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Zr-Ni INTERMETALLIC COMPOUNDS*

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Atomistic Simulations of Point Defects in Zr-Ni Intermetallic Compounds

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Abstract

The properties of point defects, including stable configurations, formation and migration energies, and migration mechanisms, in the ZrNi and Zr\textsubscript{2}Ni intermetallic compounds were simulated using molecular dynamics and statics, in conjunction with interatomic potentials derived from the Embedded Atom Method. We describe a method to calculate the formation energy of point defects from the program and apply the method to ZrNi and Zr\textsubscript{2}Ni. The results showed that vacancies are most stable in the Ni sublattice, with formation energy of 0.83 and 0.61 eV in ZrNi and Zr\textsubscript{2}Ni, respectively. Zr vacancies are unstable in both compounds; they spontaneously decay to pairs of Ni vacancy and antisite defect. The interstitial configurations and formation energies were also calculated, with similar behaviors. In ZrNi, vacancy migration occurs preferentially in the [025] and [100] directions, with migration energy of 0.67 and 0.73 eV, respectively, and is essentially a two-dimensional process, in the (001)
plane. In Zr$_2$Ni, vacancy migration is one-dimensional, occurring in the [001] direction, with a migration energy of 0.67 eV. In both compounds, the presence of Ni antisite defects decreases the Ni vacancy migration energy by up to a factor of ~3, and facilitates three-dimensional motion.
1. Introduction

The good corrosion resistance exhibited by Zircaloy fuel cladding in nuclear power plants is related to its precipitate microstructure, consisting of intermetallic precipitates of the types Zr(Cr,Fe) and Zr_2(Ni,Fe) embedded in the Zr matrix [1]. To understand the irradiation response of these precipitates and their propensity to undergo phase transformations such as chemical disordering and amorphization, it is necessary to have a good knowledge of the properties of point defects in these compounds. Unfortunately, information about point defects is extremely limited for most ordered intermetallics. The aim of the present work is to acquire such knowledge via atomistic simulations. It is also hoped that these computer simulation results would provide guidance to experimental investigations of atomic defects in the compounds, since it is very difficult experimentally to distinguish the defects one from the other among the many possible point defect types.

In this study, we performed computer simulations to obtain information about the properties of vacancies and interstitials, including their stable configurations, energetics, and migration mechanisms, in the intermetallic compounds ZrNi and Zr_2Ni for which realistic interatomic potentials are available. In addition, the radiation-induced amorphization behaviors of these compounds have systematically been investigated, both experimentally and theoretically [2-4].

2. Computational Procedure

The computational methods used in the present simulations were molecular statics and molecular dynamics at constant pressure. The simulation cells for ZrNi (oC8 structure) and Ni Zr_2 (C16 structure) contained 1568 and 1500 atoms, respectively, and were subjected to periodic
boundary conditions. The interactions between atoms in the compounds were governed by the potentials which had been derived from the Embedded Atom Method (AEM) [5,6] and used in the previous studies of defect-induced amorphization [3,4].

The perfect lattice was first equilibrated for 10,000 time steps (25 ps) using molecular dynamics (each time step is $2.5 \times 10^{-15}$ s). Then, a vacancy or interstitial was created in a given sublattice near the center of the simulation cell using standard procedures. In the vacancy case, the most stable vacancy configuration could be found simply by relaxing the defective lattice dynamically for another 10,000 time steps. The potential energy of the system was then obtained by a local energy minimization using the Fletcher-Powell scheme, which was proven to be quite efficient [7]. The search for the interstitial’s lowest-energy configuration was, however, carried out by means of simulated annealing [8]: the system was first heated to 800K for a few hundred time steps, then energy-minimized with the Fletcher-Powell method, and the process was repeated at lower and lower temperatures, down to the desired temperature.

For pure elements, given the energies of the perfect lattice and of the lattice containing the defect, the defect formation energy can be readily calculated. In ordered compounds, the formation energies of a Frenkel pair and an antisite pair can be determined in a similar way. However, the calculation of the formation energy of a vacancy or interstitial alone is more complex because the perfect lattice and the lattice with the defect have different chemical compositions [9-11].

2.1. Calculation of Point-defect Formation Energies

In ordered compounds, the formation of a Frenkel pair (i.e., an atom is removed from a substitutional site and inserted back into a random interstitial site in the lattice) or an antisite defect pair (i.e., lattice sites of a random pair of atoms of different types are exchanged) does not
lead to a stoichiometry deviation. However, the creation of a vacancy (an atom is removed permanently from its substitutitonal site) or an interstitial (an extra atom is inserted into an interstitial site) results in a departure of stoichiometry, which must be taken into consideration in the calculation of the defect formation energies.

