

A first-principles survey of the partitioning behaviors of alloying elements on γ/γ' interface

Yun-Jiang Wang^{1,a)} and Chong-Yu Wang^{1,2}

¹Department of Physics, Tsinghua University, Beijing 100084, China

²The International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China and China Center of Advanced Science and Technology, P. O. Box 8730, Beijing 100080, China

(Received 8 January 2008; accepted 5 May 2008; published online 8 July 2008)

A first-principles approach is proposed to investigate the partitioning behaviors of the alloying elements Re, Co, and Cr, and the influence of Ru and Ir addition on them. The results show that Re, Co, and Cr all partition strongly to the γ matrix. The Ru addition decreases the γ phase partitioning trend of Re, Co, and Cr. The results are consistent with the early experimental work. Besides Ru, Ir results in Re less strongly partitioning to γ . Our study shows that the influence of Ru (or Ir) on the partitioning characteristics of alloying elements originates from the strong interactions between Ru(Ir)-Re-Ni through the $d-d$ orbitals hybridization. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2953077](https://doi.org/10.1063/1.2953077)]

I. INTRODUCTION

Single-crystal (SC) Ni-based superalloys are widely used in turbine blades for power generation and aircraft engines due to their superior mechanical properties at elevated temperature. These alloys have in common a microstructure consisting of a γ' phase ($L1_2$, ordered fcc, Ni_3Al based) surrounded by a γ matrix (disordered fcc, solid solution based on Ni). The continuing demand for developing increased temperature capacity and improved creep strength has led to alloys with an increasing amount of refractory elements. These additions have remarkably improved the creep resistance of single-crystal superalloys, but the illustrations to the mechanisms of the alloying strengthening related to these additions are still debated. Although it has been postulated that ruthenium (Ru) alters the partitioning of elements between the γ and the γ' phases in a manner called “reverse partitioning,”¹ the effects of Ru are not well understood.

It is well accepted that the lattice misfit, the precipitate morphology, and the $\gamma-\gamma'$ phase compositions are all interrelated. The composition of the phases controls the sign and the magnitude of the lattice misfit δ , which in turn determines the precipitate shape² and the microstructure evolution during high-temperature creep deformation.^{3,4} Therefore, the partitioning of alloying additions between the γ and γ' phases is of great importance to the mechanical properties of Ni-based superalloys. Early work on Ru-containing nickel-based single-crystal superalloys suggested that Ru additions alter the partitioning behaviors of elements between the two constituent phases.^{1,5–8} These works showed that Ru additions make Re and some other refractory elements (e.g., Co, Cr) partition less strongly to the matrix. Consequently, this behavior of refractory elements efficiently modulates the lattice misfit, and ultimately improves the creep strength of Ni-based single crystal superalloys. However, there still exist considerable disagreements upon whether Ru actually causes

the reverse partitioning of refractory elements.^{9–11} These previous measurements indicate that the effect of Ru on the partitioning of the other solutes is not substantial.

The partitioning behavior of Re and other refractory elements has recently come under focus because a large variation in the lattice misfit has been observed in the experiments of Ru-containing superalloys. To date, most studies in this area lie in this experiment. In the single-crystal Ni-based superalloys, the precipitation of the γ' phase creates a mount of interfacial area. The interfacial region is of high interest to the study of Ni-based superalloys. To our knowledge, the experimental technique in the vicinity of the γ/γ' interface is limited. As a result, the study of partitioning of additions near the γ/γ' interface by experiment can be very difficult. As yet, there is no direct report on the Re distribution on the γ/γ' interface in Ru (Ir)-containing Ni-based SC superalloys by experimental methods such as atom probe. As an alternative approach, we herein make the first theoretical investigation into the partitioning behaviors of alloying additions within the γ/γ' interface by fully first-principles calculations. We focus on the effect of Ru on the partitioning of Re, Co, and Cr. For comparison, we also calculate the influence of platinum group metal Ir on the partitioning behavior of Re between the two phases.

II. METHOD AND COMPUTATIONAL MODEL

The first-principles calculations presented here are based on electronic density-functional theory, and have been carried out using the *ab initio* program VASP.¹² The exchange-correlation potential adopts the generalized gradient approximation-projector augmented wave.¹³ This program is employed to study the energetics and partitioning behavior of additions, as well as the geometric characteristics of the γ/γ' interface with Ru (Ir) and Re (Co, Cr). The cutoff energy of atomic wave functions is set to be 350 eV. In the present work, the set of k points is chosen according to the size of the computational cell, and a $6 \times 6 \times 2$ with a regular Monkhorst-Pack grid of special k -points.

