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DOI:
10.1016/j.msea.2014.08.054

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Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Goswami, KN & Mottura, A 2014, 'Can slow-diffusing solute atoms reduce vacancy diffusion in advanced high-temperature alloys?', *Materials Science and Engineering A*, vol. 617, pp. 194-199.
https://doi.org/10.1016/j.msea.2014.08.054

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Materials Science & Engineering A 617 (2014) 194–199

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

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

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ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form
19 August 2014
Accepted 21 August 2014
Available online 2 September 2014

Keywords:
Nickel based superalloys
Re-effect
Vacancy diffusion
First principles calculations

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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http://dx.doi.org/10.1016/j.msea.2014.08.054
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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:

$$D_{\text{eff}} = x_i D_i + x_{\text{Ni}} D_{\text{Ni}} \tag{1}$$

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 $\tilde{D}$, 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

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

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]

$$D_i = a^2 x_{\text{v,i}} \Gamma_i f_i \tag{3}$$

where a is the equilibrium Ni lattice parameter, $x_{\text{v,i}}$ 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

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

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

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

where ν_i^* is the effective frequency associated with the vibration of the atom in the direction of the vacancy [16] and $\Delta H_{\text{m},i}$ 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]

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

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

$$D_{0,i} = f_i a^2 \nu_i^* \exp\left\{\frac{\Delta S_{\text{f}}^{\text{vib}}}{k_B}\right\} \tag{7}$$

$$Q_i = \Delta H_{\text{f},i} + \Delta H_{\text{m},i}. \tag{8}$$

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

$$D_{\text{v}} = a^2 \Gamma_{\text{v}} f_{\text{v}} \tag{9}$$

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:

$$\Gamma_{\text{v}} = x_i \Gamma_{\text{i}} + x_{\text{Ni}} \Gamma_{\text{Ni}}. \tag{10}$$

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

x_i is the mole-fraction of solute i, f_v is given by [19]

$$f_v = 1 - \frac{2}{M_0}\frac{(M_0+2)x_{Ni}x_i(D_{Ni}-D_i)^2}{(M_0+2)(x_{Ni}D_{Ni}+x_iD_i)^2 - 2D_{Ni}D_i} \quad (11)$$

where M_0 is a numerical constant, and is equal to 7.15 for *fcc* crystals. Note that the model breaks down for dilute levels of solute atoms which diffuse faster than the solvent. Hence, for these solutes, we use an alternate expression [19]:

$$f_v = \frac{x_i\Gamma_i f_v^i + x_{Ni}\Gamma_{Ni} f_v^{Ni}}{x_i\Gamma_i + x_{Ni}\Gamma_{Ni}} \quad (12)$$

where f_v^i is the partial vacancy correlation factor for i and is given as

$$f_v^i = \frac{f_i}{0.78146} \quad (13)$$

where f_i is the solute correlation factor (see Eq. (6)) and 0.78146 is the correlation factor for self-diffusion [17] in pure Ni. The partial vacancy correlation factor for Ni, f_v^{Ni} is taken as unity in the present case of dilute alloys.

2.3. Computational details

All input data was calculated from first principles, using Density Functional Theory (DFT) [20,21] as implemented in the Vienna Ab-initio Simulation Package (VASP) 5.3.2 [22]. The Projector Augmented Wave (PAW) method [23,24] was used to describe the electron–ion interactions, and the Generalized Gradient Approximation (GGA) parameterized by Perdew et al. [25] was used as exchange and correlation functional. All calculations were performed on 108-atom supercells and were spin-polarized. The electronic self-consistent loops were stopped when the total energy converged to within 10^{-6} eV and ionic positions were relaxed until all forces fell below 10^{-2} eV/Å. A Methfessel–Paxton smearing width [26] of 0.1 eV was used. Calculations were run with an energy cutoff of 400 eV and a $5\times5\times5$ k-point mesh following the Monkhorst–Pack scheme [27]. The enthalpy of migration for the different atom-vacancy exchanges was calculated using the Nudged Elastic Band method [28]. The effective frequencies were calculated within the harmonic approximation as supported by VASP.

