Phase stability and mechanical property of $\gamma'$-($Ni_{1-x}Co_x$)$_3$Al$_{1-y}$Cr$_y$ alloys

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Abstract
The phase stability and mechanical property of $\gamma'$-($Ni_{1-x}Co_x$)$_3$Al$_{1-y}$Cr$_y$ phase of Ni-Co based superalloys are studied by the first-principles method. The calculated mixing enthalpies at 0 K indicate that the alloys are thermodynamically unstable against phase separation into $Ni_3AlCr$ and $Co_3AlCr$ alloys. Additions of 6.25 at% of Cr into ($NiCo_2$)Al alloy can decrease the positive mixing enthalpy by 34%, hence Cr has a significant stabilizing effect on $\gamma'$ phase. The configurational entropy can further stabilize the alloy at finite temperature. A strong tetragonal shear softening is observed for ($Ni_{1-x}Co_x$)$_3$Al$_{1-y}$Cr$_y$ alloys with large Co concentration. Cr additions could increase $C''$ of the alloys, and thus offset the softening effect of Co by a certain extent. The electronic density of states analysis demonstrates that the flexibility of Al $p$ band and synergistic alloying effect are the physics behind the stabilization the $\gamma'$ phase of Ni-Co based superalloy by Cr alloying.

1. Introduction

Ni base superalloys are widely used as blades in Turbine engines due to their high strength and corrosion resistance at high temperature [1]. Co base superalloys are usually used in static parts of turbine engines due to their better hot corrosion, oxidation and sulfidation resistance, and lower strength [2–4]. Since the discovery of $\gamma'$ hardened Co based superalloys, this class of alloys become a promising competent alloy to the well-established Ni based superalloys [5]. The $\gamma'$-$\gamma''$ structure of Co base superalloys can be stabilized by W, Mo and Ta [6–9], while addition of Ti and Ni can increase the volume fraction of $\gamma'$ phase and the solvus temperature [5, 8, 10, 11]. This Ni-Co based alloys exhibit a similar microstructure as the extensively studied Ni base superalloys, where ordered L12-$\gamma'$ phase is coherently embedded in the solid-solution fcc-$\gamma''$ phase matrix [4, 5]. The Ni-Co based alloys contain at least four main alloying components Co, Ni, Al, W in $\gamma'$ phase with small amount of alloying additives Cr, Ta, Mo, Nb and Ti [2, 4]. In other cases, several types of Tungsten free Co base and Ni-Co based superalloys with large additions of Cr, Nb and Mo are also developed [6, 7]. However, the lower strength of Co base alloy compared to that of Ni base alloy still limits their widespread applications [7, 8].

The mechanical property of superalloys is almost determined by the precipitate $\gamma'$ phase [1–4, 10, 11], therefore the explicit knowledge of phase stability and the elastic properties of $\gamma'$ phase is of particular importance. Experiment cannot directly get access into the single phase elastic properties of alloys that contains precipitates, but fortunately modern first-principles calculation can give reasonably reliable results on enthalpy of formation, elastic moduli and planar fault energies of solids [12–16]. Several computational studies have addressed the phase stability [14, 17, 18], site preference of additives [19], elastic properties [20, 21] and planar faults as well as the creep resistance [15] of the $\gamma'$ phase of Co base superalloys. But, few theoretical works [22, 23] studied the phase stability and elastic properties of the $\gamma'$ phase of Ni-Co based superalloys, where Ni and Co having similar concentration. Furthermore, the effect of Ni concentration on the mechanical properties of $\gamma'$ phase of Co base superalloys is also of great interest. Liu et al [22] studied the phase stability, elastic constant, phase diagram of Ni-Co-Al, Co-Cr-Al, Ni-Co-Cr ternary alloys to predict quaternary Ni-Co-Cr-Al alloys.
Owing to the limited structural model used in their work [22], the quaternary \( \gamma' \) phase of Ni-Co-Cr-Al alloys is not studied explicitly. First-principles study on the solid solution strengthening effect of binary Ni-Co, Ni-Cr, and ternary Ni-Co-Cr alloys [23] find that Co and Cr have different alloying effect on \( \gamma' \) phase of Ni base superalloys. To the best of our understanding, the phase stability and mechanical property are still not fully understood for \( \gamma' \) phase of Ni-Co based superalloys. In this paper, the phase stability and elastic property of \( \gamma' \) phase of Ni-Co based superalloys were studied by first-principles calculation.

