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Solid solutions under irradiation. III. Further comments on the computed solubility limit

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An error has been detected in one of the papers used as an ingredient for our model of irradiation-induced decrease of solubility. Correcting this error does not affect the conclusions of our previous work. The quantitative agreement between theory and experimental data in the AlZn system can still be achieved with the use of a new set of parameter values for describing solute diffusion by a dumbbell mechanism. The model accounts well for the observation of homogeneous irradiation-induced precipitation in AlZn, AlAg, and possibly AlSi, and for the absence of this effect in AlGe and AlMg.

I. INTRODUCTION

We proposed recently a model for irradiation-induced metastability.[1] This model was applied to AlZn which exhibits a decrease of Zn solubility under electron irradiation.[2] The numerical estimation of the reduced solubility relied on a model for solid solutions under irradiation, based on existing theories for diffusion by vacancy[3] and dumbbell interstitial mechanisms.[4]

Detailed application of the model to new experimental results[5] led us to the discovery of a transcription error in Ref. 4 which altered the expression of the solute diffusion coefficient by dumbbell interstitial mechanism, a central quantity in the solubility limit model of Ref. 1. In this brief report, the correctly computed solubility limit is presented as well as applications of the model to yet unpublished experimental data.[5]

All trends experimentally observed are still well accounted for by the model. A reasonable quantitative agreement may be obtained by a proper choice of those parameters which describe the jumps of the dumbbell.

II. REASSESSMENT OF THE MODEL FOR THE Zn SOLUBILITY LIMIT IN Al UNDER IRRADIATION

As shown in Ref. 1, the solubility limit under irradiation $\tilde{C}$ is proportional to that without irradiation $\bar{C}$,

$$\tilde{C} = B_\infty \bar{C} , \tag{1}$$

with

$$B_\infty = [1 + (D_B^I / D_B^v)^x]^{-1} , \tag{2}$$

where D_B^I (or D_B^v) is the solute diffusion coefficient by the interstitial (or vacancy) mechanism; $x = -1$ if the occupation probability of a precipitate-matrix interfacial site by an interstitial is larger than that by a vacancy and $x = +1$ when the reverse is true.

The expression of D_B^I for the dumbbell diffusion mechanism has been derived by Barbu[4] and should be written as

$$D_B^I = C_I K_{\text{pa}} D_{\text{pa}} \tag{3}$$

TABLE I. Input parameters of the model.

Vacancy formation energy	0.65 eV	
Vacancy formation entropy	$0.80 k_B$	Ref. 9
Vacancy migration energy	0.63 eV	
Mixed dumbbell binding energy	>0.43 eV	Ref. 8
Interstitial jump frequencies	See text	Ref. 7
α coupling coefficient between vacancy and solute fluxes	0.5	Estimated
$1/\beta$ solute diffusion correlation coefficient	0.5	Ref. 10

where C_I is the free interstitial concentration, $K_{\rm pa}$ and $D_{\rm pa}$ are appropriate functions of the various jump frequencies of the dumbbell in the vicinity of the solute. Equation (3) was improperly transcripted in Ref. 4 [Eq. (A3) of Ref. 4] and was used under its wrong form in Ref. 2.

Using the correct expression of D_B^I [Eq. (3)] instead of the improper one [Eq. (A3) of Ref. 4] results in a decrease of D_B^I by a factor $(1+K_I n_B)$ where n_B is the total solute concentration and K_I the total interstitial-solute association constant.[4] Since D_B^I only enters the calculations of Ref. 2 via Eq. (2), it is easy to discuss the consequences of the use of Eq. (3):

(i) All qualitative trends of the solubility limit under irradiation which were discussed in Ref. 2 remain: the solubility limit decreases when the irradiation flux increases; the precipitation process poisons itself.

