Atomistic modeling of the order-disorder phase transformation in the Ni₂Cr model alloy

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Abstract

Mechanical property degradation due to the disorder to order phase transformation is of potential concern for alloys based on the Ni-Cr binary system, particularly in nuclear power applications where component lifetimes can exceed 80 years. In the present research, the disorder-order phase transformation has been studied in the Ni-33 at% Cr model alloy by a combined experimental and computational approach. The multiscale modeling framework utilizes grand canonical and kinetic Monte Carlo simulation techniques based upon density functional theory calculations to treat both the thermodynamic and kinetic aspects of the phase transformation. The simulation results are used to generate a simple model for the ordering kinetics based upon the Kolmogorov-Johnson-Mehl-Avrami equation. Experimental measurements of the change in lattice parameter as a function of aging time and temperature are obtained in order to assess the model accuracy. The resulting model shows reasonable agreement with experimental data at 470 and 418 °C, however additional experimental data at longer aging times are needed to confirm the accuracy of the model at lower temperatures. The model predicts that the initiation of the ordering transformation will occur in Ni-33Cr at temperatures and timescales relevant to nuclear power systems, though longer times are required for the transformation to proceed to completion.

Key Words: Nickel alloys; Monte Carlo; Phase transformations; Long-range ordering; Atomistic modeling

1 Introduction

Alloys based on the Ni-Cr binary system are an important class of structural materials due to their strength, toughness, and excellent corrosion resistance. Alloys such as alloy 690 and its weld metals are used extensively for structural components (e.g. piping) in nuclear power systems, where they will face service lifetimes exceeding 40 years in current reactors and up to 80 years under some proposed reactor lifetime extensions. The long-term thermal stability of these alloys is therefore of critical importance. The Ni-Cr system exhibits an ordered phase at low temperatures (below about 570 °C) at the stoichiometry Ni_2Cr , and the evolution of this phase is one mode of thermal degradation that

may be cause for concern. This is a first-order phase transformation, and the ordered structure is of the MoPt_2 archetype in the $Immm$ space group [1]. This structure is depicted in Fig. 1, along with an inscribed fcc unit cell demonstrating how the ordered structure maps onto the parent fcc lattice. With respect to the fcc lattice, the ordered structure may be thought of as alternating $\{110\}$ planes in a pattern of 2 planes of Ni atoms for everyone 1 plane of Cr atoms. Ordering in this system can lead to hardening and embrittlement [2], as well as an increased susceptibility to environmentally assisted cracking [3, 4]. Furthermore, the molar volume of the ordered phase is smaller than the disordered alloy phase, and the lattice contraction associated with the phase transformation can lead to elevated stresses or the loss of dimensional tolerances [5, 6].

In addition to the binary Ni-Cr system, both short and long range ordering associated with the Ni_2Cr phase have been detected in Ni-Cr-Fe model alloys [7], and commercial grades (e.g., alloy 690) have shown evidence of Ni_2Cr -like short range ordering when aged above typical operating temperatures to accelerate their kinetics [5, 8-10]. The Ni_2Cr ordering transformation and the resulting impact on material properties is therefore of potential concern in commercial Ni-Cr alloys. However, due to the considerable breadth of components and compositions spanned by this class of alloys, the Ni-Cr model system alone, upon which many commercial grades are based, has been the focus of the present study . While the Ni-33Cr model alloy is itself not an alloy of interest for engineering applications, it may provide a lower bound for the timescale of the formation of Ni_2Cr -like long-range order. If it can be demonstrated that ordering is of no concern in Ni-33Cr, then ordering can most likely be dismissed for more complex commercial alloys in which the kinetics are generally slower at temperatures relevant to pressurized water reactor (PWR) operation [7, 8, 11].

The kinetics of the disorder-order phase transformation are relatively slow. In stoichiometric binary alloy Ni-33Cr, the ordering reaction takes on the order of 1,000 hours to proceed to completion at 450 °C [5, 6], while in more complex alloys aging times of tens of thousands of hours may be required before there is any evidence of Ni_2Cr associated long range ordering [10]. At typical PWR operating temperatures near 325 °C, the kinetics are much slower and the ordering process may take

decades. It is therefore quite difficult from an experimental standpoint to study ordering kinetics at operating temperatures directly to determine whether it will be of concern on the timescale of the operational lifetime of a nuclear power system. Instead, the strategy has been to collect data at higher temperatures where the kinetics are significantly faster, and then use this data to fit empirical models to predict the timescale of the ordering transformation at the lower temperatures of interest [9, 10].

The ordering kinetics in such models typically depend upon an exponential term with an effective activation energy, and model predictions are highly sensitive to this parameter: values for Ni_2Cr ordering models are typically on the order of 100-200 kJ/mol (about 1-2 eV/atom), and a variation of only 10 kJ/mol (0.10 eV/atom) can result in a factor of 5-10 difference in predicted ordering times between 325 and 450 °C if all other model parameters are fixed [10]. Even near 450 °C, well above typical operating temperatures of interest, the ordering reaction may take many months or years depending upon alloy composition [8, 10]. It is therefore difficult to generate enough data to sufficiently constrain the model parameters, even for relatively simple empirical models. In a study of the ordering kinetics in alloy 690 (Ni-30Cr-10Fe), Delabrouille et al. [10] found that it was possible to obtain a similar quality of fit to ordering data at 420 °C and 360 °C with activation energy values ranging from 78.5 to 124 kJ/mol, depending on the value of the athermal preexponential term. However, at 325 °C, this same range in model parameters results in predicted ordering times spanning approximately 30 to 110 years. As the lifespan of a typical PWR is 40 to 80 years, the need for a more rigorous prediction is clear.

The present study was undertaken to provide a more robust model as well as to gain a better physical understanding of the kinetics of the ordering process in Ni-Cr alloys. The goal of this study is to utilize density functional theory (DFT) calculations combined with Monte Carlo simulations to develop a simple model for ordering in the Ni-33Cr alloy that is based upon first principles. This computational approach allows for the generation of a large body of simulated ordering data that covers a wide range of temperatures and has resulted in a well-constrained model that shows good quantitative agreement with data available in the literature as well as experimental data generated as a

part of this study. Furthermore, insights gained from the atomic-level resolution of the simulations lend physical significance to the resulting model parameters and provide guidance for future model development.

The remainder of this document is organized as follows: in section 2, the ordering model is described, and the details of the computational and experimental methods are recounted. Section 3 presents the significant thermodynamic and kinetic results derived from the Monte Carlo simulations. These simulation results are then used to construct the full first principles-based ordering model, and model predictions are compared with experimental measurements. Finally, concluding remarks are presented in section 4 regarding the success and limitations of the model, and the implications for component lifetimes in PWR systems.

2 Methods

2.1 Kolmogorov-Johnson-Mehl-Avrami model for ordering in Ni-33Cr

The model used in this study to describe ordering in the Ni-33Cr alloy has the form of a Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation [12-16]. This expression is used to describe a variety of phase transformations and related phenomena, and has the following general form:

$$S(t, T) = 1 - \exp[-(k(T)t)^n] \quad (2.1)$$

where $S(t, T)$ is a progress variable that varies continuously from 0 to 1 as the transformation proceeds from start to completion. The term $k(T)$ is a kinetic coefficient to which is typically described by an Arrhenius form [13].

$$k(T) = k_0 \exp\left[\frac{-Q}{k_B T}\right] \quad (2.2)$$

Here, k_0 is the preexponential factor and Q is the effective activation energy for the ordering transformation. The time exponent n is known as the Avrami exponent, and typically relates to the nucleation and growth mechanism and the geometry of the newly growing phase. This parameter often

assumes an integer value, though this is not always the case [17]. The ordering model thus has three adjustable parameters (k_0 , Q , and n).

