

Vacancy Wind Factor of Diffusion of 13 Binary Metallic Solid Solutions

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Abstract

A systematic analysis was performed of Manning's vacancy wind factor on diffusion of 13 binary solid solutions whose experimentally measured tracer diffusion coefficient data collected from the literature are reliable and comprehensive. Some straightforward yet interesting observations are reported, including a value of ~ 1.85 for the diamond cubic Ge-Si binary solid solution. It is recommended that the vacancy wind factor not be included in the CALPHAD diffusion coefficient (mobility) assessments since the effects have essentially been included in the fitting parameters. For those who use diffusion coefficients directly, the factor may still be ignored for both fcc and bcc solid solutions since the maximum effects are only 28% and 38% increase in diffusion coefficients. The factor may be included for low diffusion coefficient systems of the diamond cubic phases at low temperatures and especially for those systems whose tracer diffusion coefficients differ by orders of magnitude.

Keywords: Diffusion coefficients, vacancy wind factor, tracer diffusion coefficients, kinetics, solid solutions.

Diffusion is a fundamental process in nature. Mathematical models of diffusion coefficients are essential to simulate diffusion-controlled processes in metals and alloys such as casting, precipitation, and homogenization. Darken in 1948 performed an elegant phenomenological analysis of binary diffusion coefficients and beautifully separated the thermodynamic contributions to diffusion from the purely kinetic contributions, leading to the famed Darken's equation (Eq. 1) that relates the tracer diffusion coefficients D_A^* and D_B^* , the interdiffusion (chemical diffusion) coefficient \tilde{D} , and the thermodynamic factor φ in a binary solid solution formed between elements A and B [1]:

$$\tilde{D} = (x_A D_B^* + x_B D_A^*) \varphi \quad (1)$$

where x_A and x_B are the mole fractions of A and B in the A-B solid solution, respectively.

Manning further introduced a correction factor to the Darken's equation to take into account the influence of the net vacancy flux on the enhancement of the intrinsic diffusion coefficient of the faster diffusion element and the deceleration of the diffusion rate of the slower element [2,3], leading to an overall increase of the interdiffusion coefficients. Manning derived the overall vacancy wind factor W_{AB} (Eq. 2) as:

$$W_{AB} = 1 + \frac{2x_Ax_B(D_A^* - D_B^*)^2}{M_0(x_A D_B^* + x_B D_A^*)(x_A D_A^* + x_B D_B^*)} \quad (2)$$

(2)

where M_0 is a constant depending on the crystal structure of the phase and is 7.15, 5.33, 3.77, and 2 for face-centered cubic (fcc), body-centered cubic (bcc), simple cubic, and diamond cubic, respectively. The theoretical upper limit of W_{AB} is $1 + 2/M_0$, and is 1.28, 1.38, 1.53, and 2 for the above crystal structures, respectively.

The Manning revised Darken's equation (Eq. 3) is thus:

$$\tilde{D} = (x_A D_B^* + x_B D_A^*) \varphi W_{AB} \quad (3)$$

Several prior studies of the vacancy wind factor W_{AB} of *binary solid solutions* focused on only one or a couple of binary systems each time [4–9]. It is hard to appreciate the overall behavior of W_{AB} across the entire composition range and over a range of temperatures from these prior studies that were conducted more than 45 years ago when the experimental tracer diffusion data were relatively limited.

During the recent development of a simple Z-Z-Z model for diffusion coefficients of binary alloy systems, experimental data of 18 completely soluble binary solid solutions were collected from the literature and analyzed systematically [10]. Among them, 13 systems have very reliable and ample experimental tracer diffusion coefficient data to be used to compute W_{AB} for these binary systems at various temperatures across the entire compositions. This short article briefly reports the W_{AB} results of these 13 systems.