2. Computational details

The model superalloy \( \gamma' \cdot (\text{Ni}_{1-x} \cdot \text{Co}_{x})_3 \cdot \text{Al}_{1-x} \cdot \text{Cr}_x \) has a fcc-L1\(_2\) structure with two different atomic sites, respectively, face center site (A site) and corner site (B site). Both Experiment [24] and calculation [12, 13, 19, 22] confirmed that Co and Ni prefer A site, Al always occupies B site, and Cr shows a B site preference in both Ni based [12, 13] and Co based [19, 22] superalloys. Therefore, in the current model superalloy, Ni/Co randomly occupy the A sites and Al/Cr randomly occupy the B site, respectively.

The total energy related to this study was calculated by the Exact Muffin–Tin Orbital method (EMTO) [25–27] in the framework of Density Functional Theory (DFT) [28, 29]. The EMTO method is an improved KKR method using the screened spherical wave [25]. The one-electron Kohn–Sham equation [29] was solved within the scalar-relativistic approximation and the soft-core scheme. The Green’s function was calculated for 16 complex energy points distributed exponentially on a semicircular contour containing the valence states below the Fermi level. The self-consistent calculations were performed within the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof [30]. The Ni-3\(d^8\)s\(^2\), Co-3\(d^7\)s\(^2\), Cr-3\(d^3\)s\(^2\), and Al-3s\(^2\)3p\(^1\) were treated as valence, EMTO base set included s, p, d, and f orbitals. Spin-polarized calculations were carried out for all the alloy composition to take into account the possible magnetic ordering. For all the calculations, total energy was converged to \(10^{-7}\) Ry. The equilibrium volume and Bulk modulus were determined by fitting nine total energy points for different volumes to Morse type of equation of state [27]. The chemical disorder of the alloy system is treated with Coherent Potential Approximation (CPA) [31, 32]. The EMTO-CPA method was successfully applied in the first-principles study of the physical properties of Fe-based alloys [33, 34], Heusler alloys [35] and multicomponent high entropy alloys [36]. Several comparative studies on the coherent potential approximation and special quasirandom structure method for the disordered alloys [37, 38] demonstrate that CPA can give accurate elastic moduli and lattice constants of alloy materials even though local lattice distortion and short-range order cannot be taken into account. The EMTO-CPA method was also successfully applied in the alloys with sublattice disorder and got quite good results [35, 39]. And further, the reliability of CPA on the enthalpy of formation calculation of alloys with sizeable atomic size difference was also confirmed [37]. Therefore, the CPA is being a reliable and efficient tool for current research that concentrates on the enthalpy of formation and elastic property of (NiCo)\(_3\)(AlGr) alloys with sublattice disorder.

The two cubic shear moduli \( C' \) and \( C_{44} \) were calculated by applying volume conserving orthorhombic and monoclinic distortions, respectively:

\[
\begin{pmatrix}
1 + \varepsilon_x & 0 & 0 \\
0 & 1 - \varepsilon_y & 0 \\
0 & 0 & 1 - \varepsilon_z
\end{pmatrix}
\]

and

\[
\begin{pmatrix}
1 + \varepsilon_m & 0 & 0 \\
0 & \varepsilon_m & 0 \\
0 & 0 & 1 - \varepsilon_m
\end{pmatrix}
\]

