

Effects of alloying Re and Ru in the edge-dislocation core of the Ni/Ni₃Al interface*

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Investigations of alloying Re and Ru in the [110](001) dislocation core of the Ni/Ni₃Al interface were conducted within the framework of density functional theory. The energetic calculations show that both elements can stabilize the [110](001) dislocation core. In the dislocation core region, Re and Ru prefer to substitute for Ni on the site in the γ -phase. Re is easier to segregate into the dislocation core region as compared with Ru; it especially prefers to substitute for Ni on the γ -(Ni)1 site.

Keywords: nickel alloys, dislocation-structure, *ab initio* electron theory

PACC: 6155H, 6170G, 6185, 7115A

1. Introduction

Ni-based solid solution is widely used in turbine blades and vanes in the most advanced gas turbine engines for its high-temperature applications.^[1] It is of great interest for its good oxidation resistance and excellent ductility.^[2] γ -Ni has a face-centred cubic (fcc) structure with a lattice constant of 3.524 Å. γ' -Ni₃Al is of great interest for its attractive applications in the aerospace and power industries as a high-temperature structural material. It exhibits an ordered fcc L1₂ structure (with a lattice constant of 3.570 Å). Ni and Ni₃Al not only have similar structures but also have close unit cell lattice constants (the misfit of γ/γ' is below 1.3%). In this article, combining Ni and Ni₃Al could produce Ni-based single crystal (SC) superalloys. Creep rupture strengths of SC superalloys were reported to be improved by adding W, Re and Ta.^[3,4] W and Re are reported to participate in the dendrite core,^[5] which will lead to the formation of topologically close packed (TCP) phases,^[6] and causes considerable degradation of the mechanical properties. A recent experiment^[7] showed that the TCP phases could be eliminated through the addition of Ru. Thus, it is necessary to investigate the effects of alloying with Re and Ru, because the addition of elements could promote the overall performance of γ/γ' superalloys. Theoretical works^[8–12]

studied the strengthening effects and synergetic effect of Re and Ru in the coherent region of the γ/γ' interface. However, it is known from transmission electron microscopy (TEM) experiments^[13–15] that γ/γ' interface is associated with $\langle 110 \rangle$ Burgers vector misfit dislocations. As an important structural defect widely present in Ni-base SC superalloys, misfit dislocations have strong interactions with impurities, and the interactions greatly affect the mechanical properties of the alloy. To our knowledge, experimental techniques to study the vicinity of the γ/γ' interface are limited. As a result, there is no direct report on the study of alloying Re and Ru in the dislocation core of Ni-base SC superalloys by experimental methods. Although many theoretical works^[16–20] investigating dislocations have been conducted, none of the results come from density functional theory (DFT). Thus, we herein make a theoretical investigation of the effects of alloying elements in the dislocation core of γ/γ' superalloys by *ab initio* calculation.

In this paper, the DFT method is used to investigate the occupancy sites of Re and Ru in the coherent and dislocation core region, and the segregation properties of dopants surrounding the dislocation core. The rest of this paper is organized as follows. In Section 2, we give details of the methods and models. In Section 3 we provide the energetic analysis. In Section 4 we draw conclusions.

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2. Model and methods

Total-energy calculations were performed within the framework of the DFT, which is implemented in the plane wave-based Vienna *ab initio* simulation package (VASP).^[21,22] In all of the calculations, the Perdew–Wang 91 exchange–correlation functional^[23] within the generalized gradient approximation (GGA) is taken into account; a plane-wave cutoff energy of 500.0 eV for all the models and the electron–ion interaction potential described by the projector augmented wave method^[24] are used. The k point is set to be

$16 \times 16 \times 16$ for the bulk and $6 \times 6 \times 1$ for the interface model. Due to the large number of atoms in the dislocation core, we only use Γ point in the calculations. The interface and dislocation are modelled with the supercell model, and the thickness of the vacuum layer is 12.0 Å. The equilibrium geometry is determined by relaxation until forces are less than 0.04 eV/Å. We use the Murnaghan equation^[25] to obtain the lattice constant a_0 and the bulk modulus B_0 . The reliability of our approach is demonstrated by the excellent agreement between calculated and experimental lattice parameters, as listed in Table 1.

