

Effects of Alloying on the Interface Energy of the γ'' -Phase in Nickel-Based Superalloys



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Nickel-based superalloys of the 718 type have been extensively used in the production of engine parts which operate at high temperatures. The alloy is strengthened by the precipitation of small γ'' -phase particles with a large lattice distortion in the γ matrix. These γ'' -phase particles, however, may transform to the more thermodynamically stable δ -phase. Such transformation might be mitigated by adding other alloying elements. In this work, we used density functional theory calculations at 0 K to study the influence of relevant alloying elements on the interface energy of the γ''/γ coherent interfaces. By replacing an atom either in the γ'' -phase or at the interface and calculating the corresponding interface segregation energy, we assessed the favorable replacement position of each alloying element. Implications of our results on the γ'' -phase growth are also discussed.

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I. INTRODUCTION

DUE to their high strength at elevated temperatures, wrought nickel-based alloy-718-like superalloys have been widely used in the manufacture of highly loaded parts of aircraft engines.^[1–4] The excellent strength is due to the precipitation of the strengthening γ'' -Ni₃Nb-phase^[5] which usually takes the form of disk-shaped particles in the γ matrix. Because of the orientation relationships $(001)_{\gamma''} \parallel \{001\}_{\gamma}$ and $[100]_{\gamma''} \parallel \langle 100 \rangle_{\gamma}$, γ'' -phase particles usually have (001) and (100) interfaces with the γ matrix.^[5]

At temperatures above 650 °C, the γ'' -Ni₃Nb phase (lattice structure D0₂₂), however, transforms to the δ -Ni₃Nb phase (lattice structure D0_a) which is more thermodynamically stable. Since the δ -phase does not confer the high strength provided by the γ'' -phase, other alloying elements are usually added to stabilize the γ'' -phase.^[6]

Previous studies using density functional theory (DFT) have reported the effect of aluminum and transition group elements on the stability of the γ'' -phase in the γ -matrix.^[7,8] Of the elements relevant to γ'' -strengthened alloys (Al, Co, Cr, Hf, Mo, Ta, Ti, W, and Zr), only Co has a lower energy on a Ni site than on

a Nb site in the γ'' -phase, but its energy is still lower when it is in the γ matrix.^[7] Other alloying elements prefer to replace a Nb atom. Moreover, while Ti, Al (γ' -phase strengtheners), and Cr can be used for stabilizing γ'' -phase, both Mo and W, which are usually used as solid solution strengtheners in superalloys,^[9] prefer the δ -phase over the γ'' -phase.

Recently, we have studied the interface energy of γ/γ'' using DFT.^[10] With the magnetic effects included in the calculations, the interface energies of the γ/γ'' 001 and 100 interfaces were put at ~ 48 and ~ 24 mJ/m², respectively, which are within the range of the dynamic interface energy reported by Moore *et al.*^[11] and are, however, smaller than the experimental value given in Reference 12. Moreover, switching off the magnetic effects (by using non-polarized calculations) led to negative values of the interface energy. We note that any comparisons between these results are to be taken with caution since only fully coherent pure γ/γ'' interfaces were investigated in the mentioned DFT study, which are very different from experimental semi-coherent interfaces where other alloying elements exist in the γ matrix as well as in the γ'' -phase precipitates.

The effects of alloying elements on the interface energy and phase stability of Ni-based superalloys have been reported extensively for variations of interfaces. For example, Xue *et al.*^[13] found that solute segregation can lead to a reduction in grain boundary energy and, thus, stabilize grain boundaries in nickel-based superalloys. Using DFT calculations to investigate γ -Ni/ γ' -Ni₃Al interface, Ahmed *et al.*^[14] also showed that many alloying elements improve the stability of the interface and increase its fracture strength. For the γ/δ and γ/η interfaces, the effects of alloying on the interface

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energy have also been reported^[15] recently, together with a model to relate the relevant interface quantities to the solution energy and elastic energy.

In this study, we carried out DFT calculations at 0 K to study the influence of the relevant alloying elements on the γ/γ'' interface energy. These calculations allow us to see whether these alloying elements prefer to stay in the γ'' bulk phase or at the interface. We also discuss the implication of our results, in connection with previous studies,^[7,16] on the design of alloys where γ'' -strengthening is of interest.