these deformations lead to total energy changes: \(E(\varepsilon_x) = E(0) + 2VC'\varepsilon_x^2 + O(\varepsilon_x^3)\) and \(E(\varepsilon_m) = E(0) + 2VC_{44}\varepsilon_m^2 + O(\varepsilon_m^3)\). Six deformation strains \(\varepsilon = 0.00, 0.01, \ldots, 0.05\) were used to fit the elastic moduli \(C'\) and \(C_{44}\). To explore the ductile behavior in this alloy, the polycrystalline shear moduli were obtained from the calculated single-crystalline elastic constants according to the Voigt–Reuss–Hill averaging scheme [40]. The polycrystalline bulk modulus \(B\) and shear modulus \(G\) of Voigt and Reuss averaging method for the cubic structure are given by \(B_V = B_R = (C_{11} + 2C_{12})/3\), \(G_V = (C_{11} + C_{12} + 3C_{44})/5\), \(G_R = 5C_{44}(C_{11} - C_{12})/[4C_{44} + 3(C_{11} - C_{12})]\). Then the Poisson’s ratio \(\nu\), elastic anisotropy \(A_{VR}\) can be defined as \(\nu = (3B_R - 2G_R)/2(3B_R + 2G_R), A_{VR} = (G_R - G_B)/(G_V + G_B)\). The intrinsic ductile to brittle criterion can be expressed by Pugh ratio \(B/G > 1.75\) (Pugh criterion) [41], Poisson’s ratio \(\nu > 0.26\) and Cauchy pressure \(C_{12} - C_{44} > 0\) (Pettifor criterion) [42].

3. Results and discussions

3.1. Ground state properties

The calculated lattice parameter (\(a\) in Å) and bulk modulus (\(B\) in GPa) of \(\gamma' \cdot (\text{Ni}_{1-x} \cdot \text{Co}_{x})_3 \cdot \text{Al}_{1-x} \cdot \text{Cr}_x\) are shown in figure 1. Increasing Co concentration expands the lattice, while increment of Cr content tends to decrease the
lattice constant. The lattice parameter increases almost linearly as a function of Co content as the Cr is less than 0.1. Nonlinearity arises in $a \sim x$ curves for Cr concentration larger than 0.1, especially at lower Co content.

The bulk modulus (shown in figure 1(b)), which describes the compressibility of alloy, shows complicated behaviors for $x$ smaller than 20 at%. For (Ni$_{1-x}$Co$_x$)$_3$Al alloy, the bulk moduli show a minimum at $x \sim 20$ at%, this is closely related to the change of Fermi surface topology [43] at this alloy composition. A similar phenomenon is also observed for alloys with other compositions. It is noteworthy that both the lattice parameters and the bulk moduli show an increasing trend as a function of Co composition, which is quite unusual since lattice expansion usually accompanied by a decrease of bulk modulus [44].

The nonlinear behavior of lattice constant and anomalous Co/Cr concentration dependence of bulk modulus can be understood from the magnetic effect [43]. The total magnetic moment and the local atomic moments of atoms are shown in figure 2 as a function of Co concentration $x$ and Cr concentration $y$. As observed in figure 2(a), Globally, the (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys are ferrimagnetic with the magnetic moment of Co and Ni align in the same direction, while Cr has a moment antiparallel to those of Co and Ni. The Cr moment changes significantly with Co concentration for $x < 0.2$ (see in figure 2(c)), this effect leads to a competition of ferromagnetic and antiferromagnetic order, and which is closely related to the nonlinearity of $a \sim x$ curve and complex Co/Cr concentration dependence of bulk modulus.

As shown in figure 2(a), the total magnetic moment of (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys increases linearly for $x > 0.1$. The total magnetic moment decreases with the increment of the Cr concentration, which is due to the antiferromagnetic coupling of Cr with the nearest neighboring Co and Ni atoms. This can be seen from the negative moment shown in figure 2(c). The total magnetic moment of Ni$_3$Al$_{1-y}$Cr$_y$ disappears when Cr concentration is larger than 0.1. In this circumstance, both Ni and Cr atoms have zero moments, namely, the alloys are nonmagnetic. This is due to the severe shrinkage of cell volume with the increment of Cr content (see figure 1(a)). The absolute value of atomic moments $\mu_{\text{Ni}}$, $\mu_{\text{Co}}$, and $\mu_{\text{Cr}}$ increases with the increment of Co concentration, while $\mu_{\text{Ni}}$, $\mu_{\text{Cr}}$, and $\mu_{\text{Co}}$ decrease with the increment of Cr concentration. The alloys with high Cr
content have smaller cell volume. In the case of a large overlap of electronic wave functions, the spin degenerate state is more stable in energy, resulting in weaker spin polarization.