^{a)}Author to whom correspondence should be addressed. Electronic mail: wangyunjiang05@mails.tsinghua.edu.cn.

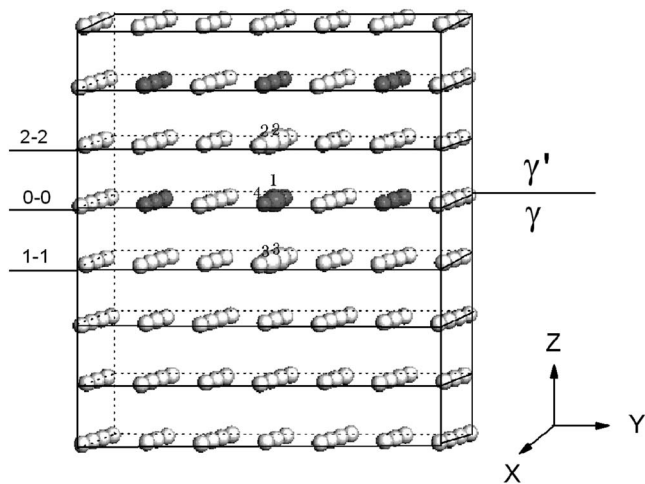


FIG. 1. The 144-atom supercell model of the γ/γ' interface for VASP calculation. The white and black balls denote Ni and Al atoms, respectively. The larger black atom labeled by the Arabic numeral 1 is Al (or Ru, Ir additions) atom. The larger white atoms labeled by 2 and 3 are Ni (or Re, Co, Cr additions) atoms in the γ and γ' phases separately.

A supercell model of the γ/γ' interface consisting of 144 atoms is devised for the present study of the partitioning of refractory additions. The atomic arrangements in the γ/γ' interface are shown in Fig. 1. The lattice parameters of the supercell are taken to be equal for γ and γ' blocks due to the assumption of complete coherence.^{14,15} The supercell interface models consist of an upper Ni_3Al region and a lower Ni region, representing the γ' and γ matrix, respectively. A transition layer (1–1) of Ni atoms exists between the two regions, which can be regarded as either the lowest plane of the Ni_3Al region or the highest plane of the Ni region. Here, we define this transition layer as the uppermost plane of the lower Ni region, and the (0–0) layer contains the atom labeled by 1 and 4 as the lowest plane of the Ni_3Al region. In our calculations, the atoms labeled by “1” are Al (Ru, Ir). The Ni atoms labeled by 2 and 3 are the Ni atom sites which are substituted by Re (Co, Cr) atoms in the quaternary Ni–Al–Ru (Ir)–Re (Co, Cr) Ni-based SC superalloys. Atoms 2 and 3 are located in the γ' and γ phases, respectively. There are two atoms labeled by 2 and 3 due to the maintenance of symmetry of the superball model and for deriving obvious partitioning behaviors of Re (Co, Cr) between the γ and γ' phases. The γ/γ' interface without any additions is used as the baseline for our calculation. All the atomic positions except the uppermost and lowest layers in the supercell have been relaxed according to the total energy, based on the cell optimization criterion (accuracy for electronic minimization is 10^{-4} eV, and ionic relaxation is 10^{-3} eV). The calculation of the total energy and electronic structure is followed by cell optimization, with a stopping criterion for electronic convergence of 10^{-5} eV.

III. RESULTS AND DISCUSSION

A. The partitioning coefficients of Re, Co, and Cr

In order to study the distributions of Re, Co, and Cr additions to Ni-based SC superalloy in the vicinity of the γ/γ' interface, we first substitute two Ni atoms labeled by 2

TABLE I. The binding energies (in eV) of the γ/γ' systems without and with substituting atoms Re (Co, Cr) in the γ and γ' phase, respectively. ΔE denotes the difference in the binding energies between the interface with the Re (Co, Cr) substitution and the pure γ/γ' interface system. (γ/γ') denotes the pure interface model without additions; (γ/γ')-Re2- γ means the γ/γ' interface with Re2 in the γ phase, and so on.

