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Atomistic modeling of the order–disorder phase transformation in the Ni_2Cr model alloy

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Abstract

Mechanical property degradation due to the disorder–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, a 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.

Keywords: 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 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 ~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 $MoPt_2$ prototype in the *Immm* space group [1]. This structure is depicted in Fig. 1, along with an inscribed face-centered cubic (fcc) unit cell demonstrating how the

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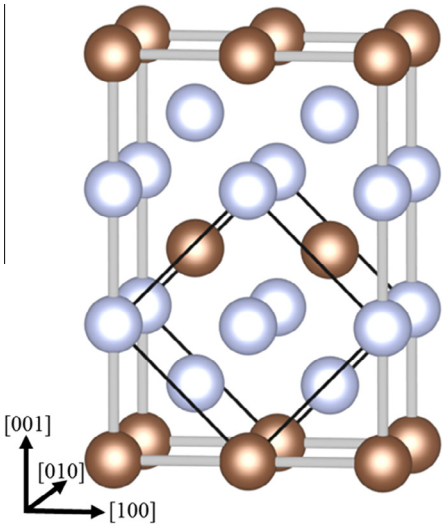

Fig. 1. Two body-centered tetragonal unit cells of the Ni_2Cr ordered structure side by side along the [1 0 0] direction. Cr atoms are rust colored, while Ni atoms are silver. The inscribed cubic cell demonstrates how the ordered structure is mapped to the fcc lattice of the Ni–Cr solid solution phase. Image created using VESTA [54]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ordered structure maps onto the parent fcc lattice. With respect to the fcc lattice, the ordered structure may be thought of as alternating {1 1 0} planes in a pattern of two planes of Ni atoms for everyone 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 are 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 1000 h 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^{-1} (~1–2 eV per atom), and a variation of only 10 kJ mol^{-1} (0.10 eV per 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^{-1}, depending on the value of the athermal pre-exponential term. However, at 325 °C, this same range in model parameters results in predicted ordering times spanning ~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 first-principles model for ordering in the Ni–33Cr alloy. 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