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First principles study of effect of lattice misfit on the bonding strength of Ni/Ni₃Al interface

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By using a discrete variational X_α (DV-X_α) method, the electronic structures and bonding strengths of Ni/Ni_3Al (or γ/γ') interface with different lattice misfits (δ) were calculated in the framework of the nonrelativistic first-principles theory. In order to describe the effect of δ on the interfacial binding strength and the structural stability of coherent γ/γ' interface, we calculated the interfacial binding covalent bond density (CBD) and the local environmental total bond overlap population (LTBOP). Very obvious effects of lattice misfits on the electronic structures of coherent γ/γ' interface were found. On one hand, less than -0.6% negative lattice misfit can increase the binding strength of the γ/γ' interface. On the other hand, the local environmental total bonding strength of the γ/γ' interface decreases with increasing magnitude of δ. Therefore, the magnitude and sign of lattice misfit must be carefully controlled to balance the high-temperature creep strength of Ni-base single crystal superalloy and the structural stability of the γ/γ' interface when one designs new alloys. © *2004 Kluwer Academic Publishers*

1. Introduction

Superalloy turbine blades and vanes are currently being used in the most advanced gas turbine engines for civil and military aircrafts and helicopters. Ni-base single crystal superalloys are most promising for their excellent oxidation resistance and high-temperature strength. The benefits of single crystal over polycrystalline superalloys derive from effective removal of grain boundaries as a result of the alignment of the $\langle 001\rangle$ direction parallel to the solidification direction, leading to the great improvement of creep resistance and thermal fatigue resistance. Ni-base single crystal superalloys mainly consist of γ' precipitates coherently dispersed on a γ matrix. The γ' precipitates (an intermetallic phase of stoichiometry based upon Ni_3Al) possess an $L1_2$ type ordered face-centred cubic structure. The γ matrix has a disordered fcc (A1) structure. Key factors that strongly affect the creep strength or creep rupture life of Ni-base superalloys include the size and shape of the γ' precipitates, the fractions and compositions of the γ and γ' phases, and the magnitude and sign of lattice misfit δ between the γ and the γ' phase. In particular, when plate-like γ' precipitates perpendicular to the tensile stress form during creep, a drastic improvement of the creep rapture life is resulted [1, 2]. The mechanism of formation of the plate-like γ' precipitates is a directional coarsening that results from the negative lattice misfit (i.e., $a_\gamma > a_{\gamma'}$) [3, 4]. Service experiments and failure analyses have showed that the weakest region of Ni-base single crystal superalloy is the γ/γ' phase boundary when a Ni-base single crystal superalloy is subjected to stress at elevated temperature, and the negative lattice misfit is responsible for improvement in creep strength of Ni-base single crystal superalloys [5, 6]. Although considerable theoretical effort has been devoted to understanding the strengthening mechanisms underlying these alloys with different lattice misfit [3, 4, 7–9], no systematic first principles calculation of the binding strength of the γ/γ' interface has been carried out up to now.

In order to probe into the mechanism of strengthening related to lattice misfit between γ' precipitates and the γ matrix, we simulated the local atomic environment at γ/γ' interface with atomic clusters and performed a non-relativistic first principles calculation of the electronic structures. The investigation focused on establishing the relation of lattice misfit to the interfacial binding strength of Ni-base single crystal superalloy and the structural stability of the γ/γ' interface.

2. Procedures of calculation

Non-relativistic first-principles molecular-orbital (MO) calculations were made by a discrete-variation DV-X$_\alpha$ method [10, 11] using a program code SCAT [11]. MOs were constructed by a linear combination of atomic orbits (AOs) as

$$\phi_\mathrm{l}(r_\mathrm{k}) = \sum_i C_\mathrm{il}\chi_\mathrm{i}(r_\mathrm{k}) \tag{1}$$

where $\chi_\mathrm{i}(r_\mathrm{k})$ denotes the AO, and r_k is one of the sampling points in the DV calculation. The number of the sampling points is chosen to be 500 per atom. The numerical basis functions were obtained by solving the radial part of the Schrödinger equations. Minimal numerical basis sets, i.e., 1s-3d for Al and 1s-4p for Ni, were used.

