Correlation between cohesive energy and mixing rate in ion mixing of metallic bilayers

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We have compared the mixing rate of several 5d-4d metal bilayers which form ideal solutions. We observe a strong correlation between the mixing rate and the average cohesive energy of each bilayer. A model based on the thermal spike concept is proposed to explain this behavior. The model leads to a general expression describing mixing rates in metallic bilayers.

In the usual theoretical description of cascade mixing, the mixing rate is assumed to be inversely proportional to the effective displacement energy $E_d$ inside the cascade volume. However, due to the complexity of the ion mixing process, the mixing rate actually depends on many factors. Recently, a relationship between the mixing rate and the heat of mixing $\Delta H_m$ was established for a series of transition metal bilayers by the present authors. By eliminating chemical effects (i.e., taking systems with $\Delta H_m = 0$), we now can investigate the role of $E_d$ directly.

The systems we have chosen to study are metallic 5d-4d bilayers of Au-Ag, Pt-Pd, Hf-Zr, W-Mo, and Ta-Nb. Due to their isoelectronic structure, similar Goldschmidt radii and density, ideal solution behavior, and corresponding near zero heat of mixing, these binary systems are well suited for studying those effects which are not related to the chemical effects examined earlier. Furthermore, all 5d and 4d elements have nearly the same atomic number and mass, while the mass difference between the top (5d) and bottom (4d) layer of each couple is sufficient to resolve their signals and study the intermixing process by backscattering spectrometry.

Thin bilayer films were prepared by e-gun evaporation in an oil-free vacuum system with a base pressure below $10^{-7}$ Torr. All bilayers consisted of a layer of the 5d metal on top of a 2000-Å-thick layer of the 4d metal sequentially evaporated on a SiO$_2$ substrate. The top layer thickness was adjusted to the projected range of 600 keV Xe$^{2+}$ ions. To reduce sputtering effects, a thin layer of Si (100 Å) was evaporated on top of the samples. Ion mixing was performed at LN$_2$ temperature in order to minimize radiation enhanced diffusion. The vacuum during the irradiation was maintained below $5 \times 10^{-7}$ Torr. Irradiation doses ranged from $10^{13}$ to $1.5 \times 10^{16}$ Xe$^{2+}$ ions/cm$^2$ at a flux of about 200 nA/cm$^2$. Different samples were irradiated simultaneously to a specific dose in order to avoid dose and dose rate variations. Backscattering analysis was performed with 3-MeV He$^{2+}$ ions and a target tilted at 60°. Different samples were placed on the same holder to cancel uncertainty in tilt angle.

The observed diffusion profiles were smooth and showed no steps that would indicate the presence of a layered compound. The high-energy backscattering edge of each bottom layer was transformed numerically to concentration versus depth profiles, assuming lateral uniformity over the mixed interface. The transformed profiles were least squares fitted to complementary error functions, using the expression

$$Y = a(3) \text{erfc}[(x - a(1))/a(2)] + a(4),$$

where $a(1)$, $a(2)$, $a(3)$, and $a(4)$ are fitting variables. The good quality of the erfc fits to all intermixing profiles is a direct indication of an unbiased random walk process, as would be expected for systems with nearly zero heat of mixing. The result of such an analysis of the experimental data is shown in Fig. 1. A linear relationship between $a(2)^2 = 4Dt$ and dose ($\phi$) is observed in all cases. The straight lines in Fig. 1 are fits obtained by linear regression analysis. The slope of each line $d(4Dt)/d\phi$ characterizes the mixing rate of the corresponding bilayer. The nonzero value of $4Dt$ at $\phi = 0$ is due to the finite extension of the interface of the as-deposited samples and the limited instrumental resolution.

A theoretical estimate of the mixing rate for the systems under consideration can be derived from the well-known formula for cascade mixing in the binary collision approxima-
where $\epsilon_D$ is the energy deposited per unit path length, $N$ is the atomic density of the material, $E_0$ the effective displacement energy, $\langle R_e \rangle^2$ is the mean square range of a displaced atom, $\Gamma_0 = 0.608$, and $\xi_{2d} = [4m_1 m_2/(m_1 + m_2)^2]^{1/2}$. The difference in mixing rate would be expected for the various bilayers involved if conventional values for $R_e$ ($10 \text{ Å}$) and $E_d$ ($\sim 30 - 40 \text{ eV}$) were used, whereas the experimental values vary by an order of magnitude.