The overall vacancy wind factor W_{AB} of 8 fcc solid solutions is calculated and plotted in Fig. 1 for various temperatures as a function of composition according to Eq. 2 using the collected experimental tracer data that are fitted to the Z-Z-Z model. One can see from Fig. 1 that as temperature decreases, W_{AB} generally increases as a direct result of lower tracer diffusion coefficients D_A^* and D_B^* , and thus lower values of the denominator in Eq. 2 (the numerator has the $(D_A^* - D_B^*)^2$ term which does not decrease as much as the denominator with decreasing temperature for most binary solid solutions examined in this study). When the D_A^* and D_B^* values are similar as in the cases of Fe-Pd, Co-Ni, Ag-Au, and Fe-Ni, the maximum W_{AB} value is only around 1.004, 1.025, 1.04 and 1.06 respectively for the temperatures at which experimental measurements are available. In other words, the effect of W_{AB} only leads to a maximum of 6% increase interdiffusion coefficients in the temperature ranges studied for the above 4 binary fcc solid solutions. In these cases, the small values of the numerator in Eq. 2 render low W_{AB} values. When the differences in the D_A^* and D_B^* values are larger and especially at relatively low temperatures, the W_{AB} values start to creep into approximately 1.11, 1.175, 1.175 and 1.20 for Co-Fe, Cu-Ni, Cu-Pt, and Au-Ni, respectively, as shown in Fig 1. The upper bound of W_{AB} for the fcc crystal structure is 1.28. Even at the limit, the effect of 28% increase in interdiffusion coefficients is within the degree of uncertainties in experimental measurements. It is noted that W_{AB} may be reduced to unity at some alloy compositions when the tracer diffusion coefficients of the two components are equal, as observed in the Co-Ni and Fe-Pd systems, creating quite complex W_{AB} curves, as shown in Fig. 1(d) and 1(h).

The composition and temperature dependences of W_{AB} in 4 completely soluble bcc solid solutions are shown in Fig. 2. The general behaviors observed in the 8 fcc solid solutions are also present in the 4 bcc solid solutions. For Ti-V, the maximum effect is only ~4% increase in interdiffusion coefficients even at 700 °C due to similar values of D_{Ti}^* and D_V^* . As a matter of fact, these tracer diffusion coefficients reach similar values at some alloy compositions in the Ti-V binary system and reduce W_{AB} to unity at certain compositions and temperatures as shown in Fig. 2(d). Even for Nb-V, the maximum effect of W_{AB} is only ~6% increase of diffusion coefficients at 1250 °C; and it would be higher values at lower temperatures. The maximum W_{AB} values for the Nb-Ti bcc solid solution reach ~1.16 at 900 °C. The W_{AB} values of the Nb-Zr bcc solid solution reach ~1.32 at relatively low temperatures (e.g. 700 °C), approaching the theoretical maximum of $W_{AB} = 1.38$ for the bcc crystal structure due to the fact the D_{Nb}^* and D_{Zr}^* are 6 orders of magnitude apart at some compositions and temperatures. Even at the theoretical limit of $W_{AB} = 1.38$, the maximum effect of W_{AB} in increasing the interdiffusion coefficients by 38% is still negligible considering the uncertainty in the diffusion coefficient measurements.

Fig. 3 shows the computed W_{AB} of the diamond cubic Ge-Si solid solution, which reaches ~1.85 at about 90 at.% Si and 550 °C, closed to the upper limit value of $W_{AB} = 2$ for the diamond cubic crystal structure. In this case, the effect of W_{AB} is appreciable.

Unfortunately, no systematic and reliable data were found for hcp solid solutions for a careful analysis as above.

A few somewhat straightforward observations are summarized here:

- The lower the temperature, **generally** the higher the W_{AB} since the lower the tracer diffusion coefficients at lower temperatures for both elements and thus lower values for the denominator in Eq. 2 (**the numerator has the $(D_A^* - D_B^*)^2$ term which does not decrease as much as the denominator with decreasing temperature for most binary solid solutions examined in this study**);
- The larger the difference of tracer diffusion coefficients, the larger the W_{AB} as a result of a larger numerator in Eq. 2;
- When tracer diffusion coefficients are equal for both elements at some compositions, W_{AB} becomes unity at those compositions; and
- The largest values of W_{AB} are for those systems with low diffusion coefficients and large disparity in tracer diffusion coefficients of both elements (W_{AB} as high as ~1.85 has been computed for Ge-Si) and thus W_{AB} may become appreciable for low diffusion coefficient systems such as hcp Ti-based and Zr-based systems at low temperatures.