The overlap population between the ith and the jth AO at the lth MO is given by:

$$Q^\mathrm{l}_\mathrm{ij} = C_\mathrm{il}C_\mathrm{jl}\sum_k \omega(r_\mathrm{k})\chi_\mathrm{i}(r_\mathrm{k})\chi_\mathrm{j}(r_\mathrm{k}) \tag{2}$$

where $\omega(r_\mathrm{k})$ is the integration weight or reciprocal point density at r_k. The sum of Q^l_ij with respect to l for occupied orbitals provides the net overlap population between the ith AO the jth AO, i.e.,

$$Q_\mathrm{ij} = {\sum_l}' Q^\mathrm{l}_\mathrm{ij} \tag{3}$$

where $\sum_\mathrm{l}'$ denotes summing over all occupied AOs. The bond overlap population (BOP) between atom A and B is given by

$$Q^\mathrm{l}_\mathrm{AB} = \sum_{\mathrm{i}\in\mathrm{A}}\sum_{\mathrm{j}\in\mathrm{B}} Q^\mathrm{l}_\mathrm{ij} \tag{4}$$

Overlap population diagrams are made by broadening of Q^l_AB at individual MOs using Gaussian functions of 1.0 eV full width at half maximum (FWHM). The orbital population of the ith orbital is given by

$$Q_\mathrm{i} = {\sum_l}'\sum_j Q^\mathrm{l}_\mathrm{ij} \tag{5}$$

The net charge of each atom ΔQ_A is obtained by

$$\Delta Q_\mathrm{A} = Z_\mathrm{A} - \sum_{i\in A} Q_\mathrm{i} \tag{6}$$

whereZ_A is the electron number of atom A.

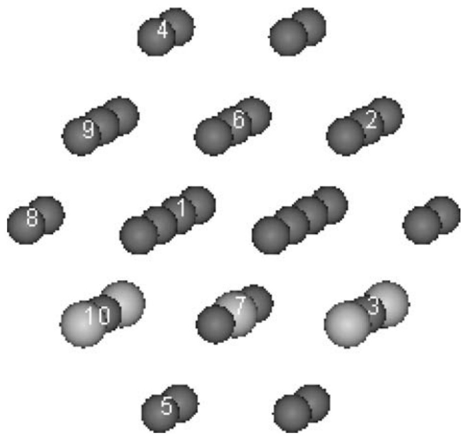

Figure 1 Model cluster of γ/γ' interface with 10 types of nonequivalent atomic positions. Big balls denote Al atoms and small balls denote Ni atoms.

Calculations were made for a 38-atom model cluster with a chemical formula of $Ni_{33}Al_5$. Atomic arrangements in the cluster of γ/γ' interface are shown in Fig. 1. The {002} plane is taken as a coherent interface of the γ and γ' phases based on the experimental results reported by Harada *et al.* [12]. The upper part of the cluster represents the γ phase and the lower part the γ' phase. Atoms in the cluster are distinguished to 10 kinds of nonequivalent positions according to a C4v symmetry perpendicular to the interface. Because the {002} atomic plane can be regarded as either the lower surface of the γ block or the upper surface of the γ' block, for the $Ni_{33}Al_5$ model cluster there exist two constructional modes, namely Ni_{25}-Ni_8Al_5 and Ni_{13}-$Ni_{20}Al_5$, corresponding to the orientation relationship of $\{002\}_\gamma//\{001\}_{\gamma'}$, $\langle 001\rangle_\gamma//\langle 001\rangle_{\gamma'}$ and $\{001\}_\gamma//\{002\}_{\gamma'}$, $\langle 001\rangle_\gamma//\langle 001\rangle_{\gamma'}$, respectively. In order to investigate the electronic structure of corresponding interfacial separations, several "surface clusters" with chemical formulae of Ni_{25},Ni_8Al_5, Ni_{13} and $Ni_{20}Al_5$ were also employed. According to previous calculations of Morinaga *et al.* [13] and Liu *et al.* [14], we take $a_\gamma = a_{\gamma'} = 0.3570$ nm as the lattice constants of the γ and γ' phases in fully coherent interfacial clusters and then moderately increase the magnitude of $a_\gamma$or $a_{\gamma'}$ from 0.3570 to 0.3590 nm so as to obtain a semi-coherent γ/γ' interfacial cluster with positive or negative lattice misfit ($\delta = 2(a_{\gamma'} - a_\gamma)/(a_{\gamma'} + a_\gamma)$). For all interfacial and surface model clusters the C4v point group symmetry was preserved. The divergence in self-consistent calculation is limited to smaller than 0.001e in the sum of transferred electrons.