Let us consider an ordered compound $A_xB_y$. The chemical potential of A is defined as the change in the Gibbs free energy, $G$, with respect to the molar fraction of the element A, $n_A$, at constant temperature, $T$, pressure, $P$, and molar fraction of B, $n_B$:

$$
\mu_A = -\frac{\partial G}{\partial n_A} \Bigg|_{T,P,n_B}
$$

(1)

Any change in the chemical composition will cause a variation in the system total energy. This difference consists of two contributions: the defect formation energy and the change in the Gibbs free energy due to the chemical potential.

In order to determine the effective defect formation energy, $E_f$, it is necessary to calculate the defect concentration, $n_j$, as a function of temperature $T$. $E_f$ is then given by the slope of the Arrhenius plot [10,11]:

$$
E_f^j = -k \frac{d[\ln(n_j)]}{dT}
$$

(2)

where $j$ stands for the type of defect (i for interstitial or v for vacancy) and $k$ is the Boltzmann's constant. The defect formation energy may be temperature dependent; however, this effect is considered to be weak and is disregarded, i.e., the Arrhenius plot is a straight line. The validity of this assumption is verified later.

The concentration $n_j$ is obtained from the numerical solution of a system of nonlinear equations proposed by Foiles and Daw [10] and adapted by us to take into account the presence
of interstitials. The total energy, \( U \), of a system of \( N \), atomic sites is given by the perfect-crystal energy, \( U_0 \), plus the contributions from different defects (assuming that their concentrations are low enough so that the defects are noninteracting):

\[
\frac{U}{N^2} = \frac{U_0}{N^2} + n_v^A H_v^A + n_i^A H_i^A + n_v^B H_v^B + n_i^B H_i^B
\]  

(3)

where \( n_j^k \) is the atomic fraction of defect \( j \) (\( = v,i,a \) for vacancy; interstitial and antisite defect) on the \( k \) sublattice (\( = A, B \)), and \( H_j^k \) is the energy difference between the perfect crystal and the crystal containing a defect \( j \) on sublattice \( k \).

The introduction of defects into the perfect crystal increases the configurational entropy which is defined by [12]:

\[
S \frac{N}{N^2} = m^k \left[ s \left( \frac{n_v^i}{m^k} \right) + s \left( \frac{n_i^i}{m^k} \right) + s \left( \frac{n_i^v}{m^k} \right) + m^l \left[ s \left( \frac{n_v^i}{m^l} \right) + s \left( \frac{n_i^i}{m^l} \right) + s \left( \frac{n_i^v}{m^l} \right) \right] \right]
\]

(4)

where \( m^k = z/(z+y) \); \( m^l = 1 - m^k \); \( k = A \) when \( l = B \); and

\[
s(x) = - \left[ x \ln x + (1-x) \ln(1-x) \right]
\]

(5)

The total number of \( k \)-atoms is given by their total number in the perfect crystal, \( m^k N^k/N \) (where \( N^k \) is the number of lattice sites on the sublattice \( A \) or \( B \)) minus the number of vacant sites in the \( k \) sublattice, \( n_v^k \), and the number of \( k \) sites occupied by wrong atoms, \( n_a^i \), plus the number of \( k \) atoms at wrong sublattice sites, \( n_a^a \), and the number of \( k \) atoms occupying interstitial positions, \( n_i^k \):

\[
n^k = \frac{N^k}{N^s} \left( m^k - n_v^k + n_a^k - n_a^i + n_i^k \right)
\]

(6)

The Grand-Canonical potential is given by:
\[ \bar{\varepsilon} = U - kT S - \sum_k i_k N_k \] (7)

Inserting Eqs. (3) and (4) into Eq. (7) and minimizing it with respect to \( n_j^{A,B} \), we arrive at the following expressions for the concentration of each defect type:

\[ n_v^k = m^k \frac{\exp \left( -\frac{H_v^k + 1^k}{kT} \right)}{1 + \exp \left( -\frac{H_v^k}{kT} \right)} \] (8)

\[ n_a^k = m^l \frac{\exp \left( -\frac{H_a^k + 1^l - 1^k}{kT} \right)}{1 + \exp \left( -\frac{H_a^k + 1^l - 1^k}{kT} \right)} \] (9)

\[ n_i^k = m^k \frac{\exp \left( -\frac{H_i^k - 1^k}{kT} \right)}{1 + \exp \left( -\frac{H_i^k - 1^k}{kT} \right)} \] (10)

Equations (8), (9), (10) have their respective counterparts in the other sublattice written by exchanging \( k \) and \( l \), as well as Eq. (6). The final set of 10 equations to be solved consists of Eqs. (3), (4), (6), (8), (9) (10) and the counterparts of equations (6), (8), (9), (10), for the variables \( n_V^A, n_V^B, n_i^A, n_i^B, n_a^A, n_a^B, N_A, N_B, \mu^A, \) and \( \mu^B \). The temperature is a parameter.

