ATOMISTIC SIMULATION OF AN f.c.c./b.c.c. INTERFACE IN Ni–Cr ALLOYS

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Abstract—The embedded atom method is applied to study the atomic structure and energy of an f.c.c./b.c.c. interface in Ni–Cr. The two phases are oriented in a Kurdjumov–Sachs orientation relationship, and the interface considered is the (1 2 1) habit plane adopted by precipitate laths of the b.c.c. phase. The interfacial energy and coherent strain energy at 0 K are calculated for boundaries between an f.c.c. Ni–Cr solid solution and b.c.c. Cr. The calculated interfacial energy varies from 216 mJ/m² when the f.c.c. phase is pure Ni to 200 mJ/m² when the f.c.c. phase is Ni–50 at.% Cr. Atomic relaxations appear limited to atoms in contact with the interphase boundary. Most of the interfacial energy is attributed to the structural difference across the f.c.c./b.c.c. boundary, and the chemical contribution to the energy is estimated to be less than 20% of the total energy. The values of the calculated energies and the widespread occurrence of the (1 2 1) habit plane in a variety of alloy systems indicate this boundary orientation has a relatively low interfacial energy. © 1997 Acta Metallurgica Inc.

INTRODUCTION

The embedded atom method [1] (EAM) is a convenient method for investigating the atomic structure [2] and energy of defects in crystals from a knowledge of interatomic potentials. It is particularly effective for studying aspects of defects that are difficult to measure experimentally. The structure and energy of a boundary between two phases are two such examples [3]. Interphase boundary structure and energy affects precipitate nucleation, growth, and coarsening, yet these quantities remain difficult to measure experimentally. The objective of this study is to evaluate the atomic structure and energy of an f.c.c./b.c.c. interphase boundary in Ni–Cr using a molecular statics approach and EAM potentials.

A number of alloys [4–6] in which f.c.c./b.c.c. transformations occur exhibit a (1 2 1) precipitate habit plane† when the two phases are in a Kurdjumov–Sachs orientation relationship (K–S OR) [7]: (111)f||(101)b, and [010]f||(T1)f. Both structure calculations [8] and high resolution electron microscopy (HREM) observations [9] have demonstrated substantial portions of this interface are free of misfit dislocations in a Ni–45 wt% Cr alloy. A detailed description of the structural characteristics of the interface are provided elsewhere [10, 8].

To calculate the structure and energy of this boundary, the EAM is applied to a simulation block consisting of a b.c.c. crystal oriented in the K–S OR between two f.c.c. crystals. The b.c.c. crystal is separated from the f.c.c. crystals by two boundaries parallel to the (1 2 1)b plane. The atoms are located initially in sites corresponding to bulk crystals. The internal energy of the simulation block is calculated from EAM interatomic potentials, and the atom positions are then relaxed until the simulation block reaches a configuration with a minimum energy. The interfacial energy is obtained by subtracting the internal energy of perfect f.c.c. and b.c.c. crystals and an elastic strain energy from the energy of the simulation block. The b.c.c. crystal is assumed to be pure Cr, and the f.c.c. crystals are a Ni–Cr solid solution. By changing the Cr concentration in the f.c.c. crystals, the interface stability and energy is studied as a function of the f.c.c. composition.

PROCEDURE

Interatomic potentials

A description of the embedded atom method can be found in Ref. [1]. The total energy, $E_{tot}$, for a
collection of atoms is expressed as:

$$E_{ext} = \sum_i F(p_{io}) + \frac{1}{2} \sum_{i \neq j} \phi_s(R_{ij})$$

(1)

where $F_i$ is a function of $p_i$, $\rho_{io}$ is the total host electron density of atom $i$ with a $p_i^k$ contribution from atom $j$, and $\phi_s$ is the potential pair function at a distance $R_{ij}$ apart. The DEVIL molecular statics code [11] was employed to optimize the configuration of atoms in the simulated block and to find a minimum in the total energy of the block. This provides the relaxed positions of the atoms relative to the positions assumed initially.

The pair part of the potentials used in the simulations is shown in Fig. 1. The Ni potential was originally developed by Voter and Chen [12]. The Cr potential was developed by Pasianot et al. [13] with the addition of angular terms using an "embedded defect" technique. For the present work, we chose this Cr potential without the addition of angular terms. This reproduces the lattice parameter, cohesive energy, and bulk modulus for Cr correctly, but it does not fit the elastic constants ($C_{11}$, $C_{12}$, and $C_{44}$) with the same accuracy since chromium has a negative Cauchy pressure and cannot be modeled using the standard embedded atom technique (Table 1).