3. Results

Calculations were initially done on the pure Ni system to obtain the self-diffusion coefficient in Ni, using a value of 3.52 Å as lattice parameter. A $D_{0,Ni}$ value of 10.1×10^{-7} m^2/s was obtained, while Q_{Ni} was computed at 2.52 eV (or 243 kJ/mol). It should be noted that the calculations presented in this work do not consider the full effects of vibrational entropy and hence we do not expect them to replicate the experimental results at the highest temperatures. The calculated values produce a self-diffusion coefficient (see Fig. 1) which agrees with available data in the literature in the intermediate temperature regime [29] and is within an order of magnitude in the high temperature regime [30]. The experimental values for $D_{0,Ni}$ and Q_{Ni} are commonly obtained by fitting the self-diffusion data to the Arrhenius relationship. As a result, these values may not be necessarily expected to match the pre-factor and activation energy values obtained from first principles. Indeed, a large scatter is observed in the experimental values for $D_{0,Ni}$ and Q_{Ni} reported in the literature. We chose to compare only to data (see Table 1) obtained from single-crystal Ni samples tested over a range of temperatures [29,30].

Calculations were then run for Re, W and Ta as solute atoms in 108-atom supercells. All the terms in the pre-factors ($D_{0,i}$) and activation energies (Q_i) have been tabulated in Table 1. It should be emphasized that the correlation factor (f_i), although featuring in the diffusion pre-factor term, is not temperature-independent. The correlation factor was calculated using the ν_i^* and $\Delta H_{m,i}$ values given in Table 1. For all jumps, except for the solute-vacancy exchange, a ν_i^* of 2.57 THz was used. In the temperature range of interest (1173–1573 K), the correlation factor varies only slightly for all solute atoms. It can also be noted that the correlation factors for Re and W are higher than the correlation factor in pure Ni, while the correlation factor for Ta is much lower. This is expected since the lower energy barrier for a Ta-vacancy exchange results in a higher Ta-vacancy exchange frequency and, in turn, a higher probability that any Ta-vacancy jump is followed by a reverse jump. The opposite is true for Re and W.

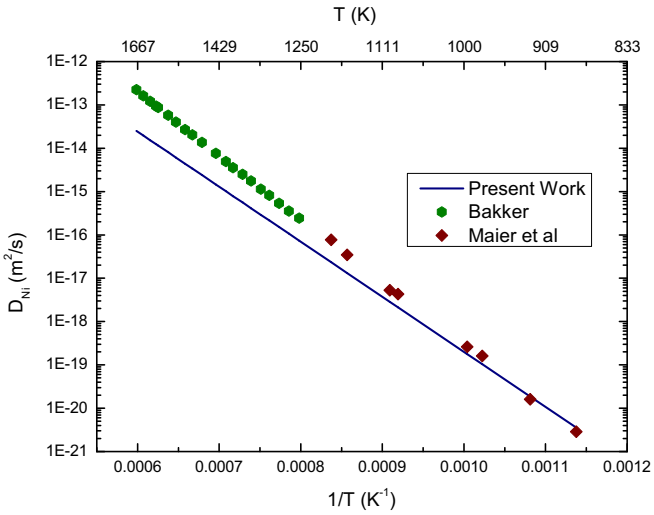

Fig. 1. The self-diffusion coefficient of Ni calculated from first principles compared to experimental values [29,30].

