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Rapid Communications

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Vacancy formation energies in disordered alloys

S. M. Kim

Atomic Energy of Canada Research Company, Chalk River Nuclear Laboratories,
Chalk River, Ontario, Canada KOJ 1JO

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A theory of vacancy formation in disordered alloys has been formulated. It is shown that when the vacancy concentration in an alloy is characterized by a formation energy, the formation energy increases with temperature. In the light of the present work, serious shortcomings in the previous theories have been identified. The present theory satisfactorily describes the observed composition dependence of the vacancy formation energies in various alloys as well as the very small vacancy-solute binding energies observed in many dilute aluminum alloys.

For a clear understanding of the many physical and metallurgical properties of alloys, such as diffusion, creep, and radiation effects, it is essential to know the properties of vacancies and other defects. In recent years, considerable effort has been made to understand the vacancy properties in ordered[1,2] and disordered[3-14] alloys. For the ordered bcc (CsCl structure) alloys, a theory based on the nearest-neighbor bond energy concept has been shown to satisfactorily describe the various observed vacancy properties.[1,2] In this Rapid Communication, we formulate a theory of vacancy formation in disordered alloys, also using the nearest-neighbor bond energy model. Although this type of model has been very useful for the theoretical understanding of the various statistical thermodynamic properties of alloys, it is not free from difficulties. When applied to pure metals, for example, it predicts that the formation energy of a vacancy should be equal to the cohesive energy, which is far from being correct in real metals. Despite the overly simplistic nature of the model, it is, nevertheless, quite satisfactory in many respects, and it is the best available model we have at the present time.

We define N as the total number of atoms, n as the number of vacancies, C_A as the fraction of A atoms, C_B as the fraction of B atoms, z as the number of nearest-neighbor atoms, and ϵ_{ij} as the bond energy between the ith and jth atoms. We then have $\epsilon_{AB}=(\epsilon_{AA}+\epsilon_{BB})/2+\epsilon$, where ϵ is the interaction energy.[15] If ϵ is positive the alloy tends to order, and if negative the alloy tends to cluster. In this paper we limit our discussion to nonordering and nonclustering disordered alloys, where $\epsilon=0$. The assumption $\epsilon=0$ is not a serious limitation on the applicability of the theory to many real disordered alloys, since even for the alloys which order or segregate below room temperature ϵ is only of order 0.01 eV, while the bond energy between two atoms is usually greater than 0.1 eV. For a completely disordered alloy, the probability that any site is occupied by an A (B) atom is given by C_A (C_B). The probability that this site is coordinated with i A atoms and $z-i$ B atoms will be given by

$$\frac{z!}{(z-i)!\,i!}C_A^i C_B^{z-i} \quad (0 \leq i \leq z) \ . \tag{1}$$

In an AB alloy, there exist $2(z+1)$ different types of sites. In each of these types of sites, vacancies can be created in $2(z+1)$ ways, by moving the atoms to the surface or by having the atoms jump into vacancies in other types of sites. In addition, the vacancies in each of these types of sites can be nullified by atoms jumping in from any of the other types of sites. We have found that all these vacancy formation processes can be taken into account accurately in the theory for vacancy concentrations greater than about 10^{-6}. If we define N_{2i} (N_{2i+1}) as the number of A (B) atoms coordinated with i A atoms and $z-i$ B atoms ($0 \leq i \leq z$), and $N_{V(k)}$ as the number of vacancies on N_k sites ($0 \leq k \leq 2z+1$), we have

$$N_{2i}=NC_A\frac{z!}{(z-i)!\,i!}C_A^i C_B^{z-i} \ , \tag{2}$$

$$N_{2i+1}=NC_B\frac{z!}{(z-i)!\,i!}C_A^i C_B^{z-i} \ . \tag{3}$$

The configurational free energy at a temperature T is given by

$$F=E-TS \ , \tag{4}$$

where E is the total bond energy and S is the configurational entropy. The derivation of the total bond energy in the presence of n vacancies is rather lengthy, but fairly straightforward mathematically, and thus will not be given here. For vacancy concentrations greater than about 10^{-6}, we obtain to an excellent approximation

$$E=-E_0+\frac{z\epsilon_{BB}}{2}\sum_i(N_{V(2i)}+N_{V(2i+1)}) + \frac{\epsilon_{AA}-\epsilon_{BB}}{2}\sum_i i(N_{V(2i)}+N_{V(2i+1)}) \ , \tag{5}$$

where E_0 is the total bond energy in the absence of vacancies.