In principal the KJMA equation can be used to compute the extent of the disorder-order phase transformation at any time and temperature. Therefore, predicting the transformation kinetics during very long service lifetimes is straightforward once the KJMA equation has been parameterized. However, for these predictions to be accurate the parameters k_0 , Q , and n must be determined by fitting Eqn. 2.1 to measurements of the ordered phase fraction that span a large breadth of temperatures and aging durations. At present, experimental measurements of the transformation kinetics below 450 °C are not available. We will therefore utilize atomistic simulations to generate a large set of measurements of the ordered phase fraction across several temperatures. Values of k_0 , Q , and n are then obtained from fitting to these simulation results. This process is described in greater detail in section 3.

2.2 Methodology for the thermodynamic and kinetic simulation of ordering in Ni-33Cr

A complete description of the ordering process requires consideration of both the thermodynamic and kinetic aspects of the phase transformation. In this study, these aspects are addressed separately by distinct but related simulation techniques: the thermodynamics are treated using grand canonical Monte Carlo (GCMC) [18], while the kinetics are treated using kinetic Monte Carlo (KMC) [19]. Both simulation techniques were performed using the Cluster Assisted Statistical Mechanics (CASM) software package [20-22]. CASM is an integrated tool suite that is used to assemble a Hamiltonian in the cluster expansion formalism [23-25] and then use this Hamiltonian to implement lattice-based GCMC and KMC simulations. The requisite steps for implementing these tools are described in the following subsections.

2.2.1 Construction of the Ni-Cr-Vacancy cluster expansion

The GCMC and the KMC simulations, as implemented here, are fixed lattice methods in which the simulated system consists of atoms and vacancies occupying sites on a perfect, rigid lattice. In this

study, fcc is the chosen lattice archetype; these simulations are therefore capable of representing any systems which are topologically equivalent to the fcc lattice, which includes the disordered Ni-Cr and Ni₂Cr ordered phases. Because the ordering transformation occurs via vacancy-mediated atomic migration, vacant sites on the fcc lattice must also be included in the model. Thus, the simulated system consists of Ni atoms, Cr atoms, and dilute monovacancies distributed on an fcc lattice. The GCMC and the KMC simulations require a method to rapidly calculate the energy of any arbitrary arrangement of these species on an fcc lattice, and the means to do this is provided by the cluster expansion Hamiltonian, which has the following general form:

$$E(\mathbf{s}) = m_0 v_0 + \sum_{\alpha} m_{\alpha} v_{\alpha} \phi_{\alpha}(\mathbf{s}) \quad (2.3)$$

Here, $E(\mathbf{s})$ is the energy of configuration $\mathbf{s}$ of Ni, Cr, and vacancies the fcc lattice. The subscript α refers to the clusters or combinations of lattice sites that make up configuration $\mathbf{s}$, i. e., single lattice sites, pairs, triplets, etc. The basis functions $\phi_{\alpha}(\mathbf{s})$ are taken as products of an occupation variable σ_i for each site in a cluster α , and the occupation variable is equal to 1 if the site is occupied by species i and 0 otherwise. This choice of basis is referred to as the occupation basis. One species, in this case Ni, is taken as the reference occupation for each site and forms a reference state of zero energy. With this choice no terms of the form σ_{Ni} enter the basis functions. Therefore, for the Ni-Cr binary component of the cluster expansion, these basis functions are products of σ_{Cr} , while for the Ni-Cr-vacancy component these are products of σ_{Cr} and σ_{vac} . The formalism behind this occupation basis cluster expansion is discussed in detail in Refs [26-28].

The coefficients m_{α} are multiplicity factors which account in the summation for all possible symmetry equivalents of the cluster α . The coefficients v_{α} are the effective cluster interactions (ECIs) per multiplicity, while the product $m_{\alpha} v_{\alpha}$ is referred to as the complete ECI V_{α} . These ECIs are the unknown parameters to be determined when constructing the cluster expansion Hamiltonian. To do this, it is first necessary to determine the energies of a finite representative set of Ni-Cr-vacancy

structures. This was done via density functional theory (DFT) calculations using the Vienna Ab Initio Simulations Package (VASP) [29-32]. All calculations were performed in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional [33] and the projector-augmented wave method [34]. An energy cutoff of 479 eV and k-point meshes of between 5000 and 7000 k-points per reciprocal atom in the Monkhorst Pack scheme were used, and all calculations were spin polarized. By this method, formation energies (from reference states of pure fcc Ni and pure fcc Cr) of 111 structures ranging in size from 1 to 108 atoms and spanning compositions from 0 to 50 % Cr were calculated. These formation energies were then used to fit the Ni-Cr cluster expansion in the occupation basis using CASM. The resulting cluster expansion Hamiltonian consists of 8 ECIs, and has a cross validation (CV) score and root mean square (RMS) error of 0.039 and 0.023 eV per atom, respectively. The former value captures the ability of the cluster expansion to predict energies of structures not included in the fitting, while the latter is a measure of the error between predicted and calculated energies when all structures are included in the fitting. Both the CV score and RMS error are on the order of 10-20% of the formation energy of the Ni_2Cr ordered structure. While the CV score and RMS errors are somewhat high, these errors are due mostly to poor fitting of high energy structures far from the convex hull. Fig. 2 depicts the formation energies of all Ni-Cr structures as predicted by the cluster expansion and as calculated via DFT as a function of alloy composition. For structures near the convex hull, the predictions of the cluster expansion and the DFT values are reasonably close. Both the DFT calculations and the cluster expansion Hamiltonian correctly predict the ground state at Ni-33Cr.

To capture interactions involving a vacancy, the binary cluster expansion was extended to include vacancy-Cr interactions following an approach similar to that used by Van der Ven et al. [26]. The additional vacancy-Cr interactions within the binary Ni-Cr cluster expansion can be determined by fitting to alloy vacancy formation energies defined as the formation energy difference between a given Ni-Cr structure with a single vacancy and the same structure where the vacancy has been replaced by a Ni atom, where again the structure formation energies are taken with respect to pure Ni and pure Cr

reference states. Because the energy of the defected structure is taken with respect to a non-defected structure containing the same atomic interactions, the resulting cluster expansion captures only the atom-vacancy interactions. The alloy vacancy formation energies as defined above of 15 structures were calculated and used to fit the vacancy cluster expansion in the occupation basis. The resulting cluster expansion Hamiltonian consists of 3 additional ECIs not already contained within the Ni-Cr cluster expansion, and has a CV score and RMS error of 0.0037 and 0.0003 eV, respectively. The CV score is on the order of 10 % of the Cr-vacancy interaction energies, which are around 50 meV in magnitude. The complete Ni-Cr-vacancy cluster expansion Hamiltonian thus contains 11 ECIs. These are presented in Table 1. The complete cluster expansion includes both Cr-Cr and Cr-Vac interactions, and can be written as follows:

$$\begin{aligned}
E(\mathbf{s}) = & m_0 v_0 + \sum_{n=1, L=0} m_{1-1} v_{1-1} \phi_{1-1}(\mathbf{s}) + \sum_{n=2, L=2.51} (m_{2-1} v_{2-1} \phi_{2-1}(\mathbf{s}) + m_{2-2} v_{2-2} \phi_{2-2}(\mathbf{s})) + \\
& \sum_{n=2, L=3.55} (m_{2-3} v_{2-3} \phi_{2-3}(\mathbf{s}) + m_{2-4} v_{2-4} \phi_{2-4}(\mathbf{s})) + \sum_{n=2, L=4.35} m_{2-5} v_{2-5} \phi_{2-5}(\mathbf{s}) + \\
& \sum_{n=3, L=2.51} m_{3-1} v_{3-1} \phi_{3-1}(\mathbf{s}) + \sum_{n=3, L=4.35} (m_{3-2} v_{3-2} \phi_{3-2}(\mathbf{s}) + m_{3-3} v_{3-3} \phi_{3-3}(\mathbf{s})) + \\
& \sum_{n=4, L=3.55} m_{4-1} v_{4-1} \phi_{4-1}(\mathbf{s})
\end{aligned} \tag{2.4}$$

where each sum is taken over all lattice site clusters of size n and max inter-site length L (Å) in lattice configuration $\mathbf{s}$.

