Discovering chemical site occupancy- modulus correlations in Ni based intermetallics via statistical learning methods

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ABSTRACT

We show how one may extract spectral features from the density of states (DOS) of $L1_2$-Ni_3Al alloys that can serve as signatures or electronic "fingerprints" which capture the correlation between site occupancy of dopants and elastic properties. Based on this correlation, we have developed a computational approach for rapidly identifying the impact of the selection of dopant chemistries on bulk moduli of intermetallics. Our results show for example that Cr preferentially occupies the Al site in Ni_3Al which is confirmed by scanning transmission electron microscopy (STEM) energy dispersed X-ray spectroscopy (EDS) analysis. We further show that this preference is due to a sensitivity of Cr to the DOS at −1.7 and 0.2 eV relative to the Fermi energy. In terms of similarity in chemistry-property correlations, we find Cr has a similar effect to Ce when occupying an Al site, while Cr occupying a Ni site has similar correlation as La on a Ni site. This logic can be utilized in targeted design of new alloy chemistries based on similar property correlations and for targeted DOS modification.

1. Introduction

In this paper, we extract the signatures of the DOS spectra which dictate the elastic moduli of alloys. Further, the DOS signatures of alloying site preference are identified, with the focus here on Ni-based alloys. In our previous work, we developed the relationship between the chemistry and crystal structure and the DOS signatures based on the characteristics of the elemental constituents [1–3]. Combining these threads, we are able to accelerate the chemical design of multicomponent systems for targeted properties by developing chemistry-electronic structure-property relationships, thereby reducing the number of electronic structure calculations required by rapidly screening the enormous chemical search space.

Nickel-based superalloys, which are of interest for their high-temperature behavior, have two phases present: γ-Ni matrix and γ′-Ni_3Al. The Ni_3Al phase has an $L1_2$ structure with Al at the corners and Ni at the face centers, and is the principal reason for the high temperature strength of superalloys due to the yield stress anomaly, where the yield stress increases with increasing temperature up to a limit [4]. Different alloying elements can modify the elastic properties of Ni_3Al [5–7], with

the superalloys having a complex composition with generally around 10 alloying elements. It is important to investigate the alloying behavior of the different elements in terms of their site-preference and elastic properties. A method for predicting site preference of a dopant atom in this Ni_3Al phase was suggested by Ruban and Skriver [8], based on the energy change of moving an atom X from a Ni site to an Al site ($E_X^{Ni \to Al}$). Later, Gleeson et al. [9] showed that this single parameter $E_X^{Ni \to Al}$ can be used to predict the site preference of a dopant atom. This parameter has been studied for many transition elements [7–10]. This method assumes the Wagner-Schottky model to be true [11] according to which the formation enthalpy of the ternary alloy Ni-Al-X is a linear function of the formation enthalpy of Ni_3Al and that of the point defect.

$$\Delta H = \Delta H_{Ni_3Al} + \sum_d H_d x_d \qquad [1]$$

Here d is the point defect under consideration, and x_d its atomic concentration. H_d is the formation enthalpy of the defect.

The energy change is defined as:

$$E_X^{Ni \to Al} = E(Ni_{24}Al_7X) + E(Ni_{23}AlAl_8) − E(Ni_{23}XAl_8) − E(Ni_{24}Al_8) \qquad [2]$$

When this quantity is negative, the atom preferentially occupies the Al site, while when it is positive the atom occupies either the Ni site or both sites. More precisely,

a) $E_X^{Ni \to Al} < 0$, X occupies Al site
b) $E_X^{Ni \to Al} > H_{AlNi} + H_{NiAl} = 1.12$ eV [7], X occupies Ni site
c) $0 < E_X^{Ni \to Al} < H_{AlNi} + H_{NiAl}$, X atoms can occupy both sites

Some dopants of interest for Ni_3Al include B for enhanced mechanical strength [12,13], Cr for improved oxidation resistance [4,13], and Ce for both better mechanical strength and oxidation resistance [12,14]. Zr provides strengthening and resistance to creep [15,16] and La has shown to improve resistance to oxidation and hot corrosion [13]. While it is established that Ce forms a second phase $CeNi_5$ at concentrations exceeding 0.63 wt% Ce [17], Ce addition contributes to the desired properties. However, it is a rare earth element and a challenge exists to replace Ce with a non-rare earth element while maintaining the desired properties. While Ce and Cr are substitutional, B occupies interstitial voids owing to its small size. As a result, the replacement of Ce with Cr and B for oxidation resistance and mechanical strength is not possible, due to their different site occupancies. This defines the challenge that is addressed by this paper, namely to assess the change in properties that result due to changes to both composition and site occupancy.

The following doping chemistries and sites discussed here are: undoped Ni_3Al, Ce, La, Cr and Zr doped on the Ni site, Ce, La, Cr and Zr doped on Al site, and B doped on tetrahedral interstitial and octahedral interstitial voids. Beyond the properties of interest, these chemistries were selected so that their additional differences such as size differences and periodic table groups are integrated into the informatics analysis. For each of these compounds, the electronic Density of States (DOS) and bulk modulus (B_m) were calculated via Density Functional Theory (DFT). An informatics analysis is then applied to the DOS spectra for assessing the possible compound chemistries that can exist, comparing behavior of different dopant chemistries, and linking dopant site occupancies with mechanical behavior. We have previously applied an informatics analysis to the DOS spectra [1–3], although those previous works did not consider site occupancies. Other approaches combining informatics algorithms with electronic structure calculations sought to accelerate the calculations so that data can be generated in a high-throughput manner, and to search for appropriate crystal structures or structure determination from the significantly increased knowledge-base [18–20]. An alternate informatics approach for predicting the bulk and shear moduli has recently been demonstrated by de Jong et al. [21,22], where a massive number of property values were predicted based on series of descriptors including formation energy, volume-per-atom, other elemental properties, and relative elemental positioning within the periodic table.

