

First principles study of the diffusional phenomena across the clean and Re-doped γ -Ni/ γ' -Ni₃Al interface of Ni-based single crystal superalloy

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Density functional theory calculations in conjunction with the climbing images nudged elastic band method are conducted to study the diffusion phenomena of the Ni-based single crystal superalloys. We focus our attention on the diffusion processes of the Ni and Al atoms in the γ and γ' phases along the direction perpendicular to the interface. The diffusion mechanisms and the expressions of the diffusion coefficients are presented. The vacancy formation energies, the migration energies, and the activation energies for the diffusing Ni and Al atoms are estimated, and these quantities display the expected and clear transition zones in the vicinity of the interface of about 3–7 (002) layers. The local density-of-states profiles of atoms in each (002) layer in the γ and γ' phases and the partial density-of-states curves of Re and some of its nearest-neighbor atoms are also presented to explore the electronic effect of the diffusion behavior.

Keywords: diffusion, interface, Ni-based superalloy, First-principles calculation

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1. Introduction

Ni-based superalloys represent a very important class of engineering material, and they have widespread applications in critical components within the gas turbine engines used for jet propulsion and electricity generation. This is due to their low specific weight, high melting point and good chemical stability.^[1,2] It is well-known that these alloys are hardened by γ' precipitates (L1₂ structure) which are coherently embedded in a nickel solid solution γ matrix (face-centered cubic (fcc) structure). The γ' cuboids are generally aligned along $\langle 001 \rangle$ lattice directions and have a cube-cube relationship with the matrix γ phase.^[3,4]

The structure of the interface plays an important role in determining properties in multiphase systems.^[5–7] Several experimental and theoretical studies of the interface between an ordered precipitate and disordered matrix in a Ni-based superalloy indicated that the interface is not abruptly changed on an atomic scale but confirmed the existence of a structural transition zone across the interface. Srinivasan *et al.*^[8] have determined a clear order–disorder transition zone at the γ/γ' interface of Ni based superalloy Rene' 88 DT where the long-range order decreases roughly over 6–8 atomic {002} plane (approximately 10 Å to 13 Å). They also conducted a three-dimensional atom probe (3DAP) experiment on the same sample, and the results exhibited an order-disorder transition zone ~ 4 –6 {002} plane wide (7 Å–10 Å). Mishin^[9]

obtained the atomic structure of the interface by grand canonical Monte Carlo simulations on a 1536-atom supercell containing a coherent (100) γ/γ' interface, and the results showed that the long-range order decays gradually over 4–6 (200) layers around the interface. Kitashima *et al.*^[10] reported that the segregation of Al in the γ/γ' interface region extends over 10 atomic layers in Ni–Al–Mo system.

Abundant observations indicated that extensive diffusion occurs across the γ/γ' interface.^[11,12] As is well known, various solid-state reactions, phase transformation, microstructural changes and the process of mass transport occurring in materials are diffusion controlled.^[13,14] Watanabe *et al.*^[15] pointed out that the main factors controlling the stability of the supercell are lattice misfit, interface structure between the two phases and diffusion phenomena across the interface. As a result, it is reasonable to assume that there might be a close relationship between the interfacial transition zone and the diffusional phenomena across the γ/γ' interface.

Alloying elements, such as Co, Cr, Mo, Re, Ru, Ta, W, etc. are added to the Ni-based superalloys to enhance the high-temperature properties. A considerable body of experimental research indicates that, among the different alloying additions, Re imparts the most potent creep strengthening.^[16] Murakami *et al.*^[17] and Warren *et al.*^[18] showed that there was a Re enrichment in the γ matrix around the γ/γ' interface. Therefore, the Re alloying could interfere with the diffusion process at the interface and might act as an efficient obstacle for the atomic

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movement.

The understanding of the diffusion mechanism, improved analysis, theory and modelling are needed. In the present paper, we try to identify the affected areas of the clean and Redoped γ/γ' interfaces from a diffusional point of view. We focus our attention on the vacancy mediated diffusions of Ni and Al atoms in the γ and γ' phases along the direction perpendicular to the γ/γ' interface. The vacancy formation energy, the migration energy and the activation energy at 0K are estimated by using density functional theory calculations in conjunction with the climbing images nudged elastic band method. The trend of the variations of the above three quantities across the interface could determine clear influence areas of the phase boundary. The results are followed by an explanation from the electronic structures.

The rest of this paper is organized as follows. In Section 2 we describe the theoretical model for the four cases of the vacancy-mediated diffusion. In Section 3, we explain our computational details. In Section 4 we give our calculated results and some further discussion.

2. Theoretical model

In the diffusional phenomena across the γ/γ' interface, the processes of Al atoms diffusing out of the γ' phase and then into the γ phase and Ni atoms diffusing out of the γ phase and then into the γ' phase can be decomposed into four cases, i.e., the diffusion of Al atoms in the γ' phase, the diffusion of Al atoms in the γ phase, the diffusion of Ni atoms in the γ phase, and the diffusion of Ni atoms in the γ' phase. In what follows, we will discuss the four diffusion mechanisms separately.

2.1. Diffusion of Ni atoms in the γ phase

The diffusion of Ni atoms in the γ phase apparently belongs to the self-diffusion process which is mediated by vacancy-type defects in metals.^[19] Its self-diffusion coefficient $D_{\text{Ni}-\gamma}$ can be described by an Arrhenius relation^[20]

$$D_{\text{Ni}-\gamma} = fga^2\Gamma, \quad (1)$$

where f is the correlation factor, which yields 0.781 for an fcc lattice, g is a geometrical factor, which equals unity for the vacancy mechanism in cubic metal, a is the lattice parameter, and Γ is the exchange rate of a matrix atom jumping to a particular neighboring site. Γ can be written as

$$\Gamma = ZC_V^{\text{eq}}\omega = Z\exp\left(-\frac{E_F^V}{k_B T}\right)v^0\exp\left(-\frac{E^M}{k_B T}\right), \quad (2)$$

where Z is the coordination number; C_V^{eq} represents the probability to find a vacancy on an arbitrary but particular lattice site in thermal equilibrium condition, which increases via the

Boltzmann factor k_B with increasing temperature T , and is primarily due to the Ni vacancy formation energy term E_F^V in Eq. (2); ω denotes the successful jump rate of the diffusing atom to its nearest vacancy site; v^0 is called the attempt frequency, which is of the order of the Debye frequency; E^M is the migration energy characterized as the difference in energy between the maximum energy configuration and the initial configuration.