2.2.2 Grand canonical Monte Carlo simulation

Once a suitable cluster expansion has been generated, it can be used to perform GCMC simulations in the CASM suite. Simulations were performed using a supercell consisting of 12x12x12 primitive fcc cells, for a total of 1,728 lattice sites. This supercell was initialized with all lattice sites occupied by Ni, and 10,000 passes were set aside for equilibration. During each pass, each lattice site is visited, on average, once to consider changing lattice occupancy based on the Metropolis algorithm for determining the correct probability for accepting or rejecting the occupancy change. After equilibration, an additional 80,000 passes were performed to compute thermodynamic averages.

The remaining input parameters for the GCMC simulations are the temperature and the chemical potentials for each species in the system (μ_{Ni} , μ_{Cr} , and μ_{Vac}), which altogether define the coordinates in thermodynamic space of a given simulation. Because the number of lattice sites is fixed, not all three chemical potentials can be varied independently. In this study, we have chosen to consider Ni as the solvent species, and Cr and vacancies as solutes. We therefore use the following differences of chemical potentials as independent thermodynamic variables in the GCMC simulations:

$$\tilde{\mu}_{Cr} = \mu_{Cr} - \mu_{Ni} \text{ and } \tilde{\mu}_{Vac} = \mu_{Vac} - \mu_{Ni}.$$

The difference $\tilde{\mu}_{Cr}$ largely determines the equilibrium alloy composition of the simulated system: as it is increased, the equilibrium composition will become more Cr-rich. In general, for a fixed value of $\tilde{\mu}_{Cr}$, the equilibrium alloy composition of the disordered phase will vary as a function of temperature, however in this case this variation was quite small: using a constant value chosen to yield a composition of Ni-33Cr at just above the order-disorder transformation temperature, the equilibrium simulated alloy composition remained within ± 1 at% of Ni-33Cr between 600 and 1400 K (i. e., from well below the critical transformation temperature to well above it).

For a fixed value of $\tilde{\mu}_{Cr}$, the chemical potential difference $\tilde{\mu}_{Vac}$ determines the vacancy concentration in the simulated alloy. In real alloys at equilibrium, vacancies are not a conserved species, they may be emitted or absorbed freely by internal vacancy sources and sinks such as dislocations. Consequently, the equilibrium vacancy chemical potential is equal to zero and in principle the value of $\tilde{\mu}_{Vac}$ should be selected such that this condition for equilibrium is satisfied [35, 36]. However, equilibrium vacancy concentrations in real alloys are generally very dilute and computationally challenging to resolve via GCMC simulations. In this study, we have instead chosen $\tilde{\mu}_{Vac}$ such that there are many times the equilibrium concentration from real alloys but still, on average, fewer than one vacancy in the GCMC simulation cell at all temperatures. This is to avoid any vacancy-vacancy interactions, which are not fit in the cluster expansion, and enable the approximations

used below. The following additional manipulations were then used to estimate the vacancy concentration in the real Ni-33Cr alloy based upon the GCMC simulation results.

Van der Ven et al. [36] have derived the following expression for the vacancy fraction in GCMC simulations where the vacancies are sufficiently dilute that lattice configurations with more than one vacancy can be neglected:

$$C_{vac} = -\frac{1}{Mk_B T} \langle \Delta\Phi_{vac}(\mathbf{p}) \rangle \quad (2.5)$$

where the quantity $\Delta\Phi_{vac}(\mathbf{p})$ is referred to by Van der Ven et al. [36] as the coarse-grained vacancy free energy. This quantity is defined by

$$\Delta\Phi_{vac}(\mathbf{p}) = -k_B T \sum_{\mathbf{q}(\mathbf{p}) \neq \mathbf{p}} \exp \left[-\frac{\Delta\Omega(\mathbf{q}(\mathbf{p}))}{k_B T} \right] \quad (2.6)$$

Here, $\mathbf{p}$ specifies a binary Ni-Cr lattice configuration, $\mathbf{q}(\mathbf{p})$ specifies a configuration where a single vacancy has been inserted into configuration $\mathbf{p}$, and $\Omega(\mathbf{q}(\mathbf{p}))$ is the grand canonical energy of configuration $\mathbf{q}(\mathbf{p})$. The grand canonical energy is determined from the cluster expansion Hamiltonian, and is defined as

$$\Omega(\mathbf{s}) = E(\mathbf{s}) - N_{Cr}(\mathbf{s})\tilde{\mu}_{Cr} - N_{vac}(\mathbf{s})\tilde{\mu}_{vac} \quad (2.7)$$

where $N_{Cr}(\mathbf{s})$ and $N_{vac}(\mathbf{s})$ are the numbers of Cr atoms and vacancies in configuration $\mathbf{s}$, respectively, and $E(\mathbf{s})$ is the cluster expansion energy of configuration $\mathbf{s}$. The change in grand canonical energy $\Delta\Omega(\mathbf{q}(\mathbf{p}))$ is the energy associated with introducing a vacancy into configuration $\mathbf{p}$, and is defined as.

$$\Delta\Omega(\mathbf{q}(\mathbf{p})) = E(\mathbf{q}(\mathbf{p})) - N_{Cr}(\mathbf{q}(\mathbf{p}))\tilde{\mu}_{Cr} - \tilde{\mu}_{vac} - \Omega(\mathbf{p}) \quad (2.8)$$

In Eqn. 2.8, we have implicitly assumed that the number of vacancies in all configurations $\mathbf{q}(\mathbf{p})$ is equal to 1. Combining Eqns. 2.5-2.8, we may now write the vacancy fraction as

$$C_{Vac} = \frac{1}{M} \exp \left[\frac{\tilde{\mu}_{Vac}}{k_B T} \right] \left\langle \sum_{\substack{\mathbf{r} \\ q(\mathbf{p}) \neq \mathbf{p}}} \exp \left[- \frac{E(\mathbf{q}(\mathbf{p})) - N_{Cr}(\mathbf{q}(\mathbf{p})) \tilde{\mu}_{Cr} - \Omega(\mathbf{p})}{k_B T} \right] \right\rangle \quad (2.9)$$

Let $C_{Vac}^*(C_{Cr})$ be the vacancy fraction determined via GCMC simulation in an alloy of Cr composition C_{Cr} , for an arbitrary value of $\tilde{\mu}_{Vac}$ chosen to yield a sufficiently dilute vacancy fraction. Further, let $R^*(C_{Cr})$ be the ratio $C_{Vac}^*(C_{Cr})/C_{Vac}^*(0)$ evaluated for a fixed value of $\tilde{\mu}_{Vac}$. From Eqn. 2.9 it is evident that the value of $R^*(C_{Cr})$ will be independent of the chosen value of $\tilde{\mu}_{Vac}$ due to cancelation. The vacancy fraction corresponding to any value of $\tilde{\mu}_{Vac}$ can be expressed as

$$C_{Vac}(C_{Cr}) = R^*(C_{Cr}) C_{Vac}(0) \exp \left[\frac{\tilde{\mu}_{Vac}(C_{Cr}) - \tilde{\mu}_{Vac}(0)}{k_B T} \right] \quad (2.10)$$

where $\tilde{\mu}_{Vac}(C_{Cr})$ is the value of $\tilde{\mu}_{Vac}$ that results in the vacancy fraction $C_{Vac}(C_{Cr})$.