### 3.2. Phase stability

To understand the thermodynamic stability of at γ'- (Ni\(_{1-x}\)Co\(x\))\(_3\)Al\(_{1-y}\)Cr\(_y\) phase at low temperature, we calculated the enthalpy of formation \(\Delta H_f\) and mixing enthalpy \(\Delta H_m\) of alloys. \(\Delta H_f\) and \(\Delta H_m\) are, respectively, defined as follows,

\[
\Delta H_f = \sum_x E_x - \sum_y E_y - 3E_{Ni} - 3xE_{Co} + 3yE_{Cr}
\]

and

\[
\Delta H_m = \sum_x E_x - \sum_y E_y - E_{Ni_{1-x}Co_x_3Al_{1-y}Cr_y} - (1 - x)E_{Ni_3Al_yCr_y} + xE_{Co_3Al_yCr_y}
\]

Here \(E_{Ni_{1-x}Co_x_3Al_{1-y}Cr_y}\), \(E_{Ni_3Al_yCr_y}\), and \(E_{Co_3Al_yCr_y}\) are, respectively, total energies of \((Ni_{1-x}Co_x)_3(Al_{1-y}Cr_y)\), \(Ni_3(Al_{1-y}Cr_y)\), and \(Co_3(Al_{1-y}Cr_y)\) alloys. And \(E_{Ni}, E_{Co}, E_{Al}\), and \(E_{Cr}\) are, respectively, atomic energies of fcc Ni, hcp Co, fcc Al and bcc Cr.

The enthalpy of formation \(\Delta H_f\) and mixing enthalpy \(\Delta H_m\) of \((Ni_{1-x}Co_x)_3(Al_{1-y}Cr_y)\) alloy are shown in figure 3. The enthalpy of formation \(\Delta H_f\) is always negative, demonstrating that formation of the alloys is exothermic, and thus the alloys are thermodynamically stable. The absolute value of \(\Delta H_f\) decreases linearly as a function of Co and Cr content from \(\sim 120\)–95 mRy to \(\sim 45\)–35 mRy, indicating that the increasing Co content destabilizes the γ’ phase. The slope of \(\Delta H_f\) vs x curve decreases gradually as a function of Cr. The calculated enthalpy of the formation for \(L1_2\) (NiCo)\(_3\)Al by Liu et al [22] is also shown in figure 3(a) for comparison. The PAW method [22] gives lower \(\Delta H_f\), but almost parallel to the curve (left triangular) for (NiCo)\(_3\)Al alloy obtained in this work.

The \((Ni_{1-x}Co_x)_3(Al_{1-y}Cr_y)\) alloys can be considered as a mixture of ternary Ni\(_3\)AlCr and Co\(_3\)AlCr alloys, therefore, mixing enthalpy \(\Delta H_m\) could be a measure of the stability of \((Ni_{1-x}Co_x)_3(Al_{1-y}Cr_y)\) alloys against decomposition. The mixing enthalpies (see figure 3(b)) of all the alloy composition considered in the present work are small positive values, indicating that alloys would decompose into Ni\(_3\)AlCr and Co\(_3\)AlCr alloys, namely, \((Ni_{1-x}Co_x)_3(Al_{1-y}Cr_y)\) alloys are thermodynamically unstable. The mixing enthalpies reach their maxima

