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Effect of interactions between elements on the diffusion of solutes in Ni—X—Y systems and γ′-coarsening in model Ni-based superalloys

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ABSTRACT

The effect of elemental interactions between solute elements on diffusion in Ni—X—Y (X, Y: Al, Ti, Nb, Ta, Cr, Co, Mo, W, Re, Ru) systems and γ′-coarsening in model Ni-based superalloys are investigated by performing first-principles calculations and high-temperature thermal exposure experiments. The ternary interactions are important for the diffusion barrier of a solute in Ni—X—Y and the coarsening rate of precipitates. These results are related not only to the electronic structure but also to chemical bonding.

Nickel-based single-crystal superalloys with γ′-Ni_3Al precipitate strengthening have been widely used to make turbine blades in high-temperature jet engines and land-based gas turbines. However, there are many microscopic effects that can degrade the superior performance of the Ni-based superalloys. One of these is the diffusion-mediated coarsening of the γ′ precipitates for the creep properties of superalloys [1–3]. Based on the classical Lifshitz–Slyozov–Wagner (LSW) coarsening theory [4–6], γ′ coarsening is influenced mainly by the diffusion rates of solute elements in the matrix.

Experiments have revealed that the γ-matrix phase in multicomponent alloys can contain solute element contents of 50 at.% or more [7,8]. As the concentration of solute elements in the matrix phase is too high, these elements will inevitably affect the diffusivity and thus affect the coarsening of γ′ precipitates. Although the size misfit of elements can be related to solid-solution strengthening, the rate-controlling diffusion behavior of each alloying element and the interaction between them with respect to phase stability may play an important role. Because diffusion is important in high-temperature thermally activated processes such as homogenization, dislocation climb, TCP precipitation, and γ′ phase coarsening, it is essential to understand how alloying elements diffuse in nickel-based superalloys in order to better design the alloy composition, perform solution heat treatment, and understand operating degradation. However, the elemental interactions (ternary interactions) influence the diffusion in the Ni matrix in a manner that is not yet fully understood.

In this work, the vacancy-formation and migration energies of solutes in the Ni—X—Y systems (X, Y: Al, Ti, Nb, Ta, Cr, Co, Mo, W, Re, Ru) were calculated by the first–principles. Furthermore, the high-temperature thermal exposure experiments were used to verify the effect of elemental interactions on the diffusion.

We used density-functional theory (DFT), implementing the Vienna ab-initio simulation package (VASP) code [9], to investigate the vacancy-formation and migration energies. All calculations were performed using the projector augmented-wave method [10,11] and the generalized gradient approximation in the Perdew–Burke–Ernzerhof form (GGA-PBE) [12]. The minimum plane wave energy cutoff was 350 eV. The convergence accuracy of the total energies of electronic self-consistency was 10^{-5} eV. Brillouin zone integration was performed with a $5 \times 5 \times 5$ Monkhorst–Pack [13] k-point scheme. Full ionic relaxation was performed until the maximum Hellmann–Feynman force was below 0.02 eV/Å. The migration energy was calculated using the climbing image nudged elastic band method (CI-NEB) [14]. Three image CI-NEB calculations were used to determine the minimum energy path. The vacancy-formation and migration energies for the Ni—X and Ni—X—Y systems were calculated for nearest-neighbor (NN) pairs in a $3 \times 3 \times 3$ (108 lattices) cubic fcc supercell for γ-Ni. For detailed calculations and models introduced above, see supplementary material. Note that the distance between elements in γ matrix of multicomponent alloys is close to the distance of the first-nearest neighbor (FNN), then two solutes X and Y are placed at FNN positions (see Fig. S1 in Supplementary material). In

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Table 1
Compositions (wt%) of the model alloys investigated in this work.

wt%	Ni	Al	Ru	Co	Re
M0	Bal.	8.8	–	–	–
M2	Bal.	8.3	–	–	5.0
M3	Bal.	8.2	3.0	–	5.0
M6	Bal.	8.4	–	5.8	5.0

order to verify the effect of elemental interactions on diffusion, four model superalloys were prepared for the high-temperature thermal exposure experiments. Table 1 lists the nominal compositions of the Ni-based alloys. The sample preparation and characterization procedures were described in detail in supplementary material.

In the γ-Ni matrix, the diffusion of alloying elements seems to be driven primarily by vacancies, which falls into the vacancy formation and vacancy-atom exchange process. Fig. 1 illustrates the effect of elements on the vacancy-formation and migration energies of solutes (the values are tabulated in supplementary material). The activation energies which is governed by the vacancy-formation and migration energies of solutes were summarized in Table 2 and compared with values available in literature. Our diffusion barriers for the solute elements are generally less than that obtained by CALPHAD methods or experiments, but the corresponding order is almost consistent and the values are comparable. Note that, the diffusion activation energy calculated by first-principles corresponds to the impurity diffusivities under very dilute conditions, which is different from the activation energy for interdiffusion coefficient. This may be the main reason for the source of the discrepancies. Further discrepancies between the values might be the deficiencies of the PBE exchange-correlation functional, or the polycrystalline samples in the experimental setup.