3. Results and discussion

3.1. Bond overlap population analysis

The magnitude and sign of both ionic and covalent bonding between atoms at the centre of a γ/γ' interfacial cluster were calculated by using Mulliken's population analysis method [15]. It is found that the net charge of atoms at the centre of the interfacial cluster is very small (e.g., −0.001e for Ni_1, −0.045e for Ni_6 and +0.028e for Al_7 in the coherent γ/γ' interfacial cluster.

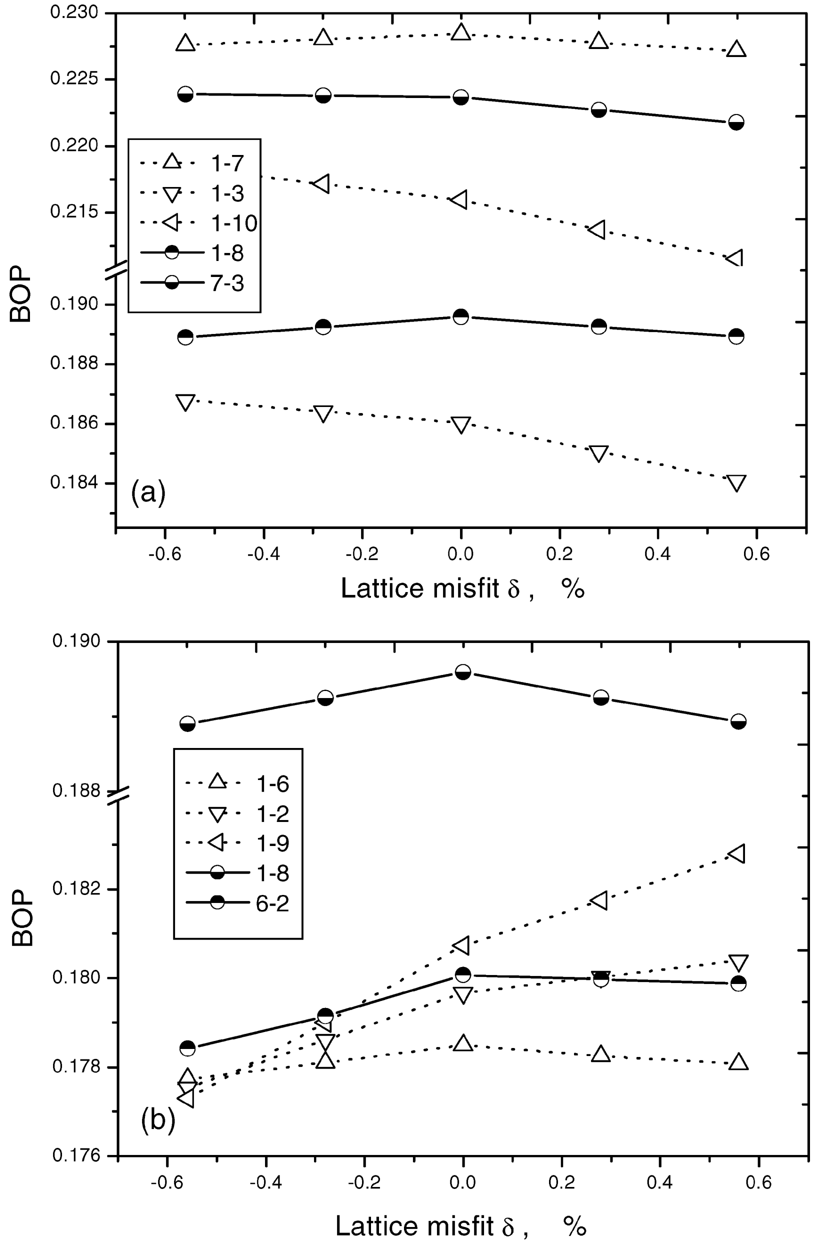

Figure 2 Correlation of bond overlap population (BOP) and lattice misfit for (a) Ni_{25}-Ni_8Al_5 mode and (b) Ni_{13}-$Ni_{20}Al_5$ mode of the interfacial cluster. Pairs of numbers represent corresponding atom pairs as indicated in Fig. 1.

Note that the subscripts here indicate the designation of nonequivalent atoms in the cluster of Fig. 1; throughout this paper subscripts of single element smaller then 10 have similar meaning whereas subscripts larger then 10 denote the number of atoms in the "surface clusters" defined in Section 2). This indicates that the interactions of Ni—Ni and Ni—Al are mostly of covalent bonding. Hence we mainly evaluate the bond overlap population (BOP) between atoms at the centre of the γ/γ' interface. The BOP around the γ/γ' interface calculated using the $Ni_{33}Al_5$ clusters with different lattice misfit are summarized in Fig. 2. In the case of the Ni_{25}-Ni_8Al_5 model cluster, the BOP changes with the type of atom pairs (Fig. 2a). For example, the BOP between Ni_1 and Al_7 atoms is larger than that between Ni_1 and Ni_3; the BOP between Al_7 and Ni_3 larger than that between Ni_1 and Ni_8. In addition the influence of bonding direction on the bonding strength can be seen as well. In the Ni_{13}-$Ni_{20}Al_5$ model cluster (Fig. 2b) it is very obvious that the BOP between Ni atoms across the interface such as Ni_1-Ni_9 or Ni_1-Ni_6 is smaller than the BOP along the interface such as Ni_1-Ni_8. These results partially explain why the introduction of the γ' phase with strongly covalent Ni-Al bonds can strengthen the Ni-base superalloy from an electron structural point of view. The bonding anisotropy also imply that in Ni-base single crystal superalloys microcracks with crack face parallel to the phase boundary would tend to emerge at γ/γ' interface, leading to interphase fracture.

3.2. Interfacial binding strength

When calculating the interfacial binding strength, we should take into account the number of effective bonds around the interface besides the strength of single bond. In addition modification of other bonds near the