![Figure 2. Total and atomic magnetic moment of γ’- (Ni\(_{1-x}\)Co\(_x\))\(_3\)Al\(_{1-y}\)Cr\(_y\) alloy.](image-url)
close to \( x \sim 40 \) at %, and the \( \Delta H_m \)s are decreased with increasing Cr content. For the Cr added alloys, \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_{0.25}\text{Cr}_{0.25}\) alloy has the lowest mixing enthalpy of 0.4564 mRy/atom, \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_{0.95}\text{Cr}_{0.05}\) alloy has the largest. The maximum value of mixing enthalpy of \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}\) alloy is 0.6868 mRy, namely, 25 at.% of Cr could lower the mixing enthalpy by 34%, therefore, Cr has a significant stabilizing effect on \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}\) alloy. The above discussions on mixing enthalpy did not include the entropy effect, which is expected to stabilize \((\text{Ni}_{1-x}\text{Co}_x)_{3-2y}\text{Al}_y\text{Cr}_y\) alloys further at finite temperature against phase separation. The disordered occupation of Ni and Co at A site could introduce the configurational entropy,

\[
\text{S}_{\text{config}} = k_B \ln (1 - x) \ln (1 - x).
\]

If the energy term \( TS_{\text{config}} \) is taken into account, one can get the mixing Gibbs free energy, \( \Delta G = \Delta H - TS_{\text{config}} \). The lower panel of figure 3(b) shows the mixing Gibbs free energy \( \Delta G \) of \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_{0.95}\text{Cr}_{0.05}\) alloy at elevated temperatures. It is observed that the \( \Delta G \) becomes negative at all Co composition when \( T \geq 200 \) K. Therefore, the \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_y\text{Cr}_y\) alloys are stabilized by configurational entropy at finite temperature.

### 3.3. Elastic moduli and mechanical properties

The calculated two cubic shear moduli \( C' \) and \( C_{44} \) of the \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_y\text{Cr}_y\) alloys are shown in figure 4. Severe softening of \( C' \) with the increment of Co concentration was observed. For \( \text{Ni}_3\text{Al} \), the increase of Co concentration decreases \( C' \) gradually to a negative value for \( \text{Co}_3\text{Al} \). Negative \( C' \) suggests that this alloy is mechanically unstable. This is in line with the previous studies \[14, 15, 22\]. Interestingly, alloying small amount (\( \sim 5 \) at %) of Cr into \( \text{Co}_3\text{Al} \) can increase \( C' \) to a positive value, and increment of Cr concentration increase the \( C' \) of \( \text{Co}_3\text{Al} \) alloy gradually. Namely, Cr can improve the mechanical stability of this alloy. For \((\text{Ni}_{1-x}\text{Co}_x)_3\text{Al}_y\text{Cr}_y\) alloys, \( C' \) increases with \( x \) below 10 at.\% of Co, and then decreases gradually at larger concentrations. But Cr has a positive effect on the shear modulus \( C' \), which increases gradually with the increment of Cr concentration. The effect of Co and Cr on elastic moduli can be partly understood from the volume effect (see figure 1). Co increases the volume but Cr tends to decrease volume. Cr and Co occupy different sublattices and the interplay between Co and Cr leads to the observed composition dependence of \( C' \). From the picture of electronic structure, the severe tetragonal lattice softening is mostly owing to the magnetic pressure \[44\], which expands the cell volume and thus leads to a reduction of tetragonal shear modulus. On the other hand, Cr introduces additional covalent
like bonding with nearest neighboring Co/Ni atoms [12], and thus $C'$ increases with Cr concentration at a certain Co/Ni ratio.

A decreasing rate, defined as $\eta(x, y) = \left[ C'_{\text{Ni}_3\text{AlCr}}(y) - C'_{\text{Ni}_{1-x}\text{Co}_x\text{Al}_{1-y}\text{Cr}_y}(x, y) \right] / C'_{\text{Ni}_3\text{AlCr}}(y)$, is used to evaluate the effect of Co and Cr concentration on $C'$. If one set $x = 1.0$, the relative difference of $C'$ between Ni$_3$AlCr and Co$_3$AlCr alloys would be $\eta(1.0, y) = 94\%, 81\%, 68\%, 57\%, 52\%$ for $y = 0.05–0.025$. This result indicating that Cr can suppress the softening effect of Co on $C'$ significantly. In technological applications, Ni-Co based superalloys contain about 40 at.% of Co at A site and 10–20 at.% of Cr at B site in $\gamma'$ phase [8–11, 45–47]. At this circumstance, $\eta(0.4, y) = 12.6\%, 4.4\%$ and 3.7% for $y = 10$ at.%, 15 at. % and 20 at.%. Therefore, one can conclude that the $C'$ of Ni-Co based superalloys are not changed that much even though Co has a strong softening effect on $C'$ of Ni$_3$Al (see figure 4(a) and also [12]) due to the hardening effect of Cr. Since we used the sublattice atomic concentration, only $\sim0.15$ Cr atoms in the cell can overwrite the softening effect of $\sim1.2$ Co atoms, namely Cr has an essential effect on elastic properties of Ni-Co based superalloys.

