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Point defect energetics in the ZrNi and Zr_2Ni intermetallics

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Abstract

A systematic study of the properties of point defects has been conducted in the ZrNi and Zr_2Ni intermetallic compounds using molecular dynamics. These properties include the stable defect configurations, formation and migration energies, and vacancy migration mechanisms. Zr vacancies (interstitials) are unstable in both compounds; they spontaneously decay to pairs of Ni vacancy (interstitial) and antisite defect. The stable Ni vacancies have formation energies of 0.83 and 0.61 eV in ZrNi and Zr_2Ni, respectively. In ZrNi, vacancy migration occurs preferentially in the [0 2 5] and [1 0 0] directions, with migration energies of 0.67 and 0.73 eV, respectively, and is essentially a two-dimensional process, in the (0 0 1) plane. In Zr_2Ni, vacancy migration is one-dimensional, occurring in the [0 0 1] direction, with a migration energy of 0.67 eV. The stable interstitial configurations for both compounds consist of a Ni atom lying on the (0 0 1) plane between two out-of-plane nearest-neighbor Zr atoms. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

There has been great recent interest in the irradiation response of intermetallic compounds, especially in regards to disordering and amorphization [1]. The radiation-induced amorphization behavior of these compounds have systematically been investigated, both experimentally and theoretically [1–3]. The irradiation response of these compounds is governed by the balance between the irradiation damage and the annealing response of the material. The latter phenomenon is controlled by the migration rate, and migration paths, of point defects in the ordered compound. In an effort to understand the dynamic recovery of these intermetallic compounds during energetic irradiation, we have performed computer simulations to obtain information about the point defect properties in the intermetallic compounds ZrNi and Zr_2Ni, for which realistic interatomic potentials are available. These properties include the antisite defect energies, and the stable configurations, energetics, and migration mechanisms of vacancies and interstitials.

In a recent paper [4], the calculational procedure and initial results of the properties of vacancies and interstitials were reported. The reader

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is referred to this reference for further information on the molecular dynamics and statics techniques used in the calculations. In this communication, we present additional details on the defect configurations and energetics, which complement the previous work and present a more complete picture of defect behavior in these compounds.

2. Defect properties

The intermetallic compound ZrNi exhibits an orthorhombic B33-type structure, with lattice parameters $a = 0.410$ nm, $b = 0.327$ nm and $c = 0.994$ nm [5], while Zr_2Ni exhibits a body centered tetragonal C16 structure, with lattice parameters $c = 0.524$ nm and $a = 0.650$ nm [5]. The interatomic potentials used to simulate this compound have been described previously [2,3]. The simulation cells contained 1568 and 1500 atoms, respectively, with periodic boundary conditions.

2.1. Antisite defects

The formation energy of antisite defects can be calculated by simply switching a random pair of Ni and Zr atoms. This procedure does not cause any change in stoichiometry of the alloy system. Care was exercised to maintain these defects near the center of the simulation cell, to avoid periodic boundary artifacts. To calculate the formation energy of individual antisite defects, Ni(Zr) (Ni atom on a Zr site) and Zr(Ni) (Zr atom on a Ni site), we used the procedure described in [4], so as to take into account the variation in stoichiometry. We have performed all of these calculations, and the results obtained for the formation energies of antisite defects in these two compounds are summarized in Table 1.

Table 1
Defect formation energies (eV)

Defect type	ZrNi	Zr_2Ni
v(Ni)	0.83	0.61
v(Zr)	1.99	1.45
i(Ni)	1.67	2.11
i(Zr)	2.75	3.01
Ni(Zr)	0.84	0.61
Zr(Ni)	1.38	1.53
Ni(Zr) + Zr(Ni)	2.22	2.14
v(Ni) + i(Ni)	2.50	2.74
v(Zr) + i(Zr)	4.73	4.48

2.2. Vacancies

Vacancies are introduced by randomly removing a Zr or Ni atom from a lattice position. In both compounds, the Ni vacancy, v(Ni), is stable, while the Zr vacancy decays according to the reaction

$$\mathrm{v(Zr)} \rightarrow \mathrm{v(Ni)} + \mathrm{Ni(Zr)} \tag{1}$$

The relative positions of the resulting defects are given in Figs. 1 and 2.