With Eqs. (1) and (2), we can obtain

$$\begin{aligned} D_{\text{Ni}-\gamma} &= fga^2Zv^0\exp\left(-\frac{E_F^V + E^M}{k_B T}\right) \\ &= D_{\text{Ni}-\gamma}^0\exp\left(-\frac{Q}{k_B T}\right), \end{aligned} \quad (3)$$

where $D_{\text{Ni}-\gamma}^0$ is the pre-exponential constant and $Q = E_F^V + E^M$ is the diffusion activation energy.

2.2. Diffusion of Al atoms in the γ phase

The diffusion of Al atoms in the γ phase belongs to the vacancy-mediated solute diffusion category, which can be analyzed by employing the transition state theory within the Lidiard's five-frequency exchange model.^[21,22] Diffusion coefficient $D_{\text{Al}-\gamma}$ can be expressed as

$$D_{\text{Al}-\gamma} = fga^2\Gamma, \quad (4)$$

where g and a in Eq. (4) have the same meaning as described in Eq. (1). While the solute correlation factor f is no longer a constant, depending on the lattice geometry as in the case of self-diffusion. It depends on the jump rates of the vacancy with the solute Al atom and the host Ni atoms. Conceptually, in the five-frequency exchange model, the five jump frequencies ω_0 – ω_4 are defined as follows (Fig. 1). ω_1 is the jump frequency of a vacancy from a nearest-neighbor site of a solute to another nearest-neighbor site, ω_2 is the frequency for a solute-vacancy exchange, ω_3 is the frequency for vacancy jumps from a nearest-neighbor to non-nearest-neighbor position, and ω_4 is the frequency of the reverse jump of ω_3 , and ω_0 is the host atom jump in the absence of an impurity.^[23]

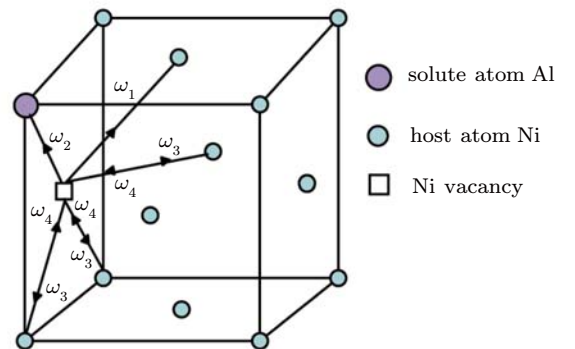


Fig. 1. (color online) Five-frequency model in the case of the fcc γ phase with a dilute solute Al atom. The arrows indicate the direction of the vacancy jump.

An exact expression for f was derived by Manning^[24] as follows:

$$f = \frac{\omega_1 + 7F_3\omega_3/2}{\omega_2 + \omega_1 + 7F_3\omega_3/2}, \quad (5)$$

where F_3 is called the escape probability, representing the probabilities of the vacancy returning from second, third and fourth nearest-neighbor positions to its original position. Man-

ning derived the following numerical expression for F_3

$$7F_3(\alpha) = 7 - \frac{10\alpha^4 + 180.5\alpha^3 + 927\alpha^2 + 1341\alpha}{2\alpha^4 + 40.2\alpha^3 + 254\alpha^2 + 597\alpha + 436}, \quad (6)$$

where $\alpha = \omega_4/\omega_0$.

In Eq. (4), Γ can be expressed as

$$\begin{aligned} \Gamma &= p\omega_2 = ZC_V^{\text{eq}} \exp\left(\frac{E^B}{k_B T}\right) \omega_2 = Z \exp\left(-\frac{E_F^{\text{V(Ni)}} - E^B}{k_B T}\right) v^0 \exp\left(-\frac{E^M}{k_B T}\right) \\ &= Zv^0 \exp\left(-\frac{E_F^{\text{V(Ni)}} - E^B + E^M}{k_B T}\right) = Zv^0 \exp\left(-\frac{E_F^{\text{V}} + E^M}{k_B T}\right), \end{aligned} \quad (7)$$

where $p = ZC_V^{\text{eq}} \exp(E^B/k_B T)$ is called the Lomer relation which denotes the probability that a vacancy occupies a nearest-neighbor site of the solute, $E_F^{\text{V(Ni)}}$ represents the Ni vacancy formation energy in the pure host system, E^B is the energy of binding between the solute atom and the vacancy, and $E_F^{\text{V}} = E_F^{\text{V(Ni)}} - E^B$ is the formation energy of the Ni vacancy adjacent to a solute atom.

Therefore the diffusion coefficient $D_{\text{Al}-\gamma}$ can be expressed as

$$D_{\text{Al}-\gamma} = f(\omega_0, \omega_1, \omega_2, \omega_3, \omega_4) g a^2 Z v^0 \exp\left(-\frac{E_F^{\text{V}} - E^B + E^M}{k_B T}\right) = D_{\text{Al}-\gamma}^0 \exp\left(-\frac{Q}{k_B T}\right). \quad (8)$$

2.3. Diffusion of Ni atoms in the γ' phase

The L1₂-type ordered structure on which Ni₃Al is based can be decomposed into two sublattices. The major element Ni occupies the face-center sites, constituting the α sublattice, and those of the minor element Al occupy the cube-corner sites, constituting the β sublattice. While an α sublattice site is coordinated with eight α sites and four β sites, a β site is surrounded entirely by α sites.^[25] Ni diffusion can occur by exchange of an Ni atom for a neighboring vacancy on the Ni site without creating disorder.^[26] Thus, it is quite natural that the diffusion of the majority component Ni in L1₂ compound Ni₃Al is by a sublattice vacancy mechanism. The diffusion coefficient is expressed as

$$D_{\text{Ni}-\gamma'} = \frac{2}{3} f g a^2 Z \omega C_V^{\text{eq}} = \frac{2}{3} f g a^2 Z v^0 \exp\left(-\frac{E_F^{\text{V}} + E^M}{k_B T}\right) = D_{\text{Ni}-\gamma'}^0 \exp\left(-\frac{Q}{k_B T}\right), \quad (9)$$

where the correlation factor f equals 0.689.^[27] The expression for the self-diffusion coefficient in the fcc lattice differs from the above only in numerical factor and the correlation factor, the numerical factor is unity instead of 2/3, reflecting the difference in coordination numbers.

