

DETERMINATION OF SOLUTE-INTERSTITIAL INTERACTIONS IN NI-CR BY FIRST PRINCIPLES

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ABSTRACT

Interstitial point defects play a key role in the microstructural evolution of irradiated alloys, however, their thermodynamic and kinetic properties in multi-component systems are largely unknown. First-principles electronic structure techniques are powerful tools for obtaining insight into interstitial properties that cannot be resolved experimentally, such as solute-interstitial binding enthalpies. In this paper, first-principles methods are used to calculate formation and binding enthalpies of interstitials in the nickel (Ni)-chromium (Cr) binary system for different Cr configurations and concentrations. This work reveals that the $\langle 100 \rangle$ dumbbell interstitial is the most stable configurations for interstitials with 0, 1, or 2 Cr present in the local environment. However, the $\langle 111 \rangle$ and $\langle 110 \rangle$ interstitial dumbbells become increasingly stable with increasing Cr concentration, which could reduce the rotation barriers for Ni-Cr and Cr-Cr dumbbells and thereby enhance interstitial diffusion. Strong binding is observed for 1-3 Cr in or near the $\langle 100 \rangle$ dumbbell and configurations with Cr in the dumbbell are most stable. The Ni-Cr mixed dumbbell and Cr-Cr dumbbell have binding enthalpies of 0.50 and 0.92 eV, respectively. These high binding enthalpies are expected to hinder dissociation of the Cr-interstitial complex, suggesting that even isolated Cr solutes could serve as temporary traps for interstitials. Temporary trapping of interstitials could aid in recombination with vacancies in the system and reducing radiation assisted microstructural changes. This trapping mechanism is reinforced with an additional Cr atom present in the local environment, which strengthens the Cr-interstitial binding and will further hinder dissociation of the solute-interstitial complex.

Key Words: interstitial, binding, first principles

1. INTRODUCTION

Non-equilibrium interstitials, along with vacancies, play a key role in the microstructural evolution of irradiated materials through the formation of dislocation loops and clusters and through the redistribution of elements during migration. Microstructural changes result in altered chemical and mechanical properties that are often significant. Improved understanding of basic properties of interstitials and vacancies is necessary for more accurate predictions of microstructural evolution in irradiated materials. Interstitial properties are significantly less well

understood than those of vacancy defects, partly due to difficulties in generating experimental data. Even in pure substances, basic properties such as, formation enthalpies, entropies and diffusion coefficients are often uncertain. In multi-component systems these properties are even less reliable if known at all. For example, migration barriers and binding energies of different species and configurations in an alloy, which are important in understanding the role of interstitials in microstructural evolution, often cannot be resolved by experimental techniques. Solute-interstitial interactions can significantly impact interstitial diffusion properties. Strong binding can trap interstitials at solute atoms, hindering the formation of loops and aiding in vacancy-interstitial recombination.

First-principles electronic structure techniques are powerful tools for obtaining insight into interstitial properties. In this paper, first-principles methods are used to calculate the formation enthalpies of different interstitial configurations in the Ni-Cr binary system, with 0, 1, or 2 Cr present in the interstitial or dumbbell position, to determine the stable interstitial configuration as a function of Cr concentration. First-principles methods are also used to calculate the binding enthalpy between 1, 2 or 3 Cr solutes with the $\langle 100 \rangle$ dumbbell interstitial in order to assess the role of Cr solutes as sites for interstitial trapping.

2. METHODOLOGY

All first principles calculations were performed with the Vienna *Ab initio* Simulation Package (VASP) [1,2], a quantum mechanical code. All VASP calculations were run with the generalized gradient approximation, the Perdew-Burke-Ernzerhof exchange-correlation functional [3], and the projector-augmented wave method [4,5]. Interstitial formation and binding enthalpy calculations were run with plane waves corresponding to a 270 eV energy cutoff, 108(+1) atom periodic simulation cell and a 3x3x3 k-point mesh. The cumulative errors associated with k-point mesh, energy cutoff and cell size convergence, are estimated to be less than 25 meV for formation and binding enthalpies [6]. All calculations were spin polarized and allow for antiferromagnetic ordering. The volume and shape of each simulation cell was fixed but ionic relaxations were allowed within the cell, unless stated otherwise. The magnetic moments on individual atoms are determined by integrating the charge density within the Voronoi volume [7].