Table 1. The calculated lattice constant a_0 and bulk modulus B_0 . Other DFT, EAM (embedded atom method) calculated results and experimental results are listed for comparison.

	Ni		Ni ₃ Al	
	$a_0/\text{\AA}$	B_0/GPa	$a_0/\text{\AA}$	B_0/GPa
our results	3.526	196.8	3.570	180.8
other DFT results ^[26]	3.540	191.6	3.564	182.4
EAM results ^[27]	3.520	181.0	3.571	N/A
experiment ^[c),28]	3.520	181.0	3.570	240.0

To obtain the optimized structures of the dislocation core, we need to investigate the interface first. The coherent manner of the interface directly influences the physical properties of γ/γ' superalloys. Figure 1 shows the atomic structure of bulk Ni₃Al, and the fcc structure of bulk Ni is the same as that of Ni₃Al. According to fcc structure, there are two series of models for $\langle 001 \rangle$ oriented interfaces. One is the hollow site model and the other is the top site model. The two models investigated in our calculations are given in Figs.2(a) and 2(b) respectively. In the previous work,^[29] the two models have been compared with each other, and the hollow site model is more energetically stable than the top site model.

We construct a γ/γ' $[110](001)$ edge dislocation model as follows. A hollow site model is selected as the initial model. The misfit between the γ and γ' -phases is 1.3%, so we construct a misfit interface model with $67 \times 67 \times 10$ γ unit cells and $66 \times 66 \times 10$ γ' unit cells, in the x , y , z , directions. Then the interface model is relaxed according to empirical molecular dynamics using the Voter–Chen potential.^[30,31] A periodic boundary condition is applied to the x and y directions and a free surface boundary condition to the z direction.

The relaxation reveals the dislocation network, which is in agreement

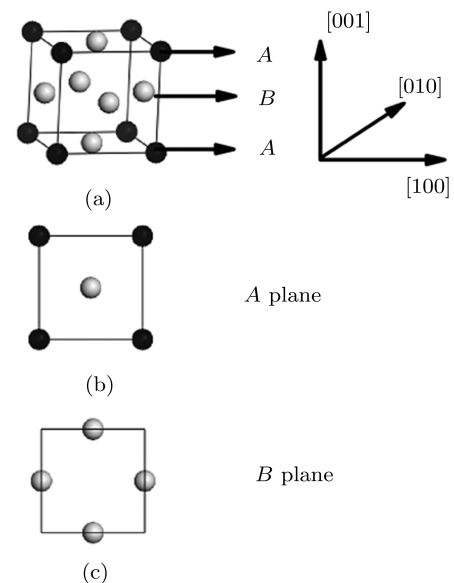


Fig.1. Ni₃Al bulk orientated $[001]$ direction. The black ball denotes the Al atom, and the grey ball denotes the Ni atom. (a) Perfect Ni₃Al bulk with the stacking sequence (ABABAB...); (b) Atomic structure of A plane; (c) Atomic structure of B plane.

^{c)} Available from: <http://www.webelements.com/>

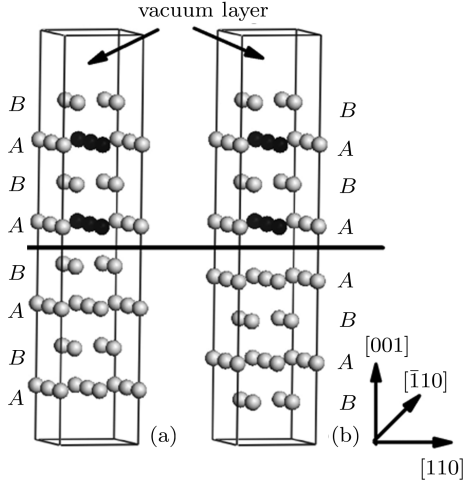


Fig.2. The geometry of the γ/γ' interface model. The black ball denotes the Al atom, and the grey ball denotes the Ni atom. (a) The hollow site (001) interface model, Ni and Al atoms in the γ' -phase placed in the vacancy site of Ni atoms in the γ -phase. ([001]: γ : ABAB ... AB|interface|[001]: γ' : ABAB ... AB) stacking; (b) The top site (001) interface model, Ni and Al atoms in the γ' -phase placed directly on the top site of Ni atoms in the γ -phase. ([001]: γ : BABA ... BA|interface|[001]: γ' : ABAB ... AB) stacking.