Because the equilibrium vacancy chemical potential is equal to zero, the chemical potential difference $\tilde{\mu}_{Vac}$ at equilibrium is equal to $-\mu_{Ni}$. By inserting this substitution into Eqn. 2.10, the equilibrium vacancy concentration in the Ni-33Cr alloy can be expressed as

$$C_{Vac}\left(\frac{1}{3}\right) = R^*\left(\frac{1}{3}\right) C_{Vac}(0) \exp \left[\frac{-\Delta\mu_{Ni}\left(\frac{1}{3}\right)}{k_B T} \right] \quad (2.11)$$

The value of $R^*\left(\frac{1}{3}\right)$ may be determined from GCMC simulations of pure Ni and the Ni-33Cr alloy, using a fixed value of $\tilde{\mu}_{Vac}$ that results in a sufficiently dilute vacancy fraction, and $C_{Vac}(0)$ can be drawn from experimental measurements of the vacancy concentration in pure Ni. The quantity $\Delta\mu_{Ni}\left(\frac{1}{3}\right) = \mu_{Ni}\left(\frac{1}{3}\right) - \mu_{Ni}(0)$ is the difference between the chemical potential of Ni in pure Ni and in the Ni-33Cr alloy, which can be determined from GCMC simulation results in the Ni-Cr binary system (i. e., without vacancies) via thermodynamic integration according to the following method [37].

In a Ni-Cr alloy consisting of a fixed number of lattice sites, the chemical potentials of Ni and Cr can be expressed as follows [35]:

$$\begin{aligned}\mu_{Ni}(C_{Cr}) &= g(C_{Cr}) - C_{Cr} \frac{\partial g(C_{Cr})}{\partial C_{Cr}} \\ \mu_{Cr}(C_{Cr}) &= g(C_{Cr}) + (1 - C_{Cr}) \frac{\partial g(C_{Cr})}{\partial C_{Cr}}\end{aligned}\tag{2.12}$$

where $g(C_{Cr})$ is the free energy per lattice site of the alloy. This free energy can be determined by the following integration:

$$g(C_{Cr}) = g(0) + \int_0^{C_{Cr}} \frac{\partial g(C'_{Cr})}{\partial C'_{Cr}} dC'_{Cr}\tag{2.13}$$

Inspection of Eqn. 2.12 reveals that the partial derivative $\frac{\partial g(C_{Cr})}{\partial C_{Cr}}$ is equal to the chemical potential difference $\tilde{\mu}_{Cr} = \mu_{Cr} - \mu_{Ni}$, which is fixed for any given GCMC simulation. Therefore, in practice the free energy can be evaluated by first performing a large number of GCMC simulations on a grid of $\tilde{\mu}_{Cr}$ values in order to populate a table of $\tilde{\mu}_{Cr}$ vs. C_{Cr} up to the alloy composition of interest, fitting a polynomial function $\tilde{\mu}_{Cr}(C_{Cr})$ to this data set, and computing the integral in Eqn. 2.13. Once the free energy $g(C_{Cr})$ has been determined, Eqn. 2.12 can be used to evaluate the chemical potential $\mu_{Ni}(C_{Cr})$. By following this procedure, the chemical potential difference $\Delta\mu_{Ni}(\frac{1}{3})$ can be calculated and subsequently used in Eqn. 2.11 to determine the equilibrium vacancy fraction in the real Ni-33Cr alloy.

In addition to the vacancy concentration, the GCMC simulations provide two other pieces of information that we make use of in this study. The first is the average grand canonical energy of the simulated Ni-Cr alloy as a function of temperature. While not of interest in itself, it is possible to identify the order-disorder transition temperature by observing the discontinuity in the average grand canonical energy of the simulated Ni-33Cr alloy, which is associated with the phase transformation. The second set of useful outputs are sample lattice arrangements of the equilibrated system, which can be used to calculate an ordering parameter and quantify the actual ordering of the simulated alloy. We define an ordering parameter as follows. In the ordered phase, all Ni atoms have 7 Ni neighbors and 5

Cr neighbors, while all Cr atoms have 10 Ni neighbors and 2 Cr neighbors. In this study, we consider the atoms in the system that have the “correct” neighbors to be “ordered atoms,” and the extent of ordering is quantified by the fraction X_o of ordered atoms in the system. This leads to the following definition of the KJMA progress variable in Eqn. 2.1:

$$S(t, T) = \frac{X_o(t, T) - X_{o, \min}}{1 - X_{o, \min}} \quad (2.14)$$

where $X_{o, \min}$ is the fraction of ordered atoms in the disordered phase just above the Ni₂Cr order-disorder critical temperature, and $X_o(t, T)$ is the ordered fraction in the system at time t and temperature T . While time is not a meaningful parameter in the GCMC simulations, it is included here for clarity, as this same definition of the progress variable will be used for analyzing the results of the KMC simulations. Note that this variable changes from 0, for the equilibrium state of the disordered phase at just above the critical temperature, to 1, for the perfect ordered phase.

2.2.3 Kinetic Monte Carlo simulation

The KMC functionality of the CASM software package was used to study the kinetic aspects of the ordering transformation in Ni-33Cr. The KMC method as implemented in CASM simulates the time evolution of the system that occurs due to the migration of a single vacancy, thus the vacancy concentration in the simulation is implicitly determined by the selection of the system size. In the present study, the KMC simulation supercell consisted of 27x27x27 primitive fcc cells, for a total of 19,683 lattice sites. Unlike in the GCMC simulations, for KMC simulations the atomic composition of the simulated system is entered by the user explicitly; for all simulations, a composition of Ni-33Cr was used in a random initial lattice arrangement.

The frequencies of atomic migration events are determined by the KMC algorithm using the familiar expression from standard transition state theory [38]:

$$\omega_{i \rightarrow j} = \nu \exp \left[-\frac{E_{i \rightarrow j}}{k_B T} \right] \quad (2.15)$$

where $\omega_{i \rightarrow j}$ is the hopping frequency for a given atom from configuration i to configuration j , ν is the attempt frequency, and $E_{i \rightarrow j}$ is the migration energy for the hop. Most estimates for attempt frequencies in metals range from 10^{12} - 10^{13} Hz. In this study we have used an approximate value of 10^{13} Hz for all events. The migration barrier $E_{i \rightarrow j}$ is approximated dynamically by the kinetically resolved activation barrier (KRA) method [39, 40]:

$$E_{i \rightarrow j} = E_0 - \frac{1}{2}(E_i - E_j) \quad (2.16)$$

where E_0 is the averaged migration barrier between forward and backward hops, and E_i and E_j are the energies of the initial and final state configurations as determined by the cluster expansion Hamiltonian. E_0 values of 1.04 eV and 0.83 eV were used for Ni and Cr, respectively. The former is the experimentally determined value for pure Ni self-diffusion [41], and the latter is the migration barrier for Cr in pure Ni determined via DFT [42]. While this neglects any potential effect of the local chemical environment on the baseline migration barrier (E_0), we assume that the majority of the effect of the local environment on the total activation barrier will be captured by the KRA treatment. This approach has been demonstrated to be a reasonable approximation in other systems [43]. Additionally, experimental measurements of Ni and Cr tracer diffusion coefficients covering a temperature range of 950 °C to 1250°C in Ni-Cr alloys show only weak concentration dependence, each changing by less than 30% with respect to their dilute values over the concentration range of 0-40 at% Cr [44]. Furthermore, the ratio of the Ni and Cr tracer diffusion coefficients is virtually constant over that composition range, suggesting that any changes in the diffusion coefficients with composition can be accounted for by changes in the vacancy concentration, rather than changes in atomic migration barrier energies. Thus, while assuming a fixed value for E_0 as a function of composition may not be an appropriate approximation in all alloy systems, there is evidence that for the Ni-Cr system it is reasonable.