The Ni potential of Ref. [12] is not in the effective pair scheme; that is, the first derivative of the embedding function, $F'(\rho)$, is not equal to zero at the electronic density in the perfect lattice of a pure metal ($\rho_0$). To be consistent with the Cr potential, the Ni potential was transformed according to an "effective pair scheme" [14] as described by Farkas et al. for Ni–Al [15]. The transformation applied is as follows:

$$F^d(\rho) = F(\rho) - \rho F'(\rho_0)$$

$$\phi^d(R) = \phi(R) + 2\rho R F'(\rho_0)$$

(2)

In addition, the electronic density for the perfect Cr lattice was normalized to 0.34, close to that used for pure Ni (0.38 [12]), to permit development of a mixed Ni–Cr potential. The embedding functions and pair potentials yield a lattice parameter of 0.352 nm for f.c.c. Ni and 0.287 nm for b.c.c. Cr; reported values for these phases are 0.35241 and 0.28847, respectively [16]. The cohesive energies modeled by these potentials are −4.45 eV/atom for Ni and −4.10 eV/atom for Cr.

Since the embedding functions can be developed based upon the pure metals, the only function needed for the mixed interaction is the mixed pair function ($\phi_{NiCr}$). For the mixed Ni–Cr potential, the EAM scheme used by Voter and Chen [12] for the Ni–Al potential was followed. The Ni–Cr interaction potential was expressed empirically as a linear combination of the Ni and Cr pair potentials (Fig. 1):

$$\phi_{NiCr}(a + bx) = A[\phi_{Cr}(c + dx) + \phi_{Ni}(e + fx)]$$

(3)

where $x$ has a value between zero and unity and represents the fractional interatomic distance between minimum separations ($a$, $c$, and $e$ for $\phi_{NiCr}$, $\phi_{Cr}$, and $\phi_{Ni}$, respectively) and the maximum separations ($a + b$, $c + d$, and $e + f$ for $\phi_{NiCr}$, $\phi_{Cr}$, and $\phi_{Ni}$, respectively). The parameters, $A$ and $a$–$f$, are fitted to experimental enthalpies of mixing and Vegard’s law (linear dependence of lattice parameter on composition) using a series of Ni–Cr solid solutions.

The disordered f.c.c. and b.c.c. solid solutions were simulated using at least 10 different starting configurations with random distributions of Cr and Ni atoms. The best fit values obtained for these parameters are given in Table 2. In Fig. 1, the interatomic distance that gives rise to the minimum potential are similar for the three pair potentials. Using the parameters of Table 2, the predicted f.c.c. lattice parameter of the equiatomic Ni–Cr disordered solid solution is 0.360 nm, and the cohesive energy is −4.22 eV. This implies a heat of mixing of 0.06 eV/atom; the value given by Hultgren et al. [17] at 1550 K is 0.07 eV/atom. The stability of the NiCr and Ni3Cr phases [18–20] was also evaluated. Neither of these are stable using the current atomic and pair potentials. The disordered f.c.c. has a lower cohesive energy at these stoichiometric compositions.

To predict the lattice constant of the f.c.c. solid solution as a function of Cr concentration, multiple

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Table 1: Experimental and calculated results of elastic constants for pure b.c.c. Cr (units in GPa)

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental</strong> [27]</td>
<td>391.0</td>
<td>89.6</td>
<td>103.2</td>
</tr>
<tr>
<td><strong>Calculated</strong></td>
<td>234.2</td>
<td>149.8</td>
<td>130.1</td>
</tr>
</tbody>
</table>

Table 2: Parameters used for the NiCr mixed interaction potential

<table>
<thead>
<tr>
<th>$A$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>$e$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.100</td>
<td>0.400</td>
<td>0.099</td>
<td>0.397</td>
<td>0.100</td>
<td>0.379</td>
</tr>
</tbody>
</table>
Fig. 2. The f.c.c. lattice parameter as a function of Cr concentration. The data points were obtained from the simulations, (- - -) is a quadratic fit [equation (4)].