Based on the results of these 13 binary systems, it is recommended that W_{AB} not be included in the CALPHAD (CALculation of PHAse Diagrams) diffusion coefficient (mobility) assessments as it has been the case ever since the start [11,12]. Since the atomic mobilities (which are equivalent to the tracer diffusion coefficients) of elements are fitted anyway, the W_{AB} effects have essentially been included already. For those who use diffusion coefficients directly and do not use the CALPHAD-type mobility treatment, W_{AB} may still be ignored for both fcc and bcc solid solutions since the maximum effects are only 28% and 38% increase in diffusion coefficients respectively. W_{AB} may be included for low diffusion coefficient systems of the diamond cubic phases at low temperatures and especially for those systems whose tracer diffusion coefficients differ by orders of magnitude.

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Since *tracer* diffusion coefficients are required in Eq. 2 to compute W_{AB} , yet they are often not measured experimentally for most binary solid solutions to allow the direct calculation of W_{AB} . The recently developed Z-Z-Z model enables the calculation of W_{AB} even for binary solid solutions that have *interdiffusion* coefficient data only. The Z-Z-Z model allows one to fit a single constant $\Phi^{A,B}$ from experimentally measured *interdiffusion* coefficients \tilde{D} using Eq. 4:

$$\tilde{D} = [x_B \exp(x_A \ln D_A^A + x_B \ln D_A^B) + x_A \exp(x_A \ln D_B^A + x_B \ln D_B^B)] \cdot \varphi \exp(\Phi^{A,B} x_A x_B / RT) \quad (4)$$

where D_A^A and D_B^B are self-diffusion coefficients of elements A and B, and D_A^B and D_B^A are the impurity (dilute) diffusion coefficients of A in B and B in A, respectively.

After the constant $\Phi^{A,B}$ is obtained by fitting the experimentally measured *interdiffusion* data using Eq. 4, the composition-dependent *tracer* diffusion coefficients D_A^* and D_B^* can be computed via Eq. 5.1 and 5.2:

$$D_A^* = \exp(x_A \ln D_A^A + x_B \ln D_A^B) \exp(\Phi^{A,B} x_A x_B / RT) \quad (5.1)$$

$$D_B^* = \exp(x_A \ln D_B^A + x_B \ln D_B^B) \exp(\Phi^{A,B} x_A x_B / RT) \quad (5.2)$$

The D_A^* and D_B^* can then be used in Eq. 2 to compute W_{AB} . The reliability of such computation of *tracer* D_A^* and D_B^* from *interdiffusion* coefficients \tilde{D} has been demonstrated for binary solid solutions [10].