System	Binding energy (eV)	ΔE
(γ/γ')	–752.70	
(γ/γ')-Re2- γ	–765.86	–13.16
(γ/γ')-Re3- γ'	–764.06	–11.36
(γ/γ')-Co2- γ	–755.73	–3.03
(γ/γ')-Co3- γ'	–755.62	–2.92
(γ/γ')-Cr2- γ	–761.02	–8.32
(γ/γ')-Cr3- γ'	–759.35	–6.65

corresponding to Fig. 1 with Re(or Co, Cr) in the γ' phase of the alloys, and then do the same operation on the γ phase, namely, two Ni atoms labeled by 3 substituted by two Re (or Co, Cr) atoms. The calculated binding energies of the systems are presented in Table I. It is interesting to find that with the Re, Co, and Cr substitution for Ni atoms, the binding energies of the systems decrease, which indicates the promotion of microstructure stability from a energetics point of view. Among them, Re appears to give the best alloying stability effect. We also notice that the binding energies of interface systems with addition in the γ phase are lower than that of in the γ' phase, indicating that all three additions have a greater tendency to partition to the γ matrix.

According to the statistical thermodynamics, the equilibrium concentration of a point defect at a given temperature in crystal may be evaluated as

$$C_d = A \exp(-E_f/kT), \quad (1)$$

where E_f is the formation energy of a point defect and A is a constant.¹⁶ In order to study the partitioning behaviors of the additions, we compare their formation energies of the cases when they replace the Ni_3 atoms in the γ phase and Ni_2 atoms in the γ' . A larger value of formation energy will give a lower addition concentration. We define the partitioning coefficient of the addition X (Re, Co, or Cr) as

$$K_{X\text{-add}}^{\gamma/\gamma'} = C_{d-\gamma}/C_{d-\gamma'} = \exp[(E_{f\gamma'} - E_{f\gamma})/2kT], \quad (2)$$

where $C_{d-\gamma}$ is the concentration of element X in γ , $C_{d-\gamma'}$ is the concentration of element X in γ' , $E_{f\gamma'}$ is the formation energy of two substituting X atoms for Ni_2 atoms in the γ' phase, and $E_{f\gamma}$ is the formation energy of two substituting X atoms for Ni_3 atoms in the γ phase corresponding to Fig. 1, respectively. There exists a factor of 1/2 before the formation energy term since two Ni atoms are substituted in the constituent phases. When the X atoms substitute the Ni_3 atoms in the γ phase or the Ni_2 atoms in the γ' phase, the external environment remains the same. Therefore, we can rewrite the equation for the partitioning coefficient $K_{X\text{-add}}^{\gamma/\gamma'}$ as

$$K_{X\text{-add}}^{\gamma/\gamma'} = \exp[(E_{b\gamma'} - E_{b\gamma})/2kT]. \quad (3)$$

Here, we replace the formation energy of the doped atoms by the binding energies of the systems. Our purpose of the

TABLE II. The partitioning coefficient $K_{X-\text{add}}^{\gamma/\gamma'}$ and $K_{X-\text{add}}^{\gamma/\gamma'-\text{Ru(Ir)}}$ of additions Re, Co, and Cr between the γ and γ' phase at 1000 K.

Addition X	$K_{X-\text{add}}^{\gamma/\gamma'}$	$K_{X-\text{add}}^{\gamma/\gamma'-\text{Ru}}$	$K_{X-\text{add}}^{\gamma/\gamma'-\text{Ir}}$
Re	3.40×10^4	6.33×10^3	7.99×10^3
Co	1.89	1.50	
Cr	1.60×10^4	1.18×10^3	

present work is to give the partitioning trend of the alloying elements qualitatively; thus this transformation can be reliable. If $K_{X-\text{add}}^{\gamma/\gamma'} > 1$, the addition X (Re, Co, or Cr) partitions more strongly to the γ matrix. Similarly, $K_{X-\text{add}}^{\gamma/\gamma'} < 1$ indicates the X element partitions preferentially to the γ' phase. We list the partitioning coefficient $K_{X-\text{add}}^{\gamma/\gamma'}$ of X (Re, Co, Cr) between the γ and γ' phase at 1000 K in Table II. As the literature reported, Re, Co, and Cr all partition preferably to the γ matrix. The order of preference is $\text{Re} > \text{Cr} > \text{Co}$. The results derived from our calculations are consistent with the experiments.^{10,17-19} Thus, our method is reliable in predicting the distribution of additions between the γ matrix and γ' precipitate in the Ni-based SC superalloys.