In order to account for changes in volume due to composition, a volume fit has been performed over 149 calculated Ni-Cr alloy structures to give an average volume per atom as a function of solute concentration. The 149 structures were initiated with cubic symmetry but both volume and cell shape changes were allowed during the minimization procedure. The number of atoms in each structure ranged from 1 to 108, though most structures contained less than 12 atoms. The volume calculations were run with plane waves corresponding to a 479 eV energy cutoff and with 4096 k-points per reciprocal atom. Any structures that underwent effective relaxations of 10% or more were discarded in order to exclude the structures that significantly deviated from cubic symmetry. The volume per atom versus solute concentration is shown in figure 1. Each data point in figure 1 represents a specific decoration of the face-centered cubic (fcc) lattice for a given Cr concentration. The construction of the atomic configurations and assessment of relaxations were performed with the Alloy-Theoretic Automated Toolkit (ATAT) code [8,9].

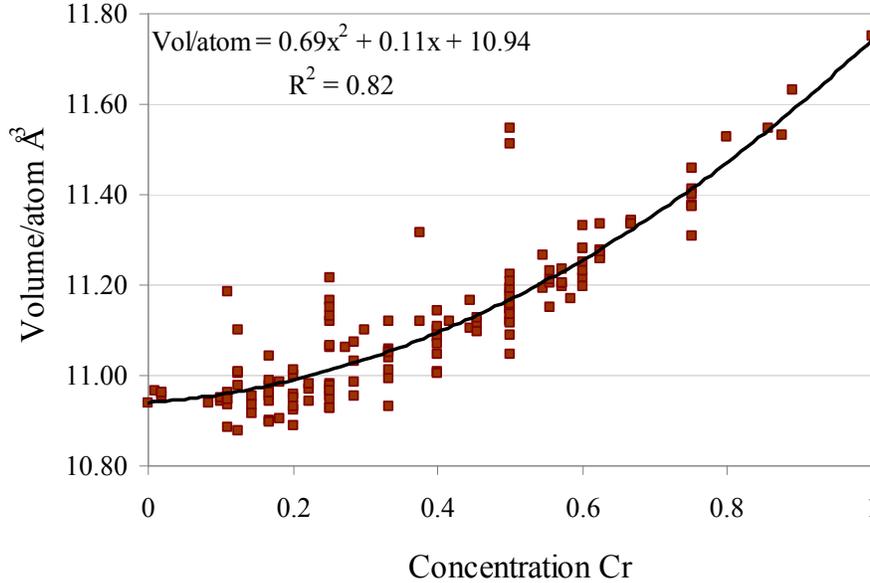


Figure 1. Volume per atom with increasing Cr Concentration.

The data in figure 1 was fit with a quadratic function of x in $\text{Ni}_{1-x}\text{Cr}_x$ where, x denotes the concentration of the Cr in the alloy and ranges from $[0, 1]$. The quadratic equation for volume per atom with concentration of Cr is given in equation 1. Note that fcc is not the ground state crystal structure at high Cr concentration but these structures have been included here to improve the fitting parameters.

$$\text{Volume/atom} = 0.69x^2 + 0.11x + 10.94 \quad (1)$$

Equation 1 was used to determine the volume of the supercells containing different solute concentrations. The volumes of simulation cells that contain an interstitial atom were based on the volume of the crystal with the same solute concentration and no interstitial atom, and were then scaled by $(N+1)/N$, where N is the number of atoms in the perfect crystal (no interstitial), to account for the extra atom in the cell. This scaled volume approximates the volume expansion due to interstitial introduction *i.e.*, interstitial formation volume. The interaction between strain fields induced by the periodic images of the interstitial becomes negligible as N becomes large.