Unlike defect creation in pure metals, the introduction of vacancies in ordered intermetallic compounds causes a change in their stoichiometry, which changes the overall potential energy of the system. To calculate the effective defect formation energy in these compounds, it is necessary to use the procedure described in [4], so as to account for the resulting change in chemical potential. The

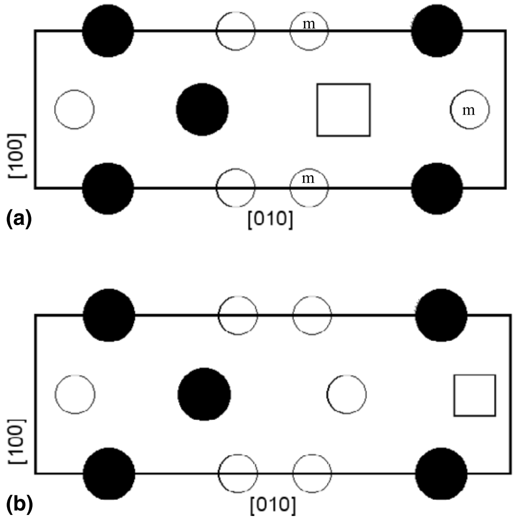

Fig. 1. Schematic depiction along the 0 0 1 direction of the conversion reaction expressed in Eq. (1) in ZrNi. In (a) the v(Zr) is formed and any one of the three atoms labeled 'm' can jump into the vacancy, giving rise to the more stable defect configuration shown in (b). Vacancy: □, Ni atom: ○, Zr atom: ●.

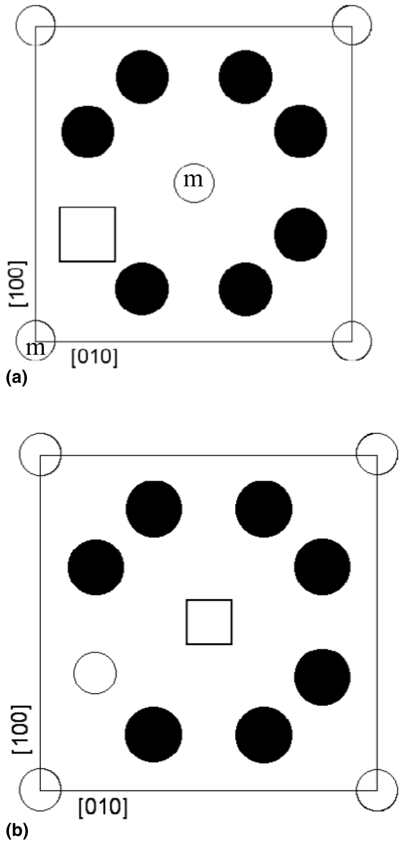

Fig. 2. Schematic depiction along the 0 0 1 direction of the conversion reaction expressed in Eq. (1) in Zr_2Ni. In (a) the v(Zr) is formed and the atom labeled 'm' can jump into the vacancy, giving rise to the more stable defect configuration shown in (b). Vacancy: □, Ni atom: ○, Zr atom: ●.

Table 2
Characteristics of Ni vacancy migration in ZrNi and Zr_2Ni

Direction	Saddle-point energy (eV)	Jump distance (Å)
ZrNi		
[0 2 5]	0.67	2.51
[1 0 0]	0.73	3.22
[1 3 4]	2.46	4.19
[0 0 1]	2.66	4.02
Ring	~2	4.18
Zr_2Ni		
[0 0 1]	0.67	2.62
[1 1 0]	2.92	4.45
Ring	1.81	4.50

calculated values for the vacancy formation energies in both sublattices in ZrNi and Zr_2Ni are shown in Table 1.

The migration energies for the stable Ni vacancies were calculated by minimizing the system energy with the jumping atom constrained at various points along the jump path, as explained in [4]. The calculated values of the migration energies along different directions are shown in Table 2.

In ZrNi, the lowest energy for vacancy migration to a nearest-neighbor site is 0.67 eV, in the [0 2 5] direction. The energies for direct vacancy jumps to Ni sites at second-, third- and fourth-neighbor distances (in the [1 0 0], [0 0 1] and [1 3 4] direction) are 0.73, 2.66 and 2.43 eV, respectively. The difference of migration energy between the [0 2 5] and [1 0 0] directions is small enough that a significant fraction of the jumps is likely to occur in the latter direction, thus causing defect migration to be two-dimensional, in fully ordered ZrNi. Indirect vacancy migration to the third-neighbor site involves a ring mechanism (shown in Fig. 3), which requires an energy of about 2 eV.