Simulations were run of lengths varying from 1 to 100 passes, in increments of 5 passes, where a pass is defined as one vacancy hop for every lattice site in the system. At the end of each simulation, the final simulation time was collected and the final configuration of the lattice was used to compute the value of the progress variable $S(t, T)$. Thus, each point in S-time-temperature space represents a separate, independent simulation. Simulations were performed at 327 °C, 375 °C, 423 °C, and 471 °C, with 5 sets of simulations at each temperature and each length in number of passes. The resulting values of $S(t, T)$ as a function of time and temperature were used to fit the values of the parameters k_0 , Q , and n in Eqn. 2.1.

2.3 Experimental measurement of the ordering kinetics in Ni-33Cr

In order to provide a benchmark for the model results, a set of experimental data on the ordering kinetics of Ni-33Cr was gathered between 333 °C and 470 °C for aging times up to 10,000 hours. While sufficient experimental data exists for temperatures above 450 °C [6, 8] the present study will provide critical lower temperature data points, so that model predictions can be validated across a wider temperature range. Because ordering is an atomic scale phenomenon, it can be difficult to characterize by direct observation techniques such x-ray diffraction due to the close scattering properties of Ni and Cr. It is therefore most often characterized indirectly by measuring some other property of the material that changes in response to the ordering process, such as hardness, fracture properties, or electrical resistivity [5]. In this study, the change in the lattice parameter is used to quantify the ordering process.

The model alloy was fabricated by arc melting 300 g buttons at the nominal composition Ni-33Cr. After melting, the buttons were annealed for 24 hours at 1093 °C and hot rolled between 982-1093 °C from approximately 10 mm to 5 mm in thickness in three passes, with the rolling direction of the second pass aligned perpendicular to the first and third passes. Following rolling, the buttons were annealed at 1093 °C for one hour and then quenched.

Once the specimens were fabricated, 1.25 cm square samples were machined and grouped for isothermal aging at 4 temperatures: 333 °C, 373 °C, 418 °C, and 470 °C. The cubic lattice parameters of select samples were measured prior to aging, and all samples were measured after aging increments of 10, 30, 100, 300, 1,000, 3,000, and 10,000 hours. Lattice parameters were determined via X-ray diffraction, performed with a PANalytical X'Pert Pro Theta-Theta diffractometer and Cu K α radiation. Parallel beam optics and high angle diffraction peaks (the (3,3,1) and (4,2,0) planes at $\approx 140^\circ$ and $\approx 150^\circ$ 2 θ , respectively) were used to minimize instrumental errors. In addition, an Alloy 690 external standard was tested periodically to check for instrumental errors.

3 Results and Discussion

3.1 Determination of the critical temperature and the fraction of ordered atoms from GCMC simulations

One immediate assessment of accuracy of the cluster expansion Hamiltonian is the predicted critical temperature T_c for the order-disorder transition. Fig. 3 depicts the grand canonical energy of the simulated Ni-33Cr alloy as a function of temperature, as determined via GCMC simulations. Temperatures were sampled with both heating and cooling scans in order to place upper and lower bounds on the simulated critical temperature. The sharp discontinuities at 677 °C for the cooling scan and 877 °C for the heating scan indicate phase transformations during the simulations. On the secondary vertical axis in Fig. 3 the fraction of ordered atoms in the system is plotted as a function of simulation temperature during the cooling scan. The sharp increase from 0.28 to near 1 as the system is cooled through approximately 677 °C verifies that this phase transformation is the transition between the disordered alloy phase and the ordered Ni₂Cr phase. While not shown, a similar hysteresis to that of the grand canonical energy is observed in the fraction of ordered atoms upon heating. The predicted value for T_c is thus between 677 and 877 °C. This is higher than the experimental values of 570-590 °C [6, 8, 45]. This discrepancy may be due to errors in the ab initio energies, the cluster expansion, or vibrational and magnetic contributions to the free energy that are neglected in the computation of the

grand canonical potential. In light of these approximations the predicted value of T_C is reasonable, and indicates that the cluster expansion Hamiltonian adequately describes the phase transformation.

In a truly random Ni-33Cr alloy, the average fraction of atoms having the “correct” numbers of Ni and Cr neighbors by happenstance is about 0.17. It is noteworthy that the ordered fraction just above the critical temperature $X_{O,min}$ in Fig. 3 is about 0.28, which is somewhat higher than the random alloy value. This reflects the persistence of some degree of short-range order above the critical temperature.

3.2 Determination of the KJMA parameters from KMC simulations

In order to construct the first principles-based KJMA model, we first introduce a slightly altered form of the kinetic coefficient $k(T)$:

$$k(T) = k_0 C_{vac} \exp\left[-\frac{Q_{mig}}{k_B T}\right] \quad (3.1)$$

where C_{vac} is the vacancy concentration in the Ni-33Cr alloy. We assume that the order-disorder phase transformation proceeds via discrete atom-vacancy exchanges [46], so we assume here that the kinetic coefficient is proportional to the vacancy concentration, analogous to vacancy-mediated diffusion. The activation energy Q_{mig} is then the portion of the activation energy associated with these atom-vacancy exchanges. In a real alloy, the vacancy concentration will have a strong temperature dependence that will be reflected in the total effective activation energy Q in Eqn. 2.2, however in the KMC simulations the vacancy concentration is determined implicitly by the selection of the system size, as discussed in section 2.2.3.

The first principles-based KJMA model was constructed by performing a least squares fit of Eqn. 2.1 to values of the order parameter $S(t, T)$ determined from KMC simulations, using pre-exponential factor k_0 , the activation energy Q_{mig} , and the Avrami exponent n as fitting parameters.

Values of the order parameter as a function of time are plotted in Fig. 4 from KMC simulations at four

different temperatures. The data points represent values measured from KMC simulations, while the solid lines are values from the best-fit KJMA model. The best fit model in Fig. 4 provides the following values for the KJMA parameters: $k_0 = 2.04 \times 10^{11}$ Hz, $Q_{mig} = 0.9$ eV, and $n = 1$. Because these parameters are independent of the system size, the results of this model may be compared directly to experimental measurements of the ordering kinetics by inserting the vacancy concentration of the real Ni-33Cr alloy into Eqn. 3.1. A precise value of this vacancy concentration is unavailable for the Ni-33Cr alloy, however GCMC simulations can be utilized to estimate how much this value might differ from the vacancy concentration in pure Ni, which has been determined experimentally, as described in Sec. 2.2.2. The results of this estimation approach will be presented in Sec. 3.4.