Simulations were performed using an f.c.c. block of 108 atoms containing a specified number of Cr atoms randomly distributed among Ni atoms. Figure 2 shows the average lattice parameter of the relaxed f.c.c. simulation block at several Cr concentrations. Although the pair potentials were developed assuming a linear relationship between the lattice constant and Cr concentration, the relaxed parameter obtained from the simulations deviates slightly from linearity. The predicted lattice parameter was thus fitted to a quadratic equation for use in subsequent calculations:

\[ a_{c} (\text{nm}) = 0.352 + 0.0178X_{C} - 5.97 \times 10^{-1}X_{C}^{2} \tag{4} \]

where \( X_{C} \) represents the mole fraction of Cr and \( a_{c} \) is the f.c.c. lattice parameter determined from the simulations.

The composition dependence of the f.c.c. and b.c.c. cohesive energies are shown in Fig. 3. The cohesive energies of the two phases are the same at a Cr concentration of 51 at\%. For greater Cr concentrations, the b.c.c. phase is more stable than the f.c.c. phase, for lower concentrations, the b.c.c. structure is unstable and its energy could not be calculated.

**Configuration of the interphase boundary simulation block.**

The \( \{1 \bar{2} 1\} \) habit plane of a b.c.c. precipitate formed during aging of a Ni–45 wt\% Cr alloy at 950°C is shown in Fig. 4(a). The parallel planes of the K–S OR can be seen by comparing Fig. 4(a) with the schematic of Fig. 4(b), which also shows the initial positions of atoms in the interface region used in the simulation block. At the atomic level, the \( \{1 \bar{2} 1\} \) habit plane is not flat, but consists of structural ledges [21] composed of \( \{111\} \) and \( \{020\} \) facets. The “corners” of the structural ledges were chosen to coincide with intersections of \( \{111\} \) close-packed planes [vertical f.c.c. planes in Fig. 4(b)] with \( \{022\} \) b.c.c. planes [the near-vertical b.c.c. planes in Fig. 4(b) tilted 79° from the overall habit plane]. Although the locations of the ledge corners are arbitrary, the relative lengths of the two ledge facets is dictated by the orientation of the overall interphase boundary.

Two interphase boundaries were included in the simulation block to maintain periodic boundary conditions. The two boundaries were created by sandwiching a b.c.c. crystal between two f.c.c. crystals. The three orthogonal directions of the simulation block, \( x, y, \) and \( z \), were chosen along the \( \{111\} \), \( \{121\} \), and \( \{101\} \) crystal directions, respectively; this assignment placed the \( y \)-direction perpendicular to the two interphase boundaries. The dimensions of the two f.c.c. crystals were: \( 3\{111\} \) or \( 3\sqrt{3}a_{c} \) in the \( x \) direction, \( 2\{121\} \) or \( 2\sqrt{6}a_{c} \) in \( y \), and \( \{101\} \) or \( \sqrt{2}/2a_{c} \) in \( z \) for a total of 72 atoms in each f.c.c. crystal. The periodicity in the \( x \)- and \( z \)-directions for the b.c.c. crystal was chosen close to those of the f.c.c. crystals to ensure coherency. In the K–S OR, the \( x \)-dimension of the f.c.c. crystal, \( [333]_{\parallel} \), is close to \( [154]_{\parallel} \), so the periodicity of the b.c.c. crystal in the \( x \)-direction was chosen as \( \sqrt{2}a_{c} \). Similarly, the f.c.c. \( z \)-direction, \( [101]_{\parallel} \), is parallel to \( [111]_{\parallel} \), so the \( z \)-periodicity of the b.c.c. crystal was selected as \( \sqrt{3}/2a_{c} \). The periodicity of the b.c.c. crystal along the \( y \)-direction, or the thickness of the b.c.c. crystal, varied in the simulations but was always an integer multiple of \( [321]_{\parallel} \), or \( \sqrt{14}a_{c} \) to maintain periodicity along the parallel \( [121]_{\parallel} \) direction in the f.c.c. crystal. The minimum size of the b.c.c. crystal (and each increment in size) was 42 atoms, and a b.c.c. crystal of this size is hereafter termed a b.c.c. module. The boundary conditions on the simulation block during energy minimization were periodic in the \( x \) and \( z \) directions and fixed in the \( y \) direction (perpendicular to the habit plane) to represent the \( \{1 \bar{2} 1\} \) interphase boundary of b.c.c. precipitate constrained within an f.c.c. matrix.

According to the Ni–Cr phase diagram [16], the equilibrium f.c.c. composition for a two phase alloy at 950°C is 38 at\% Cr and the equilibrium b.c.c. composition is 95 at\% Cr. The composition of the b.c.c. crystal in the simulations was chosen as 100 at\% Cr for convenience. The Cr concentration in the f.c.c. crystals was varied systematically from 0 to 50 at\% (the upper limit of a stable f.c.c. phase in the simulations). For each concentration, at least 10 random configurations of the Cr atoms were used to
obtain an average energy for the disordered f.c.c. structure.

