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Phase behavior and mechanical properties of Ni–W studied by first-principles calculations and ab initio based thermodynamics

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Abstract

The substitutional ordering phenomena of face-centered cubic Ni-rich Ni–W alloys are investigated by means of cluster-expansion Hamiltonians based on density functional theory calculations. We observe a strong tendency for ordering in Ni–W characterized by the formation of tungsten chains along the $\langle 100 \rangle$ direction. While previous studies only report a $D1_a$-type compound at a stoichiometry of Ni_4W with this $\langle 100 \rangle$-ordering tendency, we predict that within the solubility range of tungsten in nickel, structures with tungsten $\langle 100 \rangle$-chains are the predominant form of short-range order even at elevated temperatures. In particular, we find a Pt_8Ti-structured compound (which also shows this $\langle 100 \rangle$-ordering) to be stable in Ni–W at low temperatures and low tungsten contents. Even at high temperatures, Ni–W solid solutions are found to exhibit strong remnant order. The implications of these findings are discussed from a metallurgical perspective with an emphasis on the stiffening effect of tungsten alloying on Ni-rich matrices. Using these insights on the short-range order, we then determine a parametrization of the composition-dependent stiffening $\overline{c_{ij}}(x_W)$ and $\partial\overline{c_{ij}}/\partial x_W$.

Keywords: Cluster expansion; Nickel-tungsten; Density functional theory; Elastic properties; Thermodynamics

1. Introduction

While not as potent in its toughening as pure rhenium, tungsten is still a prototypical superalloy strengthener and certainly a useful and widely used ingredient in many modern alloy compositions [1]. Furthermore, as of 2013, no publication directly supplies the elastic stiffness coefficients $\overline{c_{ij}}(x)$ of Ni–W as function of the tungsten content x_W.[1] One of the major obstacles is that the growth of large single-crystalline Ni–W shards is problematic, partly due to the shape of the liquidus/solidus curves [2]. The growth of specimens large enough to perform bending or ultrasonic measurements to obtain elastic tensors is nearly impossible and data sets on Ni–W are exceptionally sparse, i.e. completely lacking in most major databases (cf. [3]). Calculating the elastic tensor and/or the compliance tensor from first principles is of course conceptually possible. However, the formation of low-temperature structures in Ni-rich Ni–W is largely driven by the peculiar electronic structure of face-centered cubic (fcc) nickel [4] and the resulting ground-state line is potentially complex. Using the wrong superstructure representation for an alloy will almost certainly lead to an elastic tensor that is too soft [5].

Although some valid concerns about the W-rich part of the Ni–W phase diagram were recently raised by Cury et al. [6], the Ni-rich part of the phase diagram is well accepted. While tungsten itself is unstable in the fcc lattice [7], it can

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[1] It is implicitly understood that all concentrations given in this work are given in atomic per cent, and all fractions are molar fractions, not weight or volume fractions.

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dissolve in appreciable molar fractions in the fcc-based matrices of γ-Ni or γ'-Ni$_3$Al phases (cf. ternary phase diagram in Ref. [8]). In the presence of tantalum, tungsten tends to partition primarily into the fcc-based Ni-rich matrix and not in the $L1_2$ structured $\gamma\prime$-precipitates [1], which opens the door for ab initio studies of binary Ni–W without having to include γ'-forming elements such as Al, Ta or Ti in the density functional theory (DFT) supercells.

Exploiting these fortunate circumstances, we have performed exhaustive ground-state searches within the fcc configuration space using the cluster-expansion (CE) method with first-principles input structures (cf. Section 2). The methodology used to identify the most stable structures will be described in Section 3 of this paper, while Section 4 will be dedicated to the ground-state compounds revealed in the process.

To ensure the reliability of the Hamiltonian for describing the correct ordering in single-crystalline Ni–W specimen, we have used the CE Hamiltonian and have subjected it to a (canonical) simulated annealing procedure at variable temperature; the resulting order can be directly compared to measurements of the Ni–W short-range order in a single crystalline Ni$_{92}$W$_8$ shard published in reference [4]. Then, using grand canonical Monte-Carlo simulations based on this Hamiltonian, an approximate phase diagram was calculated, which will be presented in Section 5, along with a detailed discussion of the composition dependent short-range order.