2.2. Calculation of Vacancy Migration Energy

The vacancy migration energies were calculated by minimizing the system energy with the jumping atom constrained at various points along the jump path. This procedure consists basically of taking an atom and pushing it into the neighboring vacant site. This move was done
in a series of small steps. With a reaction coordinate $\eta$ defined, the point $r(\eta)$ along the jump path was specified by:

$$r(\eta) = r_1 + \eta [r_2 - r_1] .$$  \hspace{1cm} (11)

At $r(\eta)$, the “migrating” atom was confined to the plane normal to $(r_2 - r_1)$ while the surrounding ones were allowed to relax [7,11]. The mapping of the energy barrier for migration, $E(\eta)$, was then obtained by repeating the calculation for different values of $\eta$, and the highest saddle-point energy (i.e., the maximum value of $E(\eta)$ for $\eta$ in the range $[-1,1]$) was taken to be the vacancy migration energy, $E^m_v$. All calculations were carried out for zero temperature.

3. Results and Discussion

3.1. Defect Formation Energies

In both compounds, the vacancy was found to be most stable in the Ni sublattice. Zr vacancies were highly unstable; if a Zr atom was removed from the Zr sublattice to form a Zr vacancy [$v(Zr)$] a neighboring Ni atom jumped right into it, giving rise to a stable pair of Ni vacancy [$v(Ni)$] and Zr-antisite defect [$Zr(Ni)$]. Similarly, Ni interstitials [$i(Ni)$] were much more stable than the Zr counterparts: the Zr interstitial [$i(Zr)$] also decomposed into a Ni interstitial [$i(Ni)$] plus a Zr-antisite defect [$Zr(Ni)$]. The most stable configurations for the interstitial in ZrzNi and ZrNi are shown in Figure 1.

The interstitial in ZrzNi occupies the position labeled as $i(Ni)$ in Figure 1, regardless the extra atom is Zr or Ni. Nonetheless, as explained above, the Zr interstitial is unstable. It tends to displace a neighboring Ni atom to the position labeled $Ni^i$. The interstitial atom is situated at same distance of atoms labeled 1 and 2, on the axis that connects them both. Obviously there is
some distortion of the surrounding atoms outward the interstitial. For the sake of clarity we do not represent this distortion in the Figure.

The right hand side of Figure 1 shows the interstitial configuration in ZrNi. The interstitial is located on the ab-plane immediately below atom labeled 3. Once more the lattice relaxation around the interstitial is not shown. The Zr interstitial tends to locate itself on the cb-plane, but quickly displaces the closest Ni atom which is be driven to the ab-plane as shown in the picture.

Figures 2 and 3 show the Arrhenius plots of the concentrations of vacancies and interstitials in $\text{Zr}_2\text{Ni}$ and $\text{ZrNi}$, respectively. We note that the assumption made in section 2 that the formation energy does not depend on temperature is verified by the straight slope of the curves. The formation energies for these defects, calculated from the slopes of the corresponding plots, are summarized in Table 1. Since almost all vacancies are in the Ni sublattice, the effective vacancy formation energies are 0.61 and 0.83 eV in the respective compounds.

