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Diffusion coefficients of transition metals in fcc cobalt



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ABSTRACT

Using first-principles density functional theory (DFT), we calculate the diffusivities of 32 different solute elements—all transition metals, together with Al and Si—in fcc cobalt within the formalism of the five-frequency model. For self-diffusion in fcc cobalt, we compare the accuracy of various approximations to the exchange-correlation energy functional of DFT in estimating the activation energy, and find that only the Perdew-Burke-Ernzerhof (PBE) approximation agrees well with experimental reports and all other functionals largely overestimate it. Our calculations also show that an accurate estimation of the self-diffusion coefficient requires explicit calculation of the effective jump frequency and vacancy formation entropy via phonons. Using accurate self-diffusion data and scaling all solute-related attempt frequencies with respect to the attempt frequency for self-diffusion using a simple relation involving the atomic mass and melting temperature of the solute yields solute diffusivities in excellent agreement with experiments, where such data is available. We find that large solutes spontaneously relax toward the nearest neighbor vacancy to relieve the misfit strain, and the extent of this relaxation correlates negatively with the migration energy. Thus, in general, larger solutes have lower migration energies and diffuse faster than smaller solutes in fcc cobalt. However, extremely large solutes, e.g., group III elements Sc, Y, Lu, tend to be trapped in an energy valley located halfway toward the vacancy, and monovacancy mediated diffusion may no longer be valid in such cases. Finally, for all the solutes considered, we systematically tabulate the diffusion-related quantities calculated—diffusion prefactors, migration and activation energies—constructing an extensive and accurate first-principles database for solute diffusion in fcc cobalt.

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1. Introduction

The discovery of γ/γ' -Co₃(Al,W) precipitates with the L1₂ structure [1] has opened pathways to develop a new class of high-temperature fcc-based cobalt-based superalloys with performance potentially superior to those of traditional nickel-based ones. The cobalt alloys can offer about 150 °C higher solidus and liquidus temperatures than those of advanced nickel-based superalloys [1,2]. However, their practical application has not materialized due to limited mechanical properties and issues related to the narrow γ/γ' phase stability region [2–5]. Their properties continue to be improved via innovative processing techniques, microstructural modifications, and alloying additions [6,7]; all these techniques heavily depend on diffusional behavior of solute atoms in the fcc cobalt host alloy. Therefore, knowledge of diffusion of various solutes in fcc cobalt is crucial to understanding the

macroscale properties of cobalt superalloys, such as diffusional phase transformations, nucleation, creep resistance, recrystallization, homogenization of alloys, and thermal oxidation [6,8–12].

A database of diffusion related quantities such as impurity formation energies, solubilities, solute-vacancy binding energies, and diffusion coefficients of various solutes in the host alloy, and understanding various physical and chemical factors influencing these quantities is vital for the development and design of new alloys. Such data is available for many technologically important host alloys such as Al, Mg, Cu, and Ni [13–23]. While properties such as impurity formation energy and solute-vacancy binding energy for various solutes in fcc cobalt have recently been studied [24], similar work on diffusion coefficients has not been done. Recently, Neumeier et al. [25] measured the diffusion coefficients of 12 solutes in fcc cobalt, and also performed kinetic Monte Carlo based calculations for 4 of the solute elements considered.

In the present work, using density functional theory (DFT) based calculations, we calculate the diffusion coefficients of a large number of 32 solutes in fcc cobalt for dilute concentrations. The solutes consist of almost all 3d, 4d, and 5d transition metal (TM)

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elements, together with Al and Si. Only vacancy-mediated diffusion through nearest-neighbor hops, which is known to be the dominant diffusion mechanism in most fcc metals [26–29], is considered. The diffusion coefficients of all the dilute solutes in fcc cobalt were determined using the so-called five frequency model proposed by Lidiard and LeClaire [30–32]. This model has proven to be very accurate [13,16,22,23,33–36] in dilute limit when compared to techniques such as kinetic Monte Carlo [37] and molecular dynamics [38]. We analyze the results of our calculations to search for the key physical effects that influence the diffusion coefficients of solutes (D_s), solute activation energies (Q), and solute diffusion prefactors (D_s^0). We also pay special attention to self-diffusion in fcc cobalt focusing on the effect of different approximations to the exchange-correlation functional of DFT on the vacancy formation energy, migration energy, and self-diffusion activation energy (Q) in fcc cobalt, and identify Perdew–Burke–Ernzerhof (PBE) approximation provide the best agreement with experiment. We find that the migration energies for various solutes vary parabolically across a transition metal series, reaching an extremum at the middle of the series, correlating well with d -band filling. We analyze the effect of entropic contributions on the accuracy of the calculated diffusion coefficients and identify the approximation of Neumann and Hirschwald [39] to effective frequencies to be sufficiently accurate while being computationally relatively inexpensive compared to full phonon calculations. We also find that larger solutes spontaneously relax toward a neighboring vacancy to relieve misfit strain resulting in lower migration barriers and higher diffusivities when compared to smaller solutes.