The interstitial formation energy, H_{if} , is calculated in pure Ni by comparing the enthalpy of a cell containing an interstitial to that of a pure Ni (scaled by $(N+1)/N$ to conserve the number of atoms). Equation 2 provides the equation for calculating the interstitial formation enthalpy in pure Ni in a $108(+1)$ atom cell.

$$H_{if}(\text{Ni}) = H_{\text{int}}^{109\text{Ni}} - \frac{109}{108} H^{108\text{Ni}} \quad (2)$$

In equation 2 and the equations that follow, the numbers in the superscripts denote the number of each element present in the simulation cell. If an interstitial is present in the cell it is noted in the subscript (int for a Ni interstitial and *Cr* int for a Cr interstitial), otherwise all atoms are on fcc lattice sites. In general, a triplet (*Cr*, int, *Xnn*) is used to designate a Cr solute as a X^{th} nearest-neighbor to the Ni interstitial.

The formation enthalpy of an interstitial next to a solute atom was obtained by adding the binding enthalpy, H_{bind} , of a solute-defect complex to the formation enthalpy of that defect in pure Ni. This is equivalent to forming an interstitial in bulk Ni far from the solute atom and then bringing it near the solute. Equation 3 gives an example for calculating the formation enthalpy of an interstitial as a first nearest-neighbor (1nn) to a Cr solute in a Ni host.

$$H_{f}(Cr, \text{int}, 1nn) = H_{f}(Ni) + H_{bind}(Cr, \text{int}, 1nn) \quad (3)$$

The solute-interstitial binding enthalpies were calculated based on four different *ab initio* calculations where the enthalpies of the interstitial and solute atom are subtracted separately from the enthalpy of the system where they interact. Equation 4 demonstrates how to determine the binding enthalpy of a Ni interstitial with a first nearest neighbor Cr atom.

$$H_{bind}(Cr, \text{int}, 1nn) = H_{Cr, \text{int}, 1nn}^{108Ni, 1Cr} - H^{107Ni, 1Cr} - H_{int}^{109Ni} + H^{108Ni} \quad (4)$$

On the right side of the equation, the first term represents the enthalpy of a cell where the interstitial and the solute are interacting as first nearest-neighbors, as denoted by the subscript. The second term represents the enthalpy of the cell containing an isolated substitutional Cr solute in a Ni matrix, the third term represents the enthalpy of the cell containing a Ni interstitial, and the fourth term is the enthalpy of a pure Ni cell and represents a mass balance that accounts for the extra bulk Ni atoms subtracted in the second and third term. In this formalism a negative binding enthalpy denotes binding and positive values denote repulsion.

In this work, it is also necessary to determine the binding enthalpy of configurations with multiple solute atoms interacting with the interstitial. For this case, the energetic contribution of each solute is subtracted separately, as if they were initially isolated in the Ni matrix and then moved near the interstitial. An example is given in equation 5 for a Cr interstitial interacting with a first nearest-neighbor Cr atom.

$$H_{bind}(Cr, Cr \text{ int}, 1nn) = H_{Cr, Cr \text{ int}, 1nn}^{107Ni, 2Cr} - 2H^{107Ni, 1Cr} - H_{int}^{109Ni} + 2H^{108Ni} \quad (5)$$

The subscript in the first term on the right hand side denotes the relationship between the Cr atoms and the interstitial. The second term and fourth terms have the same meaning as in equation 4 but are included twice to account for the additional Cr atom. The reference states for all binding energy calculations are isolated solutes and an isolated Ni interstitial in the Ni matrix. The use of a consistent reference state allows for the direct comparison of all calculated binding enthalpies, and the energy to transform between difference bound states is given by the difference in their binding enthalpies.

3. RESULTS

As a first step in studying solute-interstitial binding, it is necessary to identify the most stable interstitial configuration as a function of alloy concentration. In pure fcc Ni the $\langle 100 \rangle$ dumbbell has been determined experimentally [10] and through first-principles calculations [11] to be the most stable configuration. The formation energies of interstitials on six high symmetry sites in the fcc lattice were calculated in order to assess the stability of the $\langle 100 \rangle$ dumbbell in Ni-Cr alloys. These six configurations have been formerly identified as candidate stable interstitial sites in fcc materials [12] and are illustrated below in figure 2, where the black atom represents the interstitial atom. Three configurations are sites where the interstitial resides between lattice atoms, the octahedral, tetrahedral and crowdion, and three configurations are interstitial dumbbells, the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$, where the interstitial atom shares a lattice site with another atom.