Adapting Hausleitner-Hafner interatomic potentials to the $\text{ZrNi}$ compound, Teichler [13] calculated the formation energy of $v(\text{Ni})$ and $v(\text{Zr})$ to be 1.51 and 3.38 eV, respectively. The effect of deviation from stoichiometry was, however, not taken into consideration in these calculations, and the results are clearly much higher than ours. Also, for the sake of comparison, the vacancy formation energy in pure Ni was calculated to be $\sim 1.5$ eV [14-16] and experimentally measured to be 1.60 - 1.80 eV [17,18], while the value measured for pure Zr is 1.75 eV [19]. Likewise, the effective interstitial formation energies are 2.11 and 1.67 eV in $\text{Zr}_2\text{Ni}$ and $\text{ZrNi}$, respectively. These values are roughly half the interstitial formation energy calculated for pure Ni, 4.08 eV [14] or 4.16 eV [15]. The formation energies of antisite defects [$\text{Ni(Zr)}$ and $\text{Zr(Ni)}$, for Ni occupying Zr site and vice versa] were also determined in the same
manner. Their values are also given in Table 1. In both compounds, it is significantly easier to form a Ni-antisite defect, Ni(Zr), than a Zr-antisite defect, Zr(Ni). The formation of antisite pairs [Ni(Zr) + Zr(Ni)] and Frenkel pairs [v(Ni)+i(Ni) or v(Zr)+i(Zr)] does not change the stoichiometry of the system. Therefore, their formation energies were calculated by taking the differences in the total potential energy before and after the defect creation. They are tabulated in Table 1. As expected, the Frenkel pair formation energy matches perfectly the sum of the interstitial and vacancy formation energies. The same happens for the antisite pairs: their formation energy is equal to the sum of the formation energies of the two individual antisite defects. The values in parentheses were reported earlier by Devanathan et al. [3,4], using the same interatomic potentials. Employing different potentials, Teichler [13] found 2.24, 3.59, and 2.47 and 7.51 eV for the formation energy of Ni(Zr), Zr(Ni), and [v(Ni)+i(Ni)] and [v(Zr)+i(Zr)] in ZrNi, respectively.

3.2. Vacancy Migration Mechanisms and Energies

Since the stable interstitial configurations are relatively complex, a systematic investigation of interstitial migration has not been undertaken as yet. In the following, we report only the results of our vacancy migration simulations. Moreover, since Zr vacancies are highly unstable and almost all the vacancies are in the Ni sublattice, only the migration of Ni vacancies to neighboring Ni atoms is discussed.

Typical plots of the energy barrier, $E(\eta)$, along the migration path, i.e. $\eta = -1$ to 1, are shown in Figs. 4 and 5. These are for the jump of a Ni vacancy toward a Ni atom in the [001] and [100] direction in Zr$_2$Ni and ZrNi, respectively. The ground state at $\eta = -1$ and $\eta = 1$ is simply the minimum total potential energy when the vacancy (or jumping atom) is in its rest position.
The maximum value of $E(\eta)$ defines the saddle-point energy which is the energy that the vacancy must acquire in order to jump to a nearest-neighbor site.

Tables 2 and 3 summarize the vacancy migration energies obtained for different jump directions and jump distances in Zr$_2$Ni and ZrNi, respectively. In the former compound (Table 2), the vacancy migrates easily by exchanging with nearest-neighbor Ni atoms along the [001] direction, with a migration energy of 0.67 eV. This type of motion is thus one-dimensional and does not involve any antisite defect formation. Direct vacancy jump to a Ni atom at second-neighbor distance, in the [110] direction, is highly improbable, requiring an energy of 2.92 eV. However, indirect jumps, i.e. via a ring mechanism, are possible; the migration energy for the complete sequence is 1.81 eV. This indirect process involves transient formation of antisite defects in the intermediate steps. In the ZrNi case (Table 3), the energy for vacancy migration to a nearest-neighbor site (in the [025] direction) is 0.67 eV, identical to that found for Zr$_2$Ni. The energies for direct vacancy jumps to Ni sites at second-, third-, and forth-neighbor distances (in the [100], [001], and [134] direction) are 0.73, 2.66, and 2.43 eV, respectively. There are thus two directions for easy vacancy jumps in this compound, [025] and [100]. Therefore, vacancy migration is essentially two-dimensional in fully-ordered ZrNi. Indirect vacancy migration to the third-neighbor site involves a ring mechanism, and requires an energy of about 2 eV.

Chemical disorder can greatly enhance the vacancy migration. In fact, as shown in Figs. 6 and 7, the vacancy migration energy in both compounds drops significantly if a few Ni antisite defects are present on the Zr sublattice neighboring the vacancy. In Zr$_2$Ni (Fig. 6), for example, the vacancy migration energy decreases by a factor of 3 when two Ni antisites are introduced. Nearest-neighbor jumps are now very fast, with a migration energy of ~0.2 eV, and direct vacancy jumps to second-neighbor Ni sites (in the [110] direction) are also easier, requiring only
-0.9 eV. In ZrNi (Fig. 6), on the other hand, four Ni antisite defects must be present near the vacancy in order to induce a factor-of-3 drop in the energy for vacancy migration to a first-neighbor Ni site in the [025] direction. Jumps in the [010] direction toward second-neighbor sites are, however, already much faster -- with a factor-of-3 decrease in energy -- even with only one antisite defect in the close vicinity. The presence of Ni antisite defects thus facilitates random motion of vacancies in the compounds.