The resulting diffusion coefficients for Re, W and Ta are shown in Fig. 2, and agree with both experimental and simulated data available in the literature (see Table 1) [31,32]. The diffusivity of Re and W are respectively roughly two orders and one order of magnitude lower than the diffusivity of the host. In contrast, Ta is expected to diffuse an order of magnitude faster than the host. It must be noted that the reported experimental data [31] in Table 1 was determined from the interdiffusion coefficients $\tilde{D}$ in these systems. However, experiments were conducted by these authors over a range of composition in the dilute regime (<3.5 at.%), and it was observed that $\tilde{D}$ remained independent of composition in all the three systems in the dilute regime. Assuming the thermodynamic factor in the Darken's second equation to be equal to unity, the interdiffusion coefficients $\tilde{D}$ in the dilute regime should be approximately equal to (within an order of magnitude) the solute diffusion coefficients D_i.

Using the diffusion coefficients for self-diffusion of Ni and solute diffusion in Ni, the effective diffusion coefficient in a dilute binary alloy, D_{eff}, can be estimated (see Fig. 3, computed for 1373 K). Predictably, adding 5 at.% Re and W reduces D_{eff} albeit by a small amount (less than 5% when compared to the diffusivity in pure Ni) and it transpires that Re is just as effective as W at reducing effective diffusion in the γ phase of Ni-based superalloys. This simple model for effective diffusivity is only a first-order approximation and it does not explicitly account for how the presence of solute atoms may affect the diffusivity of vacancies. It is therefore necessary to apply Manning's random alloy model to obtain the vacancy diffusion coefficient.

Before applying Manning's random alloy model, its validity for the current system must be ensured. First, Manning's model

Table 1
The calculated terms for self-diffusion and solute diffusion in Ni.

Solute	ν_i^* (THz)	f_i (1373 K)	D_0^i ($\times 10^{-7}$m^2/s)	$\Delta H_{f,i}$ (eV)	$\Delta H_{m,i}$ (eV)	Q_i (eV)	$\Delta H_{rot,i}$ (eV)	$\Delta H_{dis,i}$ (eV)	$\Delta H_{ass,i}$ (eV)
Ni_{self}	2.57	0.781	10.1 920 [29] 1770 [30]	1.44	1.08	2.52 2.88 [29] 2.955 [30]	1.08	1.08	1.08
Re	1.67	0.996	8.37 8.2 [31]	1.48	1.48	2.96 2.64 [31] 3.50 [32]	1.10	1.05	1.06
W	2.36	0.966	11.44 80 [31]	1.46	1.25	2.71 2.74 [31] 3.05 [32]	1.18	1.02	1.01
Ta	2.56	0.338	4.35 219 [31]	1.36	0.755	2.11 2.60 [31] 2.34 [32]	1.35	0.985	0.88

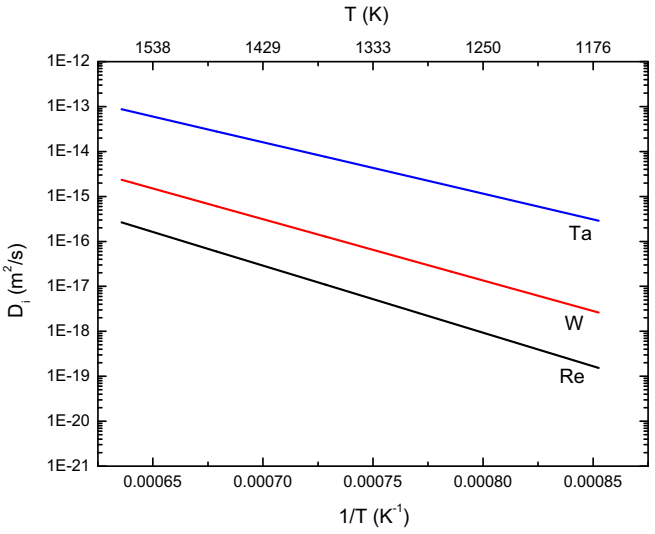

Fig. 2. The solute diffusion coefficients in Ni as a function of temperature.