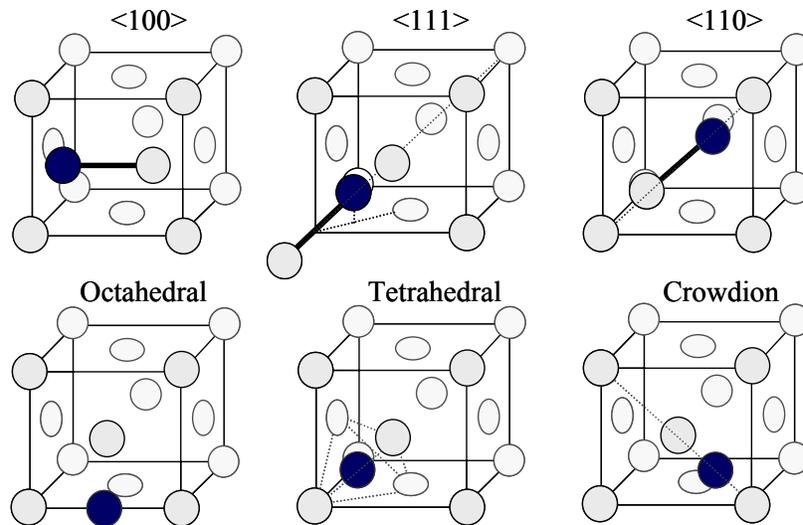


Figure 2. High symmetry interstitial configuration in the fcc crystal lattice.

The formation enthalpies are calculated using equations 2-5 for cells containing 0, 1 or 2 Cr atoms, where the Cr is located in the interstitial position or dumbbell. In cells containing 2 Cr atoms, both atoms are in the dumbbell, forming a Cr-Cr dumbbell. Also for the 2 Cr case, the octahedral, tetrahedral and crowdion formation enthalpies were not calculated because the presence of 2 Cr atoms in the simulation cell breaks the symmetry and would require a large simulation cell to maintain the basic fcc symmetry far from the interstitial site. For each concentration studied (0, 1 or 2 Cr), the $\langle 100 \rangle$ configuration was found to be the most stable configuration and serves as the reference state for all other interstitial configurations of that concentration level. The absolute values of the $\langle 100 \rangle$ formation enthalpies for each concentration are given in table I for reference.

Table I. Relative formation enthalpies of interstitials in Ni-Cr

Interstitial Formation Enthalpies Differences (eV)	Pure Ni [8] Ref. 4.11 eV	1Cr in Ni Ref. 3.61 eV	2Cr in Ni Ref. 3.19 eV
<100> Dumbbell	0.00	0.00	0.00
Octahedral	0.18	0.19	-
<111> Dumbbell	0.62	0.33	0.22
Tetrahedral	0.62	0.33	-
<110> Dumbbell	0.91	0.75	0.08
Crowdion	0.91	0.75	-

Table I shows that increasing the Cr concentration in the interstitial (0, 1 or 2 Cr) reduces the total formation enthalpy for a given configuration, except for the octahedral configuration, which remains essentially unchanged for 0 to 1 Cr. As the concentration of Cr increases, the relative relationship between configurations (*i.e.*, <100> versus <111>) also decreases. This decrease in relative formation energy indicates that the presence of Cr is flattening the energy surface between the different interstitial configurations. For the Cr-Cr interstitial the ordering of the <111> and the <110> dumbbell interstitial configurations are inverted, indicating a change in shape of the energy surface that could lead to a migration or rotation mechanism change.

Since the <100> dumbbell has been identified as the most stable interstitial configuration for all concentrations studied, the majority of interstitials are expected to exist in the <100> dumbbell configuration. Therefore, it is important to understand the stability of this interstitial configuration with solute atoms in its immediate environment. The binding enthalpies of various Cr-interstitial configurations have been determined using equations 4 and 5. The case in which the Cr atom(s) and the Ni-Ni <100> dumbbell are far apart from each other (isolated) has no binding by definition and will serve as the reference case. Cases including up to 3 Cr solutes interacting with a <100> dumbbell were calculated in different configurations. The various configurations studied and the corresponding binding enthalpies are shown in figure 3.