The configurational entropy for the alloy pertaining to vacancies can be written as

$$S = k \ln \prod_i \frac{N_{2i}!}{(N_{2i} - N_{V(2i)})! N_{V(2i)}!} \times \frac{N_{2i+1}!}{(N_{2i+1} - N_{V(2i+1)})! N_{V(2i+1)}!} \quad . \tag{6}$$

Substituting Eqs. (5) and (6) into Eq. (4) and minimizing the free energy with respect to $N_{V(2i)}$ and $N_{V(2i+1)}$, we obtain the following equation after neglecting terms of order $(n/N)^2$ and higher:

$$\frac{n}{N} = \sum_i \frac{z!}{(z-i)!i!} C_A^i C_B^{z-i} \exp\{-[z\epsilon_{BB} + i(\epsilon_{AA} - \epsilon_{BB})]/2kT\}$$
$$= [C_A \exp(-\epsilon_{AA}/2kT) + C_B \exp(-\epsilon_{BB}/2kT)]^z \quad . \tag{7}$$

The vacancy concentration in an AB alloy is thus a surprisingly simple function of the bond energies between two like atoms. Thus, if the vacancy formation energies in the two constituent pure metals are known, the vacancy concentration in any composition can be readily calculated, since $E_f^A = (z/2)\epsilon_{AA}$ and $E_f^B = (z/2)\epsilon_{BB}$, where $E_f^A(E_f^B)$ is the vacancy formation energy in metal A (B). If we characterize n/N by an exponential function of the vacancy formation energy, $n/N = \exp[-E_f(T)/kT]$, the formation energy is temperature dependent and increases with temperature. In many disordered alloys in existence, however, this increase is small (a few percent or less) within reasonable temperature limits where the vacancy concentration is appreciable. We note that the vacancy concentration of Eq. (7) is only from the configurational part of the free energy, and thus for the total vacancy concentration, Eq. (7) must be multiplied by $\exp(S^v/k)$, where the vibrational entropy S^v is expected to be of order $1.5k$, similar to the values in pure metals.

For a very dilute alloy, $C_B << 1$ and thus we have

$$\frac{n}{N} = \exp(-z\epsilon_{AA}/2kT) \times \{1 - zC_B + zC_B \exp[(\epsilon_{AA} - \epsilon_{BB})/2kT]\} \quad . \tag{8}$$

The above equation is in the same form as that written down by Lomer nearly thirty years ago[16] if we identify

$$E_B = \frac{\epsilon_{AA} - \epsilon_{BB}}{2} \quad , \tag{9}$$

where E_B is the vacancy-solute binding energy. Thus, E_B can be either positive or negative depending on the sign of $\epsilon_{AA} - \epsilon_{BB}$, and E_B will be larger for the alloys where $E_f^A - E_f^B$ is larger.

In the light of the present work, we examine some of the shortcomings in the previous theories of vacancy formation in disordered alloys. In the first model of Krivoglaz and Smirnov[15] as well as in the smeared displacement model and the simple displacement model of Cheng, Wynblatt, and Dorn[17] it was assumed that all the A atom sites as well as B atom sites are equivalent and have a single average vacancy formation energy. Since the vacancy concentration is an exponential function of the formation energy, and since the $2(z+1)$ different configurations in a disordered alloy will, in general, have appreciably different vacancy formation energies, the above models are very unrealistic and yield, in some cases, orders of magnitude smaller vacancy concentrations than those calculated from the present theory. Krivoglaz and Smirnov[15] also calculated the vacancy concentration in disordered bcc alloys using the quasichemical approximation. The final expression obtained by these authors is, however, in error since it is not invariant under the relabelling of A and B atoms. In the modified vacancy energy model of Cheng *et al.*,[17] the energy to form a vacancy in $2(z+1)$ different types of sites was assumed to be all different, similar to the present theory. In their model, however, the redistribution of atoms following creation of vacancies was not taken into account, and also it was arbitrarily assumed that the vacancy formation energy for each type of sites is one-half the bond energy in the crystal. Thus, they obtain for the A atom sites coordinated with z B atoms, a formation energy of $(z/2)\epsilon_{AB}$ instead of $(z/2)\epsilon_{BB}$ in the present theory. The fact that the above sites have a formation energy lower than $(z/2)\epsilon_{AB}$ in an alloy, where $\epsilon_{AB} > \epsilon_{BB}$, can be readily shown as follows. First, if vacancies are created by taking A atoms to the surface and these A atoms form clusters on the surface, the formation energy is $(z/2)\epsilon_{BB}$, lower than $(z/2)\epsilon_{AB}$. Secondly, if A atoms are taken to the surface together with B atoms having the same nearest-neighbor configuration, the formation energy of a vacancy is also $(z/2)\epsilon_{BB}$. Since the above processes are allowed in creating vacancies, the assumption of Cheng *et al.* that the formation energy is one-half the bond energy in the crystal is in error.