B. The influence of Ru (or Ir) on the partitioning behaviors of Re, Co, and Cr

Some early work on Ru-containing Ni-based superalloys suggested that Ru additions alter the partitioning of the element between the γ and γ' phases.^{1,7} In order to study the influence of Ru on the partitioning behavior of Re, Co, and Cr, we replace the Al1 atom shown in Fig. 1 within the interface region by a Ru atom as a Ru-containing superalloy. For comparison, we also substitute Al1 with Ir, which is regarded as a promising candidate for the fifth-generation Ni-based SC superalloys,²⁰ to study its influence on the partitioning of Re. The binding energies of the systems and the partitioning coefficients of Re, Co, and Cr in the Ru (or Ir)-containing alloys at 1000 K are listed in Tables III and II, respectively.

From Table III we notice that Re (Co, Cr) additions in the Ru (Ir)-containing superalloys decrease the binding ener-

TABLE III. The binding energies (in eV) of the γ/γ' systems with two categories of additions. ΔE denotes the difference in the binding energies between the interface with the Re (Co, Cr) substitution and that of no such additions. (γ/γ' -Ru1) denotes the interface model with Ru additions at the Al1 atomic site; (γ/γ' -Ru1)-Re2- γ stands for the γ/γ' interface with Ru1 at the Al1 atomic site and Re2 in the γ phase, and so on.

System	Binding energy (eV)	ΔE
(γ/γ' -Ru1)	-756.06	
(γ/γ' -Ir1)	-755.97	
(γ/γ' -Ru1)-Re2- γ	-769.80	-13.74
(γ/γ' -Ru1)-Re3- γ'	-768.29	-12.23
(γ/γ' -Ir1)-Re2- γ	-769.71	-13.74
(γ/γ' -Ir1)-Re3- γ'	-768.16	-12.19
(γ/γ' -Ru1)-Co2- γ	-759.25	-3.19
(γ/γ' -Ru1)-Co3- γ'	-759.18	-3.12
(γ/γ' -Ru1)-Cr2- γ	-764.84	-8.78
(γ/γ' -Ru1)-Cr3- γ'	-763.62	-7.56

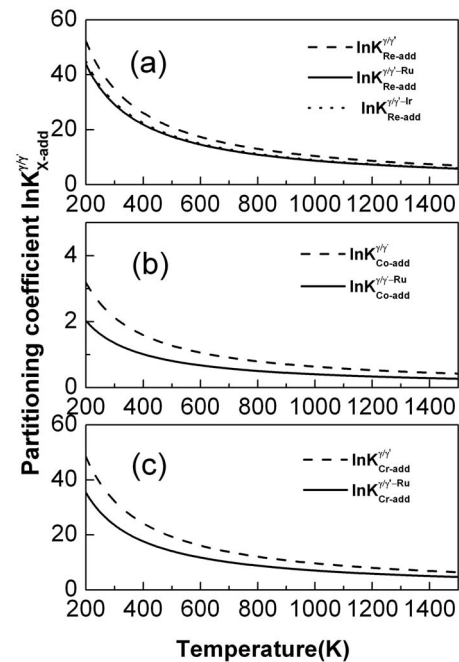


FIG. 2. The partitioning coefficient of X (Re, Co, Cr) as a function of temperature. The dashed lines, solid lines, and dotted denote the partitioning coefficients of X in Ru (Ir)-free, Ru-containing, and Ir-containing alloys, respectively.

gies as well as the Ru (Ir)-free ones, but the difference between the binding energies of Re (Co, Cr) in the γ and γ' phase is changed. These changes are reflected in Table II, where the partitioning coefficients of Re in the Ru (Ir)-containing alloys decrease at 1000 K compared to the Ru (Ir)-free alloys. It shows that Ru and Ir alter the partitioning behavior of Re, decreasing the Re content of the γ matrix. The addition of Ru also affects the partition of Co and Cr, the γ/γ' partitioning ratio decreasing from 1.89 to 1.50, and 1.64×10^4 to 1.18×10^3 due to the Ru addition, respectively.