In an effort to understand the origin of this discrepancy, we have plotted $[d(4Dt)/d\phi]^{-1}$ versus the average cohesive energy of each bilayer (Fig. 2). The latter was estimated from the heat of sublimation of the pure elements. A striking correlation suggests that values of $E_d$ and/or $R_e$ deduced from binary collision experiments are inappropriate for ion mixing under the present conditions. To understand why we need to examine the physical basis of $E_d$ in the case of ion mixing experiments, the displacement energy may be considered to consist of two major contributions. The first is the minimum energy required to remove an atom from its site and is therefore close to the formation energy of a vacancy (few eV); the second contribution is the extra energy needed to move the atom some specific distance away from the vacancy and avoid spontaneous recombination. In a low-density cascade with only one type of atoms present (such as in electron or proton bombardment of pure elements) $E_d$ is normally derived from the resulting concentration of stable radiation-produced vacancy-interstitial pairs. Each such pair has to be separated by a minimum distance (about 10 Å) below which vacancies and interstitials would mutually annihilate each other. To move an atom this distance, an energy of some tens of eV is needed. Therefore, $E_d$ in low-density cascades is dominated by the second part of the contribution to the displacement energy and the defect production is well described by a Kinchin–Pease type model.

In ion mixing with heavy projectiles, the situation is different. Because of the high density of the cascade, correlated motions of neighboring atoms are possible and the medium becomes liquid-like. Therefore, the second contribution to $E_d$ is reduced. Furthermore, an atom ejected from its site and displaced by one or more atomic distances may contribute to ion mixing whereas in a one-component system, an atom must be sufficiently displaced to make a stable vacancy-interstitial pair. These differences between the two types of experiments sug-

![Graph](image1)

**TABLE I. Comparison between calculated values of $d(4Dt)/d\phi$ from Eq. (4) and experimental observations.**

<table>
<thead>
<tr>
<th>System (A–B)</th>
<th>$-\Delta H_{\text{mav}}^*$ (kJ/g at)</th>
<th>$-\Delta H_{\text{cav}}^*$ (eV/particle)</th>
<th>$\epsilon_D^*$ (eV/Å)</th>
<th>$\rho_0$ ($10^{-2}$ Å$^{-1}$)</th>
<th>$d(4Dt)/d\phi_{\text{exp}}^*$ (10$^4$ A$^{-4}$)</th>
<th>$d(4Dt)/d\phi_{\text{cal}}^*$ (10$^4$ A$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt–Ti</td>
<td>122</td>
<td>6.60</td>
<td>4.45</td>
<td>6.14</td>
<td>1.28</td>
<td>1.07</td>
</tr>
<tr>
<td>Pt–V</td>
<td>68</td>
<td>6.27</td>
<td>4.91</td>
<td>6.92</td>
<td>0.68</td>
<td>0.78</td>
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<tr>
<td>Pt–Mn</td>
<td>43</td>
<td>4.82</td>
<td>5.31</td>
<td>7.40</td>
<td>0.73</td>
<td>1.19</td>
</tr>
<tr>
<td>Pt–Cr</td>
<td>36</td>
<td>5.34</td>
<td>5.30</td>
<td>7.47</td>
<td>0.45</td>
<td>0.78</td>
</tr>
<tr>
<td>Pt–Ni</td>
<td>7</td>
<td>5.21</td>
<td>5.82</td>
<td>7.88</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>Au–Ti</td>
<td>84</td>
<td>5.20</td>
<td>4.14</td>
<td>5.78</td>
<td>1.63</td>
<td>1.48</td>
</tr>
<tr>
<td>Au–Cr</td>
<td>0</td>
<td>3.96</td>
<td>4.98</td>
<td>7.12</td>
<td>0.78</td>
<td>0.48</td>
</tr>
<tr>
<td>Au–Co</td>
<td>0–11</td>
<td>3.99</td>
<td>5.39</td>
<td>7.43</td>
<td>0.45</td>
<td>0.12</td>
</tr>
<tr>
<td>Pt–Pd</td>
<td>0</td>
<td>4.87</td>
<td>5.54</td>
<td>6.71</td>
<td>0.45</td>
<td>0.43</td>
</tr>
<tr>
<td>Hf–Zr</td>
<td>0</td>
<td>6.34</td>
<td>3.55</td>
<td>4.40</td>
<td>0.26</td>
<td>0.22</td>
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<tr>
<td>W–Mo</td>
<td>0</td>
<td>7.86</td>
<td>5.19</td>
<td>6.36</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>Ta–Nb</td>
<td>0</td>
<td>7.84</td>
<td>4.45</td>
<td>5.56</td>
<td>0.14</td>
<td>0.15</td>
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<tr>
<td>Au–Ag</td>
<td>0</td>
<td>3.38</td>
<td>4.80</td>
<td>5.88</td>
<td>2.37</td>
<td>0.84</td>
</tr>
</tbody>
</table>