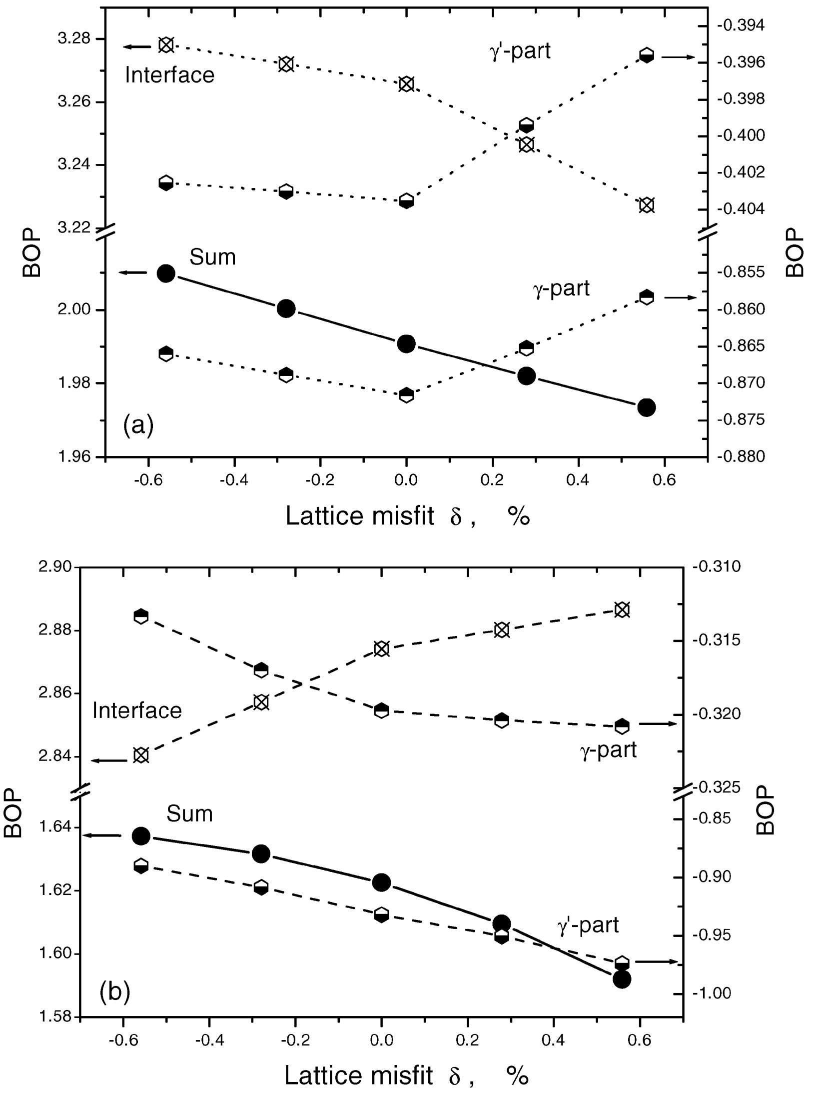

Figure 3 Sum of BOP and its components as a function of lattice misfit in (a) Ni_{25}-Ni_8Al_5 and (b) Ni_{13}-$Ni_{20}Al_5$ interfacial model clusters.

interface should also be evaluated. Fig. 3 shows the sum of BOPs in the two γ/γ' interfacial model clusters. The interfacial component plotted in Fig. 3 comprises the total bonding strengths between atoms on the lower surface of the γ block and atoms on the upper surface of the γ' block in the γ/γ' interfacial model cluster. The other two components, γ-part and γ'-part, correspond to the net bonding strengths arising in the γ block and the γ' block of the interfacial cluster, respectively. For a given mode of the interfacial cluster, the net bonding strength of the γ-part (or γ'-part) is defined as the difference between the total BOP of the γ block (or γ' block) in the interfacial cluster and the total BOP of the corresponding surface cluster of γ-Ni (or γ'-Ni_3Al) [16]. In the case of the Ni_{25}-Ni_8Al_5 mode, the major contribution to the sum of BOPs comes from the interfacial component that simply increases with increasing magnitude of the negative lattice misfit. The γ'-part and γ-part contribute negatively to the sum of BOPs, and they exhibit a minimum at $\delta = 0$. In the case of the Ni_{13}-$Ni_{20}Al_5$ mode, the major contribution to the sum of BOPs also originates from the interfacial component that decreases with increase in the magnitude of the negative lattice misfit. Although the net BOPs of the γ-part and the γ'-part in this model cluster do not decrease but slightly increase with increasing magnitude of the negative lattice misfit, the weight of the net BOPs in the sum of BOPs is still very small. It is worth noting that for both the Ni_{25}-Ni_8Al_5 and the Ni_{13}-$Ni_{20}Al_5$ mode of the interfacial cluster the sum of BOPs for the γ/γ' interface ascends with increasing magnitude of the negative lattice misfit.

As a measure against rupture of the γ/γ' interface [16], the interfacial binding strength is also affected by the volume of the γ/γ' interfacial model cluster besides the type and number of covalent bonds at the interface as well as near the γ/γ' interface. In order to eliminate this volume effect when considering the influence of lattice misfit on the interfacial binding strength of the γ/γ' interface, we herein adopt the concept of covalent bond density (CBD) to describe the interfacial binding strength. The CBD between A and B atoms was defined [17, 18] as

$$\rho_{AB} = (1/V) \cdot \sum_i N^i_{AB} \cdot Q^i_{AB} \tag{7}$$

where Q^i_{AB} and N^i_{AB} are the BOP and the number of bonds at the ith nearest-neighbour distance in a unit cell, respectively. The unit cell with volume V is selected as