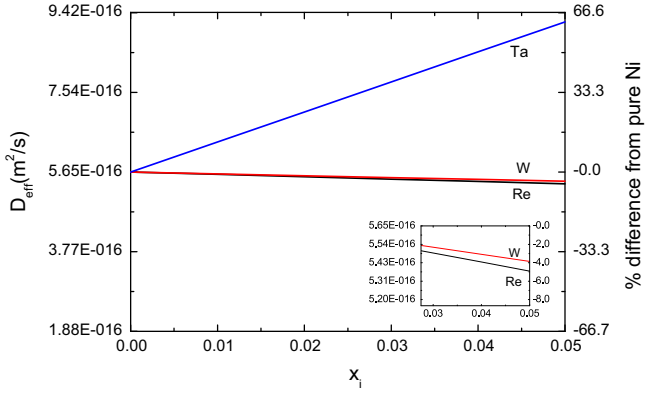

Fig. 3. Effective diffusion coefficient in Ni as a function of solute concentration at 1373 K.

assumes for the binary alloy to be random and for the solute atoms to have negligible binding energies with vacancies (*i.e.* vacancy distribution must also be random). The distribution of Re, W and Ta in Ni has been the subject of several studies [7,33,34], all confirming using a variety of techniques that the distribution of dilute amounts of these solute atoms in Ni should be expected to be random at elevated temperatures. The binding energies for solute–vacancy pairs can also be calculated from first principles (see Fig. 4). These values are small relative to the vacancy formation and migration energy, and the distribution of vacancies

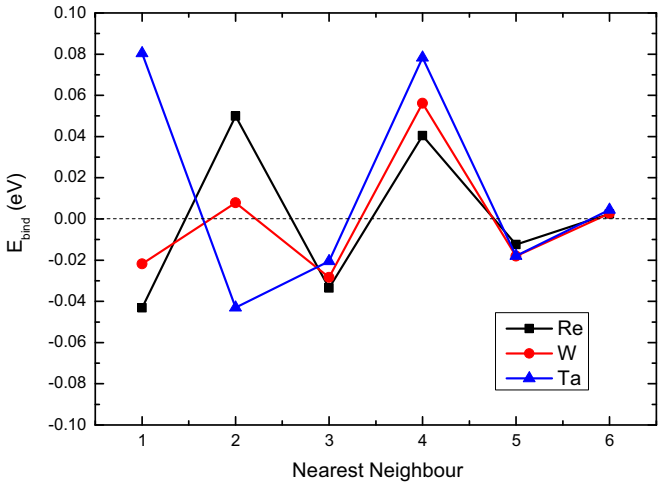

Fig. 4. The binding energies of solute–vacancy pairs at various distances in the Ni lattice.

can be assumed to be random. Second, Manning's model assumes that the exchange frequency of an atom–vacancy pair is only dependent on the atom exchanging places with the vacancy, and unbiased by the identity of neighboring atoms. In other words, the migration barriers for solute-vacancy rotation, dissociation and association should be similar to the migration barrier of the host. This is the case for Re and W (see Table 1), but not the case for Ta, which is not the primary focus of the present study. We can therefore conclude that, at least for Re and W, Manning's model for estimating vacancy diffusion is valid.

Using the values for diffusion obtained above, we can calculate the vacancy correlation factor (f_v) using in Eq. (11) as a function of temperature and composition for Re and W additions. As discussed in Section 2.2, Eq. (11) breaks down when the solute atoms diffuse faster than the host. Therefore, for Ta, we use the vacancy correlation factor calculated according to Eq. (12). The use of Eq. (12) for Re and W does not produce substantially different results when compared to the correlation factors obtained from Eq. (11). The change of f_v with solute concentration at 1373 K is shown in Fig. 5. For a pure metal, the vacancy correlation factor is unity and remains close to unity with small additions (up to 5 at.%) of Re and W. The addition of a fast-diffusing solute atom, on the other hand, results in a drop in f_v due to the fact that reverse solute-□ exchange jumps are more likely than Ni-vacancy exchange jumps.