2.4. Diffusion of the Al atoms in the γ' phase

Although a jump of the Al atom to a nearest neighbour site disturbs the ordered arrangement, an antisite Al atom can exchange its position for a vacancy on a neighboring α sublattice without causing further disordering. The review article^[28] has shown that Ni₃Al belongs to the antistructural-defect type of intermetallics, in which antisite atoms (Ni_{Al} and Al_{Ni}) are preferentially formed to accommodate the deviations from stoichiometry. In Ni₃Al vacancies are mainly formed on the Ni sublattice. So the minority element Al most likely diffuses as antisite atoms in the majority sublattice (NbO lattice).

The diffusion coefficient can be written as

$$\begin{aligned} D_{\text{Al}-\gamma'} &= \frac{2}{3} f g a^2 Z C_V^{\text{eq}} \exp\left(\frac{E^B}{k_B T}\right) \omega_2 \\ &= \frac{2}{3} f g a^2 Z \exp\left(-\frac{E_F^{\text{V(Ni)}}}{k_B T}\right) \exp\left(\frac{E^B}{k_B T}\right) v^0 \exp\left(-\frac{E^M}{k_B T}\right) \\ &= \frac{2}{3} f g a^2 v^0 \exp\left(-\frac{E_F^{\text{V(Ni)}} - E^B + E^M}{k_B T}\right) = D_{\text{Al}-\gamma'}^0 \exp\left(-\frac{Q}{k_B T}\right), \end{aligned} \quad (10)$$

and

$$f = \frac{u}{\omega_2 + u}, \quad (11)$$

where u is

$$u^{-1} = (2\omega_1 + 5\omega_3 F^X)^{-1} + (5\omega_3 F^Z)^{-1},$$

F^X and F^Z are the functions of ω_4/ω_0 .^[29]

2.5. Vacancy formation energy

Based on the above discussion, the calculation of the vacancy formation energy can be divided into two cases, i.e., $E_F^V = E_F^{V(\text{Ni})}$ for the diffusion of Ni atoms in the γ and γ' phases and $E_F^V = E_F^{V(\text{Ni})} - E^B$ for the diffusion of the Al atoms in the two phases. $E_F^{V(\text{Ni})}$ represents the Ni vacancy formation energy in the pure host system, and E^B denotes the formation energy of the Ni vacancy adjacent to the solute Al atom or the antisite atom Al_{Ni} .

In the first case, the vacancy formation energy is defined as the energy needed to remove one atom j from the host material and place it into a reservoir of the chemical potential μ_i of the same species. This energy can be written as a function of atomic potential as

$$E_F^{V(j)} = E_{\text{tot}}(\text{system}, [j]) + E_{\text{tot}}(j) - E_{\text{tot}}(\text{system}) + \mu_j, \quad (12)$$

where $E_{\text{tot}}(\text{system})$ and $E_{\text{tot}}(\text{system}, [j])$ are the total energies of the perfect solid system and the system containing one j -species vacancy, respectively, and $E_{\text{tot}}(j)$ is the total energy per atom in the elemental solid. On the condition that the j species is rich, μ_i equals zero.^[30]

As for the second case, the diffusing Al atoms in the two phases can be treated as impurities. So when calculating the vacancy formation energies, the solute-vacancy interaction should be considered, which can be written as

$$E^B = E_F^{V(\text{Ni})} - E_F^{V(\text{Al})}. \quad (13)$$

In Eq. (13), $E_F^{V(\text{Ni})}$ is the energy of vacancy formation energy in the solute-undisturbed solvent, and for Ni vacancy we have $E_F^{V(\text{Ni})} = E_F^{V(\text{Ni})}$. $E_F^{V(\text{Al})}$ is the energy of Ni vacancy formation next to a solute atom Al.^[20] So the vacancy formation energy can be expressed as

$$\begin{aligned} E_F^V &= E_F^{V(\text{Ni})} - E^B = E_F^{V(\text{Ni})} - [E_F^{V(\text{Ni})} - E_F^{V(\text{Al})}] \\ &= E_F^{V(\text{Al})}. \end{aligned} \quad (14)$$

3. Details of the calculations

Within a simple Arrhenius relation, as attempt frequencies are relatively similar, the quantity Q largely determines

the diffusion properties in close-packed structures. The activation energy for vacancy diffusion can be found by summing together the energy of vacancy formation E_F^V and the vacancy migration energy E^M . Accurate experimental determinations of these quantities can be quite challenging. The large range of vacancy formation energies reported from the different experimental methods (e.g., quenching, positron annihilation, etc.) indicates that the determination of E_F^V is non-trivial.^[31] The accuracy of E^M is dependent on method used to find E_F^V , making both quantities difficult to determine consistently and accurately.^[32,33] These difficulties partially provide the incentive to use theoretical alternatives to treat the diffusion properties of the materials.

3.1. Methodology and model

In the present paper, E_F^V and E^M were estimated by adopting the density functional theory calculations and were carried out with the plane-wave based Vienna AB initio Simulation Package (VASP)^[34,35] through using the projector augmented wave (PAW) method^[36,37] and the generalized gradient approximation (GGA) in the parametrization by Perdew, Burke, and Ernzerhof (PBE).^[38]

The computational model was a $10 \times 2 \times 2$ unit cell (160 atoms) constructed along the $\langle 001 \rangle$ direction as shown in Fig. 2. The supercell was equally divided by a (002) interface, and the two halves of the supercell were occupied by the γ -Ni and γ' -Ni₃Al phases, respectively. The lattice parameters of the supercell were taken to be equal for the γ and γ' blocks due to the assumption of complete coherence.^[39] Considering the fact that the improvement of the creep performance is mainly due to the strengthening effects of alloying element Re on the γ/γ' interface, and in order to investigate the effects of Re on the diffusion processes of Ni and Al atoms across the interface, a model with one Re atom on the γ/γ' interface was constructed. It was proved that Re mainly partitions into the γ' phase in ternary alloy,^[40,41] and a certain number of Re atoms partition into the γ' phase in multicomponent superalloy.^[42–44] Gong *et al.*^[45] pointed out that in the vicinity of the γ -Ni/ γ' -Ni₃Al interface as well as in the γ' -Ni₃Al phase, Re has a strong preference for substituting Ni atom on a (002) interfacial layer full of pure Ni atoms. So in the Re-doped interface model, one Ni atom on the (002) interfacial layer was substituted by an Re atom as shown in Fig. 2. A plane-wave cutoff of 350.5 eV was used in the calculations, which yields well converged results. The K points were sampled according to Monkhorst–Pack scheme^[46] with $1 \times 1 \times 6k$ mesh. During the simulation, the initial structures of each model without and with one Al solute atom on the layers parallel to the γ/γ' interface were relaxed with respect to the

internal coordinates, volume and shape. The structures were relaxed by minimizing the total energy with a convergence accuracy of 10^{-4} eV. The climbing image nudged elastic band (CI-NEB) (Ref. [47]) method was used to obtain the vacancy migration energy E^M of each system. Since the determina-

tions of the minimum energy path and the saddle point work reliably for a small number of images by CI-NEB, [47] we used three images in the computations for various migration paths. The images were relaxed until the maximum residual force was less than 0.02 eV/Å.

