



Full length article

# Energetics of cobalt alloys and compounds and solute–vacancy binding in fcc cobalt: A first–principles database



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## ABSTRACT

Using extensive first-principles density functional calculations, we calculate thermodynamic properties of binary fcc cobalt-based alloys with 25 different solute elements. For each solute element  $X$ , we calculate its (a) nearest- and next-nearest-neighbor solute–vacancy binding energy, (b) dilute impurity mixing energy with respect to the equilibrium and hypothetical fcc-based reference states of the solute, (c) enthalpy of formation of cobalt-rich binary ordered compounds in the Co– $X$  system, (d) solubility enthalpy, and other derived quantities. We find that the solute–vacancy binding energies of all the studied solutes in fcc cobalt are positive (indicating favorable binding), in contrast to nickel, aluminum, magnesium, and copper-based alloys, where mid  $3d$  transition metal solutes have unfavorable solute–vacancy binding. We study the physical and chemical effects influencing solute–vacancy binding energy, and find that (a) it correlates broadly with solute size—larger solute atoms possess stronger binding with vacancies—and this is understood in terms of strain relief and secondary next-nearest-neighbor interactions, and (b) it follows a parabolic trend as a function of  $d$ -occupancy across the transition metal series—falling to a minimum at the middle of the series—and this is understood in terms of a  $d$ -band filling effect. We also find this  $d$ -band filling effect in other calculated quantities such as the dilute impurity volumes and dilute impurity mixing energies. To aid in building thermodynamic databases, we tabulate all the calculated thermodynamic quantities, and compare them with experimental phase diagrams data and previous literature, and find good agreement where such data is available.

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## 1. Introduction

The field of superalloys (high-performance alloys) has received a spike in interest following the discovery of  $\gamma'$ –Co<sub>3</sub>(Al,W) precipitates with the L1<sub>2</sub> structure [1], promising a new class of Co-based high-temperature materials. These novel superalloys offer better oxidation, corrosion, and wear resistance and potentially higher operation temperatures compared to Ni-based superalloys [2,3]. Despite having some superior chemical and physical properties [1,4], alloys based on Co<sub>3</sub>(Al,W) suffer from several problems such as inferior high-temperature strength [5,6], a narrow  $\gamma + \gamma'$  two-phase region, and a low stacking fault energy [6]. Alloying additions are an effective way, at least in part, to overcome these problems and improve the mechanical properties of Co-based superalloys [3,5–10]. For example, the addition of Ta, Ti, Nb, Hf, or Ni [3,9–12] increases the stability and the stacking fault energy of

$\gamma'$ –Co<sub>3</sub>(Al,W) simultaneously, thus improving the high-temperature strength of the  $\gamma'$  phase and  $\gamma + \gamma'$  two-phase superalloys [12].

To understand the effects of alloying additions on diffusion in fcc cobalt, a detailed knowledge of the interaction between a solute atom and an accompanying vacancy (hereafter, a vacancy is indicated by  $\square$ ) is necessary [13–15]. The solute– $\square$  binding energy directly influences impurity diffusion. In an alloy with dilute solute concentrations, the solute– $\square$  binding energy controls the probability of having a vacancy at a lattice site neighboring a solute atom. Therefore, in a vacancy-mediated diffusion process, energetic binding between a solute atom and a vacancy is a key factor in the quantitative understanding of solute diffusion [13] and as well as other associated kinetic phenomena such as precipitate nucleation. For example, the observed decreased response to natural aging with microalloying additions (e.g., the behavior of Al–Cu alloys with the microalloying addition of Sn) could be understood in terms of vacancy trapping, due to a strong solute– $\square$  binding energy [13,14]. Despite its importance, this interaction is notoriously

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difficult to experimentally measure accurately [16] but can be readily calculated using first-principles electronic structure methods such as density functional theory (DFT) [14,15,17,18]. To our knowledge no such calculations exist for Co-based alloys.

In addition to kinetic phenomena, the thermodynamics of alloying behavior is also critically important in the design of new Co-based alloys. Among the computational tools available today for studying thermodynamic phase stability in alloys, calculation of phase diagrams (CALPHAD) methods are one of the most widely used [19–21]. These methods use databases of thermodynamic functions, and can accurately calculate phase diagrams of multi-component alloys. While CALPHAD methods have been successfully applied over the years to many commercial alloy systems and databases (e.g., Al-based alloys, Fe-based alloys), mature databases for similar efforts in developing Co-based superalloys are not currently available [22]. In cases where experimental data is unavailable, DFT calculations can provide a wealth of energetic and thermodynamic information (e.g., mixing energies of solid solutions, formation energies of ordered compounds, etc.) [23,24] that significantly complement CALPHAD approaches. Thus, an extensive first-principles investigation of thermodynamics in cobalt alloys would greatly accelerate the development of CALPHAD databases, and ultimately, the design of new Co-based superalloys.