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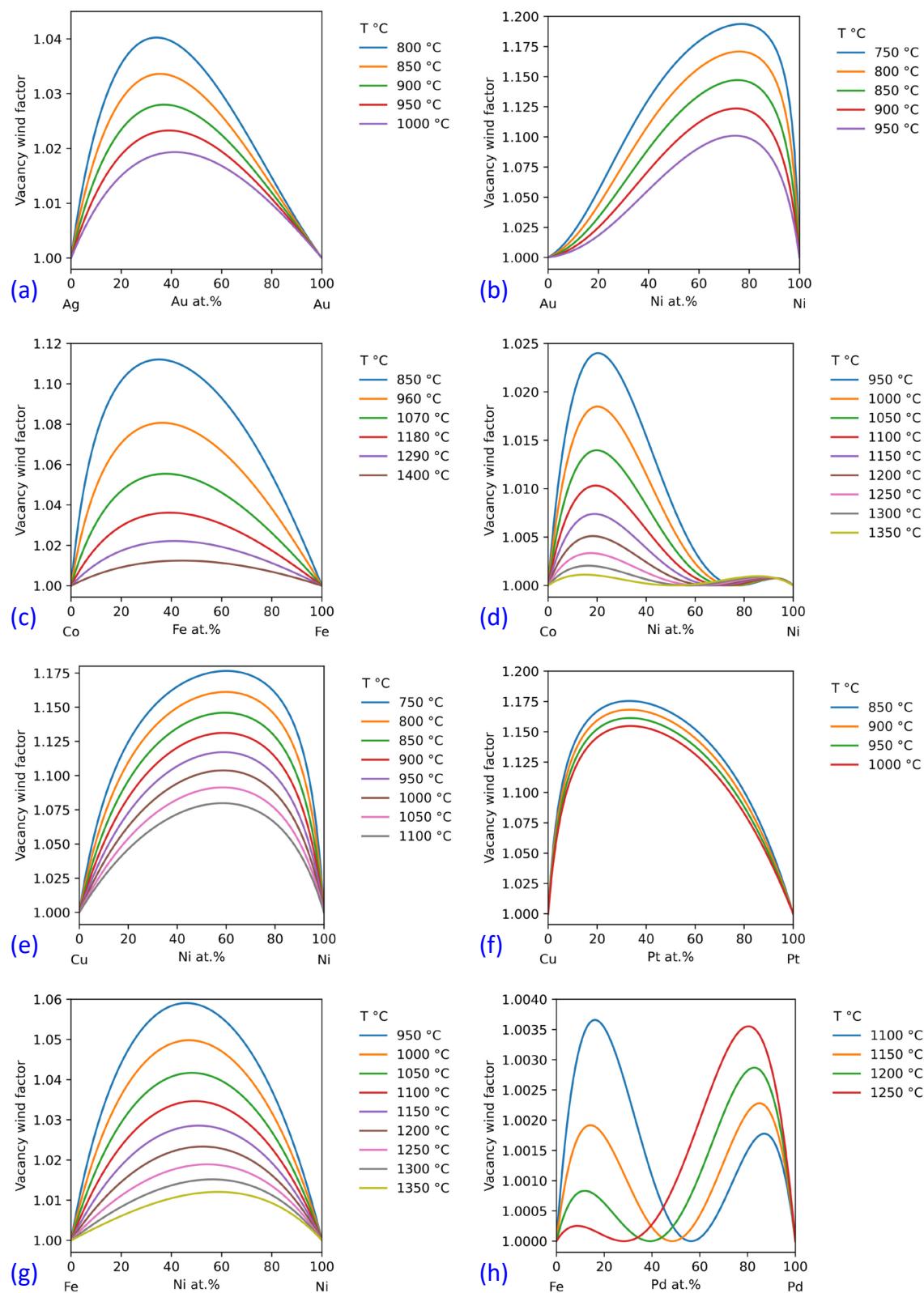


Figure 1 The vacancy wind factor W_{AB} of 8 fcc binary solid solutions: (a) Ag-Au; (b) Au-Ni; (c) Co-Fe; (d) Co-Ni; (e) Cu-Ni; (f) Cu-Pt; (g) Fe-Ni; and (h) Fe-Pd.