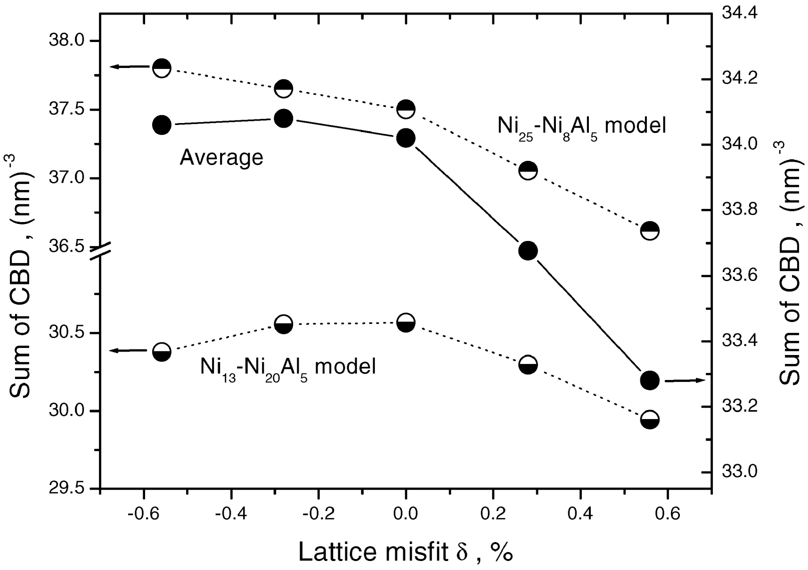

Figure 4 Sum of CBD in the γ/γ' interfacial model clusters as a function of lattice misfit.

an atomic assembly that encloses the minimum number of atoms but is representative of the local bonding environment. The total CBD may be calculated by summing up all $\rho_{\mu\nu}$ in the unit cell, i.e.,

$$\rho_{\text{total}} = \frac{1}{2}\sum_{\mu\neq\nu}\rho_{\mu\nu} + \sum_{\mu}\rho_{\mu\mu} \qquad (8)$$

where the subscripts μ and ν express the kinds of atoms. In the γ/γ' interfacial cluster model they represent the designation of nonequivalent atoms. Using an approach similar to that used in estimating the sum of BOP, we calculate the sum of the CBD in the γ/γ' interfacial model clusters. Fig. 4 illustrates the variation of the sum of the CBD in the γ/γ' interfacial model clusters with the lattice misfit δ. For positive lattice misfit, the sums of CBD for both modes of the cluster rapidly decrease with δ increasing from 0 to +0.6%. For negative lattice misfit (increasing in magnitude from 0 to −0.6%) there is merely a slow rise in the sum of CBD for the Ni_{25}-Ni_8Al_5 mode of the cluster; for the Ni_{13}-$Ni_{20}Al_5$ mode of the cluster the sum of CBD even exhibits a slight drop in the same range of lattice misfit. Because the two modes of the cluster refer to a physically identical γ/γ' phase boundary, we further give the average of the sum of CBD of the Ni_{25}-Ni_8Al_5 and the Ni_{13}-$Ni_{20}Al_5$ mode of the cluster in Fig. 4. It can be seen that the averaged sum of CBD first increases and then begins to decrease when the negative lattice misfit varies from 0 to −0.6%, and the maximum corresponds to a lattice misfit of about −0.5%. Although Mulliken's population analysis is generally considered as containing some arbitrary factors, a comparison of the γ/γ' interfacial binding strength under the condition of different lattice misfit should be efficacious. Hence this result indicates that a negative lattice misfit at the γ/γ' interface is beneficial to improving the interfacial binding strength. A number of experimental investigations [5, 6] showed that negative lattice misfit is responsible for improvement in creep strength of Ni-base single crystal superalloys. But so far the mechanism of the strengthening effect of the negative lattice misfit has not been understood. The results of this first principles study thus provide a basis at electronic structure level for understanding a phenomenon which is of great importance to the strengthening of Ni-base single crystal superalloy.