The form of Eqn. 3.1 contains a single activation energy Q_{mig} associated with the vacancy migration events. It therefore assumes implicitly that nucleation is essentially instantaneous and that the transformation is limited only by the vacancy migrations. In other words, according to Eqn. 3.1, the phase transformation will always proceed faster at higher temperatures, whereas in reality the kinetics will be reduced above a certain temperature due to the weaker driving force for nucleating ordered domains. The lattice structures resulting from multiple KMC simulations of various lengths and temperatures have been examined to ensure that the assumption of almost instantaneous nucleation is valid over the temperature range examined here. Fig. 5 depicts the ordered atoms following simulations of multiple lengths (in terms of MC steps) at 327, 471, and 575 °C. Only ordered atoms that are neighbored by at least 10 other ordered atoms are shown. The first two temperatures correspond to the lowest and highest temperatures used for fitting Eqn. 3.1, while the third is a temperature that is outside this range but still below the stability limit of the ordered phase according to Fig. 3. From Fig. 5 it is clear that the ordered phase has nucleated after relatively few MC steps at both 327 and 471 °C, while at 575 °C significant nucleation is suppressed until later simulation times. At all three temperatures, the transformation is virtually completed by 50 MC steps per lattice site (row d). Beyond the kinetics of nucleation, other qualitative differences are apparent in the morphology of

the phase transformation at the different temperatures in Fig.5. The nuclei appear to be smaller and more numerous at 327 °C compared with 471 °C, which result is consistent with a higher driving force for nucleation at the lower temperature. The stronger driving force at low temperature leads to multiple ordered domains of differing orientations in the fully ordered structure at 327 °C, while the fully ordered structures at 471 and 575 °C appear to be a single continuous domain. Finally, the fully ordered structure at 327 °C appears to have the fewest defects, with progressively more defects apparent at the higher temperature simulations.

The differences in nucleation kinetics are highlighted again in Fig.6, which compares the measured values of the order parameter $S(t, T)$ from the simulations in Fig. 5 with the corresponding predictions of Eqn. 3.1. The simulation results at 327 and 471 °C follow the predictions of Eqn. 3.1 reasonably closely, while the order parameter measured for the shorter simulations at 575 °C are well below the predicted values. This result is consistent with the delayed nucleation at 575 °C observed in Fig. 5. Based on the results in Figs. 5 and 6, the nucleation rates over the temperatures of interest in this study appear to be sufficiently fast that the assumptions inherent in Eqn. 3.1 are reasonable.

3.3 Physical interpretation of the KJMA model

The value of the Avrami exponent n is often interpreted in terms of the nucleation and growth mechanism of the growing phase. For instance, for site saturated nucleation and diffusion controlled growth, n is equal to 1, 2, or 3 and reflects the dimensionality of the growth [14-16]. In this section, we posit a simple model for the kinetics of the ordering transformation to provide a physical interpretation of the KJMA model assembled in section 3.2, specifically the value of the Avrami exponent.

In keeping with the original derivation of the KJMA equation [12], we first define a fictitious extended fraction of ordered atoms, X_{ext} , as the fraction of ordered atoms that would result if the growing domains of the ordered phase never impinged upon one another. We assume that the ordering transformation proceeds by a series of atom-vacancy exchanges that rearrange the disordered atomic

structure to the ordered structure at some constant, effective rate. Consequently, the volume growth rate of the ordered phase domains is independent of the domain size. This is in contrast with the volume growth rate under diffusion controlled growth conditions, where the growth rate is proportional to a flow of material across the interface of the domain of the newly growing phase. This flow is proportional to the interfacial area of the domain; as the domain grows, the growth rate increases according to some power law of time, depending on the dimensionality of the growth. A disorder-order transformation rate that is constant with respect to time was also proposed by Dienes [47] for a place-exchange mechanism and Vineyard [46] for a vacancy mechanism, with greater theoretical rigor than the simple model proposed here.

Subject to these assumptions, the differential change of the extended ordered fraction can be expressed as

$$dX_{ext} = C_{vac} k_{ord} dt \quad (3.2)$$

where k_{ord} is the average rate at which a one atom is transformed from a disordered atom to an ordered atom by a series of atom-vacancy exchanges. The differential extended ordered fraction is related to the differential real ordered fraction X_o by

$$dX_o = (1 - X_o) dX_{ext} \quad (3.3)$$

After combining Eqns. 3.2 and 3.3 and integrating, and recalling that $X_o(0) = X_{o,min}$, we arrive at the following expression for the ordered fraction as a function of time:

$$X_o(t) = 1 - \exp[-C_{vac} k_{ord} t] (1 - X_{o,min}) \quad (3.4)$$

Combining Eqns. 3.4 and 2.14, we recover the original functional form of the KJMA equation:

$$S(t) = 1 - \exp[-C_{vac} k_{ord} t] \quad (3.5)$$

The value of 1 for the Avrami exponent that resulted from the least squares fitting in section 3.2 is evidently a consequence of the physical growth mechanism reflected in Eqn. 3.2; namely, that the volume of the extended ordered phase fraction grows at a constant rate. It is therefore not related to

the dimensionality of the growing domains, as is conventionally assumed for diffusion-controlled phase transformations described by the KJMA equation.

3.4 Estimation of the vacancy concentration in the Ni-33Cr alloy

Before the results of the KJMA model obtained in Sec. 3.2 can be used to predict the ordering transformation kinetics in a real Ni-33Cr model alloy, a value of the vacancy concentration in the alloy must be determined. The method described in Sec. 2.2.2 was used to determine the parameters $R^*\left(\frac{1}{3}\right)$ and $\Delta\mu_{Ni}\left(\frac{1}{3}\right)$ on the temperature range between 950 and 1200 K. The results of these calculations are presented in Fig. 7a and b. The values of the ratio $R^*\left(\frac{1}{3}\right)$ are consistent with the Arrhenius expression

$$R^*\left(\frac{1}{3}\right) = R_0^* \exp\left[-\frac{E_R}{k_B T}\right] \quad (3.6)$$

where $R_0^* = 0.57$ and $E_R = 0.15$ eV. The values of $\Delta\mu_{Ni}\left(\frac{1}{3}\right)$ follow the form

$$\Delta\mu_{Ni}\left(\frac{1}{3}\right) = A + BT \quad (3.7)$$

with parameter values $A = -0.024$ eV and $B = -2.68 \times 10^{-5}$ eV/K. We have used these functional forms to extrapolate the value of the vacancy fraction to the temperature range where the disorder to order phase transformation occurs. This extrapolation from higher temperature was performed because the kinetics of the phase transformation are likely governed by the vacancy concentration in the solid solution phase, while direct evaluation by GCMC at low temperature would yield information only about the vacancy concentration in the ordered phase.

The ratio $C_{Vac}\left(\frac{1}{3}\right)/C_{Vac}(0)$ is equal to the product $R^*\left(\frac{1}{3}\right)\exp\left[-\frac{\Delta\mu_{Ni}\left(\frac{1}{3}\right)}{k_B T}\right]$, and from Eqns. 3.6 and

3.7 this ratio has a value between about 0.15 and 0.23 over the temperature range 950 to 1200 K. The vacancy concentration in the Ni-33Cr alloy is therefore predicted to be lower than in pure Ni. This result is in qualitative agreement with experimental diffusion measurements, which show that Ni and Cr diffusion coefficients decrease with increasing Cr concentration, down to a minimum near 30 at% Cr [44].