(ii) Using slightly different values (Table I) for the parameters and a more accurate expression for the effective diffusion coefficient of vacancies (see Appendix) yield a very small shift of solubility limit under irradiation [see Fig. 2(c)], but a reasonable fit of the model to the data can be achieved by a new choice of interstitial parameters. As already discussed, we use Dederich's *et al.* model[7] as a guide for the choice of the latter parameters values. According to Refs. 4 and 7 all the relevant activation energies may be deduced from the linear size effect η of the solute atom in the matrix. Setting $\eta=-3\%$ yields a binding energy of the mixed dumbbell configuration in the experimental range (greater than 0.43 eV) (Ref. 8). A good fit to the data (see Fig. 1) could be achieved by choosing for the values computed with a size effect of $\eta=-3\%$ interstitial jump frequencies according to Dederich's models, except for the activation energy for the rotation of the mixed dumbbell which was reduced by a factor $\frac{3}{2}$ (giving back the value computed from Dederich's model with the experimental size effect of $\eta=-2\%$).

The solubility limit shown on Fig. 1 was computed according to Eq. (1), following procedure depicted in Ref. 2 and using the values listed in Table I. The sensitivity of the results to the parameters is shown on Fig. 2.

The sensitivity to the poorly known vacancy mechanism parameters α and β (cf. Appendix) is low. Figures 2(a) and 2(b) show the sensitivity to the migration and the formation energy and entropy. Figure 2(c) shows the high sensitivity to the rotation energy E_R of the mixed dumbbell: reducing E_R changes x from -1 to $+1$ in Eq. (2) by

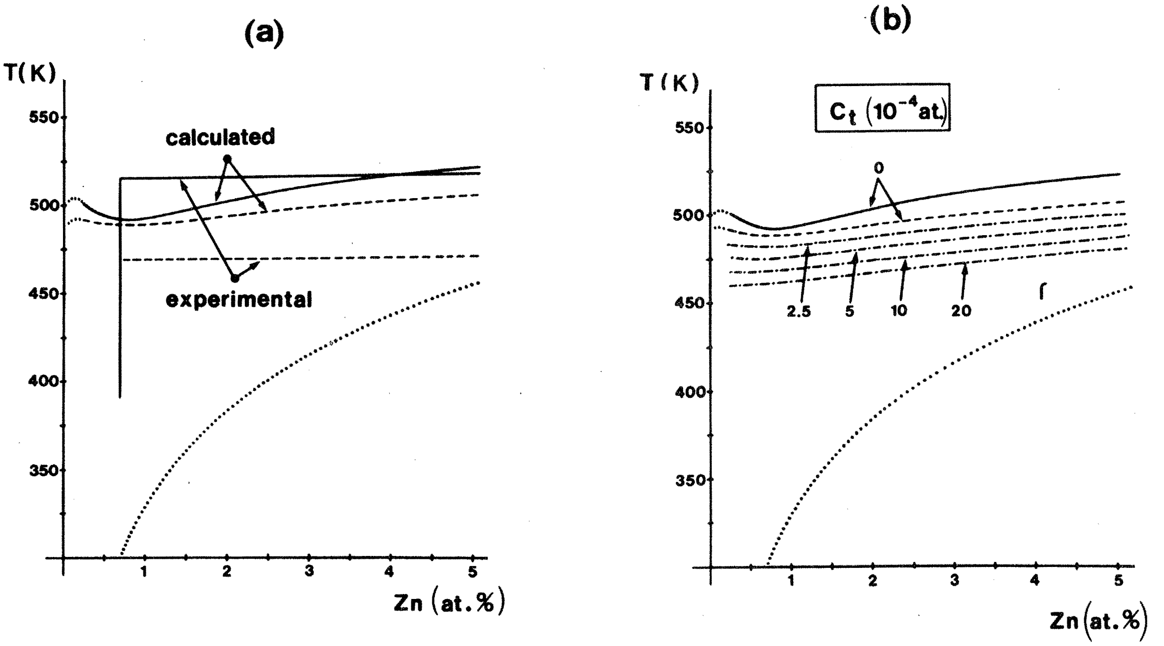
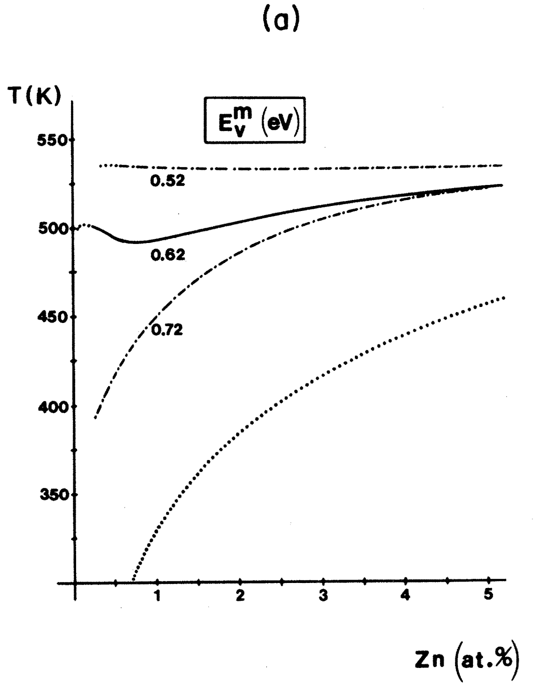