With the correct order known from the ground-state configurations deduced from the CE Hamiltonian, we were able to compute the averaged elastic tensors $\overline{c_{ij}}(\sigma)$ as a function of the atomic configuration σ and hence as a function of the tungsten content x_W. From this data, a parametrization of the composition-dependent stiffening $\overline{c_{ij}}(x)$ and $\partial\overline{c_{ij}}/\partial x_\mathrm{W}$ of tungsten alloying to a Ni-rich matrix was deduced (see Section 6).

2. First-principles methodology

A grand-total of 90 fcc-based structures in a concentration range $0 \leq x_\mathrm{W} \leq 33\%$ have been fully relaxed in two steps with the Vienna Ab initio Simulation Package (VASP) [9,10] using the PBE approximation [11] as implemented in the standard GGA-PAW potentials [12,13] supplied with VASP. These 90 structures have been selected with the help of the cluster expansion code UNCLE [14] in an iterative process that is elaborated in more detail in the next Section 3.

In order to compute the stiffness coefficients $\overline{c_{ij}}$ of these supercells in a later part of this paper, both the electronic and ionic structures of all structures were required to relax with the highest accuracy. However, increased energy cutoffs of 420 eV and relaxation criteria of $5 \cdot 10^{-6}$ eV for the electronic and 10^{-5} eV for the ionic structure have proven to be sufficient to obtain converged stress tensors and hence reasonable estimates for the elastic properties. For convergence reasons, the usual Methfessel–Paxton smearing [15] has been employed for integrations within the Brillouin zone, where a smearing width of 0.18 eV was found to yield numerically stable total energies. All calculations have been performed fully spin-polarized.

The choice of an appropriate k-mesh has proven critical. The best results were obtained using Γ-centered k-meshes with an excessively large number of k-points, especially for smaller unit cells, which frequently required $23 \times 23 \times 23$ k-points before absolute convergence was reached. Ultimately, careful convergence tests had to be carried out and the number of k-points have been set for each structure individually.

The resulting converged total energies of the aforementioned 90 fully relaxed structures make up the input database for the cluster expansion. Some of these structures, in particular structures that were confirmed to be ground states (see Section 4) were subjected to a finite-distortion scheme [16,17] using a four-point displacement method as implemented in VASP to obtain their respective elastic properties.

3. Cluster-expansion and Monte-Carlo methodology

Using the first-principles data set of 90 fully relaxed fcc-based structures and their respective total energies plus the body-centered cubic (bcc) tungsten reference, we have performed a CE [18,19] employing the UNCLE code [14]. The CE is a mathematical formalism which represents a quantity that is strictly a function of the atomic arrangement σ (such as the energy E) on a lattice as a sum over correlation functions $\overline{\Pi}_F(\sigma)$ times some expansion coefficients J_F. In this case, the heat of formation ΔH_f was expanded for binary structures σ containing x_Ni nickel and x_W tungsten. For this particular problem, the CE expands ΔH_f as

$$\begin{aligned}\Delta H_\mathrm{f}(\sigma) &= -x_\mathrm{Ni}E_\mathrm{Ni} - x_\mathrm{W}E_\mathrm{W} + E(\sigma)\\ &= -x_\mathrm{Ni}E_\mathrm{Ni} - x_\mathrm{W}E_\mathrm{W} + \sum_F J_F\overline{\Pi}_F(\sigma). \qquad (1)\end{aligned}$$

The basis functions of the cluster expansion are n-point correlations $\overline{\Pi}_F(\sigma)$, which correspond to different n-body interactions F. The prefactors J_F in the Hamiltonian Eq. (1) can be understood as effective interaction strengths of the respective many-body interactions. In this work, these expansion coefficients J_F are fitted to first-principles total energies, which can be repeated iteratively, each iteration yielding a preliminary Hamiltonian. After each step, the latest preliminary Hamiltonian can then be used to suggest a new set of low-energy structures to be relaxed and added to the input set. This approach essentially guarantees an enrichment of input structures near the ground-state line as the Hamiltonians increase in quality. For more details on this procedure, see e.g. Ref. [20], in which a similar ansatz was employed and explained in more detail.

The reference energies for the pure elements E_Ni and E_W required in Eq. (1) were obtained by calculating the total