with that reported in Ref.[32]. From this configuration, we extract the model of the dislocation core, which is illustrated in Fig.3. We select 312 atoms around the dislocation core as our calculated model.

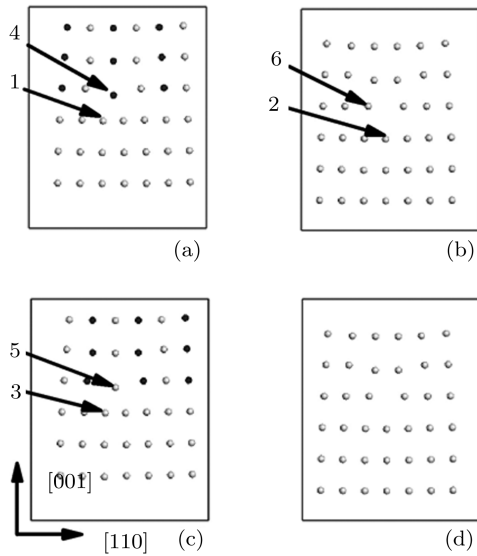


Fig.3. Atomic model of the [110](001) edge dislocation core in γ/γ' interface. The black ball denotes the Al atom, and the grey ball denotes the Ni atom. The adjacent planes (a), (b), (c) and (d) stack consecutively along $[1\bar{1}0]$. The arrows point to the substitution sites: 1 γ -(Ni)¹, 2 γ -(Ni)², 3 γ -(Ni)³, 4 γ' -(Al), 5 γ' -(Ni)¹, 6 γ' -(Ni)².

The model has a stacking sequence of planes (abcd-abcd). The study of [110](001) dislocation in the Ni/Ni₃Al interface, despite its simplicity, is very helpful for understanding the interactions between impurity and dislocation. Assuming a very dilute solution of Re and Ru in the Ni/Ni₃Al interface, we consider a single impurity model. Substitutional states are studied with only one Re or Ru atom doped at the corresponding substitutional site within the core region. Therefore, we perform structure optimizations by using VASP with the total energy minimization. Atoms in the top and bottom layers are fixed during the relaxations to simulate a bulk environment. Atoms surrounding Re or Ru and atoms in the dislocation core have been fully relaxed in each case.

3. Results and discussion

3.1. Alloying with Re and Ru in the coherent region of the Ni/Ni₃Al interface

We model the (001) γ/γ' interface system with a repeated slab construction with a three-dimensional translational symmetry. The formation energy of interface E_f is defined as follows:

$$E_f = (E_{\gamma/\gamma'} - E_{\text{bulk-}\gamma} - E_{\text{bulk-}\gamma'})/A_i - (E_\gamma + E_{\gamma'}), \quad (1)$$

$$E_\gamma = (E_{\text{slab-}\gamma} - E_{\text{bulk-}\gamma})/A_{s-\gamma}, \quad (2)$$

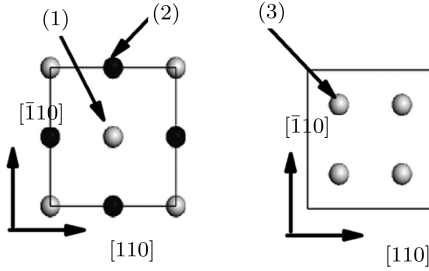
$$E_{\gamma'} = (E_{\text{slab-}\gamma'} - E_{\text{bulk-}\gamma'})/A_{s-\gamma'} \quad (3)$$

