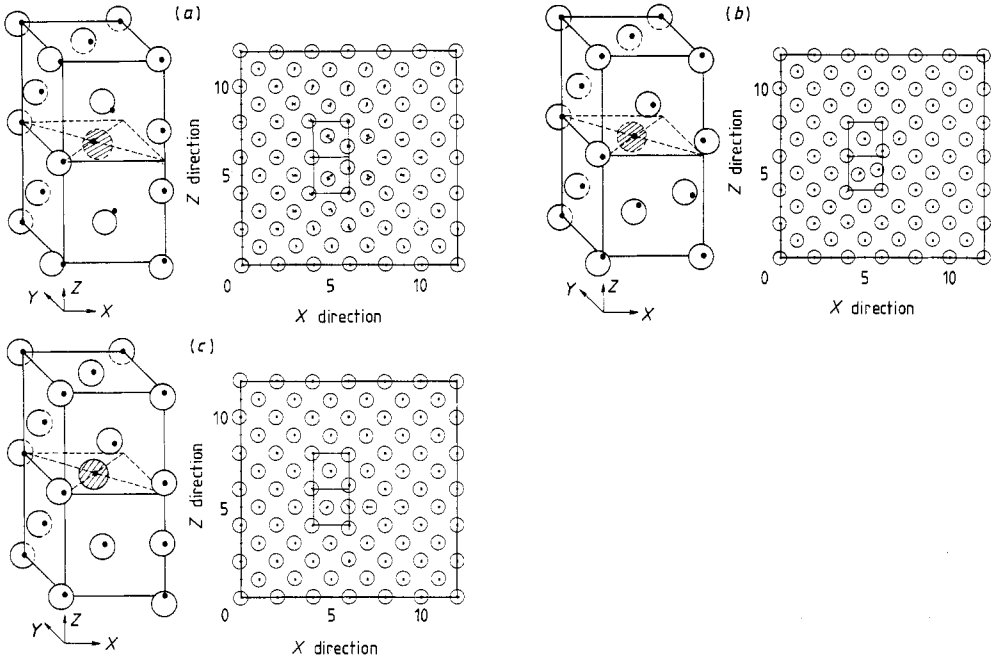
Figure 2. Rearrangement of atoms in the X–Z plane, which shows the projection of the positions of atoms situated between $Y = 5.5$ and 6.5 onto the X–Z plane, and its perspective which indicates rearrangement of atoms in the region bounded by the large square in the right-hand figure. The initial positions of the atoms are indicated by the dot and the final positions are indicated by the circles. (*a*) The dumb-bell is initially aligned in the $\langle 001 \rangle$ direction and then the atoms are relaxed without quenching: (*b*) the interstitial is initially aligned in the position of the coordinates (5.8, 6, 5.2) and relaxed finally to the coordinates (5.8, 5.9, 5.2) with quenching; (*c*) the interstitial is initially set at coordinates (6, 6, 5) and finally aligned to coordinates (5.9, 6, 5) with quenching. The solute is represented by the shaded broken circle.
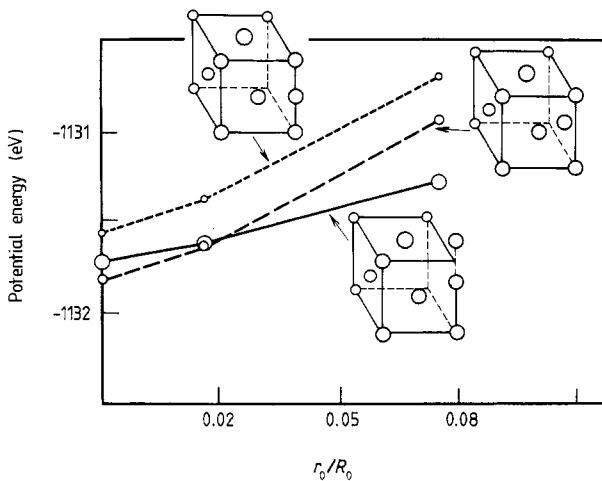