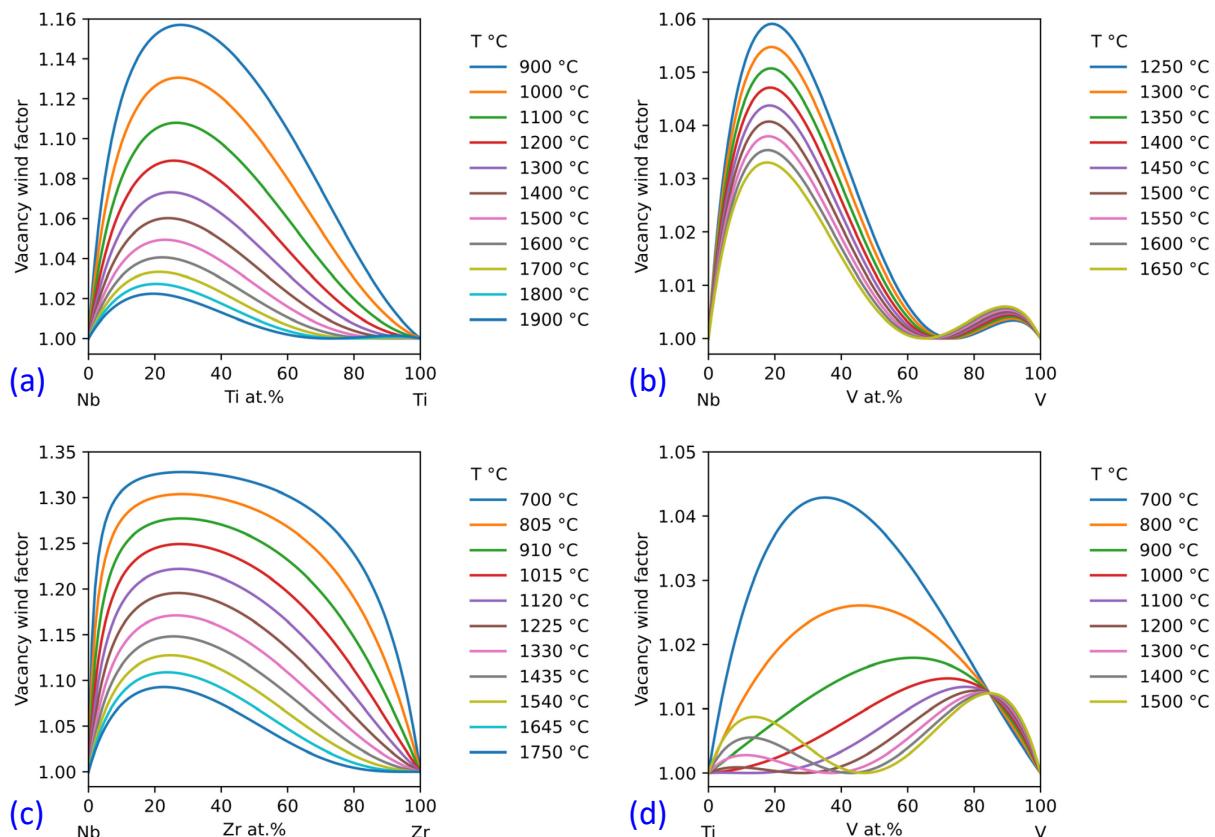


Figure 2 The vacancy wind factor W_{AB} of 4 bcc solid solutions: (a) Nb-Ti; (b) Nb-V; (c) Nb-Zr; and (d) Ti-V.

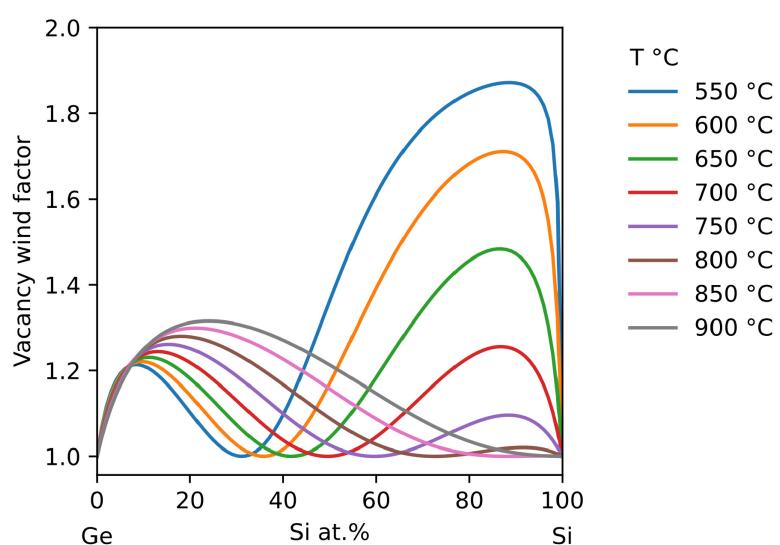


Figure 3 The vacancy wind factor W_{AB} of the diamond cubic Ge-Si solid solution.

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