II. METHODS

Here, we study the influence alloying elements on the interface energy of both coherent γ/γ'' interfaces parallel to $(001)_{\gamma''}$ and $(100)_{\gamma''}$ surfaces (referred to as 001 and 100 interfaces, respectively). For each orientation, an initial interface supercell is created by stacking two individual γ and γ'' phases along the direction normal to the interface (Figure 1), using lattice constants from [7]. The in-plane lattice constants of the two constituents of the initial supercell were averaged. These supercells contain 128 atoms.

For each interface, we replaced an atom in the supercell by an alloying element, either at the center of the γ'' phase or at the interface. As mentioned above, we studied the following relevant alloying elements: Al, Co, Cr, Hf, Mo, Ta, Ti, W, and Zr. We used results reported in^[7] to choose the replacement site. Consequently, except for Co which replaced a Ni atom (marked b in Figure 1), all alloying elements replaced a Nb atom (marked a in Figure 1).

All DFT calculations were carried out using the VASP program^[17–19] with the projector augmented wave method potentials.^[20,21] Similar to a previous

study,^[7] we used the pseudo-potential with maximum number of electrons for each alloying element. The energy cutoff was set to 520 eV which is at least 1.5 times the largest energy cut off of the used potentials. The precision parameter was set to ‘accurate.’ The real-space projection operators were calculated to the precision of 10^{-4} eV/atom. The electronic and ionic convergence criteria were set to EDIFF = 4×10^{-7} eV and EDIFFG = 4×10^{-5} eV, respectively.

For each alloying element in a particular supercell, we used the same procedure as in 7. First, we relaxed the ionic positions and cell shape at fixed supercell volume for different volumes and use a Birch-Murnaghan equation of state^[22] to get the optimal scale factor. A final calculation was then carried out for the optimal scale factor with a k-point spacing of 0.1 Å. All calculations were spin polarized where γ -phase atoms were initialized with a magnetic moment of $0.8 \mu_B$. The magnetic moments of γ'' -phase atoms were initialized to $0.05 \mu_B$, except for Co and Cr whose magnetic moments were initialized to a very large value of $2 \mu_B$. In all simulations, γ and γ'' phases converged to ferro-magnetic and non-magnetic states, respectively.

III. RESULTS AND DISCUSSION

The main results of this study are plotted in Figure 2 and given in Table I (with the alloying elements sorted by their atomic number) which show the interface segregation energy, E_{seg} , defined as the difference in the supercell energy when the alloying element replaced an atom at the interface and in the bulk, respectively. A positive E_{seg} means that the alloying element prefers to stay in the γ'' -phase bulk. Conversely, that element prefers to segregate towards the interface if $E_{\text{seg}} < 0$.

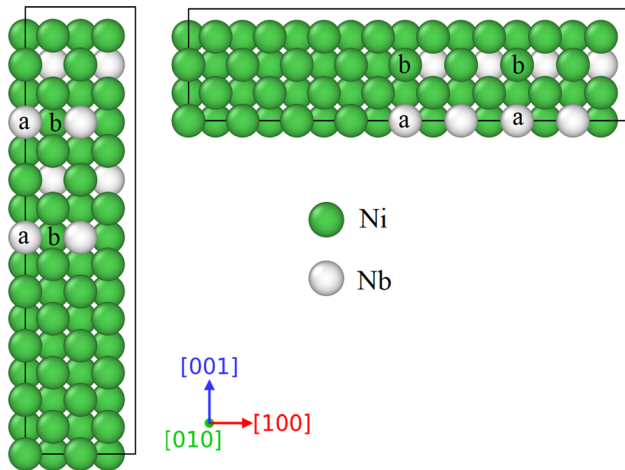


Fig. 1—Side view of the interface supercells used in this study. These interfaces were created by stacking two individual γ'' - and γ -phases along the direction perpendicular to the interface. Both coherent 001 and 100 interfaces (left and right figures, respectively) were studied. Co will replace one of the Ni sites marked by ‘b’. Other element will replace one of the Nb sites marked by ‘a’. These supercells contain 128 atoms.