4. Conclusions

In the present work, the properties of atomic defects (i.e., stable configurations, formation and migration energies, and migration mechanisms) in the intermetallic compounds ZrNi and Zr$_2$Ni have been investigated using molecular-dynamics and molecular-statics simulations. It was found that vacancies are most stable in the Ni sublattice, with formation energy of 0.83 and 0.61 eV in ZrNi and Zr$_2$Ni, respectively. Zr vacancies are unstable in both compounds, spontaneously decaying to pairs of Ni vacancy and antisite defect. The Zr interstitials are also unstable; they convert to Ni interstitials and antisite defects. In fully-ordered ZrNi, vacancies migrate rapidly in the [025] and [100] directions, with migration energy of 0.67 and 0.73 eV, respectively. Vacancy migration is thus practically two-dimensional. In fully-ordered Zr$_2$Ni, on the other hand, the vacancy migration is one-dimensional, taking place in the [001] direction, with a migration energy of 0.67 eV. In both compounds, the presence of antisite defects decreases the vacancy migration energy by up to a factor of 3, and facilitates three-dimensional motion.
Acknowledgments

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References


Figure 1. Interstitial configuration in Zr$_2$Ni (left) and ZrNi (right). The atom size varies with distance from the front plane.

Figure 2. Arrhenius plots of the concentrations of vacancies and interstitials in Zr$_2$Ni
Figure 3. Arrhenius plots of the concentrations of vacancies and interstitials in ZrNi.

Figure 4. (a) Crystal structure of Zr₂Ni, and (b) energy barrier for the migration of a Ni atom toward a vacancy in the [001] direction.
Figure 5. (a) Crystal structure of ZrNi, and (b) energy barrier for the migration of a Ni atom toward a vacancy in the [100] direction.
Figure 6. Influence of near-neighbor antisite defects on the vacancy migration energy in Zr$_2$Ni.

Figure 7. Influence of near-neighbor antisite defects on the vacancy migration energy in ZrNi.
Table 1. Effective formation energies (eV)

<table>
<thead>
<tr>
<th>Defect type</th>
<th>Zr$_2$Ni</th>
<th>ZrNi</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(Ni)</td>
<td>0.61</td>
<td>0.83</td>
</tr>
<tr>
<td>v(Zr)</td>
<td>1.45</td>
<td>1.99</td>
</tr>
<tr>
<td>i(Ni)</td>
<td>2.11</td>
<td>1.67</td>
</tr>
<tr>
<td>i(Zr)</td>
<td>3.01</td>
<td>2.75</td>
</tr>
<tr>
<td>Ni(Zr)</td>
<td>0.61</td>
<td>0.84</td>
</tr>
<tr>
<td>Zr(Ni)</td>
<td>1.53</td>
<td>1.38</td>
</tr>
<tr>
<td>Ni(Zr) + Zr(Ni)</td>
<td>2.14 (2.17)</td>
<td>2.22 (2.18)</td>
</tr>
<tr>
<td>v(Ni) + i(Ni)</td>
<td>2.74 (2.75)</td>
<td>2.50 (2.59)</td>
</tr>
<tr>
<td>v(Zr) + i(Zr)</td>
<td>4.48</td>
<td>4.73</td>
</tr>
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</table>

Table 2. Vacancy migration in Zr$_2$Ni.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Saddle-point energy (eV)</th>
<th>Jump distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>0.67</td>
<td>2.62</td>
</tr>
<tr>
<td>[110]</td>
<td>2.92</td>
<td>4.45</td>
</tr>
<tr>
<td>Ring</td>
<td>1.81</td>
<td>4.50</td>
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Table 3. Vacancy migration in ZrNi

<table>
<thead>
<tr>
<th>Direction</th>
<th>Saddle-point energy (eV)</th>
<th>Jump distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[025]</td>
<td>0.67</td>
<td>2.51</td>
</tr>
<tr>
<td>[100]</td>
<td>0.73</td>
<td>3.22</td>
</tr>
<tr>
<td>[134]</td>
<td>2.46</td>
<td>4.19</td>
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<tr>
<td>[001]</td>
<td>2.66</td>
<td>4.02</td>
</tr>
<tr>
<td>Ring</td>
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<td>4.18</td>
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