To analyze the Re (Co, Cr) partitioning behavior and the effect of Ru (Ir) addition on it, we also plot the partitioning coefficients of Re, Co, and Cr as a function of temperature from 200 to 1500 K in Fig. 2. At any given temperature, the partitioning ratio of Re in the Ru (Ir)-free alloys is larger than the Ru-containing and Ir-containing alloys. It is obvious that Ru and Ir both make Re less strongly partition to the γ matrix, and Ru is more effective than Ir in reducing the content of Re in the γ . It is also found in Figs. 2(b) and 2(c) that Ru effectively depresses the partitioning coefficient of Co and Cr, which is consistent with the result of experiments.^{1,6,21}

C. Electronic structures of the γ/γ' interface with Ru (Ir) and Re additions

In this section, we study the electronic mechanisms of alterations to the partitioning behavior of Re due to Ru (or Ir) addition, and the synergetic alloying effects of Ru-Re and Ir-Re on the γ/γ' interface strengthening of Ni-based SC superalloys. Figure 3 shows the total valence charge density contour plots on the cross section of the five coherent interfacial layers of the γ/γ' interface supercell with and without Ru (Ir)-Re. All the aforementioned cross sections are the

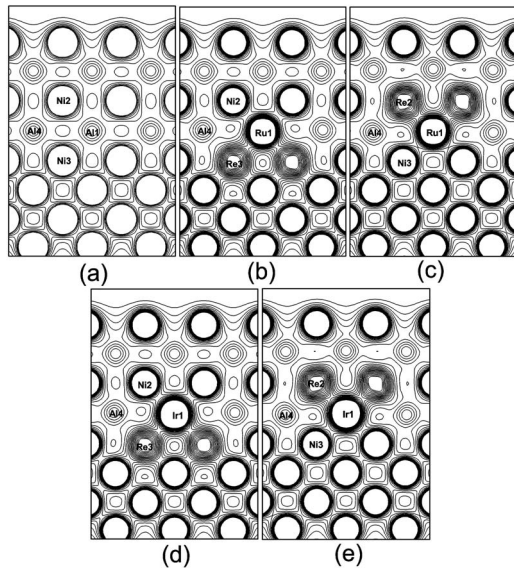


FIG. 3. The total valence charge density contour plots of the γ/γ' interface on the $(010)(x-z)$ planes for the interfaces (a) without Ru (Ir)-Re; (b) with Ru1 and Re2 in γ ; (c) with Ru1 and Re3 in γ' ; (d) with Ir1 and Re2 in γ ; (e) with Ir1 and Re3 in γ' corresponding to Fig. 1, respectively.

$(010)(x-z)$ planes, which contain the atoms labeled from 1 to 4 shown in Fig. 1. Comparing Figs. 3(b) and 3(c) with Fig. 3(a), it is obvious that the electronic interaction between the Ru1 and the two nearest-neighbor (NN) Re2 (Re3) atoms is much stronger than that of Al1 and its NN Ni2 (Ni3) atoms. This strong interaction across the interfacial region originated from the synergetic doping of Ru and Re. They considerably strengthen the γ/γ' interface. The formation of a strong bond between Ru1–Ni2 and Ru1–Ni3 effectively links

the interface 0–1 and 0–2 layers. The charge density contours in Figs. 3(d) and 3(e) take on a similar form as that of the interfaces with Ru and Re, which indicates the bonding between Ir1–Re2 (Re3) is strong as well. The Ir addition is equally useful as Ru for the strengthening of the γ/γ' interface of Ni-based SC superalloys. For all the interfaces with Ru (Ir) and Re, we notice that the bonding between Re–Ni is much stronger than that of Re–Al, which we think is the very reason why Re preferentially partitions to the γ phase. The additions of Ru and Ir influence the partitioning behavior of Re through its strong bonding with Re. The strong bonding between Ru (Ir)–Re weakens the strong γ matrix partitioning trend of Re within the interfacial region.