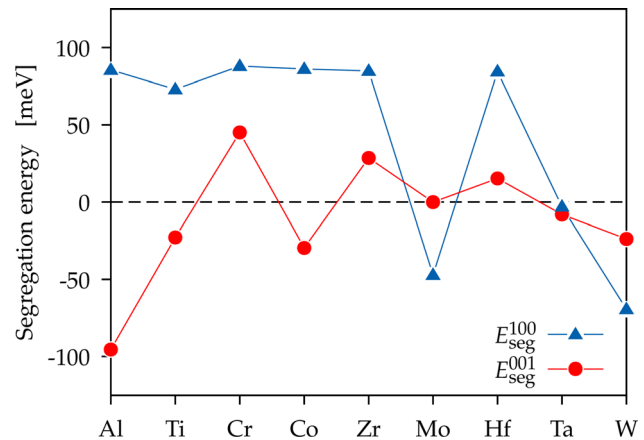


Fig. 2—Interface segregation energy of the investigated alloying elements. This figure shows the interface segregation energy, E_{seg}^{100} and E_{seg}^{001} , defined as the difference in the supercell energy when the alloying element replaced an atom at the interface and in the bulk, respectively. A negative value means that the alloying element prefers to segregate towards the interface. Vice versa, the alloying element prefers to stay in the γ'' -phase bulk if its E_{seg} is positive.

Table I. Interface Segregation Energy of the Investigated Alloying Elements

	E_{seg}^{001} [meV]	E_{seg}^{100} [meV]
Al	-95.48	85.53
Ti	-22.83	73.06
Cr	45.17	88.03
Co	-29.62	86.13
Zr	28.55	84.83
Mo	-0.06	-47.08
Hf	15.26	84.52
Ta	-8.00	-2.96
W	-23.81	-69.37

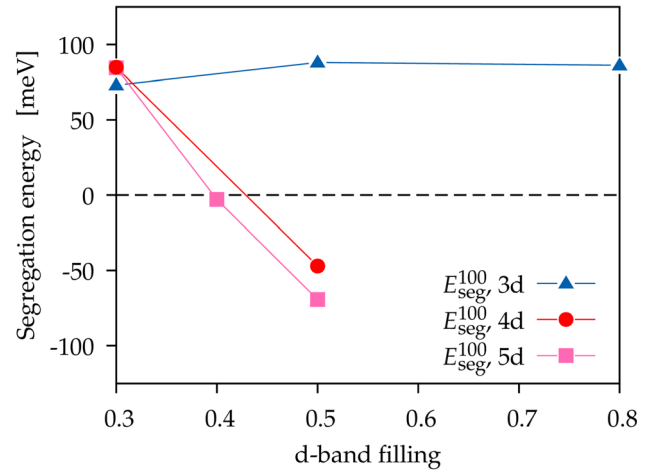
Note that E_{seg} of a particular alloying element is also the difference in the interface energy (density) when the element moves from the γ'' -phase bulk to the interface.

Figure 2 does not hint to any clear trend of the E_{seg} . Take for example the 100 interface: while $E_{\text{seg}}^{100} < 0$ for Mo and W and E_{seg}^{100} is almost 0 meV for Ta, the remaining E_{seg}^{100} values are positive and of the same order. Such an observation, however, does not occur in the E_{seg}^{001} of the 001 interface.

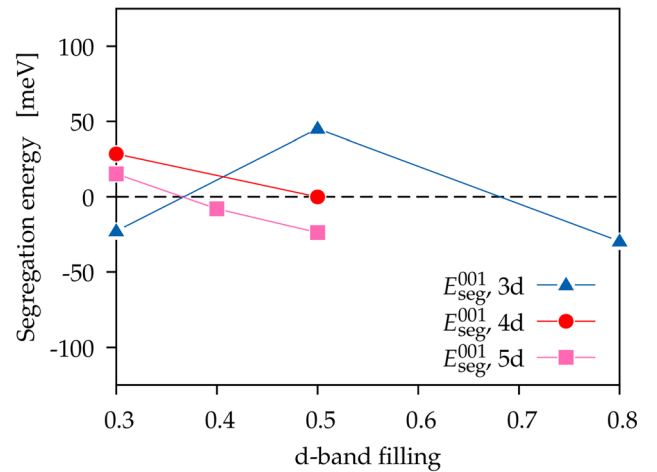
It has been found that for many dilute transition-metal alloys, the surface segregation energies of single-transition-metal impurities can be related to their d -band filling^[23,24]—though such a relation has not been confirmed in Ni(111) surface^[25] or in bimetallic alloy surfaces.^[26] Here, we also plotted the segregation energy versus d -band filling (Figure 3), with the idealized d -band filling taken from Reference 27 (Figure 3 therein). Our current dataset, however, does not reveal any relation between the interface segregation energies E_{seg} and d -band fillings. For example, while the E_{seg}^{100} values of the investigated 3d elements are more or less constant, E_{seg}^{100} of 4d and 5d elements seems to decrease with respect to d -band occupancy.