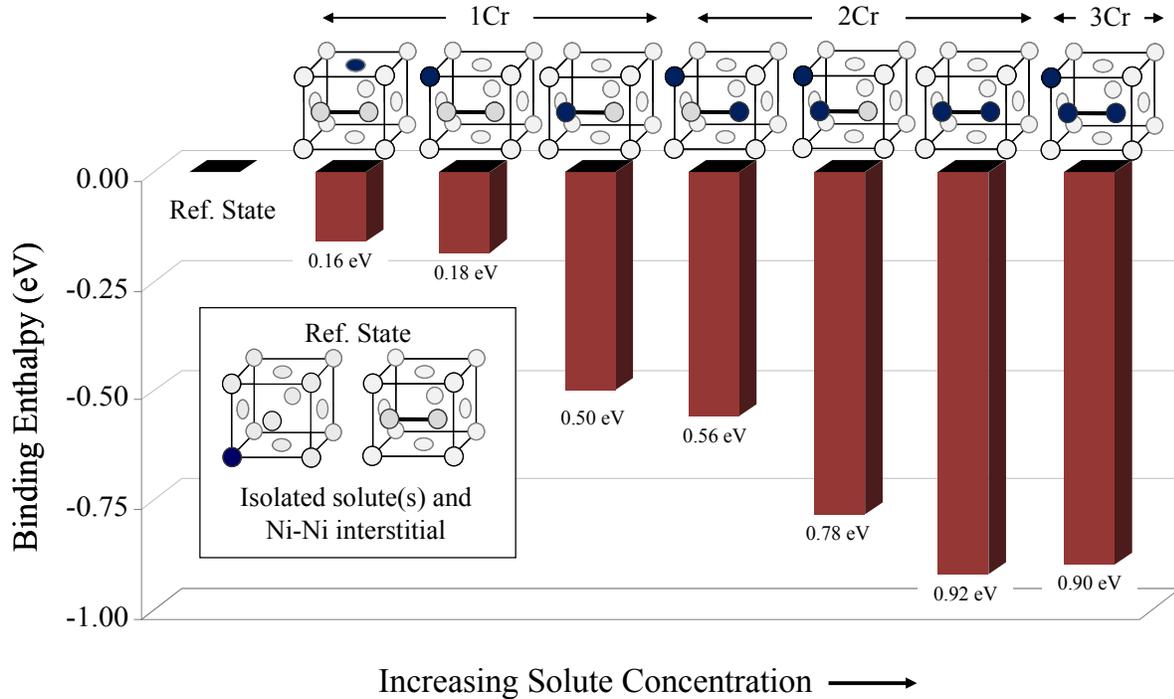


Figure 3. Binding enthalpies for various Cr solute-interstitial configurations.

Figure 3 shows strong binding (attraction) between the Cr solute(s) and the interstitial in all configurations and concentrations studied. The binding enthalpy increases with increasing Cr concentration up to 2 Cr and the most stable configurations are obtained when Cr is part of the interstitial dumbbell. The Ni-Cr mixed dumbbell is significantly more stable than other 1 Cr configurations studied with a binding enthalpy of 0.50 eV and the Cr-Cr dumbbell is the most stable configuration in this study with a binding enthalpy of 0.92 eV. These strong binding interactions can hinder the ability of the interstitial to migrate in the alloy and possibly aid in recombination. Figure 3 also shows that there is relatively strong binding between the Ni-Ni interstitial and a Cr atom when they are first nearest-neighbors. The same trend is also seen for the Ni-Cr dumbbell but not for the Cr-Cr interstitial where there is a slight repulsion (compare the last two values on the right hand side of figure 3).

