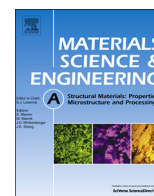




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Can slow-diffusing solute atoms reduce vacancy diffusion in advanced high-temperature alloys?



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ABSTRACT

The high-temperature mechanical properties of precipitate-strengthened advanced alloys can be heavily influenced by adjusting chemical composition. The widely-accepted argument within the community is that, under certain temperature and loading conditions, plasticity occurs only in the matrix, and dislocations have to rely on thermally-activated climb mechanisms to overcome the barriers to glide posed by the hard precipitates. This is the case for γ' -strengthened Ni-based superalloys. The presence of dilute amounts of slow-diffusing solute atoms, such as Re and W, in the softer matrix phase is thought to reduce plasticity by retarding the climb of dislocations at the interface with the hard precipitate phase. One hypothesis is that the presence of these solutes must hinder the flow of vacancies, which are essential to the climb process. In this work, density functional theory calculations are used to inform two analytical models to describe the effect of solute atoms on the diffusion of vacancies. Results suggest that slow-diffusing solute atoms are not effective at reducing the diffusion of vacancies in these systems.

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1. Introduction

Many advanced alloys rely on the presence of hard precipitates in a softer matrix phase in order to reduce creep strain rates. This is the case for, amongst others, magnesium alloys [1], near- α titanium alloys [2], and nickel-based superalloys [3]. At their respective high operating temperatures, creep plasticity in these alloys is limited to the softer matrix phase, and dislocations have to climb around the hard precipitates in order to further contribute to plasticity [1–3]. This mechanism is often referred to as climb-assisted glide.

In Ni-based superalloys this deformation mechanism is particularly important, as it controls the minimum strain rate, which is a metric of alloy performance [4,5]. Here, the harder precipitate phase (γ') remains impenetrable to dislocations during high-temperature creep, and all plasticity is restricted to the softer matrix phase (γ) [3]. The dislocation climb process that happens at the γ/γ' interfaces is diffusion-controlled and relies on vacancies being emitted or absorbed by the dislocation cores depending on the direction of climb [6]. These vacancies must diffuse from emitting cores to absorbing cores in order for deformation to continue. A prevalent hypothesis within the superalloys community is that slow-diffusing atoms in the matrix phase must severely reduce the flow of vacancies and, in turn, improve the high-

temperature creep properties [4,7]. This is currently the best explanation provided for the beneficial effect of Re additions to the superalloys (*i.e.* the rhenium-effect [7], as discussed later.

Quantitative estimations of how chemistry affects the diffusion of vacancies are also desirable since these may be used to inform deformation models at the higher length-scales. Many implementations of Discrete Dislocation Dynamics (DDD) are becoming mature enough to treat dislocation climb explicitly, and assume that the flow of vacancies to and from the cores is the rate-controlling mechanism [8,9]. Others assume a value of 10, 100 and 1000 for the ratio of the mobilities of glide and climb, expecting this ratio to be dependent on temperature and alloy composition [5]. Similarly, constitutive creep models commonly include an effective diffusion factor, which is thought to be strongly influenced by chemistry such as the presence of slow-diffusing atoms [4,10]. Zhu et al. proposed a compositionally-explicit creep model by assuming a simple model for how effective diffusivity may be affected by the chemical composition of the alloy [4]. A reliable estimate of how single solute atoms may affect vacancy diffusion is needed.

This paper aims to evaluate the effect of dilute levels of Re, W and Ta on the diffusion of vacancies in Ni, with the aim of understanding whether slow-diffusing solute atoms can improve high-temperature creep properties by reducing vacancy diffusion. Rhenium is widely regarded to be the ‘magic dust’ for Ni-based superalloys. Small additions of Re, on the order of 2–3 wt.%, have been observed to dramatically improve the creep properties of the superalloys. The effect of Re is thought to be amplified by the fact

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that Re strongly partitions to the γ phase, where most of the dislocation activity is confined at the higher temperatures. Due to the large volume fraction of the γ' phase, adding 2–3 wt.% Re to the bulk alloy composition of the alloy leads to a γ phase containing 8–12 wt.% (2–4 at.%) Re [11]. Tungsten, sitting just beside Re in the periodic table, is also regarded as a slow-diffusing solute atom in the Ni lattice, and is thought to play a similar role to Re in the γ phase of Ni-based superalloys. The effect of W is thought to be less dramatic than Re since it does not partition to either of the two phases. Finally, Ta was included in this study to test for the effect of fast-diffusing elements on the flow of vacancies and investigate trends across the periodic table.

2. Methodology

2.1. Calculation of effective diffusion coefficient

For vacancy diffusion, atoms in the γ matrix, which are predominantly Ni, need to simultaneously diffuse in the reverse direction. Thus, the effect of solute additions on an average effective diffusion coefficient should be a first-order approximation of the vacancy diffusion coefficient. In the present case, we can obtain the effective diffusion coefficient, D_{eff} , by averaging the solute diffusion coefficient in Ni (D_i) and the Ni self-diffusion coefficient (D_{Ni}), weighed by their respective atomic concentrations:

$$D_{\text{eff}} = x_i D_i + x_{\text{Ni}} D_{\text{Ni}} \quad (1)$$

This first-order approximation is not the first attempt at capturing the effects of chemical composition within an average effective diffusion coefficient, but it is fundamentally different from that used by Zhu et al. [4]. It should also be pointed out that D_{eff} must not be confused with \bar{D} , the interdiffusion coefficient as defined from Darken's equations. The interdiffusion coefficient is approximately equivalent to the solute diffusion coefficient in dilute binary alloys. In the present case, we are interested in the effect of solute additions on nickel self-diffusion.