Except for (NiCo)$_3$Al alloy, the rhombohedral shear modulus $C_{44}$ (see figure 4(b)) of (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys show a maximum at certain Co concentration, and then decrease gradually at larger Co concentrations. The Co concentration corresponding to $C_{44}$ maxima increases with the increment of Cr content. This fact is due to the competition between antiferromagnetic and ferromagnetic order respectively governed by Cr and Co atoms. For practical Ni-Co based superalloys, where Co content is about 0.4–0.6 at A site, the $C_{44}$ of the (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys are larger than those of Ni$_3$AlCr. Therefore, the co-doping of Cr and Co into Ni$_3$Al can improve the elastic properties of this alloy, even though Co has a significant lattice softening effect on Ni$_3$Al [12].

The theoretical measure of brittle versus ductile behavior of (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys are shown in figure 5. Both the Pugh ratio $B/G$ and the Poisson’s ratio $\nu$ increases as a function of Co concentration, but decrease with

![Figure 4](https://example.com/figure4.png)

*Figure 4.* Elastic shear moduli $C'$ (a) and $C_{44}$ (b) as function of Co and Cr concentration.
the increment of Cr content. The B/G is always larger than 1.75 and v is larger than 0.26, indicating that the alloys are ductile in all the composition considered in this study. B/G and v give a similar prediction of the brittle versus ductile behaviors, since these two quantities are closely connected with Pugh condition [41]. The Cauchy pressure \( (C_{12} - C_{44}) \) follows the trend of B/G and v, but a significant deviation is observed for \( C_{12} - C_{44} \) from the prediction of Pugh condition. The Cauchy pressure becomes negative for Cr content \( y > 0.05 \). Negative Cauchy pressure implies angular character in the bonding and thus characterizes covalent crystals while positive Cauchy pressure is typical for metallic crystals [42, 48]. Therefore, Cauchy pressure shown in figure 5(d) implies the covalent like bonding between Cr and Ni/Co, this is in line with the discussions on elastic constants. A large deviation of Cauchy pressure from Pugh condition is closely related to the large elastic anisotropy \( A_{VR} \) which is usually smaller than 0.2 for metallic system, but in current alloys \( A_{VR} \) is always larger than 0.2 and it reaches almost 0.9 for Co\(_3\)Al\(_{0.9}\)Cr\(_{0.1}\). The elastic anisotropy can also be characterized by \( C_{44}/C' \), which is 1 for isotropic crystal and larger than 1 for anisotropic crystals. In the current case, \( C_{44}/C' \sim 60 \) for Co\(_3\)Al\(_{0.9}\)Cr\(_{0.1}\) alloy, which is in line with the prediction of \( A_{VR} \). Such large elastic anisotropy is originated from the very small \( C' \sim 2 \) GPa of Co\(_3\)Al\(_{0.9}\)Cr\(_{0.1}\) alloy. For practical Ni-Co based superalloys containing x \( \sim 0.4 \) of Co at A site and y \( \sim 0.15 \) of Cr at B site, the brittle versus ductile measures are \( B/G \sim 2.1, v \sim 0.3, C_{12} - C_{44} \sim -1.5, A_{VR} \sim 0.27 \) and \( C_{44}/C' \sim 4.9 \), implying that the superalloys are ductile and with moderate elastic anisotropy.