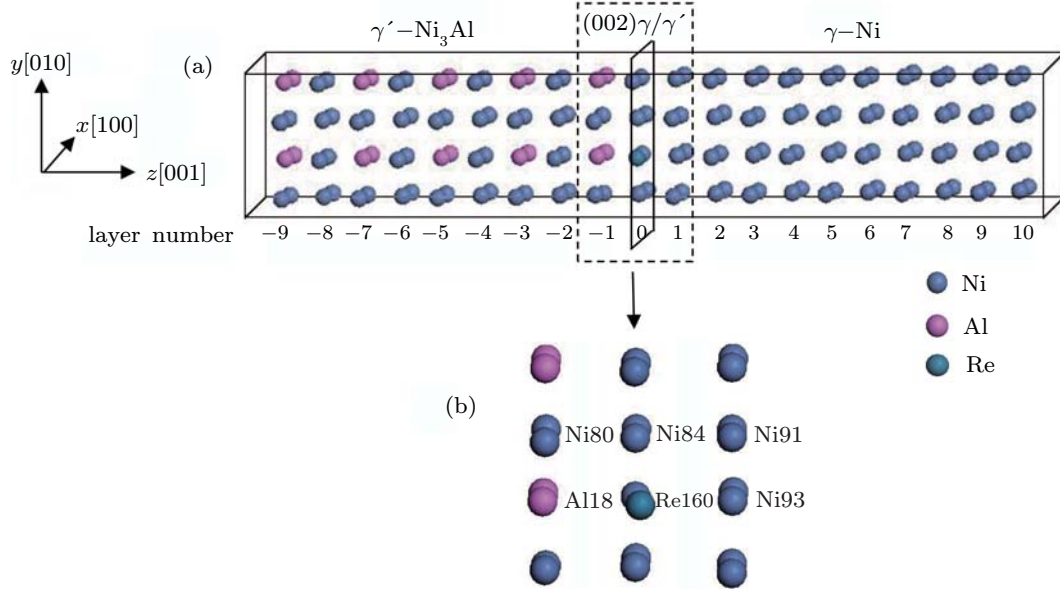


Fig. 2. (color online) (a) The 160-atom supercell model constructed along the $\langle 001 \rangle$ direction. The periodic boundary conditions are applied in the x and y directions while a vacuum layer of 12 Å is imposed in the z direction. The supercell is equally divided by a (002) γ/γ' interface (layer number 0), and the two halves of the supercell are occupied by the γ -Ni and γ' -Ni₃Al phases, respectively. In the Re-doped interface model, one Ni atom on the (002) γ/γ' interfacial layer (layer number 0) is substituted by an Re atom, (b) Some of the first nearest-neighbor atoms of the Re atom (Re160) are marked with the arabic numerals.

3.2. Migration path

From the four diffusion mechanisms mentioned above, we can determine the migration paths of the diffusing Ni and Al atoms, respectively. When Al atom diffuses out of the γ' phase and into the γ phase, it first diffuses as an antisite atom in the Ni sublattice in the γ' phase, and then as a solute in the fcc Ni lattice via the first nearest-neighbor Ni-vacancy in the γ phase. When Ni atom diffuses out of the γ phase and then into the γ' phase, the diffusion process can occur by exchange of a Ni atom for a neighboring Ni-vacancy on the fcc Ni lattice in the γ phase and then in the NbO structure type Ni sublattice.

When considering the diffusion processes of Ni atoms in the γ and γ' phases and the Al atoms in the γ phase, atom at each atomic site in the respective (002) layer in the model can be viewed as a potent diffusing atom jumping to its nearest-neighbor Ni vacancy; while in the diffusion process of Al atom in the γ' phase, the position of the antisite Al_{Ni} atom should be tested to make sure that it should be placed in a (002) plane of pure Ni or the plane of 50% Ni and 50% Al atoms. An energetic calculation indicates that the antisite Al_{Ni} atoms have a preference to be located on the (002) plane with pure Ni atoms as shown in Table 1.

Table 1. Total energy (in unit eV) of the system with substituting an antisite Al_{Ni} atom for the Ni atom in the n -th (002) layer of the model.

	(002) planes with pure Ni atoms in the γ' -Ni ₃ Al phase		(002) planes with 50%Ni and 50%Al atoms in the γ' -Ni ₃ Al phase	
	n	E_{tot}	n	E_{tot}
Model with clean γ/γ' interface	0	-866.71	-1	-866.03
	-2	-866.24	-3	-866.09
	-4	-866.30	-5	-866.10
	-6	-866.30	-7	-866.04
Model with Re-doped γ/γ' interface	0	-873.36	-1	-872.58
	-2	-872.71	-3	-872.79
	-4	-873.02	-5	-872.82
	-6	-873.02	-7	-872.74

4. Results and discussion

4.1. Diffusional phenomena across the clean γ/γ' interface

In Figs. 3(a)–3(c), we present the calculated Ni-vacancy formation energy adjacent to the diffusing atom (E_F^V), the diffusing migration energy (E^M) and the activation energy (Q) varying with the number of the (002) γ/γ' interface layers in the clean interface model.