Finally, the vacancy diffusion coefficient in a dilute binary alloy, D_v, can be estimated. The results for 1373 K in binary Ni alloys with up to 5 at.% Re, W and Ta are shown in Fig. 6. Also in this case, Re and W are seen to decrease the vacancy diffusion coefficient,

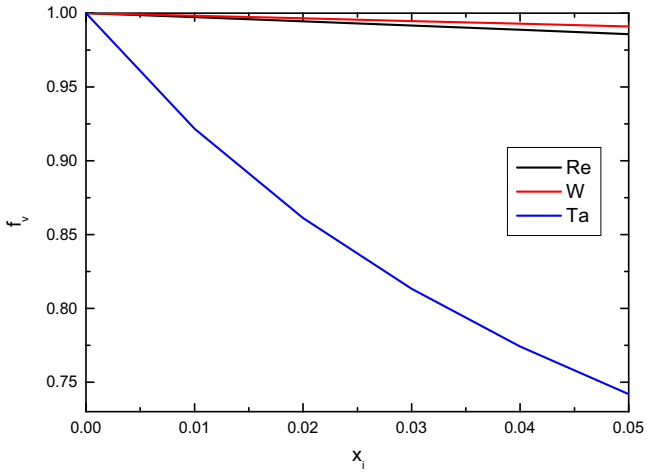

Fig. 5. Vacancy correlation factors in Ni at 1373 K.

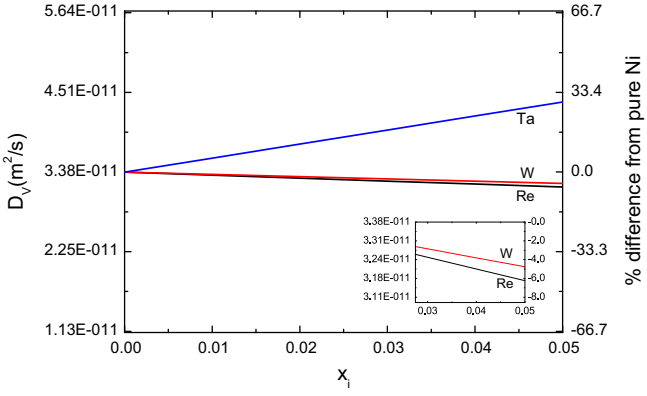

Fig. 6. Vacancy diffusion coefficients in Ni as a function of solute concentration at 1373 K.

albeit the effect is small. The addition of 5 at.% Re and W results in a reduction of vacancy diffusion coefficient of less than 10% when compared to vacancy diffusion in the pure host. The addition of Ta, as expected, increases the vacancy diffusion rate. The lower vacancy correlation factor in the presence of Ta additions does not negate the effects of the higher Ta-□ exchange frequency on the overall vacancy diffusion rate.

4. Discussion

The analytical model for vacancy diffusion developed by Manning [19] clearly indicates that small additions (<5 at.%) of slow-diffusing atoms in a host *fcc* lattice do not reduce the diffusion rate of vacancies substantially. In the case of slow diffusing solute atoms, the correlation factor for vacancy diffusion remains close to unity, and the decrease in Γ_v is minor. Indeed vacancies would rarely have to exchange with the slow-diffusing solute atom, and even in the case the solute atoms were to be absolutely immobile due to a very high solute-vacancy exchange migration barrier, the resulting effect would only be as big as the percentage of solute content.

Conversely, a larger effect on vacancy diffusion can be observed with the addition of fast-diffusing solute atoms, such as Ta. In this case, the fact that the solute-vacancy exchange frequency is an order of magnitude higher than the host means that the average vacancy jump frequency markedly increases with a small addition of solute atoms. The effect is mitigated by the correlation factor, which accounts for the fact that a higher solute-vacancy exchange frequency results in a reduced efficiency in vacancy diffusion. It must be pointed out again, however, that Manning's model is not strictly applicable in this case, as the exchange frequencies of Ni–vacancy pairs are affected by the presence of a neighboring Ta atom.