3.4. Electronic density of states

The lattice stability and mechanical property of alloy materials can be understood from the basic electronic structure. The hybridization of atomic orbitals and the density of states at the Fermi level are two main characteristics of bonding in intermetallic compounds [49]. The Projected and Total density of states (PDOS and TDOS) of Ni base, Co base and Ni-Co based alloys are visualized in figure 6. The positive and negative DOSs are denoting the spin up and spin down channels.

As shown in figure 6, Ni, Co and Cr d bands do not change significantly during alloying. Ni has 3 pronounced PDOS peak and Co has 4, they move towards lower or higher energies owing to the band hybridization and charge transfer. When Cr substitutes Al in Ni\(_3\)Al, the Al p band narrowed down and several PDOS peaks of Al disappeared and rearranged into the 2 main PDOS peaks, which implies that the metallic like bonding weakened and directional covalent like bonding become more significant, see in figure 6(c). A small Al PDOS peak at \(-0.03 \) Ry just below Fermi level disappears while a dangling bond like PDOS appears in Ni PDOS close to this energy level. This DOS evolution is closely related to the smaller \( C' \) for Ni\(_3\)AlCr compared to Ni\(_3\)Al.
A narrow p band for Al is observed in figure 6(e) for the (Ni$_{1-x}$Co$_x$)$_3$Al, the highest PDOS peak of Al spin down channel overlap with the lowest d DOS peaks of both Ni and Co spin down channels implying the p-d hybridization. From both figures 6(e) and (f), the main PDOS peaks of spin up subband of Co and Ni overlap, while spin down channels do not show such phenomena. The PDOS fingerprints of four elements are observed in PDOSs of (Ni$_{1-x}$Co$_x$)$_3$Al$_{1-y}$Cr$_y$ alloys. Positive and negative values denote spin up and spin down channels.
Comparing Al $p$ bands in different alloys, it is easy to observe that the Al $p$ band is rather sensitive to the chemical environment, both the band width and DOS peak are very different for different alloy compositions. Due to the free-like electronic states, Al band evolves to fit the chemical bonding in different alloys. Therefore, the flexibility of Al $p$ states and synergistic alloying effect due to $d$-$d$ hybridization of 3$d$ elements are the main physics behind the stabilization and strengthening of $\gamma'$- ($Ni_{1-x}Co_x$)$_3Al_1Cr_y$ alloys.

4. Conclusion

Ab initio alloy theory as formulated in the EMTO package was employed to study the phase stability and mechanical properties of $\gamma'$- ($Ni_{1-x}Co_x$)$_3Al_1Cr_y$ phase of Ni-Co based superalloys. The mixing enthalpies calculated at 0 K for all the alloy composition considered in this present work are small positive value, indicating that the alloys are thermodynamically unstable against phase separation into Ni$_2$AlCr and Co$_3$AlCr alloys. Addition of 6.25 at $\%$ of Cr into (NiCo)$_3$Al alloy can decrease the positive mixing enthalpy by 34, hence Cr has significant thermodynamical stabilizing effect on $\gamma'$ phase. The configurational entropy, which arises from the random occupation of Ni/Co at A site, can stabilize further these alloys at a temperature higher than 200 K. The continuous increase of alloying Co concentration leads to a strong tetragonal shear softening for (Ni$_{1-x}$Co$_x$)$_3Al_1Cr_y$, which is closely connected with the lower strength of Ni-Co based superalloys compared with the well-studied Ni based superalloys [7, 8]. But increasing Cr additions could increase $C'$ of the alloys and thus offset the softening effect of Co by a certain extent. For practical Ni-Co based superalloys containing $\sim$ 40 at $\%$ of Ni/Co and $\sim$ 15 at $\%$ of Cr, $C'$ of the alloys are just decreased by $\sim$ 3$\%$–5$\%$ and $C_{44}$ are increased by $\sim$ 3$\%$ compared with those of Ni$_3$Al. The electronic density of states analysis demonstrates that the flexibility of Al $p$ band and synergistic alloying effect of Co and Cr are the physics behind the stabilization of the $\gamma'$ phase of Ni-Co based superalloy by Cr alloying.

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