Effect of P-Doping on the Rupture Strength of $\gamma$-Ni/$\gamma'$-Ni$_3$Al Interfaces

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Abstract. A first-principles investigation on the rupture strength $W_0$ of $\gamma$-Ni/$\gamma'$-Ni$_3$Al interfaces with and without P-doping is conducted, and the influence of phosphorous content $x$ on $W_0$ is also evaluated. The results show P prefers to occupy Ni sublattices at the side of $\gamma$-phases rather than octahedral interstitial centers in $\gamma$ and $\gamma'$ phases. The advantages and adverse effects of phosphorous mainly depend on their inter-phase fracture sites related to doping types. With the increase of P content $x$, the Griffith rupture work $W$ of Ni/Ni$_3$Al interfaces firstly decreases and then increases, and a minimum appears at $x=0.018$ wt.%. This good agreement with the $x$ dependence of ultimate tensile strengths of IN718 superalloys indicates the $W_0$ can be applied to characterize the tensile strength of Ni-based superalloys to some extent. The analysis of electronic structures reveal the detrimental effect of P-doping mainly originates from the weakened electronic affinity between interfacial atoms, but an elevated local elastic strain energy caused by substitution of P for Ni cannot be neglected. As a result, the P-doping at octahedral interstices in $\gamma'$-phases has a higher $W$ than the substitution of P for Ni in $\gamma$-phases.

1. Introduction
Ni-based single crystal (SC) superalloys, one of key structural materials, are widely used in advanced aeroengines and gas turbines because of their outstanding high-temperature mechanical properties. Their unique microstructure, a high volume fraction of intermetallic $\gamma'$-Ni$_3$Al precipitates (L1$_2$ structure) embedded coherently in a $\gamma$-Ni (A1 structure) matrix, is a key for their remarkable high-temperature mechanical properties. In-service examination and failure analyses have shown that the structure and properties of $\gamma'$ interfaces have a great impact on the shape, size and coarsening rate of $\gamma'$ precipitates which in return strongly affect the creep strength or creep rupture life of SC superalloys subjected to stress at elevated temperatures [1]. Numerous experiments have demonstrated that trace elements and minor alloying additions, e.g. N, O, H, S, P, Si, As, Se, C, B etc., have a great influence on the strength and ductility of Ni-based SC superalloys [2]. Phosphorus used to be regarded as a deleterious trace element because it seriously segregates to the grain boundary of $\gamma$ and $\gamma'$ phases and then leads to the cohesive strength of grain boundaries to be weakened [3]. However, a big breakthrough is reported recently that P has a positive effect on some wrought superalloys, e.g., GH761 and IN718 superalloys. It is demonstrated that phosphorus plays an important role in improving creep rupture life of 718Plus alloys [4]. With the increase of phosphorus content from 0.0007 wt.% to 0.023 wt.%, the stress-rupture life of commercial GH761 alloy at 650 °C and 637 MPa is found to increase quickly [5]. Moreover, a same favorable effect is also reported, in which the phosphorus content is 0.013 wt.% corresponding to the peak life at 650 °C in IN718 alloy [6].
Several theoretical investigations have been made to detect the partitioning and segregation behavior of trace elements and minor additions as well as their roles in the strength and ductility of Ni-based SC superalloys. Wu et al. [7] firstly investigated the segregation behavior of B and H in Ni-based and Ni3Al-based alloys by means of cluster models and DV-Xα method. They suggested that both B and H may segregate to the octahedral interstices in the γ-Ni/γ'-Ni3Al interface but B has a greater segregation tendency and higher stability than H. Sanyal et al. [8] further calculated the site preference of O, H and N at the γ-Ni/γ'-Ni3Al interface and estimated their effects on the interfacial cleavage energy using Vienna Ab-initio Simulation Package (VASP). Their result showed O and H have intrinsic tendencies to segregate to the octahedral interstice constituted by 6 Ni atoms in the interfacial region. Our recent work [9, 10] on the existence probability and site preference of S and P in the γ-Ni/γ'-Ni3Al interfacial region also indicated that single S-doping or P-doping either at sub-lattice sites or at octahedral interstitial centers is energetically permissible, and both S and P atoms prefer to substitute host atoms, especially Ni atoms in γ-block.