The b.c.c. crystal was strained elastically to force coherency at the interphase boundaries. Because the f.c.c. lattice parameter changes with Cr concentration, the strain required to force coherency also varies with the f.c.c. Cr concentration. The strains applied to the b.c.c. crystal in the x- and z-directions (parallel to the interface) were determined from the ratios of the periodicities of the b.c.c. and f.c.c. crystals in these directions. For the x-direction, this ratio was \(3\sqrt{3}a_c/a_s\), which ranged from \(-1.7\) to \(1.6\)% for the Cr concentrations considered. The strain in the z-direction was between 0.09 and 3.5%.
A range of b.c.c. strains in the y-direction (perpendicular to the interface) was tested. It was found that the lowest energy corresponds to the y-strain which, together with the aforementioned x- and z-strains, produces a zero volume change in the b.c.c. crystal. That is, stretching the b.c.c. crystal in the plane of the interphase boundary causes a contraction perpendicular to the boundary just enough to maintain a constant b.c.c. volume. The same conclusion was reached in an equivalent study using Fe EAM potentials [22].

The total energy of the simulation block also depends upon a rigid body translation between the f.c.c. and b.c.c. crystals. Simulations at three f.c.c. compositions, 0, 20 and 40 at.% Cr, were made to determine the optimum rigid body translation versus the f.c.c. Cr concentration. The component of this translation in the x-direction was (-0.026 + 0.0688X_{Cr} - 0.231X_{Cr}^2) nm, and the y-component was (0.0115 + 0.00846X_{Cr} + 0.0456X_{Cr}^2) nm. Thus, the relaxed structure of the simulation block was found by minimizing the energy with respect to dilatational strain, a relative translation of the f.c.c. and b.c.c. crystals within the interface plane, and local displacements of each individual atom in the simulation block.

RESULTS

The excess energy was obtained by subtracting the cohesive energy of the f.c.c. and b.c.c. portions of a simulation block from the total energy of a simulation block. It is composed of two terms, the elastic strain and the interfacial energy [22]. The interfacial energy term does not change with the size of the block as long as the area of the interface stays constant. On the other hand, the strain energy is proportional to the volume of the b.c.c. crystal. Consequently, the excess energy increases linearly with the thickness of the b.c.c. crystal for a constant interface area. The slope of this linear relationship gives the strain energy [3]. The interfacial energy can be obtained by extrapolating the excess energy to zero b.c.c. thickness, i.e. to an infinitely thin layer of the b.c.c. phase with two interfaces.

Since the smallest b.c.c. crystal that can be simulated with the present approach contains 42 atoms, one or more b.c.c. modules of this size could be extended in the y-direction and sandwiched between two f.c.c. crystals of 72 atoms each. The number of b.c.c. atoms included in the simulation blocks was thus 0, 42, 84, and 126. The four block sizes increased the number of simulations needed to obtain an average energy at each composition from 10 to 40. These were then used to obtain the linear relationship between excess energy and b.c.c. crystal thickness from which the interfacial energy and strain energy could be calculated.

At each f.c.c. composition, the linear fit of excess energy to the number of b.c.c. modules (i.e. b.c.c. thickness) gave a correlation coefficient of 0.99 or better, and in most cases as high as 0.9996, indicating that the size of the simulation block and the number of simulations was sufficient to represent the energy of the f.c.c. solid solution accurately. Figure 5 shows the excess energy vs b.c.c. crystal size for an f.c.c. crystal composition of 25 at.% Cr (Fig. 5). The interfacial energy obtained by extrapolating the lines to zero b.c.c. thickness is 211 mJ/m² and the strain energy obtained from the slope of the line is 3.2 x 10⁴ J/m².