We now compare our theory with experimental observations. Most of the determinations of the vacancy formation energies and vacancy-solute binding energies in disordered alloys have been recently carried out using the positron annihilation technique. In this technique, the temperature dependences of certain parameters are measured and then analyzed using the trapping model[18] to yield the vacancy formation energy E_f. The vibrational entropy, discussed earlier, is absorbed in a composite parameter and cannot be determined with this technique. In most metals and alloys, some of the parameters in the trapping model cannot be determined accurately, for example, because of the onset of melting. Thus, the derived values of E_f can be uncertain by several percent.[18-20] Another method often used in determining E_f from the positron annihilation data is the following semiempirical correlation between E_f and the threshold temperature of positron trapping, T_t,[13,18,21,22]

$$E_f = 15kT_t \quad . \tag{10}$$

The excellent correlation of T_t with the observed activation energies of self-diffusion in various metals[21] suggests that the uncertainty in E_f in the above method may be less than that in the standard trapping model analysis. In addition, T_t in various alloys can be determined fairly accurately even where the statistics of the data are not good enough to yield meaningful E_f values when analyzed with the standard trapping model. Therefore, we have chosen to compare our theory with observed E_f values determined by Eq. (10). Since the above method determines E_f at temperatures near (slightly above) T_t, it can be readily compared with $E_f(T_t)$ calculated from the present theory with the equation

$$[C_A \exp(-\epsilon_{AA}/2kT_t) + C_B \exp(-\epsilon_{BB}/2kT_t)]^z = \exp(-E_f(T_t)/kT_t) \quad , \tag{11}$$