Having established that the addition of slow-diffusing solute atoms does not reduce vacancy diffusion appreciably, it remains to be discussed whether this may help explain the beneficial effects of Re additions on the creep properties of Ni-based superalloys. The creep life of commercial Ni-based superalloys has been observed to increase four-fold from the 1st to the 3rd generation superalloys above 1323 K [3]. This improvement is largely attributed to the addition of Re: 3rd generation superalloys may be expected to contain up to 5–8 at.% Re in the γ phase. The extended creep life at the elevated temperatures is associated with a drop in minimum creep strain rate; these numbers are commonly regarded to be linked by an inverse relationship under the creep conditions examined here. Therefore, in order for a four-fold increase in creep life to be achieved, the minimum creep strain rate in 3rd generation superalloys must drop to 25% of the value in 1st generation superalloys. Assuming that all other factors affecting the minimum creep strain rate are unchanged between 1st and 3rd generation superalloys, it must be concluded that additions of Re brings about a 75% drop in vacancy diffusion rates.

In light of the results presented in this paper, such a drop in vacancy diffusion rates is unrealistic, assuming no interactions between vacancies and multiple solute atoms. Both analytical models presented in this paper clearly indicate that small additions (<5 at.%) of slow-diffusing atoms in a host *fcc* lattice do not reduce the diffusion rate of vacancies substantially. Other models for how chemistry may affect an average effective diffusion coefficient, such as the one presented by Zhu et al. [4], may predict smaller or larger effects of composition on effective diffusion. This is because their model relies on averaging the pre-factor and activation energy terms separately. As a result, the approach is heavily dependent on the values of pre-factor and activation energy used, which are seen to vary greatly across different studies.

Therefore other mechanisms, beside isolated slow-diffusing solute atoms reducing vacancy diffusion, must be investigated in order to understand the effect of Re additions on the creep properties of the superalloys. First, complex arrangements of solute atoms may act as vacancy traps. Such mechanisms may become prevalent as the solute content is increased beyond the dilute levels, and in turn explain how elements such as Re and W reduce the rate of dislocation climb. It must be pointed out, however, that a variety of solute diffusion coefficients were not observed to change with increasing solute content [31], and that even very dilute levels of Re produce a beneficial effect on creep properties [35]. Consideration of more complicated local atomic environments surrounding the vacancies will require the adoption of kinetic Monte Carlo simulations coupled with an accurate description of the many possible migration barriers. Second, a number of other mechanisms, in addition to the effect of Re additions on vacancy diffusion, may act together to further reduce the minimum creep strain rate due to the addition of Re. These will be the subject of further work.

5. Conclusions

1. Two analytical models describing how climb-related diffusional processes may be affected by the presence of solute atoms were analyzed.
2. Ab initio density functional theory was used to obtain all necessary input parameters for the analytical models.

3. Results indicate that small additions of slow-diffusing solute atoms results in a reduction in vacancy diffusion coefficient and average effective diffusion coefficient.
4. The predicted small reductions in vacancy diffusion coefficient cannot, by itself, explain the abnormal creep strengthening effect observed due to small additions of Re.
5. This work assumes that interactions between vacancies and multiple solute atoms are negligible. Although single slow-diffusing solute atoms may not reduce the diffusion of vacancies appreciably, complex arrangements of solute atoms may act as vacancy traps. This will be the focus of future work.

Acknowledgments

The authors would like to acknowledge the use of the *BlueBEAR* High Performance Computing facility at the University of Birmingham for the calculations presented in this manuscript. The authors would also like to thank Prof. Ralf Drautz, Dr. Jutta Rogal and Dr. Sergej Schuwalow of the Interdisciplinary Centre for Advanced Materials Simulation at the Ruhr-Universität, Bochum in Germany for the valuable discussions.