4. DISCUSSION

The Cr-interstitial attraction in the Ni host (shown in Figure 3) is counterintuitive to the conventional arguments that correlate binding/repulsion to size and strain induced by the solute. In the Ni-Cr case Cr is thought to be oversized in the Ni matrix based on the elemental metals atomic radii. The Goldschmidt atomic radii for body-centered cubic (bcc) Cr and fcc Ni are reported to be 1.28 and 1.25 Å, respectively [13]. Additionally, figure 1 shows that Cr in the fcc Ni matrix generally increases the atomic volume per atom, providing further evidence that Cr is oversized in the Ni matrix. The atomic radii for pure fcc Cr and fcc Ni is calculated from the endpoints in figure 1 and remain to be 1.28 and 1.25 Å, respectively, based on half the nearest-

neighbor distance. Size-based arguments suggest that a Cr atom would be less stable than a Ni atom in or near the interstitial site, where atoms are compressed. However, first-principles calculations reveal that the first nearest-neighbor shell surrounding the Cr solute relaxes inward toward the Cr. The inward relaxation of the first nearest-neighbor shell causes an expansion of the second-neighbor shell outward beyond the original lattice site positions, thus explaining the overall expansion of the lattice with Cr concentration in figure 1. These relaxations suggest that the strain induced by Cr in the Ni matrix is not monotonically decreasing with increasing distance from the solute but that it goes from contraction and to expansion at a short distance from the solute site. Therefore, not only the solute atom size but also its chemical interaction with the host atom needs to be taken into account to determine the strain field associated with the solute atom at close distances. It is the combined size and chemical effects that help determine the nature (attractive versus repulsive) of solute-interstitial interactions.

Magnetism affects solute-host interactions and may also play a role in the Cr-interstitial binding. Figure 4 illustrates the local magnetic moments, obtained from the output of the VASP code, for substitutional and interstitial Cr. A substitutional Cr atom in a Ni matrix has a magnetic moment of $1.83 \mu_B$ and reduces the moments on the nearest-neighbor Ni atoms to $0.53 \mu_B$ from the pure Ni value of $0.62 \mu_B$. In the interstitial, Cr aligns antiferromagnetically with a magnetic moment of $-0.44 \mu_B$ and the surrounding Ni atom moments are reduced to as little as $0.10 \mu_B$. The dramatic change in local moment may help to stabilize the Cr in and near the interstitial site.

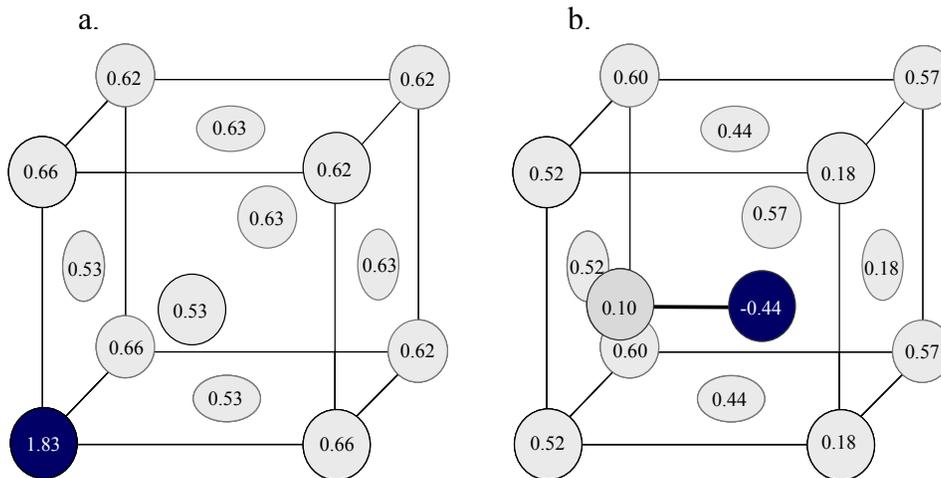


Figure 4. Magnetic moments (in μ_B) for a) substitutional Cr and b) interstitial Cr in a Ni matrix.

To gain a qualitative understanding of the extent to which magnetism may affect binding, a simple study has been performed comparing spin polarized (SP) and non-spin polarized calculations. The binding enthalpy of three Cr-interstitial configurations (shown in figure 5) were calculated with and without the affect of magnetism included. A new equilibrium lattice constant for pure Ni was determined for the non-spin polarized calculations. The affect of Cr concentration on volume was not taken into account for either set of calculations and the pure Ni

lattice constant was used or scaled by $(N+1)/N$ for cells containing interstitials. Figure 5 illustrates the configurations in the study and table II contains the binding enthalpy results.