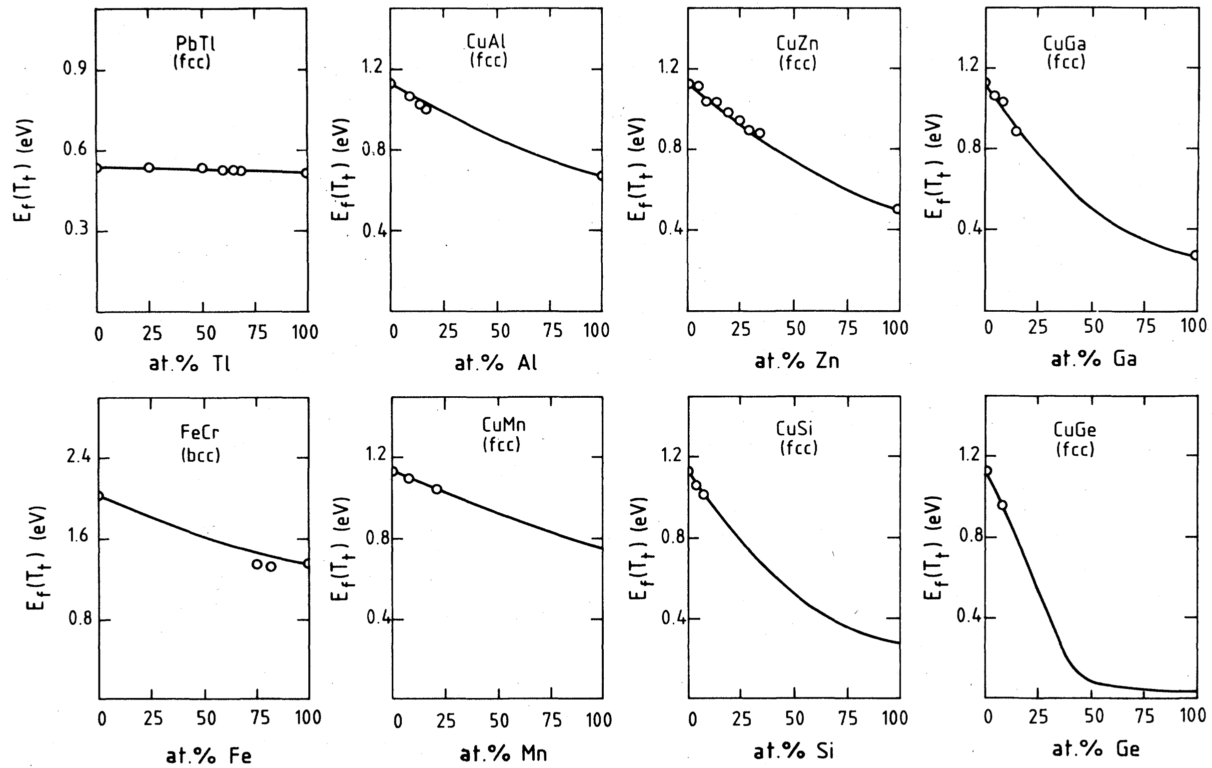

FIG. 1. The experimental (open circles) and theoretical (full curves) vacancy formation energies near the threshold temperatures, $E_f(T_t)$, in disordered fcc alloys of PbTl, CuAl, CuZn, CuGa, CuMn, CuSi, CuGe, and bcc alloys of FeCr obtained as described in the text.

where T_t is determined from the relationship $E_f(T_t) = 15kT_t$.

In Fig. 1, we have plotted the experimental and theoretical $E_f(T_t)$ determined using Eqs. (10) and (11) in pure metals Pb,[18] Tl,[23] Cu,[18] Al,[18] Zn,[18] Ga,[1] Cr,[24] and Fe[22] as well as in the fcc alloys of PbTl,[10] CuAl,[5] CuZn,[9] CuGa,[6] CuMn,[8] CuSi,[6] CuGe,[7] and the bcc alloys of FeCr.[13] We assumed that the bond energy between two Ga atoms in the fcc phase is the same as that obtained in the bcc NiGa.[1] In alloys where both ϵ_{AA} and ϵ_{BB} are known, i.e., PbTl, CuAl, CuZn, CuGa, and FeCr, the full curves are theoretical predictions for $E_f(T_t)$ calculated with Eq. (11) for the whole composition range. Since in alloys of CuMn, CuSi, and CuGe, ϵ_{BB} in the fcc phase is not known, this quantity was first determined by fitting Eq. (11) to the observed $E_f(T_t)$ in the alloy phases and then $E_f(T_f)$ was calculated for the whole composition range. It is seen that the agreement between theory and experiments is excellent. The FeCr data in Fig. 1 are those of bcc stainless steels (types 430 and 446)[13] containing 2 at.% Si, and these impurities may account for the slightly lower observed $E_f(T_t)$.

TABLE I. The vacancy-solute binding energies, E_B, in various dilute alloys obtained from the theory by using Eq. (9).

Alloy	E_B (eV)	Alloy	E_B (eV)
CuAl	0.038	AlZn	0.014
CuZn	0.052	AlSi	0.033
CuGa	0.071	AlAg	−0.027
CuMn	0.031	AlGe	0.053
CuSi	0.071	PbCu	−0.050
CuGe	0.091	PbAu	−0.037
PbTl	0.002	PbCd	0.005
FeCr	−0.083	PbAg	−0.039

It is now generally accepted that the vacancy-solute binding energies are very small, $|E_B| \lesssim 0.1$ eV, in many dilute aluminum alloys, where extensive measurements have been made.[3,4,14,25] Similar small binding energies have been observed in several lead alloys.[11,12] In fact, the threshold temperatures in all these dilute alloys studied by positron annihilation method are practically the same as those in the host pure metals. In some Cu and Ag alloys, considerably larger values of E_B have been reported, i.e., $E_B \simeq 0.15 \pm 0.1$ eV in CuAl (Ref. 26) and $E_B \simeq 0.25 \pm 0.1$ eV (Ref. 26) or 0.19 ± 0.02 eV (Ref. 27) in CuGe. The vacancy-solute binding energies in various Cu alloys, PbTl, FeCr, as well as in various Al alloys and Pb alloys obtained from Eq. (9) of the present theory are shown in Table I. It is seen that E_B is largest in CuGe, smallest in PbTl, and negative in several alloys where $\epsilon_{AA} < \epsilon_{BB}$. The magnitudes of E_B in all the aluminum and lead alloys are very small ($\lesssim 0.1$ eV), in good agreement with experimental observations. For CuAl and CuGe, however, the observed values of E_B appear to be much larger than those given in Table I.

We conclude that a theory of vacancy formation in disordered alloys based on the nearest-neighbor bond energy concept is capable of satisfactorily describing the observed composition dependence of the vacancy formation energies in various alloys as well as the observed very small vacancy-solute binding energies in many dilute aluminum alloys. It is hoped that additional precise measurements will be made in other alloys, in particular, bcc and hcp alloys, to provide further tests of the present theory.

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