With respect to the role of trace elements in the strength and ductility of Ni-based SC superalloys, Liu et al. [11] found the binding strength of doped interfaces gradually decreased in the following order: C, B, N, O, H, clean, P, S. On the basis of the calculation of Griffith rupture work of the γ-Ni/γ'-Ni3Al interface, Sanyal et al. [8] reported N, O, H are also deleterious dopants, and O is the most deleterious for the interfacial toughness. B-induced ductility and H-induced embrittlement were demonstrated to mainly originate from a different lattice misfit between γ and γ' phases [7]. Subsequently, Peng et al. [9, 12, 13] further studied the effect of S, N, B or P on the Griffith rupture work and local toughness of the γ-Ni/γ'-Ni3Al interface. Their results showed that although B [13] is beneficial to the improvement of the interfacial fracture strength, but S [9] and P [13] are deleterious for the local toughness of the interfacial regions.

It is noticed that previous investigations on P-induced embrittlement seldom took into account the influence of phosphorus contents, and the site preference of P far away from γ-Ni/γ'-Ni3Al interfaces was scarcely examined as well. Owing to a high cost and actuality difficulty in the exact control of phosphorus contents [6], it is desired to deeply understand the impact of P on the high temperature properties of Ni-based superalloys. As this reason, the deleterious influence of P-doping on the cleavage strength of γ-Ni/γ'-Ni3Al interfaces will be carefully evaluated by a series of γ-Ni/γ'-Ni3Al interfacial supercells with P-doping at various sub-lattice sites and octahedral interstitial centers.

2. Computation models and methods

Similarly to literatures [14], a completely coherent Ni/Ni3Al interfacial supercell is built on the basis of the experimental result reported by Harada et al. [15], as shown in Figure 1. Herein, the coherent (002)γ/γ' atomic plane can either be regarded as a lower surface of γ-Ni block or be treated as a upper surface of γ'-Ni3Al block. Hence, there exist two orientation relationships of (002)γ/(001)γ' and (001)γ||(002)γ' in present interfacial model. Accordingly, there are four surface models, i.e., the (002) surface model of γ-Ni phase and the (001) surface model of γ'-Ni3Al phase, and the (001) surface model of γ-Ni phase and the (002) surface model of γ'-Ni3Al phase. In the interfacial supercell, six sub-lattice sites and six octahedral interstitial centres are labelled by Arabic numerals (1, 2, 3, 4, 5 and 6) and Roman numerals (i, ii, iii, iv, v and vi), respectively. Each sub-lattice site or octahedral interstitial centre represents a set of equivalent sites with same local environments at the γ-Ni/γ'-Ni3Al interface.

A Cambridge serial total energy package (CASTEP) is adopted, in which a plane-wave pseudopotential method [16, 17] based on the density function theory (DFT) is employed. Ultrasoft pseudo-potentials [18] represented in reciprocal space with a exchange–correction function of Perdew-Burke-Emzerhof (PBE) form under generalized gradient approximation (GGA) [19] are used for all elements in our models. A finite basis set correction [20] is utilized for evaluation of energy and stress. In the calculation of self-consistent field (SCF), the cutoff energy and k-point sampling are set as 300 eV and 7×7×1, respectively. Meanwhile the Pulay scheme of density mixing [21] is adopted. All atomic positions in the supercell are optimized by Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme [22] based on the cell optimization criterion (RMS force of 0.03 eV/Å, RMS stress of 0.05 GPa and...
RMS displacement of $1.0 \times 10^{-3}$ Å. The calculation of total energy and electronic structures is followed by cell optimization with SCF tolerance of $1.0 \times 10^{-6}$ eV/atom under GGA-PBE [19].