3.3. Local environmental total bonding strength

The local environmental total bond overlap population (LTBOP), a measure of the strength of the total covalent bonding for a local environment, is generally good enough for evaluating the interface cohesion. It provides us with a local estimation of the cohesive energy as well as structural stability [14, 19]. For (002) type of γ/γ' interface an octahedron is both convenient and representative of the local interface environment [14, 19], so we selected the central octahedron of the γ/γ' interfacial cluster to evaluate the LTBOP of the γ/γ' interface at different lattice misfit. In order to accurately describe the structural stability of the γ/γ' interface, the local environmental total covalent bond density (LTCBD) was also calculated by considering the volume of the cental octahedron. The variation of the LTCBD together with the LTBOP of the cental octahedron of the γ/γ' interfacial cluster with lattice misfit is illustrated in Fig. 5. A similar tendency of variation with lattice misfit can be seen for the LTBOP and the LTCBD: Both reduce with increasing magnitude of δ. The completely coherent γ/γ' interface ($\delta = 0$) has a maximum value in the LTCBD. The smaller the coherency at the Ni/Ni_3Al interface, the weaker the local environmental total bonding strength. A large LTCBD represents strong interface cohesion [5], and hence Fig. 5 indicates that both positive and negative lattice misfits are unfavourable for structural stability of the γ/γ' interface. This conclusion is consistent with previous theoretical calculations and experiments [14, 19].

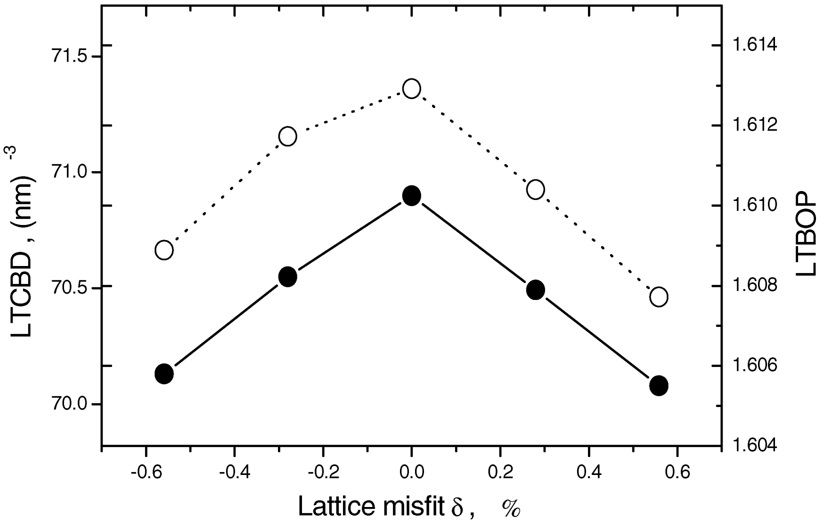

Figure 5 LTCBD (solid circle) and LTBOP (open circle) of the γ/γ' interfacial model clusters as a function of lattice misfit.