*Cohesive energy of $A_vB_{ref}$ calculated from $\Delta H_{\text{cav}} = [\Delta H_{\text{v}}^0 + \Delta H_{\text{i}}^0] + \Delta H_{\text{mav}}$ and $\Delta H_{\text{v}}^0$ and $\Delta H_{\text{i}}^0$ are obtained from C. Kittel, Introduction to Solid State Physics, 4th ed. (New York, 1976), and Ref. 6.
*Average atomic density of $A_vB_{ref}$.
*Experimental observations of $d(4Dt)/d\phi$ in Ref. 2 and present work.
*Calculated values of $d(4Dt)/d\phi$ from Eq. (4) with least-square fitted value of $K_1 = 0.037$ Å and $K_2 = 27.$
*This data point was not used in determining $K_1$ and $K_2$, since it would contribute badly to the quality of the least-square fit.
gest an alternative approach to describe the mixing process.
Our previous experiments have shown that most of the mixing
takes place when the energy of the particles is in the 1-eV
range. Such energy densities are achieved in the thermalizing
regime of the cascade, as described by various authors.
Assuming that the particle energy distribution has
reached a state of local quasi-equilibrium, we can adopt a
thermal spike picture as proposed, e.g., by Vineyard. Within
this model, ion mixing is a thermally activated diffusion
process of the form $R = A \exp(-Q/T)$. For a cylindrical
spike, Vineyard obtains the total number of jumps per
unit distance induced by one spike
$$\xi = A \left( \frac{\epsilon_D}{\kappa C Q} \right)^2,$$
where $\epsilon_D$ is the energy deposited per unit path length, while $\kappa$ and $C$ are the (temperature independent) thermal conduc-
tivity and specific heat of the lattice. $A$, $\kappa$, and $C$ are roughly
constant for the metal pairs in our bilayer experiments.
It can be argued that the activation energy $Q$ should scale with
the cohesive energy of the lattice, since the latter is a measure
of the interatomic binding forces; hence $D_t / \phi \propto (\Delta H_{coh})^{-2}$.
The results reported in Fig. 2 are in good accord with such a
dependence.

We have extended this model of ion mixing by dense
energy spikes to the case when chemical driving forces are
present and derived the following equation for the mixing rate$^{12}$:
$$\frac{4Dt} {\phi} = \frac{K_1 (\epsilon_D)^2}{\rho^{3/2} (\Delta H_{coh})} \left( 1 + K_2 \frac{\Delta H_m}{\Delta H_{coh}} \right),$$
where $\rho$ is the average atomic density, $\Delta H_m$ is the heat of
mixing parameter calculated by Miedema.$^3$ $K_1 = 0.037$ Å
and $K_2 = 27$ are two least-square fitted constants.

In Table I we compare experimental and calculated mixing rate for various metal systems. The proposed
expression clearly reproduces the experimental trend. In addition
to the data listed in Table I, it has also been observed that
several systems with $\Delta H_m > 0$ show very low mixing rates (e.g., Cu-W,$^{13}$ Cu-Bi,$^{14}$ Ta-Y$^{15}$), as expected from Eq.
(4).

In summary, we have established a direct correlation between the mixing rate of metallic bilayers and the cohesive
energy of the corresponding elements. The experiments were
designed to isolate this effect from the chemical effect estab-
lished earlier. We offer an explanation for this correlation
based on the nature of the microscopic atomic displacement
process which leads to the mixing of atoms. An expression is
proposed which predicts the mixing rate of transition metal
bilayers and includes the chemical enhancement effect. This
expression should be appropriate in the case of high-density
cascades, where the Kinchin-Pease model based on the binary
collision approximation is no longer applicable. More
generally, our results illustrate the usefulness of a thermodynamic
description of the ion mixing phenomenon. It would be
desirable to extend this description to the final stage of the
cascade, where intermetallic phase formation is taking place.
One might then hope to be able to predict the phases which
are produced by cascade mixing.$^{12}$

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