Figure 1. The $\gamma$-Ni/$\gamma'$-Ni$_3$Al interfacial model. The blue and orange balls denote Ni and Al atoms, respectively. (001)$_\gamma$, (001)$_{\gamma'}$ and (002)$_{\gamma/\gamma'}$ represent the (001) atomic layer in the $\gamma$-Ni block, the (001) atomic layer in the $\gamma'$-Ni$_3$Al block and the coherent Ni/Ni$_3$Al interfacial layer, respectively. Region-1 and Region-2 are the region bounded by (002)$_{\gamma/\gamma'}$ and (001)$_{\gamma'}$ layers and by (001)$_\gamma$ and (002)$_{\gamma/\gamma'}$ layers, respectively. Arabic numerals (1, 2, 3, 4, 5, and 6) and Roman numerals (i, ii, iii, iv, v, and vi) denote sub-lattice sites and octahedral interstitial centres, respectively.

3. Results and discussion

3.1. Site preference of P at $\gamma$-Ni/$\gamma'$-Ni$_3$Al interfaces

A series of interfacial models with P-doping at various sub-lattice sites and octahedral interstitial centers are built to examine the site preference of P at $\gamma$-Ni/$\gamma'$-Ni$_3$Al interfaces. These P-doping supercells are remarked as M-y where M=Ni, Al and O represent Ni and Al sublattices as well as octahedral interstices doped by P, respectively. y =1, 2, 3, 4, 5, 6, i, ii, iii, iv, v and vi are sublattice sites and octahedral interstitial centers. Their heats of formation $\Delta H$ and cohesive energies $E_b$ can be calculated by following expressions [23]:

$$\Delta H = \left[ E_i(n, m, k) - n \cdot E(Ni) - m \cdot E(Al) - k \cdot E(P) \right] / (m + n + k)$$ (1)

$$E_b = \left[ E_i(n, m, k) - n \cdot E_{Ni} - m \cdot E_{Al} - k \cdot E_{P} \right] / (m + n + k)$$ (2)

where $E_i(n, m, k)$ is the total energy of $\gamma/\gamma'$ supercells with n, m and k atoms of Ni, Al and P, respectively. $E$(Ni), $E$(Al) and $E$(P) are the energies per atom in fcc-Ni, fcc-Al and triclinic-P unit cells, respectively. $E_{Ni}$, $E_{Al}$ and $E_{P}$ are the energies per gaseous Ni, Al and P atoms, respectively. Table 1 tabulates the magnitude of $\Delta H$ and $E_b$ of the $\gamma/\gamma'$ interfacial model with or without P-doping. A negative $\Delta H$ indicates P-doping at the $\gamma/\gamma'$ interface is permissible from the energetic point of view. Thus, for the formation ability of P-doping $\gamma/\gamma'$ interfaces the following tendency can be deduced: Ni-3 > Ni-2 > Ni-1 > O-i > Ni-4 > O-ii > O-iii = O-v > Ni-5 > O-vi > O-iv > Al-6 > clean, in which clean represents the interfacial super-cell free of P. It is noticed that P atoms prefer to substitute host atoms, especially Ni atoms far away from the $\gamma/\gamma'$ interface at the side of $\gamma$-Ni phases, rather than occupy
octahedron interstitial centers. But a bigger negative $\Delta H$ value of doping systems than the clean interface indicates P-doping at octahedral interstitial centers [14] are also energetically permissible, and the octahedron interstitial center O-i bounded by 6 Ni atoms in $\gamma$-Ni region is the most favorable.

Table 1 shows the cohesive energy $E_b$ of P-doping $\gamma/\gamma'$ interfaces declines in the following order: O-i > Ni-3 > Ni-2 > Ni-1 > Al-6 > Ni-4 > O-ii > O-iii > O-v > O-vi > O-iv > Ni-5 > clean. A larger cohesive energy $E_b$ in doped models indicating the $\gamma/\gamma'$ interfaces with P-doping is more stable than the $\gamma/\gamma'$ interface free of P [23]. And O-i is the most stable, followed by Ni-3, Ni-2 and Ni-1 sites in $\gamma$-block. Therefore, we can conclude that P prefers to substitute Ni atoms in $\gamma$-Ni phases, but the $\gamma/\gamma'$ interfaces with P-doping at octahedral interstitial centers are also energetically permissible and structurally stable.