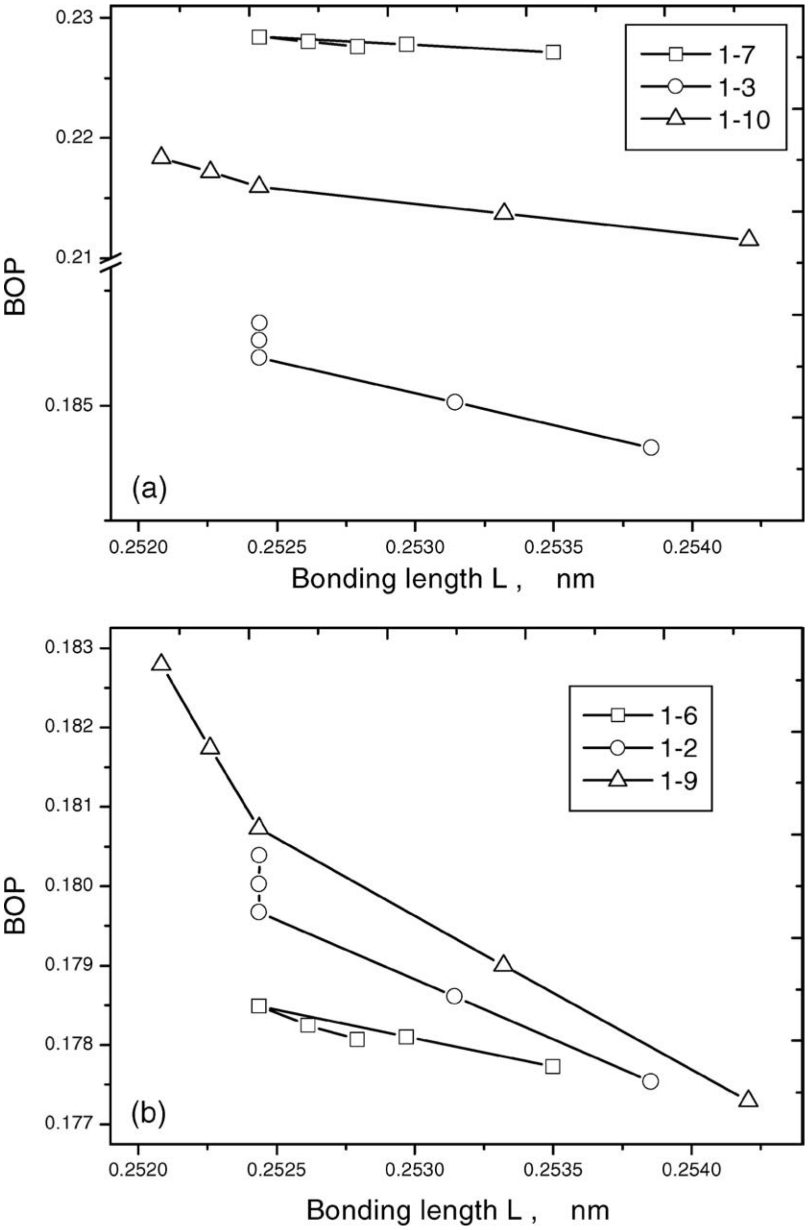

Figure 6 Correlation of BOP and bonding length for (a) Ni_{25}-Ni_8Al_5 and (b) Ni_{13}-$Ni_{20}Al_5$ interfacial model clusters.

3.4. Bond overlap population and bonding length

The variation of the BOPs between atoms at the central octahedron of the γ/γ' interfacial cluster with their bonding length is plotted in Fig. 6. It can be seen that the BOP increases as the bonding length L between atoms shortens. In fact, a similar tendency was also found in the plots of the net BOPs of the Ni-part and the Ni_3Al-part of the γ/γ' interface against their bonding length. It is clear that the influence of lattice misfit on the binding strength of the γ/γ' interface can be attributed to the changes in bonding length between atoms at the central octahedron of the γ/γ' interfacial cluster.

4. Conclusion

The electronic structures of the Ni/Ni_3Al interface with different lattice misfit were investigated systematically. The concept of covalent bond density (CBD) has been applied to discuss the relation of lattice misfit to interfacial binding strength and to the local environmental total bond overlap population (LTBOP). The main results can be summarized as follows:

The effect of lattice misfit δ on the electronic structures of coherent Ni/Ni_3Al interface is very obvious. On one hand, the negative lattice misfit between γ-Ni phase and γ'-Ni_3Al phase promotes the binding strength of the γ/γ' interface. The larger the magnitude of the negative lattice misfit between γ-Ni and γ'-Ni_3Al, the larger the binding strength of the γ/γ' interface, and the limit of the negative lattice misfit with strengthening effect on the γ/γ' interface is about $\delta \approx -0.5\%$. On the other hand, the local environmental total bonding strength of the γ/γ' interface drops when the magnitude of the lattice misfit increases. The less the coherency at the Ni/Ni_3Al interface, the weaker the bonding strength and the worse the structural stability of the interface. Therefore, the magnitude and sign of lattice misfit must be carefully controlled in order to balance the binding strength and the structural stability of the γ/γ' interface when one designs new alloys.

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