Our results show that the elements Mo and W have the tendency to move to the 100 interface: their E_{seg} are negative for both interfaces with $|E_{\text{seg}}^{100}| > |E_{\text{seg}}^{001}|$. Note that their diffusion in nickel is slow. At 900 °C, their interdiffusion coefficients with nickel are only around $10^{-17} \text{ m}^2/\text{s}$ (as a comparison, the diffusion coefficients of Ta and Hf in nickel, for example, are more than one order of magnitude larger).^[28,29] Together with our current results, this means that adding W would hinder the growth of γ'' -phase particles in the 100 direction: Any growth of the γ'' -phase particles would require the interface to carry these alloying atoms along. Moreover previous studies^[7,15,16] have already shown that, in terms of the stabilization of the γ'' -phase, it is not advisable to add Mo and W since they possibly destabilize the γ'' -phase in favor of the δ -phase.

Ta is another element whose values of E_{seg} are negative for both interfaces. However, these values are small (less than 10 meV) and thus Ta basically does not have any preferable positions and adding it will not affect the growth of γ'' -phase particles.



(a)



(b)

Fig. 3—Interface segregation energy of investigated transition elements versus d -band filling for (a) 100 interface and (b) 001 interface. Element order from left to right: Ti-Cr-Co (3d series), Zr-Mo (4d series), and Hf-Ta-W (5d series).

The γ' -forming elements Al and Ti prefer to be at the 001 interface ($E_{\text{seg}}^{100} > 0$ and $E_{\text{seg}}^{001} < 0$). Thus, having a 001-interface bordering on a region rich of (Al, Ti) might be energetically favorable. This is in agreement with the experimental results which show composite γ''/γ' precipitates in the γ matrix at low temperatures.^[30]

Co also prefers to be at the 001 interface ($E_{\text{seg}}^{100} > 0$ and $E_{\text{seg}}^{001} < 0$). However, Co has lower energy when it is in the γ matrix^[7] and, thus, it will not stay in the γ'' -phase but rather move to the γ phase and diffuse away from the interface.

The remaining alloying elements (Cr, Zr, Hf) all prefer to stay in the bulk γ'' -phase ($E_{\text{seg}}^{100} > 0$ and $E_{\text{seg}}^{001} > 0$). Here, we note that while the Cr diffusion in nickel is slow (its diffusion activation energy is about 300kJ/mol which is on par with the diffusion activation energy of W in nickel), the diffusion of Zr and Hf in nickel is much faster.^[29] Adding Cr will, thus, make the γ'' -phase growth in the 100 direction less energetically

favorable than in the 001 direction (its E_{seg}^{100} is much larger than its E_{seg}^{001}). Conversely, adding Zr and Hf will probably not suppress the growth of the γ'' -phase in any directions. However, the contents of Zr and Hf must be limited since increasing their contents might hinder the grain coalescence at grain boundaries^[31] or lead to the formation of chains of misoriented grains which causes the deterioration of creep resistance.^[32]

The present study was based on spin-polarized calculations with which the magnetic effects were included. As mentioned above, switching off the magnetic effects led to a negative γ/γ'' interface energy.^[10] Similar influence of the magnetic effects has been also reported previously by Woodward *et al.*^[33] where the authors found that non-polarized calculations led to a negative interface energy of the γ -Ni/ γ' -Ni₃Al interface. One, thus, expects that the results of the current study might change when the influence of magnetic effects is altered either by switching off all these effects altogether or by introducing other elements with strong magnetic interactions, such as Fe, Co, and Cr, into the γ matrix.

Finally, we also emphasize that obvious simplifications of the γ/γ'' interface have been made to ease the computing difficulties: Here, the interface is assumed to be fully coherent and *pure*—e.g., the γ phase contains Ni only. The existence of other elements in the alloys, as in experiments, might lead to changes in, for example, elastic energy (due to difference in sizes) and magnetic interactions (see above) and, thus, might lead to changes in the segregation energy.

IV. SUMMARY

Using density functional theory at 0K, we have calculated the interface segregation energy for γ/γ'' interface for some alloying elements which are relevant to γ'' -phase strengthening in nickel-based superalloys. The implications of these results were then discussed: For example, while Mo and W should be avoided since these elements might hinder the growth of γ'' precipitates, addition of Al, Ti, and Cr might change the shape of γ'' precipitates. Further studies are necessary to assess the influence of magnetic effects on the current results.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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