Table 1. The heat of formation $\Delta H$, the cohesive energy $E_b$ and the Griffith rupture work $W$ in Region-1 and Region-2. The bold value represents the $W$ at rupture sites

| Model   | $\Delta H$(eV·atom$^{-1}$) | $E_b$(eV·atom$^{-1}$) | $W$(J·m$^{-2}$) |
|---------|-----------------------------|----------------------|-----------------|
| Clean   | -0.252                      | -5.509               | 4.428           |
| Ni-1    | -0.677                      | -5.594               | 4.374           |
| Ni-2    | -0.681                      | -5.598               | 4.416           |
| Ni-3    | -0.683                      | -5.601               | 4.335           |
| Ni-4    | -0.645                      | -5.562               | 2.685           |
| Ni-5    | -0.596                      | -5.513               | 4.265           |
| Al-6    | -0.561                      | -5.587               | 4.063           |
| O-i     | -0.667                      | -5.617               | 4.379           |
| O-ii    | -0.603                      | -5.552               | 4.612           |
| O-iii   | -0.597                      | -5.547               | 3.970           |
| O-iv    | -0.566                      | -5.516               | 4.490           |
| O-v     | -0.597                      | -5.547               | 4.388           |
| O-vi    | -0.596                      | -5.545               | 4.640           |

3.2. Griffith rupture work of P-doping $\gamma/\gamma'$ interfaces

The Griffith rupture work $W$ [24], a reversible work needed to separate a crystal along the interface into two free surfaces, is used to evaluate the binding strength of $\gamma/\gamma'$ interfaces. $W$ can be calculated by a difference in total energy by an optimized interfacial model and its corresponding surface models:

$$W = (-1/2S_i) \cdot \left[ E_i(n, m, k) - E_b(n_{\gamma}, m_{\gamma}, k_{\gamma}) - E_b(n_{\gamma'}, m_{\gamma'}, k_{\gamma'}) \right]$$

where $S_i$ is the area of coherent atomic layers in the $\gamma/\gamma'$ interfacial model. $E_b(n_{\gamma}, m_{\gamma}, k_{\gamma})$ and $E_b(n_{\gamma'}, m_{\gamma'}, k_{\gamma'})$ are the total energies of $\gamma$ and $\gamma'$ surface models, respectively. $n, m, k$ denote the numbers of Ni, Al and P atoms, respectively, where $n = n_{\gamma} + n_{\gamma'}$, $m = m_{\gamma} + m_{\gamma'}$, and $k = k_{\gamma} + k_{\gamma'}$.

The calculated $W$ values of $\gamma/\gamma'$ interfaces with or without P-doping is listed in Table 1. Corresponding to above two orientation relationships, i.e., (002)$\gamma$|(001)$\gamma'$ and (001)$\gamma$|(002)$\gamma'$, there are two potential inter-phase fracture sites [13], i.e., Region-1 and region-2, as illustrated in Figure 1. For the mode related to (002)$\gamma$|(001)$\gamma'$, the cleavage adjacent to the coherent (002) atomic layer occurs along the (001)$\gamma$ layer of $\gamma'$-Ni$_3$Al blocks, while the split takes place along the (001)$\gamma$ layer of $\gamma$-Ni blocks in the schema of (001)$\gamma$||(002)$\gamma'$.

Table 1 shows the Griffith rupture work $W$ in region-1 is smaller than region-2 in the clean model, which means $W$=4.428 J/m$^2$ in region-1 represents the rupture strength $W_0$ of clean [25] because the fracture usually emerges at the weakest part of a material [24]. Similarly to the clean $\gamma/\gamma'$ interface, most of $W$ values in region-1 are smaller than those in region-2, e.g., Ni-1, Ni-2, Ni-4, Al-6, O-iii, O-iv and O-v, indicating their inter-phase fractures also occur along the (001)$\gamma'$ layer of $\gamma'$-Ni$_3$Al blocks.
However, in the case of Ni-3, Ni-5, O-i, O-ii and O-vi, the inter-phase fracture site is changed to region-2 because their Griffith rupture works in region-2 are low relative to region-1. That is said, as P locates at its preferential sites in the γ/γ’ interface, e.g., Ni-1 and Ni-2 in γ-Ni block, the inter-phase fracture in region-1 keeps unchanged, while it is transferred to region-2 in the case of interstitial doping, e.g., O-i, O-ii and O-vi.