In order to analyze the interaction between the alloying elements and its NN host atoms, which explains the reason why Ru and Ir influence the partitioning ratio of Re, we also calculate the partial density of states (PDOS). We plot the PDOS of atoms in the systems with Ru1 (and Ir1) and Re in the γ' , namely, at the Re2 atomic site corresponding to the supercell shown in Fig. 1. PDOS for the center Ru (and Ir)1, the NN Re2 and Ni3, and the Al4 atom in the (0–0) layer are shown in Figs. 4(a) and 4(b), respectively. It is easy to understand that the interaction between Ru (Ir)1, Re2, and Ni3 is mainly through the hybridization of d orbitals, because most of their valence electrons are from the d orbitals. It is seen from Figs. 4(a) and 4(b) that there exists a strong hybridization between Ru 4*d* (Ir 5*d*)-Re 5*d*, Ru4*d* (Ir 5*d*)-Ni 3*d*, and Re 5*d*-Ni 3*d*, which results in the strong bonding between Ru (Ir)–Re, Ru (Ir)–Ni, and Re–Ni. There also exists the Al p -Ru (Ir, Re) d hybridization, but it is not as strong as that of the d – d hybridization, resulting in the in-

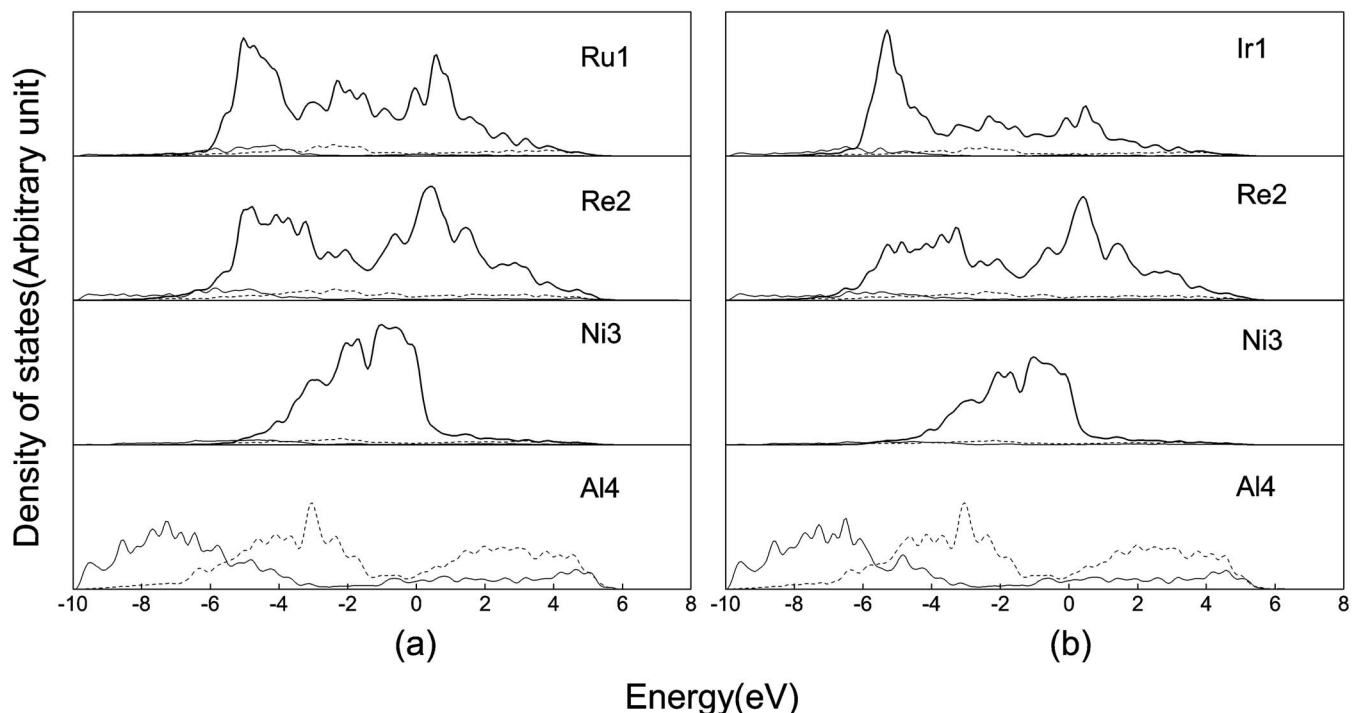


FIG. 4. The atomic partial density of states in (a) the Ni-Al-Ru1-Re2 system; Ru1, Re2, Ni3, and Al4 are corresponding to the supercell shown in Fig. 1. (b) the Ni-Al-Ir1-Re2 system; Ir1, Re2, Ni3, and Al4 correspond to the supercell shown in Fig. 1. The thick solid lines, thin solid lines, and dashed lines denote d , s , and p electronic states, respectively. The Fermi level is shifted to zero.

teraction between Al and the alloying elements being weaker than that of Ni. Quantum mechanics calculations illustrate why Re partitions strongly to the γ matrix.