Figure 6 shows how the strain energy changes with f.c.c. composition. The solid curve represents a fit to the strain energies obtained from the simulations. For comparison, the dashed curve is the elastic strain energy before relaxation of the simulation block calculated analytically using the homogeneous strains in the initial b.c.c. crystal and the elastic constants obtained from the Cr potential (Table 1). The strain energies calculated by the two approaches are similar, and they follow the same trend with f.c.c. Cr concentration. The comparatively lower strain energy of b.c.c.
energies obtained from the simulations are believed to reflect local atomic relaxations near the interface not included in the analytical calculation. Figure 7 shows the dependence of the interfacial energy on the Cr concentration in the f.c.c. crystals. The interfacial energy is essentially constant, decreasing only slightly from 216 to 200 mJ/m² as the Cr concentration increases from 0 to 50 at.%. The relaxed configurations of two representative simulations, one with pure Ni f.c.c. crystals and the other with 25 at.% Cr, are shown in Fig. 8(a) and (b), respectively (the displacements shown are enlarged by a factor of 10 for clarity). The relaxation in Fig. 8(a) shows the atomic displacements are limited to a region within two atomic layers of the interface. These relaxations are on the order of 0.015 nm; atomic displacements at locations away from the interface are less than 0.002 nm.

In the example with alloyed f.c.c. crystals, Fig. 8(b), comparatively larger relaxations are present. Atoms near the interface relax on the order of 0.02 nm, but displacements in the bulk crystals far from the interfaces are still small (~0.005 nm). The larger displacements in the bulk crystals are associated with the Cr atoms embedded in the f.c.c. crystals.

**DISCUSSION AND CONCLUSIONS**

In a study by Hopkins and Kossowsky [23], the f.c.c./b.c.c. interfacial energy was measured experimentally in eutectic Ni-Cr and reported to be 300 mJ/m², a value somewhat greater than the range calculated from the present simulations. However, the interface orientation and the f.c.c./b.c.c. orientation relationship of their samples were set during solidification and differed from those used in this study. The range of calculated (121), interfacial energies is also considerably lower than measured grain boundary energies (presumably the high-angle type) in pure Ni (866 mJ/m² [24]) and in a Ni-22 at.% Cr alloy (756 mJ/m² [25]). This indicates the good atomic matching across the (121), habit plane results in a low energy boundary.

The insensitivity of the calculated interfacial energy to the f.c.c. Cr concentration (Fig. 7) is perhaps surprising. It suggests the chemical contribution to the interfacial energy is quite small despite the large difference in composition across the boundary. This conclusion is consistent, however, with the small heat of mixing over the range of f.c.c. compositions.

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**Fig. 7.** The calculated energy of the (121) interphase boundary as a function of the Cr concentration in the f.c.c. phase (the b.c.c. phase is pure Cr).

**Fig. 8.** Two views of (a) the relaxed structure of a simulation block with pure Ni f.c.c. crystals and pure Cr b.c.c. crystals; and (b) the relaxed structure of a simulation block whose f.c.c. crystals contain 25 at.% Cr. Squares, triangles, and circles are used to represent atoms on different planes parallel to the paper ([100], and [220]). The final positions of Ni and Cr atoms are represented by empty and filled shapes, respectively. The relative relaxations (represented by lines attached to the atoms) are enlarged 10 times to show their directions more clearly.
considered (<0.07 eV/atom). It is also supported by a recent study of the coherent [100] boundary between f.c.c. Ni and L11 Ni3Al [3]. The energy of this boundary, which has only a chemical contribution, was calculated to be 22 mJ/m2 and measured to be between 14 and 21 mJ/m2 [26]. These values are similar to the change in interfacial energy between the 0 and 50 at.% Cr f.c.c. simulations of this investigation. As for the structural component of the interfacial energy, another study using the same methods [22], estimated the energy of the (121), f.c.c./b.c.c. boundary in pure Fe to be 179 mJ/m2 [22]. Since the two phases had the same composition, this energy has only a structural component. This value and those calculated in Ni–Cr alloys (200–216 mJ/m2) differ by 10–20% even though the pair potentials and embedding functions in the two cases are quite different. Thus, most of the interfacial energy in Ni–Cr is attributed to the structural difference across the boundary, and chemical effects probably contribute less than 20% of the total interfacial energy.

The interfacial energy was evaluated for a coherent interface, and this type of boundary is consistent with that found experimentally in Ni–Cr, TEM and HREM observations of the (121) habit plane [10] reveal an absence of regular misfit-compensating defects other than the structural ladders included in the simulations (Fig. 4), so the simulated interface is believed to represent a significant portion of the actual (121) habit plane.

The lattice parameter ratio varied in the simulations from 1.226 (for pure Ni f.c.c.) to 1.251 (for 50 at.% Cr in the f.c.c. crystals). Similar lattice parameter ratios are found in other alloys including Fe–Cu [4], Cu–Cr [5], and dual phase stainless steels [6]. The presence of (121) precipitate habit planes in these alloys suggests this plane has similar matching and a relatively low interfacial energy in all these systems.

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