Figure 3. Potential energies of the complexes shown in figure 2 plotted against the misfit factor of the solute calculated using the Johnson potential.
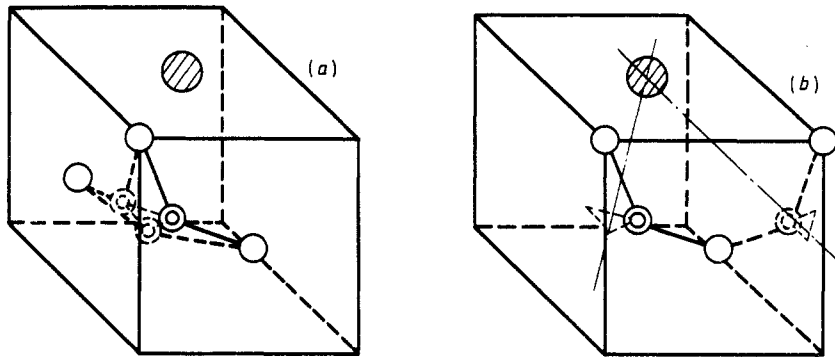
Figure 4. Schematic jump processes of a tilted dumb-bell. Relaxations of the atoms are not shown. The jumping to equivalent position (*a*) of a self-interstitial in the tilted dumb-bell under ⟨100⟩ stress at 10–12 K and (*b*) of the tilted dumb-bell under ⟨111⟩ stress at 55–60 K, where a double circle shows a self-interstitial in a tilted dumb-bell and the broken lines show the configuration after jumping. The solute is represented by a large shaded circle.

having a ⟨100⟩ direction. This model is similar to that for the cage motion of a mixed dumb-bell where localised diffusion of 'off-centre' interstitial confined to the equivalent sites occurs, although the dumb-bell consists of only host atoms in the present case. When the crystal is heated to 50–60 K, the tilted dumb-bell would reorient to a triangle around the other ⟨111⟩ direction under a stress in the ⟨111⟩ direction as shown in figure 4(*b*). The appearance is very similar to the stress-induced ordering of interstitial O in Si, where an O atom hops between six equivalent sites located in a circular arrangement around a ⟨111⟩ axis at lower temperature and it follows that an O atom reorients to any six sites around other ⟨111⟩ direction by translational jumps, breaking the nearest-neighbour bond of Si–O–Si (Nowick and Berry 1972). Judging from the experimental results that the peak temperatures, 10–12 and 55–60 K, in internal friction measurements are nearly equal in the above-mentioned alloys, the height of potential barrier for rearrangement between the equivalent sites around a solute seems to be nearly independent of the atomic size of solutes. However, the relative height of the two peaks varies for different types of alloy. The peak height at 10–12 K may be explained in terms of the length of jump between the sites forming a triangle in figure 4(*a*). Since the main internal friction peak in Al–Mg alloy has a nearly trigonal symmetry and the peak height at 12 K is very small, the length of a triangle side is very small and the interstitial is considered to occupy the octahedral site.

After annealing above 120–130 K, the complexes seem to rearrange to the other stable complexes without symmetry or dissociate since the internal friction peaks cannot be observed in Al alloys with oversized solutes such as Pb, Sn and Ge atoms. A detailed study of electrical resistivity measurements in Al–Ti alloy showed that the dissociation of a single interstitial–solute complex in Al–Ti alloy occurred at 110 K (Maury *et al* 1988).

4. Summary and conclusions

From internal friction spectra in Al–Pb, Al–Sn and Al–Ge alloys after electron and neutron irradiation at low temperatures, it is considered that there are some resemblances between the configuration of an interstitial–solute complex in these alloys. To interpret the internal friction spectrum in the Al alloys with oversized solutes, the con-

figurations of a complex are calculated. The interaction potentials used are the Morse and Johnson potentials. The interaction potential between a solute and a host atom is obtained by shifting the host atom potential by the atomic size difference between a solute and a host atom towards larger inter-ionic distances for oversized solutes. The main results are as follows.

(i) The type b first-neighbour configuration is most stable for single interstitial–solute complexes if the Morse potential is used.

(ii) When the Johnson potential is used, the tilted dumb-bell is most stable in complexes with a small misfit factor of the solute. The octahedral interstitial exists as a stable configuration, although this configuration is a saddle point.

(iii) From internal friction measurements of dilute Al alloys irradiated with 3 MeV electrons, the main internal friction peaks in Al alloys with oversized solutes seem to be due to the single interstitial–solute complex. The peak at 10–12 K seems to be due to the jumping of a tilted dumb-bell between three equivalent sites located in a triangle arrangement around a $\langle 111 \rangle$ axis and the peak at 55–60 K seems to be due to the jump process of the tilted dumb-bell to any triangle arrangement in the other $\langle 111 \rangle$ direction.

Acknowledgment

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