where $E_{\gamma/\gamma'}$ is the total energy of γ/γ' interface, which is the interface between slab γ and slab γ' , A_i is the interface area. E_{bulk} is the total energy of bulk, and E_{slab} is the total energy of a fully relaxed slab. $A_{s-\gamma}$ and $A_{s-\gamma'}$ are the areas of slab γ and slab γ' , respectively. E_γ and $E_{\gamma'}$ are surface formation energies. Interface formation energy can be viewed as the work requires to create an interface between the two bulk materials. It compares interfacial bonds to the total bonds in bulk material. To use the repeated slab model, we must guarantee that the size of the slab model is large enough. Hence, we investigate the formation energies of the Ni/Ni₃Al interface. Table 2 lists the formation energies of the hollow site (001) interface model. When the number of atomic layers N reaches 24, the formation energy gets converged. This suggests that a repeated slab model with 24 atomic layers is large enough to model the Ni/Ni₃Al interface.

Table 2. Formation energy of the hollow site (001) interface model. The formation energy unit is J/m².

N	4	8	12	16	20	24	28
E_f	-4.19	-4.20	-4.20	-4.18	-4.18	-4.15	-4.14

We consider the substitutions near the interface; the atomic structures of the interface plane are sketched in Fig.4.

**Fig.4.** The atomic structure of the interface plane. The black ball denotes the Al atom, and the grey ball denotes the Ni atom. (1) The γ' -Ni substitution; (2) The γ' -Al substitution; (3) The γ -Ni substitution.

The dopant interface coverage is 25% in our calculations. The usual defect energy for a given defect can be calculated using the formula

$$\tilde{E}_d = E(d) - E(0), \quad (4)$$

where $E(d)$ and $E(0)$ are the total energies of the model with and without the defect considered, respectively. The results calculated from a 96 atom repeated slab model for point defects in the coherent region of the Ni/Ni₃Al interface are presented in Table 3.

Table 3. The defect energy \tilde{E}_d (in eV) when alloying with Re and Ru.

X^{site}	\tilde{E}_d/eV	X^{site}	\tilde{E}_d/eV
Re γ' -(Ni)	-6.59	Ru γ' -(Ni)	-3.39
Re γ' -(Al)	-7.57	Ru γ' -(Al)	-3.82
Re γ' -(Ni)	-5.66	Ru γ' -(Ni)	-3.13

The results indicate that both Re and Ru can stabilize the Ni/Ni₃Al interface system, and alloying with Re is more energetically stable than with Ru. Among the three cases of substitution, γ' -(Al) substitution is the most energetically stable state.

3.2. Re and Ru at substitutional sites in the dislocation core

The structure of the dislocation core is very important due to its singularity. To compare with the

core structure obtained by the empirical molecular dynamics method, we perform reoptimizations of the core with the *ab initio* VASP code. During the relaxations the fixed atoms are the same as those mentioned above in Section 2. The results obtained show that only slight displacements take place in the middle atomic layers, and this conclusion indicates that the structure of the dislocation core obtained by molecular dynamics method is reliable.

To discuss the segregation of alloying elements to the dislocation line, we use the segregation energy defined as

$$E_{\text{seg}} = \frac{1}{n} \left[\left(E_{\text{dislocation}}^{\text{doped}} - E_{\text{dislocation}}^{\text{clean}} \right) - \sum_i \mu_i \Delta M_i \right], \quad (5)$$

where $E_{\text{dislocation}}^{\text{doped}}$ and $E_{\text{dislocation}}^{\text{clean}}$ are total energies of the relaxed systems with and without alloying elements in the dislocation core region, respectively; n is the number of dopants, and μ_i ($i = \text{Re, Ru, Ni, Al}$) are chemical potentials, ΔM_i are the change of number for the chemical species i .

From Fig.3, we can see six substitutional sites around the dislocation core: (i) sites 1, 2 and 3 in the compressed region in the γ -phase; (ii) sites 4, 5 and 6 in the dilated region in the γ' -phase. Only site 4 is substituted by Al, the other sites are substituted by Ni. The calculated segregation energies are summarized in Table 4.