The calculated vacancy-formation energy of pure Ni is 1.408 eV, which is close to the experimental value of 1.40 eV [15,16]. Because of the effect of solute atoms on solvent Ni, γ-partitioning elements (Cr, Co, Mo, Ru, W, Re) increase the vacancy formation energy at the NN lattice sites, while the γ′-partitioning elements (Al, Ti, Nb, Ta) reduce that. For the solute pairs, the vacancy-formation energies of most Ni—X—Y systems are larger than Ni. It is suggested that the vacancy-formation energy can increase as the local atomic environment surrounding the vacancies becomes more complicated. Specifically, the Re—W and W—Mo pairs have the strongest effects.

The calculated migration energy barrier of solvent Ni in fcc Ni is 0.96 eV, which agrees well with the experimental value of 1.0 eV [17]. The migration energies of γ′-partitioning elements (Al, Ti, Nb, Ta) in the matrix phase are less than those of refractory elements (Ru, Mo, W, Re) and can be improved by refractory elements. Among the alloying elements (Al, Ti, Nb, Ta, Cr, Co, Mo, Ru, W, Re), Re has the largest migration energy in the Ni matrix, and adding Re can increase the diffusion barrier of other elements. The activation energy for Al is larger in Ni—Al—Re (2.466 eV) than in Ni—Al (2.072 eV). The refractory elements of Mo, Ru, and W have a similar effect as Re. Mabruri et al. [18] reported that adding Ru decreases the diffusivities of Re and W in the pseudo-binary systems, indicating that our computational results agree well with experiments on diffusion couples. γ′-partitioning elements—not just refractory elements—can increase the diffusion barrier of other elements. With added Al, the diffusion barrier of Re in Ni—Al—Re increases from 3.200 eV to 3.438 eV. Besides adding elements forming the complex local atomic neighborhood, elemental diffusion would slow in the presence of covalent-like bonds between Re and Al atoms. Because γ′-partitioning elements and refractory elements Re can form intermetallic compounds [19–21], we deduce that the interatomic bonding of X—Y pairs may provide resistance against solute migration in the Ni matrix.

Interestingly, adding Co reduces the migration energy of other elements, as shown in Fig. 1(b), indicating that Co may increase the diffusivity of other elements and the coarsening rate of precipitates. To explain these behaviors, we analyzed the electronic structure of solute pairs (X—Y) at their migration initial sites. As illustrated in Fig. 2, more electrons accumulate between Re and Ru than between Re and Co, and the region of overlap (hybridization) of the d orbitals of Re with Ru states for the Ni—Re—Ru system is larger than that of Re with Co states for Ni—Re—Co system, which indicates that the interaction between Ru and Re is stronger than that between Co and Re. Note that the alloying elements *X* and *Y* can form intermetallic compounds, and their covalent-like X—Y bonds significantly inhibit the jumping process. Therefore, we suggest that a strong interatomic interaction between *X* and *Y* that would yield a high diffusion barrier.

Note that, the vacancy-formation energies appear comparable to that for Ni, but their migration energies are very different, so the difference in the activation energies among the alloying elements comes mainly from the difference in their migration energies. In addition, the vacancy-formation and migration energies of a solute generally increase as the number of components in the system increases. Therefore, the number of alloying elements being greater than ten for the Ni-based superalloys is conductive to reducing the effective diffusion coefficient of the system.

Due to elemental interactions, adding a third element would affect the diffusion barriers of elements in the matrix phase. We deduce from this behavior that changing the diffusion rate of solutes in nickel-based superalloys may change the γ′ phase coarsening rate. To study the effect of ternary interactions on the diffusion of solutes, we performed thermal exposure experiments on four model superalloys. The

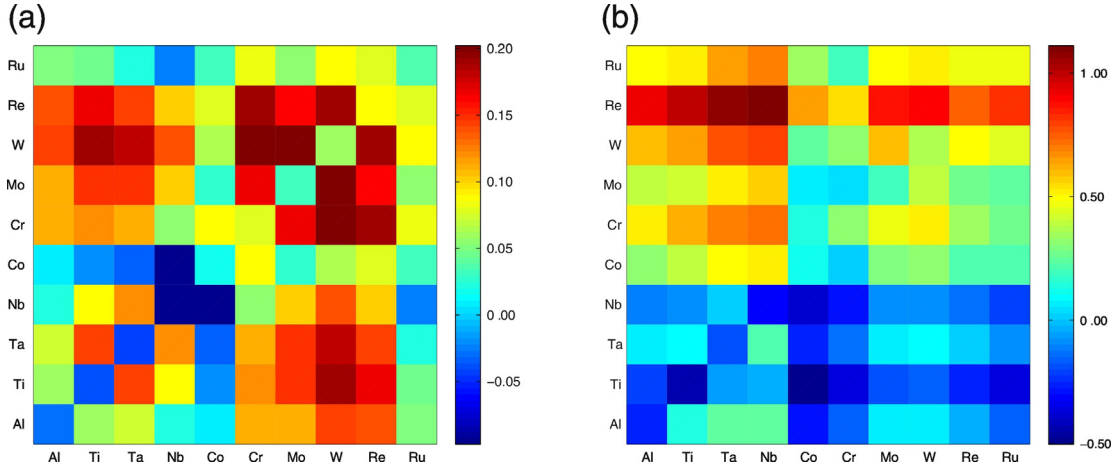

Fig. 1. Effect of *X* solutes on the (a) vacancy-formation and (b) migration energies of *Y* solutes in Ni matrix, in units of eV. Squares denote the values relative to pure Ni. Squares at the diagonal (e.g. Al—Al) denote the vacancy-formation and migration energies of the X element in the Ni—X system.