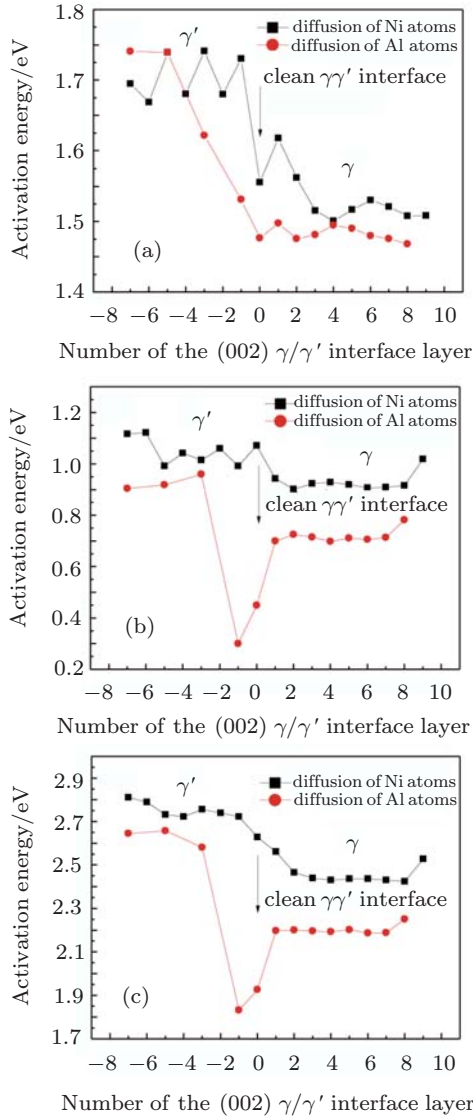


Fig. 3. (color online) (a) Variations of calculated Ni-vacancy formation energy adjacent to diffusing atom E_F^V , (b) diffusing migration energy E^M , and (c) the activation energy Q with the number of the (002) γ/γ' interface layers in the clean γ/γ' interface model.

We note that in the vicinity of the γ/γ' interface, E_F^V and E^M terms have displayed expected and clear transition areas: for the diffusion of the Ni atoms, this area ranges from -1 to -5, a total of 6 (002) layers for E_F^V , and 0 to 3, a total of 4 (002) layers for E^M ; for the diffusion of Al atoms, this area ranges from -3 to 3, a total of 7 (002) layers for E_F^V , and -3 to 1, a total of 5 (002) layers for E^M .

It is worthy to point out that the magnitudes of the formation energies of the Ni-vacancies adjacent to the diffusing Al atoms and the corresponding migration energies of the Al

atoms in both phases are obviously lower than those of the Ni atoms. This can be attributed to the size effects of the Al atom and Ni atom (Al: 1.43 Å, Ni: 1.24 Å). The Al atom acting as a solute may induce strain on the surrounding atoms. Via the neighboring vacancy, the solute atom would allow itself to relax towards the vacancy and thus go away from the other neighboring atoms. Therefore, the vacancy in a nearest-neighbor position to a large Al atom helps to relieve the strain, producing a strong solute-vacancy binding energy E^B , and hence according to Eq. (14) a lower E_F^V and also a greater probability to move towards the vacancy and complete the exchange process.

We note that between the two phases, the discrepancies in E_F^V and E^M of the Ni diffusion process are smaller than those of the Al diffusion process. These two quantities of the Al diffusion are much more sensitive to the existence of the γ/γ' interface, and has an abrupt change of about 0.3 eV for E_F^V and 0.65 eV for E^M between the two phases. This may be attributed to the ordered structure of the γ' -Ni₃Al phase that could more greatly retard the movement of the Al atoms than the fcc Ni lattice.

We emphasize that the major contribution to the variation of the diffusion activation energy Q across the γ/γ' interface comes from the variation of the diffusion migration energy E^M . Watanabe *et al.*^[15] observed in the experiment that in the Ni/Ni₃Al diffusion couple, a γ phase would be transformed from the γ' phase near the Ni/Ni₃Al interface and Kirkendall voids were visible exclusively in this γ phase. The similar formation of Kirkendall voids in the new γ phase was also reported by Janssen^[48] and Kawazoe *et al.*^[49] Our calculation results given in Fig. 3(c) might to some extent explain this phenomenon. Around the γ/γ' interface, the activation energy of the Al atom in the γ' phase has a sudden drop of about 0.8 eV which makes it easy to diffuse out of the γ' phase and into the γ phase. However, the activation energy of the Ni atom to diffuse from γ to γ' phase differs not much, which makes them possible to diffuse into the γ' phase. So the formation of the γ phase in the original γ' phase observed in the experiment can be viewed as the consequence of the atoms exchange, with Al atoms diffusing out of the γ' phase and Ni atoms diffusing in. Furthermore, from the activation energy shown in Fig. 3(c), we can see that Al atom diffusion is faster than Ni atom diffusion in the γ phase which would result in the formations of Kirkendall voids exclusively in the new γ phase. The Al atom diffusion is inhibited in the γ' phase in comparison with the γ phase, which would cause the absence of void formation in the γ' phase.

To understand the origin of the affected area of the clean γ/γ' interface, we present in Figs. 4 and 5 the local density-of-states (LDOS) profiles of atoms in each (002) layer in the γ and γ' phases, respectively. In Fig. 5, the main peaks of the LDOS of atom at layer 1 are lower at the Fermi level than those of the atoms at layers 2 and 3. The magnitudes of the LDOS for the atoms on layers 4–8 in the γ phase are then reduced again and close to the case of the bulk Ni.