As the Griffith rupture work $W$ in cleaved regions is regarded as the rupture strength $W_0$, the impact of P-doping on $W_0$ of γ/γ’ interfaces can be further evaluated. Figure 2 displays the doping site dependence of $W_0$ in doped γ/γ’ interfaces. From Figure 2, one can see that most of $W_0$ in P-doping γ/γ’ interfaces are lower than that in the clean interface, and there exists following variation order: O-vi > O-iv > clean > Ni-2 > O-v > Ni-1 > O-i > Al-6 > Ni-5 > O-iii > Ni-3 > O-ii > Ni-4. This result clearly indicates P-doping at its preferred sites, e.g., Ni-3, Ni-2, Ni-1 and O-i, is detrimental to the rupture strength $W_0$ of γ/γ’ interfaces. But, in the case of O-vi (bounded by four Ni and two Al in γ’-Ni$_3$Al region) and O-iv (bounded by five Ni and one Al at the coherent (002) interface layer), their $W_0$ respectively increase by 3.8% and 1.4% [13] relative to the clean interface, indicating P-doping at some special interstitial sites can also improve the rupture strength of γ/γ’ interfaces. Since the probability of P-doping at O-vi and O-iv sites is quite low compared with its preferred sites Ni-3, Ni-2, Ni-1 even O-i sites, thus the rupture strength of γ/γ’ interfaces can only benefit from a moderate P-doping at elevated temperatures. Moreover, it is noticed that the phosphorous contents in present substitutional and interstitial models are 3.65 wt.% and 3.40 wt.%, respectively, both of which are far more than the upper limit of 0.051 wt. % in experiments [26]. Therefore, an influence of phosphorus concentration on the $W_0$ of P-doping Ni/Ni$_3$Al interfaces will be further investigated in the following work.

![Figure 2. The site dependence of $W_0$ in P-doping γ/γ’ interfaces](image)

To evaluate the impact of phosphorus concentration $x$ on rupture strengths $W_0$ of P-doping interfaces, a virtual crystal approximation (VCA) [27] approaches is adopted. In the schema of VCA, the host atom at doped sites may be partially replaced by other atoms. Herein only substitutional models can be calculated. Corresponding to Ni-1, Ni-2, Ni-3, Ni-4, Ni-5 and Al-6, their $x$-dependences of $W_0$ are illustrated in Figure 3. From Figure 3, one can see that with the addition of phosphorus, the $W_0$ in all models firstly decrease within 0.018 wt.%, and then increase up to 0.053 wt.% , finally keep unchanged in the range of 0.053 wt.% to 0.177 wt.%. This result clearly indicates P-doping induced deleterious impact is merely sensitive to low phosphorous concentration, and there is a most disadvantageous concentration point, e.g., $x$=0.018 wt.%. Interestingly, this tendency of $W_0$ vs $x$ is just consistent with experimental results of ultimate tensile strength $\sigma_{uts}$ of IN718 superalloys [28]. In which both of $\sigma_{uts}$ of IN718 superalloys at 25 °C and 650 °C also decrease firstly and then increase, and there is a minimum $x$=0.005 wt.%. Although the theoretical minimum $x$=0.018 wt. % is bigger than experimental value, a good agreement between $W_0$ vs $x$ and $\sigma_{uts}$ vs $x$ indicates the rupture strength
$W_0$ of $\gamma/\gamma'$ interfaces can be adopted to characterize the ultimate tensile strength of Ni-based superalloys to some extent.

![Figure 3](image-url)

**Figure 3.** The rupture strength $W_0$ of the Ni/Ni$_3$Al interface. The inset is the ultimate tensile strength $\sigma_{ut}$ of IN718 alloy with different phosphorus content [28].