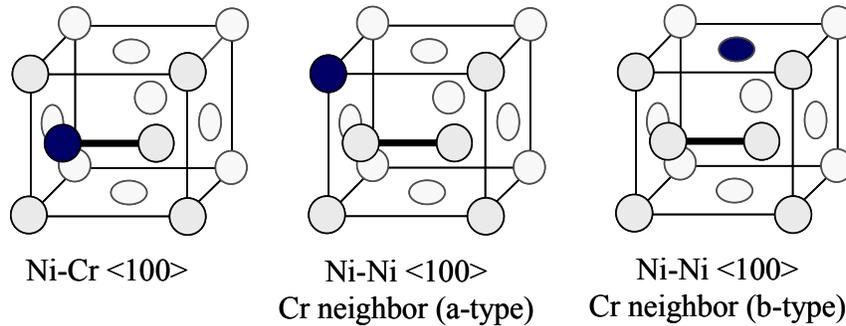


Figure 5. Three Cr-interstitial configurations for spin polarization study.

Table II. Binding enthalpy of Cr-interstitial complexes with and without spin polarization

Cr-Interstitial Binding Enthalpy (eV)	SP	Non-SP
Cr-Ni mixed <100>	-0.45	-0.38
Cr (a-type) Ni-Ni <100>	-0.14	-0.11
Cr (b-type) Ni-Ni <100>	-0.12	0.24

In table II the non-spin polarized calculations still predict binding for the Cr-Ni mixed dumbbell and the Cr a-type first nearest-neighbor cases but not the Cr b-type first nearest-neighbor case. The b-type Cr-interstitial interaction became strongly repulsive in the absence of magnetism. These data suggest that the role of magnetism in solute-interstitial binding is configuration dependent and that magnetism is not the sole source of binding present in the mixed dumbbell and the a-type Cr cases.

The strong binding of Cr solutes with interstitials, both in and near the interstitial position, indicates that dissociation of the interstitial-Cr complex will be hindered. For solute concentrations well below the percolation threshold (~ 19 at.% for fcc), interstitials will have to dissociate from the Cr solute(s) to continue to diffuse through the crystal. In dilute alloys Cr solutes could serve as temporary traps for migrating interstitials, preventing them from rapidly escaping the system and aiding in their recombination with vacancy defects. Enhanced recombination of point defects reduces their contribution to microstructural changes, possibly reducing detrimental radiation-induced effects.

5. CONCLUSIONS

In this paper *ab initio* calculations were used to identify the stable interstitial configurations as a function of Cr concentration and to determine the binding enthalpies of various interstitial-solute configurations, which are difficult to infer from experimental measurements. These calculations show that the <100> interstitial dumbbell is the most stable configuration for pure Ni, Ni-Cr and Cr-Cr dumbbells in a Ni matrix. A flattening of the energy surface between different interstitial configurations was observed with an increase in Cr concentration. It was also determined that unlike the Ni-Ni and Ni-Cr dumbbells, the <110> configuration is more stable than the <111> for the Cr-Cr dumbbells. This energetic change could indicate that the Cr-Cr dumbbell has a different rotation pathway than the Ni-Ni and Ni-Cr dumbbells. On site rotation of the <100> dumbbell on the lattice site is critical for long range diffusion of the solute in dilute alloys. Additional research is needed to confirm the rotation pathways and barriers of each type of dumbbell.

The study on solute-interstitial binding as a function of increasing Cr concentration revealed that binding energy increases with concentration up to 2 Cr solutes. The system is most stable when Cr is part of the interstitial dumbbell and the Cr-Cr dumbbell was found to be the most stable configuration studied, with a binding enthalpy of 0.92 eV. The strong Cr-interstitial binding both in and near the dumbbell will likely hinder dissociation of the Cr-interstitial complex. For the Ni-Cr dumbbell, the Cr solute could serve as temporary trap for an interstitial. This trapping mechanism is reinforced with an additional Cr atom present, forming a Cr-Cr dumbbell, which strengthens the Cr-interstitial binding and further hinders dissociation of the Cr-interstitial complex. Temporarily trapping interstitials at solutes can aid in recombination with vacancies, which may help to reduce radiation effects. Further research is needed to identify the energy landscapes associated with dissociation of the Ni-Cr and Cr-Cr interstitial complexes, which will allow for a quantitative analysis of the trapping effect.

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