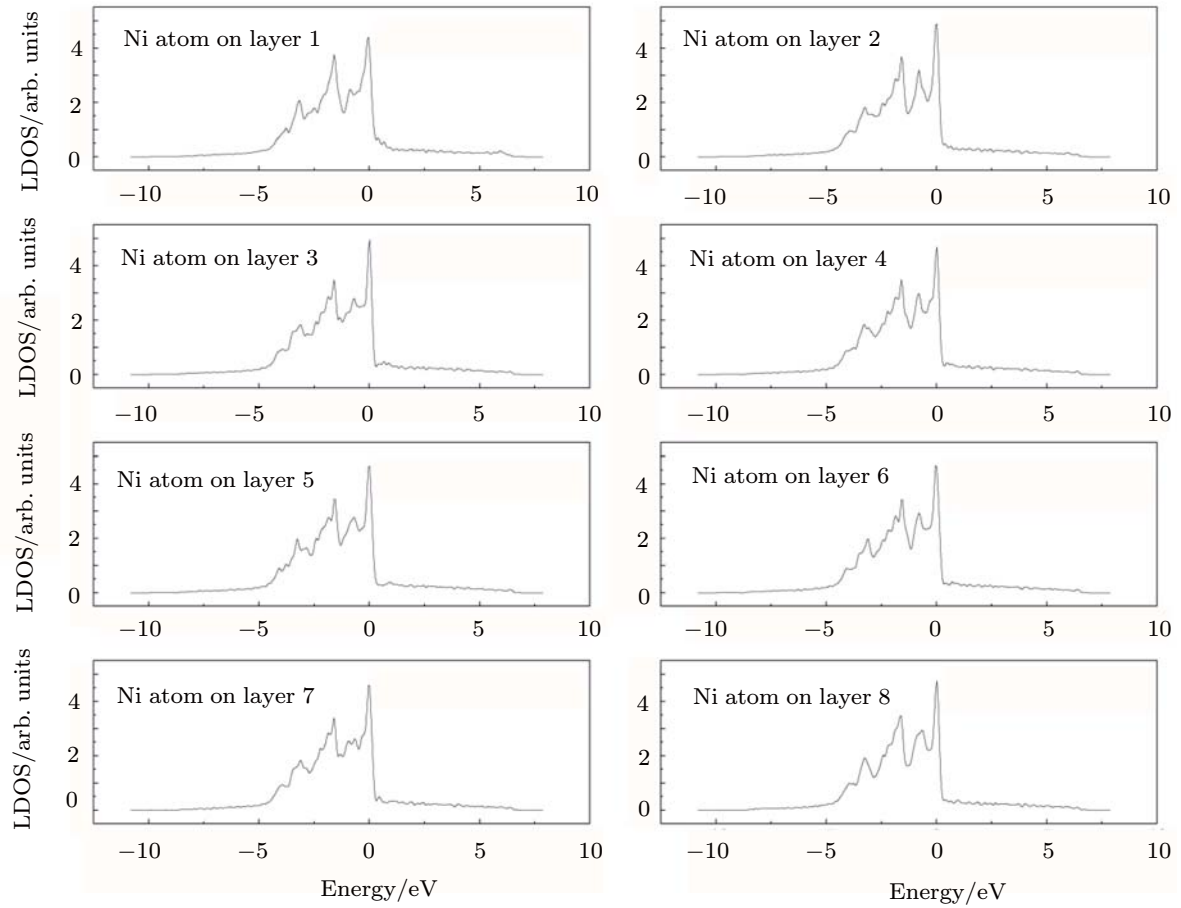


Fig. 4. LDOSs (in units of states/eV) of some particular Ni atoms on each (002) layer in the γ phase in the clean γ/γ' interface model. The Fermi level is shifted to zero.

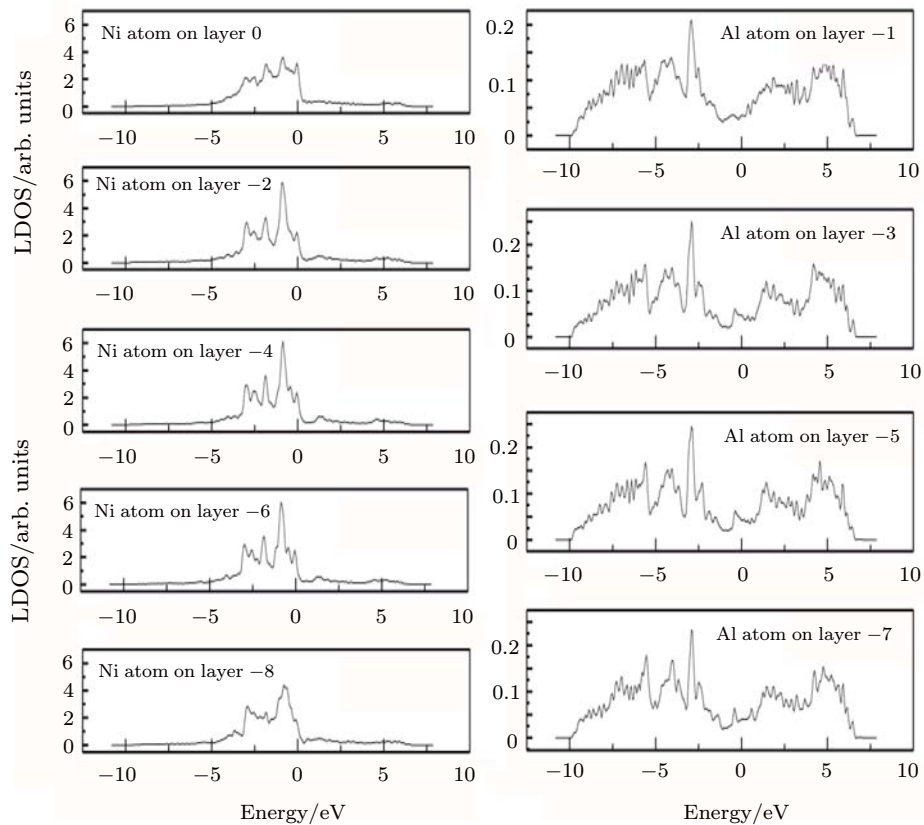


Fig. 5. LDOSs (in units of states/eV) of some particular Ni or Al atoms on each (002) layer in the γ' phase in the clean γ/γ' interface model. The Fermi level is shifted to zero.

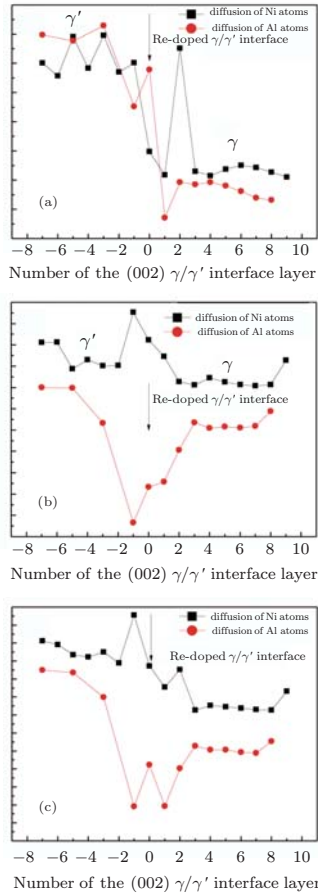


Fig. 6. (color online) (a) Calculated values of Ni-vacancy formation energy adjacent to the diffusing atom E_F^V , (b) diffusing migration energy E^M , and (c) activation energy Q varying with the number of the (002) γ/γ' interface layer in the Re-doped γ/γ' interface model.