IV. SUMMARY

In this paper, we present a novel first-principles approach to study the partitioning behaviors of alloying elements between γ and γ' phase within the interfacial region qualitatively and apply it to the Re, Co, and Cr additions. The results show that all three additions partition preferentially to the γ matrix, which agrees well with the available experimental data in the literature, demonstrating the validity of our approach. Our calculation also shows that the addition of Ru makes Re (and Co, Cr) partition less strongly to the γ phase, as was recognized. Besides Ru, Ir is equally shown to influence the distribution characteristic of Re.

Our electronic structures analysis shows that the strong interactions of Ru (Ir)-Re-Ni through the d - d orbitals hybridization are responsible for the strong γ matrix partitioning trend of Re. The Ru (or Ir) addition influences the partitioning behavior of Re between the γ and γ' phase.

ACKNOWLEDGMENTS

A financial grant of the “973 Project” (Ministry of Science and Technology of China, Grant No. 2006CB605102) is gratefully acknowledged.

- ¹K. S. O'Hara, W. S. Walston, E. W. Ross, and R. Darolia, U.S. Patent No. 5, 482, 789, General Electric Company (1996).
- ²M. Fährmann, P. Fratz, O. Paris, E. Fährmann, and W. C. Johnson, *Acta Metall.* **43**, 1007 (1995).
- ³H. Mughrabi and U. Tetzlaff, *Adv. Eng. Mater.* **2**, 319 (2000).
- ⁴R. Schmidt and M. Feller-Kniepmeier, *Scr. Metall. Mater.* **29**, 863 (1993).
- ⁵L. J. Carroll, Q. Feng, J. F. Mansfield, and T. M. Pollock, *Metall. Mater. Trans. A* **37A**, 2927 (2006).
- ⁶L. J. Carroll, Q. Feng, J. F. Mansfield, and T. M. Pollock, *Mater. Sci. Eng., A* **457**, 292 (2007).
- ⁷A. P. Ofori, C. J. Humphreys, S. Tin and C. N. Jones, in *Superalloys 2004*, pp. 787–794.
- ⁸Y.-J. Wang and C.-Y. Wang, *Mater. Sci. Eng., A* **490**, 242 (2008).
- ⁹A. Volek, F. Pyczak, R. F. Singer, and H. Mughrabi, *Scr. Mater.* **52**, 141 (2005).
- ¹⁰R. C. Reed, A. C. Yeh, S. Tin, S. S. Badu, and M. K. Miller, *Scr. Mater.* **51**, 327 (2004).
- ¹¹T. Yokokawa, M. Osawa, K. Nishida, T. Kobayashi, Y. Koizumi, and H. Harada, *Scr. Mater.* **49**, 1041 (2003).
- ¹²G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13115 (1993).
- ¹³G. Kresse and J. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁴H. Harada, A. Ishida, H. K. D. H. Bhadeshia, and M. Yamazaki, *Appl. Surf. Sci.* **67**, 299 (1993).
- ¹⁵P. Strunz, R. Gilles, D. Mukherji, A. Wiedenmann, R. P. Wahi, and J. Zrník, *Mater. Struct.* **6**, 91 (1999).
- ¹⁶J. E. Dorn and J. B. Mitchell, *Acta Metall.* **14**, 70 (1966).
- ¹⁷U. Hemmersmeier and M. Feller-Kniepmeier, *Mater. Sci. Eng., A* **248**, 87 (1998).
- ¹⁸C. Schulze and M. Feller-Kniepmeier, *Mater. Sci. Eng., A* **281**, 204 (2000).
- ¹⁹T. Murakami, H. Harada, and H. K. D. H. Bhadeshia, *Appl. Surf. Sci.* **76–77**, 177 (1994).
- ²⁰T. Kobayashi, H. Harada, M. Osawa, and A. Sato, *Jpn. Inst. Met.* **69**, 1099 (2005).
- ²¹S. Walston, A. Cetel, R. Mackay, K. O'Hara, D. Duhal, and R. Dreshfield, in *Superalloys 2004* (2004), pp. 15–24.