2.1.1. Calculation of solute diffusion coefficients

To get D_{eff} from Eq. (1), we need to calculate the solute diffusion coefficients using

$$D_i = D_{0,i} \exp\left\{-\frac{Q_i}{k_B T}\right\} \quad (2)$$

where $D_{0,i}$ and Q_i are the effective diffusion pre-factor and activation energy respectively, k_B is the Boltzmann constant and T is the absolute temperature. The activation energy (Q_i) and pre-factor ($D_{0,i}$) can be expressed analytically using solid-state principles [12]. The solute diffusion coefficient (D_i) in dilute binary alloys of Ni with *fcc* crystal structure is given by [13]

$$D_i = a^2 x_{v,i} \Gamma_i f_i \quad (3)$$

where a is the equilibrium Ni lattice parameter, $x_{v,i}$ is the probability of vacancy occurring beside an atom i , Γ_i is the solute-vacancy exchange frequency and f_i is the solute correlation factor. For self-diffusion, the Ni atom itself is the solute.

The probability of a vacancy occurring beside an atom i is

$$x_{v,i} = \exp\left(\frac{\Delta S_f^{\text{vib}}}{k_B}\right) \exp\left(-\frac{\Delta H_{f,i}}{k_B T}\right) \quad (4)$$

where $\Delta H_{f,i}$ is the enthalpy of vacancy formation adjacent to a solute and ΔS_f^{vib} is the vibrational entropy of vacancy formation. This has been calculated previously but results from different theoretical approaches differ significantly [14]. We have assumed $\Delta S_f^{\text{vib}} = 1.4k_B$, computing an average of two values reported by

Seeger et al. [15] calculated by fitting the experimental Ni-self diffusion data.

The jump frequency for a successful atom-vacancy exchange is defined as [16]

$$\Gamma_i = \nu_i^* \exp\left\{-\frac{\Delta H_{m,i}}{k_B T}\right\} \quad (5)$$

where ν_i^* is the effective frequency associated with the vibration of the atom in the direction of the vacancy [16] and $\Delta H_{m,i}$ is the enthalpy of migration or the difference between the energy at the saddle point and the starting point of the transition.

Correlation effects develop in a system as the atoms do not undergo a strict 'random walk'. The correlation factor f_i gives a measure of this reduced efficiency of diffusion. For self-diffusion in *fcc* crystals, a value of 0.78146 has been accurately determined using computer simulations [17]. In dilute binary *fcc* alloys, several different jumps are possible and f_i is estimated using Lidiard's five frequency exchange model [18]

$$f_i = \frac{2\Gamma_{\text{rot}} + 7\Gamma_{\text{dis}}}{2\Gamma_{\text{rot}} + 2\Gamma_i + 7\Gamma_{\text{dis}}} \quad (6)$$

where Γ_{rot} and Γ_{dis} are jump frequencies for the rotation and dissociation of the solute-vacancy pair respectively, and Γ_i is the solute-vacancy exchange frequency.

Therefore, we can write

$$D_{0,i} = f_i a^2 \nu_i^* \exp\left\{\frac{\Delta S_f^{\text{vib}}}{k_B}\right\} \quad (7)$$

$$Q_i = \Delta H_{f,i} + \Delta H_{m,i}. \quad (8)$$

The separation into a pre-factor ($D_{0,i}$) and exponential term (Q_i) is usually done to dissociate the temperature-dependent and temperature-independent parts of diffusion, and these values can be experimentally determined from the slope and intercept of a graph of the logarithm of diffusivity versus the inverse of temperature. It should be pointed out, however, that f_i is not strictly temperature independent, although variation of f_i with temperature is small in most cases.

2.2. Calculation of vacancy diffusion coefficient

The direct determination of vacancy diffusion coefficients is less obvious using analytical formulations. Manning's random alloy model [19] is the only available approximate method in the literature to the best knowledge of the authors. This model applies to alloys where the atoms and vacancies are distributed randomly with no energetically favored sites. Using this model, the vacancy diffusion coefficient, D_v is given by

$$D_v = a^2 \Gamma_v f_v \quad (9)$$

where Γ_v is the average vacancy jump frequency and f_v is the vacancy correlation factor. The jump frequency of a vacancy is the same as the jump frequency of the atom exchanging with the vacancy. In a binary alloy, Γ_v can be approximated by a simple arithmetic average of the jump frequencies weighted by their respective atomic concentration:

$$\Gamma_v = x_i \Gamma_i + x_{\text{Ni}} \Gamma_{\text{Ni}}. \quad (10)$$

This approach assumes that the jump frequency of a given atom i , Γ_i , depends only on i and not on the identity of other neighboring atoms, and that the lattice site occupation surrounding a vacancy is not biased relative to the average composition of the binary alloy.

The vacancy follows a random walk in a pure crystal, and hence f_v is unity for the self-diffusion case. In a random alloy of Ni where

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