Figure 6 shows that the main peaks of the LDOS curves of Ni on layer 0 and Al on layer -1 at the Fermi level are higher and located in a higher energy region than those of the

atoms away from the interface in the γ' phase. Based on the above analysis, we can see that the electronic states of the typical clean γ/γ' interface are localized within 5 (002) layers of atoms.

4.2. Diffusional phenomena across the Re-doped γ/γ' interface

Further quantitative evaluations of E_F^V , E^M , and Q for the Re-doped interface model are given in Figs. 6(a)–6(c). We can see that the addition of Re at the interface has great influences on E_F^V and E^M for both Ni and Al diffusion. It could increase E_F^V of Ni diffusion in the γ phase, E_F^V of Al diffusion in the γ' phase, and is also able to raise E^M of Ni diffusion in the γ phase and lower E^M of Al diffusion in the γ phase. As an overall effect as shown in Fig. 6(c), we find that in the vicinity of the interface, the activation energies increase and the transition regions enlarge for both Ni and Al atoms. The results indicate that the Re-doping could thus effectively retard the Al and Ni diffusion across the γ/γ' interface, which accordingly elevates the creep strength and maintains the stability of the Ni-based single crystal superalloy.

Compared with the scenario of the clean γ/γ' interface, the LDOSs of some corresponding atoms in the γ phase and γ' phase for the Re-doped interface model are shown in Figs. 7 and 8. It is found that an obvious feature of the LDOS change is that the magnitudes of the LDOS curves of Ni at layer 0 and layer 1 and Al at layer -1 at the Fermi level greatly decrease when Re replaces one Ni atom at the γ/γ' interface. The reduction of the LDOS near the Fermi level means that the transition probability of the electronic states is confined and the stability of the γ/γ interface can increase.

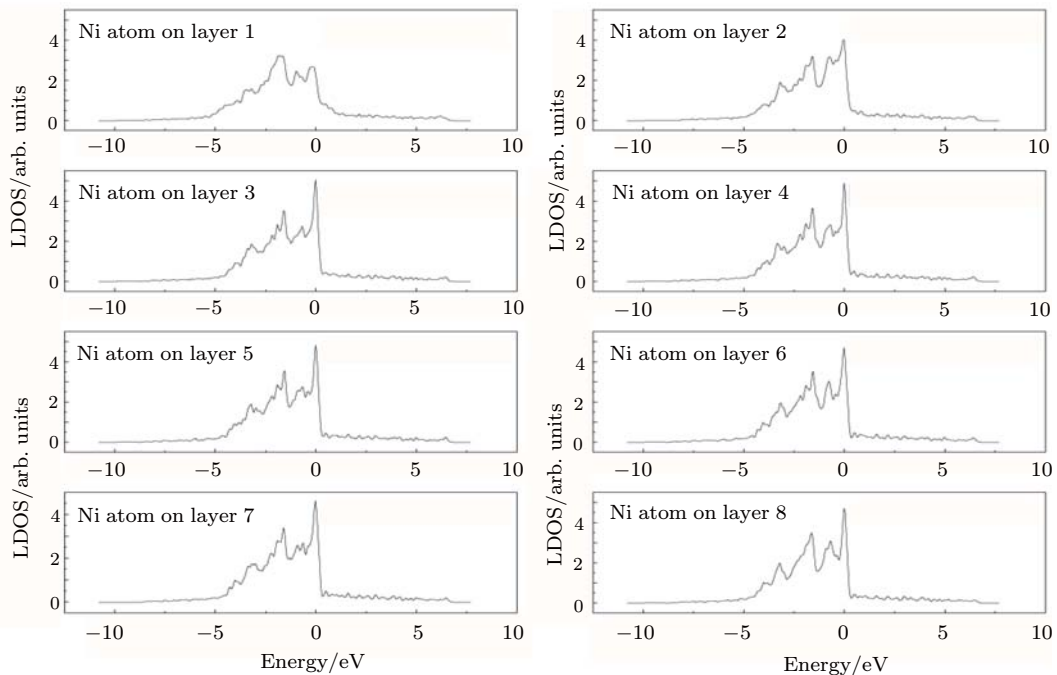


Fig. 7. LDOSs (in units of states/eV) of some particular Ni atoms on each (002) layer in the γ phase in the Re-doped γ/γ' interface model. The Fermi level is shifted to zero.

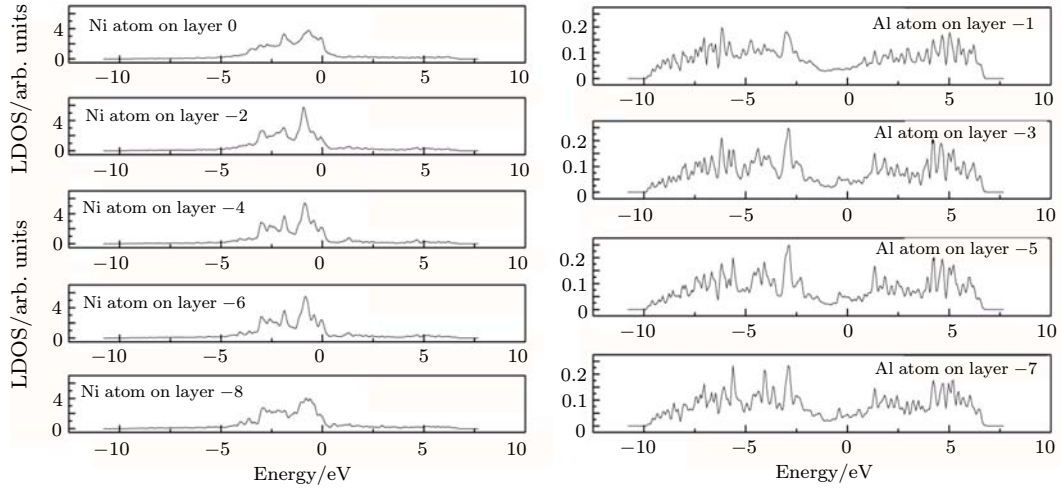


Fig. 8. LDOSs (in units of states/eV) of some particular Ni or Al atoms on each (002) layer in the γ'/γ' phase in the Re-doped γ/γ' interface model. The Fermi level is shifted to zero.