We systematically tabulate all the calculated properties—migration energy for different jumps, activation energies, diffusion coefficients—in order to aid in developing Calculation of Phase Diagrams (CALPHAD) [40–42] type diffusion mobility databases, similar to the ones that exist for Mg [43] alloys and Ni-based superalloys [44]. We hope our extensive first-principles diffusion coefficients data for solutes in fcc cobalt will greatly accelerate the development and design of new cobalt-based superalloys.

2. Computational methods

For calculations in the present work, we used the projector-augmented wave (PAW) method [45,46] as implemented in the Vienna Ab-initio Simulation Package (VASP) [47,48]. Throughout the calculations, the plane-wave cutoff energy was set to a constant value of 520 eV. The exchange-correlation energy functional was described with the spin-polarized generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) [49], unless specified otherwise. All structures were fully relaxed with respect to lattice vectors and atomic positions by minimizing the energy until the Hellmann–Feynman forces on all atoms were less than $0.01 \text{ eV } \text{Å}^{-1}$, and stresses on the cell were less than 1 kbar. The Climbing Image Nudged Elastic Band (CI–NEB) as implemented in the VTST package [50,51] was used for the calculation of migration barriers. Lattice dynamics calculations were performed using VASP and the results were analyzed using the Phonopy package [52].

We tested the convergence of calculated migration barriers with respect to the size of the supercell and the number of images along the diffusion pathway used for NEB calculations. First, we compared the calculated barriers for various jumps using a $2 \times 2 \times 2$ (with number of atoms $N = 32$) and $3 \times 3 \times 3$ ($N = 108$) supercells consisting of $N - 2$ cobalt atoms, and one solute atom with a nearest neighbor vacancy. We found that for most of the studied solutes the barriers calculated by the 32-atom supercell stay within 5% of those calculated by the 108-atom cell. Nevertheless, in the

case of E_m^3 (migration energy corresponding to the vacancy jump dissociating the solute–vacancy pair, see ω_3 in Fig. 3) of large solutes (i.e., group III and IV) the difference can be significant (e.g., 0.6 eV for Zr). Therefore, we conducted further size convergence tests using 32-, 64-, 108-, and 256-atom supercells (see Fig. S5 in the supplementary information). The results demonstrate that the calculated barriers with the 108-atom cell are converged to within 0.03 eV, thus we assert that the 108-atom supercell is sufficiently converged for all barrier calculations in this paper. Regarding the number of images required along the diffusion pathway for NEB calculations, previous studies [16,17,23] have demonstrated that due to the simple energy landscape of fcc metals, a single image is sufficient to calculate the energy barrier accurately. Nonetheless, we calculated the various jump barriers for an Al solute atom in the 108-atom unit cell using up to 5 images. Consistent with previous studies [23,35,53], we find that for the different jumps shown in Fig. 2, a single image is sufficiently accurate (migration energies within 0.01 eV of those calculated with 5 images) to determine the migration barriers. Thus, we use a single intermediate image for calculating all migration barriers in the 108-atom supercell for all solutes. Details of the convergence tests can be found in the Supplementary Information.

3. Results and discussions

In this section, we first discuss self-diffusion in fcc cobalt, briefly describing the formalism, and focusing on how different levels of approximation—different approximations to the exchange-correlation functional of DFT and explicitly calculating entropic contributions—affect the activation energy and the diffusion prefactor. Next, we extend this discussion to impurity diffusion for all the 32 solutes considered in this work. We first focus on Al and W, explicitly calculating all contributions from phonons and compare the accuracy of several commonly used levels of approximation. We identify the approximation that is computationally inexpensive but sufficiently accurate, and use it for the calculation of diffusion coefficients of the rest of the solutes.

3.1. Self-diffusion

- *Formalism:* Throughout this work we assume that the diffusion is governed solely by a monovacancy mechanism mediated by nearest-neighbor vacancy jumps. The self-diffusion coefficient for such a mechanism can be expressed as [54]:

$$D = f_0 \omega_0 a_0^2 C_0 \quad (1)$$

where a_0 is the lattice parameter, f_0 is the correlation factor (for self-diffusion on face-centered crystals, it is constant and equal to 0.7815), ω_0 is the vacancy jump frequency, and C_0 is the concentration of vacancies. The equilibrium concentration of vacancies C_0 at a given temperature T is given by

$$C_0 = \exp\left(-\frac{G_{\text{vf}}}{k_{\text{B}}T}\right) \quad (2)$$

where G_{vf} is the Gibbs energy of formation of a vacancy, and k_{B} is the Boltzmann constant. Based on the transition state theory (TST), ω_0 can be written as [55]:

$$\omega_0 = \nu_0^* \exp\left(-\frac{H_{\text{m}}}{k_{\text{B}}T}\right) \quad (3)$$

where H_{m} is the difference in enthalpy of the system in the initial

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