In Zr_2Ni, the Ni vacancy migrates preferentially along the [0 0 1] direction, with a migration energy of 0.67 eV, identical to that found for ZrNi. Direct vacancy jump to a Ni atom at second-neighbor distance, in the [1 1 0] direction, is highly improbable, requiring an energy of 2.92 eV. Because of this large difference, Ni vacancy migration is essentially one-dimensional and does not involve any antisite defect formation. We also considered vacancy migration through a ring mechanism (shown in Fig. 4). This indirect process involves transient formation of antisite defects in the intermediate steps. However, the migration energy for the complete sequence is 1.81 eV, making vacancy migration through this process highly unlikely.

The results above are valid for the perfectly ordered compounds. As shown in [4], chemical disorder can greatly enhance the vacancy migration. For both compounds, the presence of a few antisite defects in the vicinity of the migrating vacancy can reduce the migration energy by up to a factor of three.

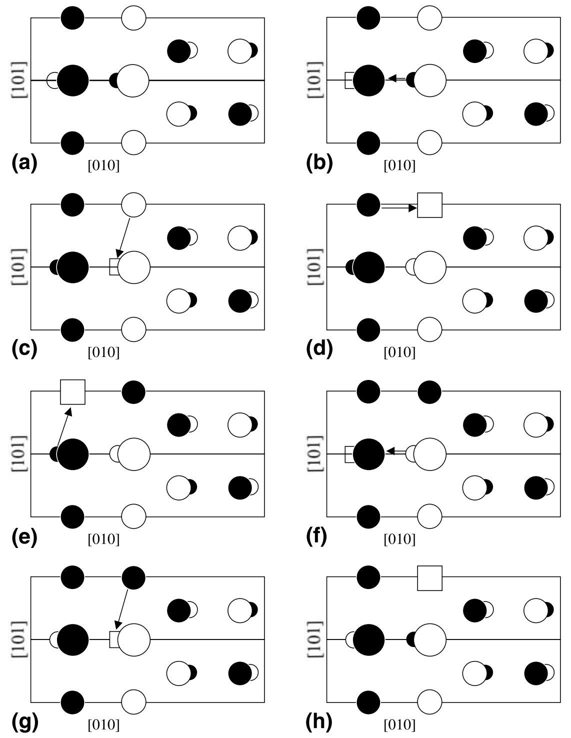

Fig. 3. Jump sequence for the ring mechanism for vacancy diffusion in ZrNi. Starting with the perfect lattice (a), a vacancy is introduced (open square symbol); the sequence of jumps indicated by the arrows (b)–(g) produces the final configuration shown in (h). The resulting jump distance is 4.18 Å. The symbol conventions are identical to those used in Fig. 1.

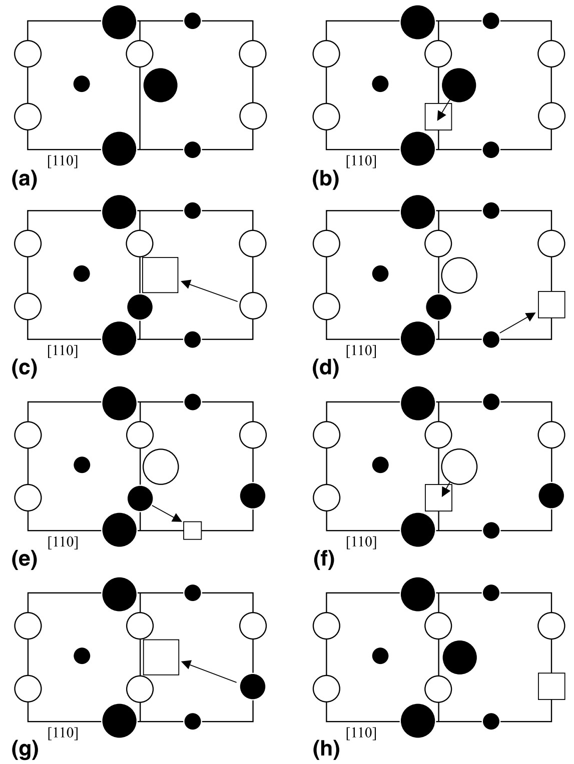

Fig. 4. Jump sequence for the ring mechanism for vacancy diffusion in Zr_2Ni. Starting with the perfect lattice (a), a vacancy is introduced (open square symbol); the sequence of jumps indicated by the arrows (b)–(g) produces the final configuration shown in (h). The resulting jump distance is 4.50 Å. The symbol conventions are identical to those used in Fig. 1.