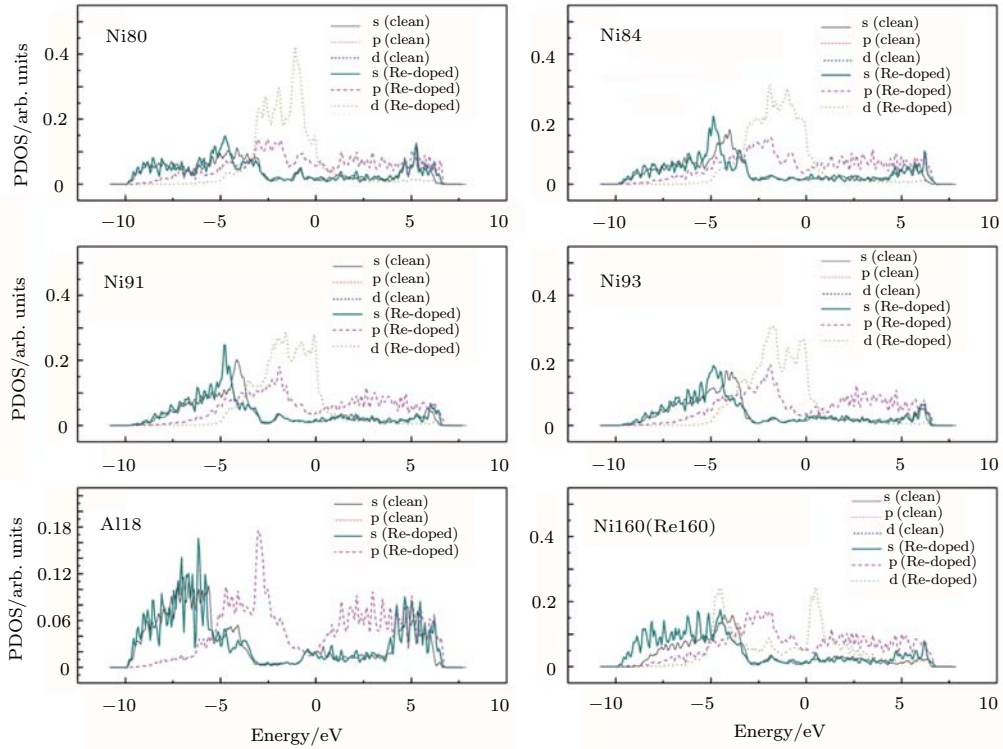


Fig. 9. (color online) PDOS curves for Ni160 (Re160) and some of its nearest-neighbor atoms in the clean and Re-doped γ/γ' interface models. The Arabic numerals in Ni80, Al18, etc., correspond to those in Fig. 2(b).

To further examine the significant role played by the doping Re at the interface, we investigate the partial density of states (PDOS) curves for Ni160 (Re160) and some of its nearest-neighbor atoms in the clean and Re-doped γ/γ' interface models. The results are presented in Fig. 9. It is found that the main peaks of s PDOS of the nearest-neighbor atoms (Ni80, Ni84, Ni91, Ni93, and Al18) in the Re-doped model are higher and located in the region of lower energy than those of in the clean interface system. The distribution of s electrons is spatially dispersed, which represents a reduction in the directionality of bonds in the Re-doped system with respect to that in the clean interface system. We note that the d electrons of Re are responsible mainly for bonding between Re and its neighboring atoms. The Re- d form strong hybridization states

with the s, p, d electrons of the adjacent atoms, showing that the interplay between Re and its neighboring atoms is very strong. The magnitude of the d PDOS of the nearest-neighbor Ni atoms at the Fermi level is reduced and moved to lower energy region when Re160 replaces Ni160, which means that the transition probability of the electronic state is inhibited. The above analyses all suggest that the Re atom on the (002) γ/γ' plane could significantly enhance the stability of the γ/γ' interface.

5. Conclusions

First principles quantum-mechanical electronic structure method is used to study the diffusional phenomena of Ni and

Al atoms across the clean and Re-doped γ/γ' interfaces of the Ni-based single crystal superalloys. The diffusional mechanisms of the four circumstances are discussed: the diffusion of Ni atoms in the γ phase belongs to the self-diffusion process which is mediated by the vacancy-type defects, the diffusion of Al atoms in the γ phase can be classified as the vacancy-mediated solute diffusion, and can be analyzed by employing the transition state theory within the Lidiard's five frequency exchange model, the Ni diffusion in the γ' phase can occur by exchange of a Ni atom for a neighboring vacancy on the Ni site, and Al atoms in γ' phase mostly likely diffuse as antisite atoms in the majority Ni-sublattice. The expressions for the vacancy formation energies and the diffusion coefficients for the four cases are also given.

The values of vacancy formation energy E_F^V , the migration energy E^M , and the activation energy Q for the Ni and Al diffusion across the clean and Re-doped γ/γ' interfaces are estimated. In the vicinity of the clean γ/γ' interface, E_F^V and E^M terms display the expected and clear transition area which varies from 3 to 7 (002) layers. The magnitudes of the E_F^V and E^M of the diffusing Al atoms in both phases are lower than those of the Ni atoms, which may be related to the electronic configuration and the atomic size. The variations of E_F^V and E^M of the Al atoms between the two phases are more sensitive to the existence of the γ/γ' interface, which can be attributed to the ordered structure of the L1₂-type Ni₃Al that hinders the movements of the Al atoms. The calculated results also indicate that the Al atom diffusion is faster than Ni atom diffusion in the γ phase, which means that the formations of the Kirkendall voids are exclusively in the γ phase, which is because the Al diffusion is hindered in the γ' phase, and thus leading to the absence of void formation in the γ' phase. With Re addition at the γ/γ' interface, the activation energy increases and the transition region enlarges for the diffusions of both Ni and Al atoms.

The LDOS profiles suggest that the electronic states of the typical clean γ/γ' interface are localized within 5 (002) layers of atoms. When Re replaces a Ni atom on the (002) γ/γ' interface, an obvious change is that for atoms around the interface the LDOS curves at the Fermi level greatly decrease, which means that the transition probability of the electronic states is confined. The PDOS curves show that the Re-*d* hybridizes strongly with the *s*, *p*, *d* electrons of its nearest-neighbor atoms, showing that the interaction between Re and its adjacent atoms is very strong, which indicates that with the Re doping the stability of the γ/γ' interface can be increased.

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