### 3.3. Electronic structures of P-doping $\gamma/\gamma'$ interfaces

Figure 4 illustrates the charge density contour plots on sections across $\gamma/\gamma'$ interfaces with various P-doping. For the clean $\gamma/\gamma'$ interface, Figure 4.a and 4.b show the charge distribution of Ni atom in $\gamma$-Ni block is nearly spherical and isotropic, which means a metallic bonding exists between first nearest neighbor (FNN) Ni-Ni atoms. However, an obvious directivity can be seen between FNN Ni-Al atoms in $\gamma'$-Ni$_3$Al block, indicating there exists some covalent bonding along the FNN Ni-Al direction. This covalent bonding mainly arises from the polarization of p electrons of Al atoms as a result of the p-d hybridization effect [29]. And the charge density in region-2 is rich but poor in region-1, which means the local electronic interaction in region-2 is stronger than that in region-1. Hence the inter-phase cleavage fracture takes place in region-1 between the (001)$\gamma'$ and (002)$\gamma/\gamma'$ layers[13, 25, 30]. Thus, the charge density contour plots provide a direct visual pattern for understanding the inter-phase rupture sites shown in Table 1.
Figure 4. Typical charge density contour plots on sections across the Ni/Ni$_3$Al interface with or without P-doping. (a) (020) plane in P-free model, (b) (100) plane in P-free model, (c) (020) plane in Ni-4 model, (d) (100) plane in Ni-4 model, (e) (100) plane in Ni-3 model, (f) (020) plane in O-vi model. The regions indicated by red and black arrows are region-1 and region-2, respectively.

Figure 4.c and 4.d further exhibit the charge density contours in Ni-4 model. In comparison with the clean γ/γ’ interface, the charge density at the (001)γ and (002)γ/γ’ layers is poor, which means the substitution of P for Ni at coherent (002)γ/γ’ layer results in the electronic bonding strength in region-1 to be weakened. Maybe, just this weakened electronic interaction leads to the decrease of $W$ from 4.428 J/m$^2$ in clean interfaces to 2.685 J/m$^2$ in Ni-4 models.

As for the preferred site of P, e.g., Ni-3 model with the substitution of P for Ni atoms at (001)γ layer, Figure 4.e shows the relative variation of charge densities to P-free interfaces is not obvious, either in region-1 or in region-2, indicating there exists some other factors for the strengthening of γ/γ’ interfaces except for electronic affinity. To evaluate the influence of local elastic strains, a displacement $z$ of doped atom and the space $l$ between atomic layers are also calculated, as shown in Table 2 and 3. One can see that the doped atom in Ni-3 model moves 10.70 % in the Z direction toward γ-Ni block, and the layer spaces in region-1 and region-2 are larger than those in γ-Ni and γ’-Ni$_3$Al blocks, which means some local elastic strain energy exists in γ/γ’ interfacial regions and a like-Frenkel defect form at the side of γ-phases [12]. Different from the clean interface, its layer space $l$ in region-2 is found to be larger than that in region-1. As a result of mutual influence of atomic bonding energy and local elastic strain energy, the change of inter-phase fracture site in Ni-3 model undoubtedly can be attributed to high local elastic strain energy in region-2 [7, 9, 13].
Table 2. Relative displacement of doped atoms z (%) in the Z-direction. Note: positive and negative values represent the displacement toward and away from the coherent interfacial layer, respectively.

| Layer     | Model | Ni-1 | Ni-2 | Ni-3 | Ni-4 | Ni-5 | Al-6 | O-i | O-ii | O-iii | O-iv | O-v | O-vi |
|-----------|-------|------|------|------|------|------|------|-----|------|-------|------|-----|------|
| γ-Ni      | +15.71| +25.61| -25.84| -47.90| +95.26|     |      |     |      |       |      |     |      |
| (001)γ    |       |      | -10.70|       | +95.26|     |      |     |      |       |      |     |      |
| (002)γ/γ' |       |      | -37.25|       | -65.96|     |      |     |      |       |      |     |      |
| (001)γ'   |       |      | -106.26| -21.74| -13.90|     |      |     |      |       |      |     |      |
| γ'-Ni3Al  |       |      |      |       |       |     |      |     |      |       |      |     |      |