2.3. Interstitials

Interstitials are created by inserting an extra Ni or Zr atom in a random interstitial position in the simulation cell. The search for the interstitial's lowest-energy configuration was, however, carried out by means of simulated annealing [6]: the system was first heated to 800 K for a few hundred time steps, then energy-minimized with the Fletcher–Powell method, and the process was repeated at lower and lower temperatures, in 100 K intervals, down to 0 K. As in the case of vacancies, interstitial generation is associated with a change in stoichiometry, and the proper procedure to be used is described in [4].

The formation energies for the Zr and Ni interstitials (denoted i(Zr) and i(Ni)), are shown in Table 1 for both ZrNi and Zr_2Ni. In both alloys the Zr interstitial is unstable and decays according to the reaction

$$\mathrm{i(Zr)} \rightarrow \mathrm{i(Ni)} + \mathrm{Zr(Ni)} \qquad (2)$$

The most stable configurations for the i(Ni) defect are shown in Figs. 5 and 6. Preliminary analysis of the stable configurations for the respective compounds indicates that, in ZrNi, the extra Ni atom lies on the (0 0 1) plane, in between the nearest out-of-plane Zr atoms, above and below it (see atom 3 in Fig. 5). For the Zr_2Ni compound, the stable i(Ni) can be described in the same manner, i.e. it also lies on the (0 0 1) plane, with a nearest Zr atom immediately above and below it (Zr atoms labeled "1" and "2" in Fig. 6). The calculation of

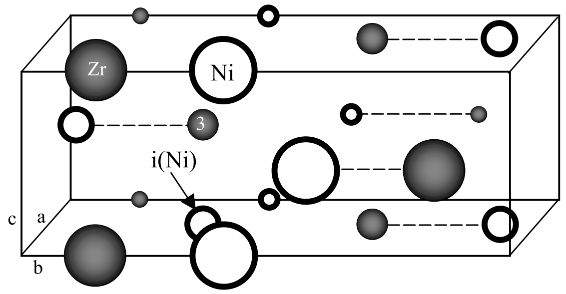

Fig. 5. Stable interstitial configuration for the i(Ni) defect in ZrNi. The Ni interstitial is co-planar with the Ni and Zr atoms in the ab plane (001) and lies halfway between two Zr atoms, one of which is indicated by “3”.

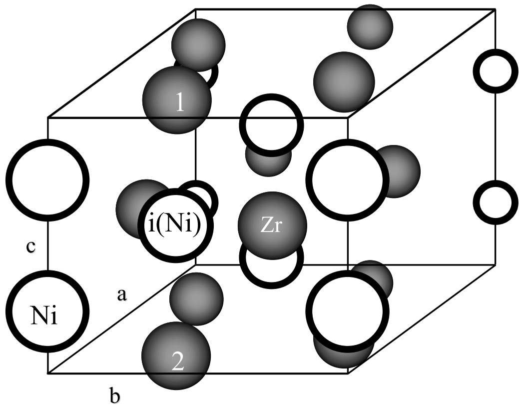

Fig. 6. Stable interstitial configuration for the i(Ni) defect in Zr_2Ni. The Ni interstitial is located between the Zr atoms “1” and “2” and is not co-planar with the other Ni atoms on plane cb (100).

interstitial migration energy and the determination of the interstitial migration mechanism are considerably more complex than the vacancy calculations. These are currently in progress.

2.4. Frenkel pairs

Frenkel pairs are introduced by removing an atom from a regular lattice site and inserting it in a random interstitial position. This procedure does not cause any change in stoichiometry of the compounds and therefore the Frenkel pair energy can be calculated directly from the increase in potential energy relative to the perfect lattice. The calculated values for both compounds are shown in Table 1. The values of the Frenkel pair formation energies agree very well with the sum of the individual formation energies of the pertinent point defects. The formation energy of the Ni Frenkel pairs, v(Ni) + i(Ni), is roughly half of that for the Zr Frenkel pairs, v(Zr) + i(Zr).

3. Conclusions

Systematic molecular dynamics calculations of point defect energetics have been performed for the ZrNi and Zr_2Ni intermetallic compounds. The main results are:

- Vacancies are most stable in the Ni sublattice, with formation energies of 0.83 and 0.61 eV in ZrNi and Zr_2Ni, 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 [0 2 5] and [1 0 0] directions, with migration energies of 0.67 and 0.73 eV, respectively. Vacancy migration is thus practically two-dimensional.
- In fully ordered Zr_2Ni, the vacancy migration is one-dimensional, taking place in the [0 0 1] direction, with a migration energy of 0.67 eV.
- Interstitial configurations are quite complex, and simulations of their migration mechanisms are under way.

Acknowledgements

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