By employing the entire DOS spectra as we do here, the span of reversible property descriptors are theoretically included without any prior assumptions. As the DOS represents all electronic interactions of a system, it should contain information on all electronic properties [23–25]. However, the understanding of how these properties are captured by the DOS is not well understood. One example of a property which is known to be at least qualitatively represented within the DOS spectra is bulk modulus [26], where the difference between Fermi energy and antibonding-bonding transition correlates to B_m. Some physical explanation of the connection between B_m and DOS spectra can thus be provided, although it remains qualitative and limited. Building on this concept is one of the primary objectives in linking DOS spectra with an informatics approach. By contrast, we use informatics approaches to relate patterns in the DOS spectra to the bonding of alloy systems and the corresponding properties.

Cr has previously been shown to have an Al site preference via calculation of $E_X^{Ni - > Al}$ [5–10]. Calculation of this quantity for Ce substitution has not been reported. To predict this site occupancy, we must understand why Cr occupies the Al site and not the Ni site. In addition to assessing the calculations at 0 K, we perform experimental analysis of Ni_3Al-Cr to ensure that the modeling of site occupancy holds at higher temperatures. While the focus of this paper is limited to site preference, we also recognize that the concentration of defects is critical to consider since the properties discussed here are largely dependent on the final equilibrium state of the system. Future work will address this added layer of consideration by including chemical potentials to describe the thermodynamic interactions between the γ and γ' phases. This paper introduces an informatics driven approach for extracting previously undefined chemistry-electronic structure-property correlations, even though the systems considered have been extensively studied previously. We discuss how this added layer of information which is not available solely from the unprocessed DFT output allows us to accelerate the design of new Ni-base alloys for specific applications.

2. Methods

2.1. Density functional theory calculations

The supercell consisted of $2 \times 2 \times 2$ unit cells of Ni_3Al, shown in Fig. 1 (a). Cr, Zr, La and Ce dopants were placed in either the Al or Ni site (Fig. 1 (b) and (c)), while B was placed in the tetrahedral and octahedral void (Fig. 1c and (d)). Cr, Zr, La and Ce were varied with concentrations of 3.125 at%, 6.25 at% and 9.375 at%, which corresponds to 1, 2 and 3 dopant atoms substituting either Ni or Al site in Ni_3Al. For B, the concentration used was 3.03 at%. The concentrations were chosen keeping in mind the compositions used in superalloys [27].

The Vienna Ab initio Simulation Package (VASP) [28–31] was used to perform the density functional theory (DFT) calculations. The exchange-correlation functional by Perdew, Burke and Ernzerhof was employed within generalized gradient approximation (PBE-GGA) [32,33]. Projector Augmented Wave (PAW) scheme [34] was used to account for the core electrons, while the energy cut-off for the plane wave basis was chosen to be 350 eV, which was determined to be a suitable value. A Monkhorst-Pack [35] K-mesh of $6 \times 6 \times 6$ was used. All calculations were spin-polarized and the atoms were relaxed with a convergence criteria of 10^{-7} eV for energy and 10^{-3} eV/Å for the forces on atoms. The elastic constants were then extracted from the stress-strain relationship by straining the relaxed structures to obtain $\overline{C_{11}}$, $\overline{C_{12}}$, and $\overline{C_{44}}$, where $\overline{C_{11}} = (C_{11} + C_{22} + C_{33})/3$, $\overline{C_{12}} = (C_{12} + C_{13} + C_{23})/3$ and $\overline{C_{44}} = (C_{44} + C_{55} + C_{66})/3$. The convergence achieved was within an error bar of 8 GPa except in the case of Ce-doped Ni_3Al on the Ni-site where the error bar range is 10–15 GPa. Complete details of the elastic constant calculations and the convergence achieved are provided in our prior report [7]. The density of states (DOS) was calculated with the energy convergence criterion increased to 10^{-8} eV and a Monkhorst-Pack K-point mesh of $9 \times 9 \times 9$ for both pure and doped Ni_3Al systems. The Fermi-energy was shifted to 0 eV for all the calculations for consistency.

2.2. Informatics

To identify the underlying governing features within the DOS spectra, we employed the entire DOS spectra to quantitatively analyze the DOS without any prior assumptions by treating the DOS as spectral data, building on our prior work in analyzing spectral data [36,37]. We apply eigenvalue decomposition techniques such as principal component analysis (PCA) [36–41]. As we have demonstrated in our earlier studies [1–3,36–38], this permits one to identify the right projection of data from which meaningful features associated with the DOS can be identified. Partial Least Squares (PLS) were further applied to this high dimensional data space [42–50]. These were used in a predictive informatics mode to link the DOS spectra with elastic constants. By applying PCA to the DOS spectra, the strongest patterns in the data can be