In order to complete the evaluation of the vacancy concentration in the Ni-33Cr alloy, the vacancy concentration in pure Ni must be established. We assume that this vacancy concentration can be described by the general form

$$C_{vac}(0) = \exp\left[\frac{-H_{vac}(0)}{k_B T}\right] \exp\left[\frac{S_{vac}(0)}{k_B}\right] \quad (3.8)$$

where $H_{vac}(0)$ and $S_{vac}(0)$ are the vacancy formation enthalpy and entropy in pure Ni. Suggested values of these parameters range from 1.55-1.8 eV [41, 42, 48-53] and from $1 - 5 k_B$ [42, 48, 51, 53], including both experimental measurements and theoretical calculations. Values of 1.6 eV and $1.1 k_B$ from within this range were chosen to yield the best model agreement with experimental measurements of ordering kinetics. It should be emphasized that this vacancy concentration corresponds to the Ni-Cr solid solution phase, and not to the vacancy concentration in the ordered phase. Given the more stable bonding which stabilizes the ordered phase it is likely that the vacancy concentration is somewhat lower in the ordered phase than in the solid solution phase. However, the transformation itself proceeds by vacancies in the disordered phase transforming the surrounding material into the ordered structure by a series of successive jumps. Thus, it is reasonable to suppose that the transformation kinetics are governed primarily by the vacancy concentration in the disordered phase, at least until the late stages of the transformation when there is little disordered material left.

3.5 Determination of the lattice parameters of the ordered and disordered phases

In order to relate the model predictions to experimental measurements of the change in lattice parameter as a function of aging time and temperature, the order parameter $S(t, T)$ must be related to a change in lattice parameter $\Delta a(t, T)$. As a first approximation, we assume that the lattice parameter changes linearly as the order parameter progresses from 0 to 1. In order to complete the model, lattice parameters of the disordered and ordered phases must be determined. This information cannot be obtained from the GCMC or KMC simulations, however the lattice parameters can be calculated directly via DFT. To best capture the lattice parameter of the disordered phase, the structure produced

by the GCMC simulations at 1000 °C was utilized. Because the GCMC simulation cell itself is far too large for a DFT calculation, several small cubic samples of this structure were carved out, each consisting of a 3×3×3 cubic fcc supercell and containing 108 atoms. The lattice parameters of these cubic sample cells were averaged to obtain the lattice parameter of the disordered phase. A supercell with the Ni₂Cr lattice arrangement of the same size and dimensions was used to determine the lattice parameter of the ordered phase. The cubic lattice parameters were calculated by first relaxing each of these supercells internally, then relaxing the volumes of the supercells without allowing the shape to change. By this method, the change in lattice parameter due to complete phase transformation from the disordered to the ordered structure was determined to be -0.26±0.02 %.

3.6 Comparison of model predictions to experimental measurement

The complete first principles-based model can now be constructed, and the results compared directly to experimental measurements of the change in lattice parameter, a , as a function of time and aging temperature. The complete model may be expressed as follows:

$$\Delta a(t, T) = \Delta a_{D \rightarrow O} \left[1 - \exp \left[- (k(T) t)^n \right] \right]$$

$$k(T) = k_{eff} \exp \left[- \frac{Q_{eff}}{k_B T} \right] \quad (3.9)$$

where Q_{eff} and k_{eff} are the effective preexponential factor and activation energy of the ordering reaction, defined as follows:

$$Q_{eff} = H_{vac}(0) + E_R + A + Q_{mig}$$

$$k_{eff} = k_0 R_0^* \exp \left[\frac{S_{vac}(0) - B}{k_B} \right] \quad (3.10)$$

The descriptions and values of the parameters in Eqns. 3.9 and 3.10 are summarized in Table 2.

Fig. 8 presents experimental measurements and model calculations of the change in lattice parameter in a Ni-33Cr alloy as a function of time during aging at temperatures between 333 °C and 470 °C (measurements of Marucco [8] taken at 475 °C). The data points represent experimental

measurements generated in this study as well as data available from the literature [6, 8], while the solid lines depict the results of the model. The error bars in on the experimental data generated in this study represent a range of one standard deviation on the individual measurements, computed using a pooled variance estimate across replicate as-fabricated specimens from the various buttons.

Reasonable agreement between the model and experiment is observed for temperatures above 373 °C, and for aging times longer than 100 hours. For shorter aging times, there is some experimental evidence of a small lattice contraction that is not captured by the model. This initial decrease in lattice parameter may be due to the population of excess vacancies present in the alloy after quenching from the annealing temperature. These vacancies would temporarily accelerate the transformation until they have been annealed out. Notably, the smallest early decrease in lattice parameter is observed in the data of Marucco [8], who heat treated specimens at 700 °C before quenching. Presumably, this would result in a much smaller population of excess vacancies compared to the present study and the study of Karmazin, in which heat treatments were performed at 1000 °C or above [6].

At 333 and 373 °C, the model predicts that there should be no significant change in the lattice parameter before 3,000 hours, in broad qualitative agreement with experimental measurements at these temperatures. While there is some measured change in lattice parameter at these temperatures, it is minor and does not follow a discernible consistent trend of increasing lattice contraction with longer aging. At 373 °C, the model predicts that a modest degree of lattice contraction will occur by 10,000 hours, in qualitative agreement with the experimental data, though the predicted lattice contraction is less than the measured amount. The model predicts that no significant lattice contraction will occur by 10,000 hours at 333 °C, although a very small contraction is measured for this aging condition. This measured lattice contraction is not significantly different from measurements taken after shorter aging times at 333 °C, and therefore does not appear to indicate that a significant degree of ordering transformation has yet occurred.

A notable discrepancy exists between the model predictions and many experimental measurements for lattice contractions larger in magnitude than about 0.2 %. This discrepancy may be

attributed to the difference between the predicted value for the maximum change in lattice parameter and experimental measurement: the DFT calculations predict a change of -0.26 ± 0.02 %, while in most cases the observed lattice contraction does not exceed about -0.24 % [6, 8]. Aside from DFT error in the lattice parameters, one other possible reason for this discrepancy is that complete ordering is typically not achieved experimentally. In a real alloy, as ordered domains grow they interact with nearby domains elastically due to misfit strains at the order-disorder interface, and this interaction impedes further growth. Consequently some small phase fraction of disordered material remains [7] and the change in lattice parameter saturates at a value smaller in magnitude than the maximum theoretical value. These elastic effects are not included in the present modeling framework, and thus there is no such impediment to full ordering in the simulated alloy.

From Fig. 8 we conclude that the model developed here presents a qualitatively accurate description of the ordering transformation between $420 - 470$ °C, however at lower temperatures the transformation may occur faster than predicted. Additional aging data is necessary to fully assess the model accuracy at the lower temperatures. At temperatures relevant to PWR conditions (about 330 °C), the model predictions in Fig. 8 indicate that while extensive ordering should not occur on the timescale of service lifetimes (40-80 years), the initiation of the ordering transformation will occur during this window.

3.6 Limitations of the first principles-based KJMA model

The model developed here has four main limitations. First, the effects of misfit strain between the ordered and disordered phases are not included. Any impact that this might have on the size or morphology of ordered domains in the real alloy will therefore not be manifested in the simulated alloy. This may contribute to the small overestimation of the maximum predicted change in lattice parameter with respect to most changes measured experimentally. Second, the KJMA model contains only a single kinetic term describing the ordering rate due to atomic migration. It is therefore only valid for conditions of sufficient undercooling that nucleation of the ordered phase is homogeneous and transformation is rate-limited by atomic migration, and not nucleation rate, i.e., below the “nose”

of the transformation diagram. The KMC simulation results discussed above indicate that this approximation is reasonable over the temperature range investigated here. Furthermore, TEM characterization reveals that nucleation is homogenous at temperatures below 500 °C [6, 7]. Above this temperature the assumptions of this model are not valid. Third, the model predictions are strongly dependent upon the vacancy concentration, and changes on the order of 100 meV in the vacancy formation energy can lead to differences of factors of 5-10 in the model predictions. While the values for this parameter used in the model are consistent with available experimental data, a precise determination of the vacancy concentration in the Ni-33Cr alloy is highly desirable to further validate the model. Furthermore, the model neglects the possible effects of excess vacancies that arise from water quenching or cold working. Finally, the simulation crystal is highly idealized with respect to the real material, and it contains no grain boundaries, dislocations, or other material defects. While these features can sometimes alter atomic migration mechanisms or provide nucleation sites for ordered domains, the experimental evidence of homogeneous nucleation suggests that the ideal, defect free crystal is a reasonable approximation of the real system, at least below 500 °C.