FIG. 1. Computed solubility limit of Zn in Al under irradiation; (——) $G=2\times10^{-2}$ dpa/s (dpa/s denotes displacement per atom per second); (- - -) $G=2\times10^{-3}$ dpa/s; (· · ·) $G=0$; thermal solvus. See Table I for the value of the parameters used. (a) Computed solubility limit compared to the experimental one. (b) Effect of the concentration (at.) C_t of trapping sites at the surface of the solute clusters on the computed solubility limit in the matrix; (— · — · — ·) $G=2\times10^{-2}$ dpa/s.



increasing the effective mobility of interstitials, and thus reducing their concentration.

Therefore, after correcting for the error found in Ref. 4, our model still depicts the qualitative behavior observed experimentally in AlZn, and may yield the right order of magnitude, using experimentally known values of vacancy diffusion parameters and relying more on values for interstitial parameters inferred from experiments.

III. APPLICATION OF THE MODEL TO OTHER Al BASE SOLID SOLUTIONS

As shown in Ref. 5, a decrease of solubility limit under irradiation has been observed in AlAg, possibly in AlSi, and was looked for and not observed in AlGe and AlMg. Ge and Mg are oversized solute in Al: One therefore expects no solute diffusion by a dumbbell mechanism (Ref. 4). $D_B^I=0$ in Eq. (2). As shown in Ref. 5, $x=+1$ in these systems and Eqs. (1) and (2) predict no shift of the solubility limit under irradiation.

Inversely Ag and Si are not oversized solutes in Al leaving the possibility for solute diffusion by a