Table 4. The segregation energy E_{seg} (in eV) of the dislocation line, doped with Re and Ru.

X^{site}	E_{seg}/eV	X^{site}	E_{seg}/eV
Re γ' -(Ni)1	-1.09	Ru γ' -(Ni)1	-0.45
Re γ' -(Ni)2	-0.78	Ru γ' -(Ni)2	-0.05
Re γ' -(Ni)3	-1.04	Ru γ' -(Ni)3	-0.4
Re γ' -(Al)	1.37	Ru γ' -(Al)	2.02
Re γ' -(Ni)1	0.2	Ru γ' -(Ni)1	0.18
Re γ' -(Ni)2	-0.14	Ru γ' -(Ni)2	0.19

For the Re substitution case, the corresponding segregation energies for sites 4 and 5 are positive (1.37 eV and 0.20 eV). This means that they are not favourable in energy. For other substitution sites, the lowest and the highest segregation energies occur, respectively, at site 1 (-1.09 eV, in the compressed region of the γ -phase) and site 6 (-0.14 eV, in the dilated region of the γ' -phase). The compressed region in the γ -phase seems to be a preferable substitutional site, showing the trapping effect of the dislocation core on Re. In the case of Ru substitution, the segregation energies for the dilated region in the γ' -phase are positive, and in the compressed region in the γ -phase the

values are negative. In particular, the lowest segregation energy appears at the same substitution site (site 1, the compressed region in the γ -phase) as in the case of doping with Re. This means that both Re and Ru prefer to segregate to the compressed region (site 1) around the dislocation core.

To discuss the distribution of alloying elements around the dislocation core, we define the dopant concentration as

$$c_{\text{dislocation}} = c_{\text{coherent}} \exp[-\Delta U/kT], \quad (6)$$

where c_{coherent} is the equilibrium concentration in the coherent regions. ΔU is the segregation energy difference between the dislocation core region and the coherent region.

$$\Delta U = E_{\text{seg}}^{\text{dislocation}} - E_{\text{seg}}^{\text{coherent}}. \quad (7)$$

In Eq.(6) k is the Boltzmann constant, and T is temperature. Table 5 lists the segregation energy difference ΔU between the dislocation core region and the coherent region when alloying with Re and Ru. The segregation energy difference is positive for the substitution on the γ' -Al site. It should be noted that both Re and Ru prefer to substitute for the atom on the γ' -Al site in the coherent region, while in the dislocation core region, the alloying elements Re and Ru may redistribute themselves into the γ -phase. The segregation energy difference on other sites is negative; this means that the concentration of dopants around the dislocation core is larger than that in the coherent region. At low temperatures, Re prefers to segregate into the dislocation core region. This exhibits the same trend as the experimental results.^[10] Re is much easier to segregate into the dislocation core than Ru. This is because doping with Re leads to lower segregation energy. Experimental results^[33,34] show that

segregation of Re onto dendrite cores can increase the possibility of forming TCP phases, which are not microstructurally stable and would be expected to result in degraded properties. Our results agree well with the experimental results^[7] that alloying with Ru could reduce the possibility of forming TCP phases, because doping with Ru leads to higher segregation energy. The addition of Ru could significantly improves the overall performance.^[6–8]

Table 5. The segregated energy difference U (in eV) between the dislocation and coherent regions when alloying with Re and Ru.

X^{site}	$\Delta U/\text{eV}$	X^{site}	$\Delta U/\text{eV}$
Re γ -(Ni)1	-1.43	Ru γ -(Ni)1	-0.79
Re γ -(Ni)2	-1.13	Ru γ -(Ni)2	-0.4
Re γ -(Ni)3	-1.38	Ru γ -(Ni)3	-0.75
Re γ' -(Al)	0.28	Ru γ' -(Al)	0.38
Re γ' -(Ni)1	-1.08	Ru γ' -(Ni)1	-0.44
Re γ' -(Ni)2	-1.42	Ru γ' -(Ni)2	-0.42

4. Summary

In this work, the effects of alloying Re and Ru in the [110](001) edge dislocation core region of the Ni/Ni₃Al interface are investigated by *ab initio* calculations. Doping with Re and Ru increases the cohesive strength of Ni-based SC superalloys. In the coherent region near the interface, Re and Ru prefer to substitute for Al on the site in the γ' -phase, while in the dislocation core region, Re and Ru prefer to substitute for Ni on the site in the γ -phase. Re is more favoured to segregate into the dislocation core region compared with Ru, and it especially prefers to substitute for Ni on the γ -(Ni)1 site.

