REPLY TO COMMENT ON SOME CALCULATIONS OF VACANCY CHARACTERISTICS IN SUBSTITUTIONAL ALLOYS

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Recently, Sprušil (1) has found some inconsistencies in the values of several energy parameters obtained from our pair approximation model (2) and the model by Kinoshita and Eguchi (3) on vacancies in alloys. Here, we would like to demonstrate that the energy values derived from our model are consistent with the results from some simple reasoning using the "broken-bond" concept.

The vacancy formation energy $E_f$ is the energy required to take an atom from inside the crystal, and to place it on the surface. Using the "broken-bond" concept, e.g. see Friedel (4), $E_f$ is simply the energy required to break the bonds necessary in creating the vacancy. If $z$ is the coordination number of a metal $A$, then $z$ number of $\sigma$-$A$ bonds are broken during extracting an atom from inside the crystal, and on the average, $z/2$ bonds are reestablished in putting the atom on the surface. Therefore, by assuming $E_{AA}$ the energy of an $A$-$A$ bond and no relaxation around the newly created vacancy, we have

$$E_f = -\frac{z}{2} E_{AA} \tag{1}$$

However, in reality, there is always some relaxation associated with a vacancy. Since relaxation reduces the free energy of the system, we may assign an apparent binding energy $E_{AV}$ for a vacancy-atom pair as some average contribution to the total reduction of free energy. Then, $E_f$ should be rewritten as:

$$E_f = z E_{AV} - \frac{z}{2} E_{AA} \tag{2}$$

which is exactly the result in our model (2) except there we have defined the bond energies $V_{ij}$ as the negatives of $E_{ij}$ here. Note that Sprušil missed a minus sign in his Eqs. (2a) and (2b).

In alloys, the vacancy concentration is also controlled by the energy factor $B$ (or $E_{VB}^B$ in Sprušil's notation). We have pointed out (2) that $B$ is essentially the energy of a pair reaction involving the dissociation of a solute-vacancy ($B$-$V$) pair, i.e.

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To show this is a "broken-bond" model, we visualize the separation of a B-V pair in the following change in local configurations

\[
\begin{array}{c}
\begin{array}{c}
\text{(a)} \\
b \end{array}
\end{array} \rightarrow \begin{array}{c}
\begin{array}{c}
\text{(b)} \\
a \end{array}
\end{array}
\]

In dilute solutions, it is reasonable to assume that both configurations are generally surrounded by the solvent A atoms. Then there are \((z-1)\) A-B bonds, \((z-1)\) A-V bonds, \((z-1)\) A-A bonds and one B-V bond in configuration (a), and \(z\) A-B bonds, \((z-2)\) A-A bonds and \(z\) A-V bonds in configuration (b). In the transition from configuration (a) to (b), one B-V bond and one A-A bond are broken, and one A-B bond and one A-V bond are created. Therefore, the transition energy is essentially the energy of the pair reaction (3)

\[
\begin{align*}
B &= E_{AV} + E_{AB} - E_{AA} - E_{BV}
\end{align*}
\]

Equation (4) is our Eq. (25) in Ref. (2) when the sign differences in bond energies are properly considered.

We have shown above that our energy values from the pair approximation are physically sound based on the broken-bond concept. If the "broken-bond" concept is correct, then the results from Kinoshita and Eguchi's model must be incorrect. We have found that the discrepancies in their values are the result of a poor approximation in estimating the entropy term, which in fact, has happened before (5). Since a general discussion on this point is quite lengthy, we will present it in a later paper.

References

1. B. Spruišil, to be published in Scripta Met. (this issue).

**The reaction direction shown in Ref. (2) is wrong and should be reversed.**