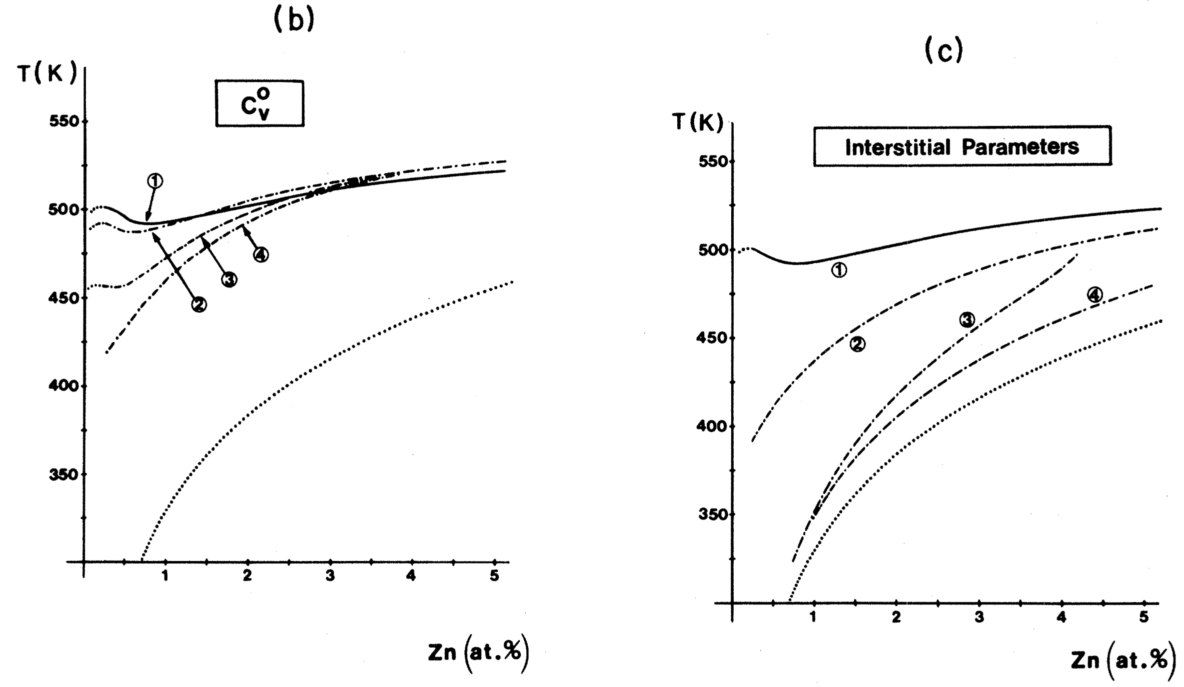


FIG. 2. Sensitivity of the computed solvus under irradiation to the values of the parameters; (· · ·) thermal solvus; (——) computed solvus of Fig. 1; $G=2.10^{-2}$ dpa/s. (a) Sensitivity to the vacancy migration energy. (b) Sensitivity to the vacancy formation energy and entropy pairs: (1) $E_v^F=0.62$ eV, $S_v^F=0.8k_B$; (2) $E_v^F=0.71$ eV, $S_v^F=1.76k_B$; (3) $E_v^F=0.76$ eV, $S_v^F=2.4k_B$; (4) $E_v^F=0.81$ eV, $S_v^F=3.12k_B$. (c) Sensitivity to the interstitial parameters: (1) $\eta=-3\%$, $Ew_R/1.5$; (2) $\eta=-2\%,Ew_R/1.5$; (3) $\eta=-3\%,Ew_R$; (4) $\eta=-2\%,Ew_R$.

dumbbell mechanism: $D_B^I \neq 0$ in Eq. (2) yields $B_\infty < 1$, which according to Eq. (1) indicates a decrease of solubility. As just seen, even in the absence of a detailed knowledge of parameter values, the model proposed in Ref. 1 and 2 gives a qualitative understanding of the shift of solubility limits under irradiation.

IV. CONCLUSION

An error was detected in one of the references (4) we used for evaluating the irradiation-induced shift of solubility of Zn in Al, according to the model we proposed (Refs. 1 and 2). Correcting this error does not change the qualitative agreement between theory and experiment; a good quantitative fit may be recovered by assuming a small rotation energy for the mixed dumbbell.

The model successfully accounts for the occurrence or (absence) of homogeneous radiation-induced precipitation in AlZn, AlAg, AlSi, AlGe, and AlMg.

APPENDIX

The vacancy diffusion coefficient $D_v(n_B)$ can be expressed using experimental parameters instead of the five classical jump frequencies w_j defined in Ref. 3. We have

$$w_3/w_4 = \exp(-\Delta g_B/kT) , \tag{A1}$$

$$a^2 w_0 = D_v(0) , \tag{A2}$$

where Δg_B is the binding free energy of a vacancy with a solute atom, a is the lattice constant, and $D_v(0)$ the vacancy diffusion coefficient in the pure metal. We define

$$\alpha = 1 - \frac{13}{2}\frac{w_3}{w_1} , \tag{A3}$$

$$\beta = 1/f_B = \frac{w_1 + w_2 + 7w_3/2}{w_1 + 7w_3/2} , \tag{A4}$$

where f_B is the correlation factor for solute diffusion and α is a measure of the coupling strength between vacancy and solute fluxes; as can be seen from Ref 6, J_B/J_V is proportional to $[1-(13/2)w_3/w_1]$ when $\vec{\nabla} n_B = 0$, so that the coupling is positive (negative) when α is positive (negative).

Then, we have

$$D_v(n_B) = \left\{ D_v(0) + C_B \left[7D_v(0) - \frac{D_B^*(0)}{C_v^0} \left[3 - \frac{6\alpha+20}{7\alpha-20} + 80\frac{(2\alpha-15)(\alpha-1)}{(7\alpha-20)(\alpha-1)} \right] \right] \right\} \Big/ (1 + k_v n_B) , \tag{A5}$$

where $D_B^*(0)$ is the solute diffusion coefficient in the pure metal and C_v^0 is the thermal-vacancy concentration in the pure metal.

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