References

- [1] Huntz A M, Lefevre B and Cassino F 2000 *Mater. Sci. Eng. A* **290** 190
- [2] Betteridge W 1977 in: *Nickel and its Alloys* (Macdonald and Evans, Estover, United Kingdom) p124
- [3] Erickson G L 1995 *A New, Third Generation, Single-Crystal, Casting Superalloy* (Warrendale, PA: JOM, TMS) **47** No4 p36
- [4] Yeh A C and Tin S 2005 *Scripta. Mater* **52** 519
- [5] Durand-Charee M 1997 *The Microstructure of Superalloys* (Canada: Gordon and Breach Science Publishers) p60
- [6] Fuchs G E 2001 *Mater. Sci. Eng. A* **300** 52
- [7] Atsushi Sato, Hiroshi Harada, Tadaharu Yokokawa, Takao Murakumo, Yutaka Koizumi, Toshiharu Kobayashi and Hachiro Imai 2006 *Scr. Mater* **54** 1679
- [8] Chen K, Zhao L R and Tse J S 2003 *Philos. Mag.* **83** 1685
- [9] Chen K, Zhao L R and Tse J S 2003 *Mater. Sci. Eng. A* **360** 197
- [10] Chen K, Zhao L R and Tse J S 2003 *Acta Mater.* **51** 1079
- [11] Peng P, Soh A K, Yang R and Hu Z Q 2006 *Comput. Mater. Sci.* **38** 354
- [12] Wang C Y, Yu S and Yu T 2007 *Acta Phys. Sin.* **56** 3212 (in Chinese)
- [13] Feller-Kniepmeier M and Link T 1989 *Mater. Sci. Eng. A* **113** 191
- [14] Lahrman D F, Field R D Darolia R and Fraser H L 1988 *Acta Metall.* **36** 1309
- [15] Singh A K, Louat N and Sadananda K 1988 *Metall. Trans. A* **19** 2965
- [16] Cao L X, Wang C Y, Wen Y H and Zhu T 2003 *Acta Phys. Sin.* **52** 2520 (in Chinese)

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- [17] Xie H X, Wang C Y, Yu T and Du J P 2009 *Chin. Phys. B* **18** 251
- [18] Wang S F 2006 *Chin. Phys.* **15** 1301
- [19] Geng C Y, Wang C Y and Zhu T 2005 *Acta Phys. Sin.* **54** 1320 (in Chinese)
- [20] Wang S F 2005 *Chin. Phys.* **14** 791
- [21] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** R558
- [22] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [23] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- [24] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
- [25] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 244
- [26] Wang Y, Liu Z K and Chen L Q 2004 *Acta Mater.* **52** 2665
- [27] Mishin Y 2004 *Acta Mater.* **52** 1451
- [28] Kamara A B, Ardell A J and Wagner C N J 1996 *Metall. Mater. Trans. A* **27** 2888
- [29] Wang C and Wang C Y 2008 *Surf. Sci.* **602** 2604
- [30] Voter F and Chen S P 1987 *Mat. Res. Soc. Symp. Proc.* **82** 175
- [31] Chen S P, Voter A F, Albers R C and Boring A M 1990 *J. Mater. Res.* **5**(5) 955
- [32] Zhu T and Wang C Y 2005 *Phys. Rev. B* **72** 014111
- [33] Lavigne O, Ramusat C, Drawin S, Caron P, Boivin D and Pouchou J L 2004 *Superalloys* (Warrendale, PA: TMS) p667
- [34] Yeh A C, Rae C M F and Tin S 2004 *Superalloys* (Warrendale, PA: TMS) p667-86