4 Conclusions

In this study, a first principles-based atomistic modeling framework has been developed for studying the disorder-order phase transformation in the Ni-33Cr model alloy. The alloy energetics are obtained via density functional theory calculations, which are used to construct a cluster expansion Hamiltonian. This Hamiltonian is then leveraged by grand canonical and kinetic Monte Carlo methods to simulate both the thermodynamic and kinetic aspects of the phase transformation. Based upon the results of these simulations, a Kolmogorov-Johnson-Mehl-Avrami model was assembled that allows a direct comparison to experimental measurements of the change in lattice parameter in a Ni-33Cr model alloy arising from the disorder-order phase transformation. The model exhibits reasonable agreement with experimental data available in the literature below 500 °C, as well as new data generated in this study at 418 and 470 °C. Additional long-time, low-temperature data are desirable to assess the accuracy of the model at lower temperatures.

The predictions of the model developed in this study indicate that while complete transformation should not occur in the Ni-33Cr model alloy at operating temperatures during 40-80 year service lifetimes of PWRs, the early stages of the ordering transformation will occur on this timescale. There is some experimental evidence that even a small degree of ordering may have a significant impact on susceptibility to hydrogen embrittlement [4], and that the maximum embrittlement may occur well before the ordering transformation has completed [3]. Furthermore, experimental measurements at 373 °C indicate that the ordering transformation may occur even faster at low temperatures than predicted by the model developed here. Therefore, this result suggests that ordering cannot be readily dismissed as a long-term concern in near-stoichiometric Ni-Cr alloys in PWRs. However, many engineering alloys of interest are far from the Ni₂Cr stoichiometry and contain other alloying constituents such as Fe, which appears to delay the ordering transformation or prohibit it altogether [7, 8, 10]. Further study is therefore warranted on the effects of alloy composition on the order-disorder transformation kinetics, particularly near PWR operating temperatures where there is no experimental data available.

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Captions:

Figure 1: Two bct unit cells of the Ni_2Cr ordered structure side by side along the [100] direction. Cr atoms are rust colored, while Ni atoms are silver. The inscribed cubic cell demonstrates how the ordered structure is mapped to the fcc lattice of the Ni-Cr solid solution phase. Image created using VESTA [54].

Figure 2: Comparison of cluster expansion predictions and DFT calculations of formation energies for all structures included in the Ni-Cr cluster expansion, as a function of at % Cr. The dashed lines represent the convex hulls of energies for the DFT values and the cluster expansion predictions.

Figure 3: Grand canonical energy and ordered fraction as functions of temperature, determined via GCMC for the simulated Ni-33Cr alloy.

Figure 4: KMC simulation results for order parameter $S(t, T)$ as a function of time, at 4 different temperatures. Solid lines are the best-fit KJMA model to the simulation data.

Figure 5: Structures resulting from KMC simulations of 5 (row a), 10 (row b), 20 (row c), and 50 (row d) MC steps per lattice site, at 3 different temperatures. Images created using VESTA [54].

Figure 6: Measurements of the order parameter $S(t, T)$ from the simulated structures illustrated in Fig. 5, along with the corresponding predictions of Eqn. 3.1. The lettered data points correspond to the rows of images in Fig. 5.

Figure 7a (left): Ratio $R^*(\frac{1}{3})$ determined from GCMC simulations. b (right): chemical potential difference $\Delta\mu_{\text{Ni}}(\frac{1}{3})$ determined from thermodynamic integration of GCMC simulations in the Ni-Cr binary system.

Figure 8: Change in lattice parameter of a Ni-33Cr model alloy as a function of time as measured experimentally, and corresponding predictions of the first-principles based model.

Table 1: ECIs in the Ni-Cr-Vacancy cluster expansion Hamiltonian for formation energies referenced to pure fcc phases. The Ni-Cr and Cr-Vac basis functions are in the occupation basis.

Table 2: Parameter definitions and values for the complete first principles-based model.

Table 1

Designation α	Basis Function ϕ_α	Number of sites in basis function	Max Length (Å)	Multiplicity m_α	ECI V_α (meV)	ECI/multiplicity v_α (meV)
0	Empty	0	0	1	-3	-3
1-1	σ_{Cr}	1	0	1	-141	-141
2-1	$\sigma_{Cr}\sigma_{Vac}$	2	2.51	12	643	54
2-2	$\sigma_{Cr}\sigma_{Cr}$	2	2.51	6	304	51
2-3	$\sigma_{Cr}\sigma_{Vac}$	2	3.55	6	136	23
2-4	$\sigma_{Cr}\sigma_{Cr}$	2	3.55	3	-266	-89
2-5	$\sigma_{Cr}\sigma_{Cr}$	2	4.35	12	-847	-71
3-1	$\sigma_{Cr}\sigma_{Cr}\sigma_{Vac}$	3	2.51	24	-907	-38
3-2	$\sigma_{Cr}\sigma_{Cr}\sigma_{Cr}$	3	4.35	24	938	39
3-3	$\sigma_{Cr}\sigma_{Cr}\sigma_{Cr}$	3	4.35	24	806	34
4-1	$\sigma_{Cr}\sigma_{Cr}\sigma_{Cr}\sigma_{Cr}$	4	3.55	12	-789	-66

Table 2

Symbol	Description	Value	Source
$\Delta a_{D \rightarrow O}$	Maximum lattice change	-0.26 %	DFT + GCMC
n	Avrami exponent	1	Fit of Eqn. 2.1 to KMC data
$k(T)$	KJMA kinetic coefficient		Eqn. 3.9b
Q_{eff}	Effective activation energy	2.62 eV	Eqn. 3.10a
k_{eff}	Effective preexponential factor	4.3×10^{11} Hz	Eqn 3.10b
$H_{vac}(0)$	Pure Ni vacancy formation enthalpy	1.6 eV	Best fit within range of experiments
E_R	Activation energy from Arrhenius fit to $R^*(\frac{1}{3})$	0.15 eV	Fit of Eqn. 3.6 to GCMC results
A	Intercept from linear fit to $\Delta\mu_{Ni}(\frac{1}{3})$	-0.024 eV	Fit of Eqn. 3.7 to GCMC results
Q_{mig}	Atomic migration component of the ordering activation energy	0.9 eV	Fit of Eqn. 2.1 to KMC data
$S_{vac}(0)$	Pure Ni vacancy formation entropy	1.1 k _B	Best fit within range of experiments
k_0	KJMA preexponential factor	2.04×10^{11} Hz	Fit of Eqn. 2.1 to KMC data
R_0^*	Preexponential factor from Arrhenius fit to $R^*(\frac{1}{3})$	0.57	Fit of Eqn. 3.6 to GCMC results
B	Slope from linear fit to $\Delta\mu_{Ni}(\frac{1}{3})$	-2.68×10^{-5} eV/K	Fit of Eqn. 3.7 to GCMC results