References

[1] K.U. Kainer (Ed.), Magnesium—Alloys and Technologies, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2003.
[2] C. Leyens, M. Peters (Eds.), Titanium and Titanium Alloys: Fundamentals and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2003.
[3] R. Reed, The Superalloys: Fundamentals and Applications, Cambridge University Press, UK, 2006.
[4] Z. Zhu, H. Basoalto, N. Warnken, R. Reed, Acta Mater. 60 (12) (2012) 4888–4900.
[5] S.M. Hafez Haghighat, G. Eggeler, D. Raabe, Acta Mater. 61 (2013) 3709–3723.
[6] Y. Gao, A. Cocks, Acta Mech. Solida Sin. 22 (5) (2009) 426–435.
[7] A. Mottura, M. Finnis, R. Reed, Acta Mater. 60 (6–7) (2012) 2866–2872.
[8] J. Danas, V.S. Deshpande, Model. Simul. Mater. Sci. Eng. 21 (4) (2013) 045008.
[9] D. Morderhai, E. Clouet, M. Fivel, M. Verdier, Philos. Mag. 88 (6) (2008) 899–925.
[10] B.F. Dyson, Mater. Sci. Eng.: A 25 (2) (2009) 213–220.
[11] N. Wanderka, U. Glatzel, Mater. Sci. Eng.: A 203 (1–2) (1995) 69–74.
[12] M.E. Glicksman, Diffusion in Solids: Field Theory, Solid-State Principles, and Applications, John Wiley and Sons, New York, 1999.
[13] M. Mantina, Y. Wang, R. Arroyave, L. Chen, Z. Liu, C. Wolverton, Phys. Rev. Lett. 100 (21) (2008) 215901.
[14] C.L. Zacherl, Ph.D. thesis, The Pennsylvania State University, 2012.
[15] A. Seeger, D. Schumacher, Mater. Sci. Eng. 2 (1) (1967) 31–36.
[16] G.H. Vineyard, J. Phys. Chem. Solids 3 (1–2) (1957) 121–127.
[17] K. Compaan, Y. Haven, Trans. Faraday Soc. 52 (1956) 786.
[18] A. Lidiard, CXXXIII., Philos. Mag. Ser. 746 (382) (1955) 1218–1237.
[19] J.R. Manning, Phys. Rev. B 4 (1971) 1111–1121.
[20] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864–B871.
[21] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133–A1138.
[22] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169–11186.
[23] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953–17979.
[24] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
[25] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865–3868.
[26] M. Methfessel, A.T. Paxton, Phys. Rev. B 40 (1989) 3616–3621.
[27] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188–5192.
[28] G. Henkelman, H. Jonsson, J. Chem. Phys. 113 (22) (2000) 9978–9985.
[29] K. Maier, H. Mehrer, E. Lessmann, W. Schle, Phys. Stat. Solidi B 78 (2) (1976) 689–698.
[30] H. Bakker, Phys. Status Solidi B 28 (2) (1968) 569–576.
[31] M. Karunaratne, P. Carter, R. Reed, Mater. Sci. Eng.: A 281 (1–2) (2000) 229–233.
[32] A. Janotti, M. Krčmar, C.L. Fu, R.C. Reed, Phys. Rev. Lett. 92 (2004) 085901.
[33] A. Mottura, R.T. Wu, M.W. Finnis, R.C. Reed, Acta Mater. 56 (11) (2008) 2669–2675.
[34] A. Mottura, N. Warnken, M.K. Miller, M.W. Finnis, R.C. Reed, Acta Mater. 58 (3) (2010) 931–942.
[35] A. Heckl, S. Neumeier, M. Göken, R. Singer, Mater. Sci. Eng.: A 528 (9) (2011) 3435–3444.