Table 3. Space between atomic layers l in Ni block, Ni3Al block, Region-1 and Region-2 in the Ni/Ni3Al interfacial model with or without P-doping. The bold value represents the l at rupture sites.

| Model | l/Å       | Ni block | Region-1 | Region-2 | Ni3Al block |
|-------|-----------|----------|----------|----------|-------------|
| Clean |           | 1.750    | 1.810    | 1.771    | 1.815        |
| Ni-1  | 1.745     | 1.814    | 1.745    | 1.812    |             |
| Ni-2  | 1.712     | 1.794    | 1.786    | 1.800    |             |
| Ni-3  | 1.719     | 1.812    | 1.819    | 1.806    |             |
| Ni-4  | 1.780     | 2.009    | 1.502    | 1.841    |             |
| Ni-5  | 1.675     | 1.549    | 1.775    | 1.727    |             |
| Al-6  | 1.734     | 1.788    | 1.776    | 1.787    |             |
| O-i   | 1.834     | 1.779    | 1.828    | 1.830    |             |
| O-ii  | 2.094     | 1.670    | 1.909    | 1.792    |             |
| O-iii | 1.527     | 1.413    | 1.366    | 1.315    |             |
| O-iv  | 2.243     | 1.839    | 1.799    | 1.813    |             |
| O-v   | 1.247     | 1.295    | 1.221    | 1.537    |             |
| O-vi  | 1.810     | 1.593    | 1.779    | 2.511    |             |

In the interstitial O-vi model, a similar reverse of inter-phase fracture site to Ni-3 model can be also deduced from the variation of the layer space l. Table 2 and 3 show P-doping causes Al atoms at (001)γ' layers to move toward Ni/Ni3Al interfaces and the layer space l in region-1 significantly descend. Thus, the bonding between Al atoms at (001)γ' layers and Ni atoms at coherent (002)γ/γ' is distinctly enhanced (refer to Figure 4f). In this case, although the electronic interaction and local elastic strain in region-2 is scarcely changed by P-doping, and even the Griffith rupture work W=4.598 J/m² is lower than W=4.647 J/m² in clean interfaces, its rupture strength $W_0$ of γ/γ' interfaces can benefit from the dramatic increase of W in region-1 owing to the reverse of inter-phase fracture site.

4. Conclusions

Using a first-principles calculation, the energetic and electronic structures of γ-Ni/γ'-Ni3Al interfaces with various P-doping are investigated. The heats of formation and cohesive energies show P atom prefers to occupy Ni sublattices at the side of γ-phases rather than octahedral interstitial sites in γ-Ni and γ'-Ni3Al phases. The rupture strength $W_0$ of Ni/Ni3Al interfaces is found to be very sensitive to P-doping site and concentration. Not only Griffith rupture works W of Ni/Ni3Al interfaces but also their inter-phase sites can be changed by P-doping. For the preferential substitution of P for Ni atoms in γ-Ni phases, the $W_0$ of Ni/Ni3Al interfaces are smaller than that in P-free interfaces. With the increase of P concentration $\chi$, their $W_0$ firstly decrease, and then increase, finally keep unchanged. This variation tendency is consistent with $\chi$-dependence of ultimate tensile strengths $\sigma_{uts}$ of IN718 superalloys, implying the rupture strength $W_0$ of the Ni/Ni3Al interface can be adopted to characterize the tensile strength of Ni-based superalloys to some extent. In the interstitial doping mode, a reverse of inter-phase fracture sites from region-1 in clean interfaces to region-2 in O-vi system is detected. In this
case, a mutual impact of atomic bonding energy and local elastic strain energy leads to a abrupt rise in $W$ in region-I relative to P-free interface. As a result, the rupture strength $W_0$ in O-vi model is improved. Thus, we can conclude that the strengthening of $\gamma\text{-Ni/}\gamma\text{'}\text{-Ni}_3\text{Al}$ interfaces can also benefit from the moderate P-doping at elevated temperatures.

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6. References

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