In the present work, the solute–□ binding energy, dilute mixing energy, dilute volume of mixing, compound formation energy, and solubility enthalpy of 25 substitutional solutes in fcc cobalt are calculated using DFT. We include all of the alloying elements used in Co-based superalloys [6] which consist of almost all 3d, 4d, and 5d transition metal elements — except groups 3 and 12 — together with silicon and aluminum. Some of the alloying elements considered, such as technetium and silver, may have no practical interest but provide useful data that serves to find systematic trends across the periodic table. We analyze the results of our calculations to search for the key physical effects that influence solute–□ binding, such as *d*-occupancy, solute size, and second nearest-neighbor interactions. Finally, in an effort to aid in building thermodynamic databases, we tabulate all the calculated thermodynamic properties and compare them with experimental phase diagrams data, where available.

## 2. Methodology

### 2.1. Density functional theory

For calculations in the present work, we used plane-wave DFT with projector-augmented plane-wave (PAW) method [25,26] as implemented in Vienna Ab-initio Simulation Package (VASP) [27,28]. The exchange-correlation energy functional was described with the spin-polarized generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [29]. We used the PAW potentials recommended by VASP, with a plane wave cutoff energy 1.3 times the maximum energy cutoff (“ENMAX”) listed in the PAW potentials for each system. We verified the convergence of the calculated quantities with respect to the plane wave cutoff energy by calculating all energies at a constant large cutoff of 520 eV — and found that the change in the solute–□ binding energies was negligible (<0.2%). We relaxed all structures fully, with respect to cell lattice vectors and atomic positions, by minimizing the energy until the Hellmann-Feynman forces on all atoms were less than 0.01 eV/Å, and stresses on the cell were a few kbar or less. We then used this relaxed structure for a final “static” self-consistent run to calculate the total energy. Therefore, all calculations were relaxed under constant zero pressure.

We utilized a periodic supercell in which one host atom is replaced with either a solute or a vacancy to approximate dilute

limits. As discussed in Ref. [15], a large size mismatch between the solute/defect and the host atoms can result in elastic strain on nearby atoms, in addition to spurious defect-defect interaction due to periodic boundary conditions, and minimizing this interaction requires very large supercells. Here, we found that a 108-atom supercell consisting of  $3 \times 3 \times 3$  cubic conventional cells, which separates impurity atoms by  $\approx 11$  Å, results in solute–□ binding energies converged to within 1 meV/solute atom. We performed integrations over the Brillouin zone of the 108-atom supercell using the first-order Methfessel-Paxton [30] approach with a smearing width of 0.2 eV and a  $3 \times 3 \times 3$  Monkhorst-Pack [31] k-mesh during structural relaxation, and the tetrahedron method with Blöchl [32] corrections and a  $4 \times 4 \times 4$  Monkhorst-Pack k-mesh during the final static calculation for accurate total energies.

### 2.2. Calculation of energetic quantities

We calculate the energetics of solute–□ ( $X$ –□) binding for various pair spacings (e.g., nearest and second-nearest neighbors). The binding energy  $E_{\text{bind}}$  is defined as the difference between the energy of “infinite separation” and nearest-neighbor (or second-nearest-neighbor) separation of the solute and the vacancy. We calculated this difference using four independent calculations as follows:

$$-E_{\text{bind}}(X - \square) = \frac{(E(\text{Co}_N) - E(\text{Co}_{N-1}\square_1)) - (E(\text{Co}_{N-1}X_1) - E(\text{Co}_{N-2}X_1\square_1))}{1} \quad (1)$$

where  $X$  and  $\square$  represent a solute and vacancy respectively, embedded in an  $N = 108$ -atom supercell. The two groups of terms on the right side of Eq. (1) represent the energy required to break a host-host bond (first term) and a host-impurity bond (second term) due to the introduction of a vacancy. Thus, the solute–□ binding energy can be qualitatively understood as the difference between the host-impurity and host-host bond energies. In other words, if the host-impurity (Co- $X$ ) interaction is weaker than the host-host (Co-Co) interaction, a favorable solute–□ binding can be expected. The negative sign of  $E_{\text{bind}}$  in Eq. (1) is included to follow standard convention: a positive value corresponds to a favorable binding between the solute and the vacancy.

By having all the four energy terms on the right side of Eq. (1), one can easily calculate as a “by-product”, the vacancy formation energy in fcc cobalt:

$$E_{\text{vac}}(\square) = E(\text{Co}_{N-1}\square_1) - \frac{N-1}{N}E(\text{Co}_N) \quad (2)$$

Similarly, the dilute impurity mixing energy of a solute  $X$  in fcc cobalt is also readily obtained using:

$$E_{\text{imp}}(X) = E(\text{Co}_{N-1}X_1) - \frac{N-1}{N}E(\text{Co}_N) - E(X) \quad (3)$$

where  $E_{\text{imp}}(X)$  is calculated for both  $X$  in the fcc ( $E^{\text{fcc}}(X)$ ) and its equilibrium crystal structure ( $E^{\text{eq}}(X)$ ).

In order to get a quantitative measure of the atomic size of each solute impurity,  $X$ , we also calculate the dilute volume of mixing (hereafter, simply “impurity volume”),  $V_{\text{imp}}^X$ , which is given by the difference in volume induced by substituting a single fcc cobalt atom with a solute atom:

$$V_{\text{imp}}^X = V(\text{Co}_{N-1}X_1) - V(\text{Co}_N) \quad (4)$$

We note here that after adding a solute atom to the fcc cobalt matrix, we fully relaxed the alloyed structure to its ground state; therefore, this definition of the impurity volume includes all

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