Effect of interface orientation on the adhesion strength and fracture toughness of Ni/CrN interfaces by first-principles study

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Abstract

The brittleness and relatively poor adhesion properties of CrN materials have been extensively addressed by developing Ni/CrN composites with a separate Ni phase. However, conditions at the Ni/CrN interfaces, which are the key features leading to the enhanced toughness, remain poorly understood. The present work addresses this issue by investigating the effect of interface orientation on adhesion strength and fracture toughness of Ni/CrN interfaces using first-principles calculations. To this end, we build seven Ni/CrN interface models, including Ni(100)/CrN(100), Ni(110)/CrN(110), Ni(110)/CrN(111), and Ni(111)/CrN(111), with different interface orientation and stacking orders. The results demonstrate that the interface orientation plays a predominant role in determining the mechanical properties of the Ni/CrN interfaces, while the effect of stacking order can be neglected. The Ni(111)/CrN(111) interface is demonstrated to provide the greatest adhesion strength, interfacial stability, and fracture toughness among the Ni/CrN interfaces considered, and is therefore the preferred orientation for Ni/CrN composite applications.

1. Introduction

Chromium nitride (CrN) has been widely used as a protective layer material owing to its high hardness and good resistance to wear and corrosion. However, the brittleness and relatively poor adhesion of CrN materials greatly restrict their use in industrial applications. Studies have demonstrated that the incorporation of ductile metallic phases within CrN materials is a promising approach for enhancing their mechanical properties [1–3]. To this end, Ni has been most commonly employed as a separate phase in transition metal nitrides (TMNs) [4–7]. Therefore, the development of Ni/CrN composites has received considerable attention [8–10].

The incorporation of Ni as a separate phase in TMNs dictates that the strength and failure mechanisms of the interface between the two different phases represent important factors when studying the mechanical properties of these composites. In this regard, studies have demonstrated that the enhanced toughness of multilayer TMN composites is facilitated via various phenomena occurring at the interface, such as crack deflection, stress relaxation, and energy dissipation [11, 12]. For example, Daniel et al. [3] experimentally demonstrated that the fracture resistance of TiN/SiO2 and CrN/Cr multilayer coatings was enhanced by the deflection of cracks propagating at the interfaces. Sui et al. [13] experimentally studied the effects of interfacial properties on the increased fracture toughness and adhesion strength of TiAlN/CrN multilayer coatings. Moreover, the crystal orientations at the interfaces of the composites have been demonstrated to play a key role in their mechanical properties. For example, Wiecinski et al. [14] experimentally demonstrated that the optimum crystal orientation at the interfaces of Ti/TiN multilayer coatings resulted in a decreased interfacial energy and a corresponding improvement in the mechanical properties of the coatings. A similar effect was observed for Cr/CrN multilayer coatings [15]. Therefore, obtaining detailed information regarding the interfacial characteristics of Ni/CrN...
materials with different interface orientations is imperative for developing advanced Ni/CrN composites with optimal mechanical properties.

According to the above discussion, experimental methods have demonstrated the important effect of interface orientation on the enhanced toughness of multiphase materials empirically. However, the results of experimental methods lack important details regarding the molecular mechanisms leading to this phenomenon, and the results therefore tend to be limited. This can be addressed by employing first-principles calculations based on density functional theory (DFT) [16–19]. Here, DFT calculations have been demonstrated to be a powerful method for revealing detailed information regarding atomic and electronic structures at the interfaces between two phases, and thereby facilitating predictions regarding the stability, adhesion strength, and fracture toughness of interfaces. Previous theoretical studies extensively investigated the interfacial properties of cermet composites which were influenced by atomic termination, stacking order, or interfacial doped element [20–28]. For example, Zhang et al [23] investigated atomic structure and electronic properties of Ag(111)/TiC(111) interfaces with two atomic terminations and eight stacking sites. Li et al [21] studied the interfacial bonding mechanism of Al(111)/Al2MgC2(0001) interface models with five different terminations of Al2MgC2(0001) and various four stacking sites of Al(111). Guo et al [20] investigated the effect of active Ti element on the bonding characteristic of the Ag(111)/α-Al2O3(0001) interface. However, despite this large body of interfacial research based on first-principles calculations, the interfacial properties of the cermet composites influenced by interface orientation were relatively unexplored [16]. As a result, the effect of interface orientation on the adhesion strength and fracture toughness at the interfaces of multiphase Ni/CrN materials remains poorly understood.

The present work addresses this issue by systematically investigating the effect of interface orientation on the adhesion strength and fracture toughness of Ni/CrN interfaces using first-principles calculations based on DFT. To this end, we construct seven Ni/CrN interface models, including Ni(100)/CrN(100), Ni(110)/CrN(110), Ni(110)/CrN(111), and Ni(111)/CrN(111), with different interface orientations, stacking orders, and interface misfit values less than 5%. We compare the mechanical properties of the interface models according to the calculated values of the work of adhesion, interfacial energy, and fracture toughness. However, the mechanical properties of the interfaces are particularly related to the nature of atomic bonding at the interfaces, which in turn depends on their electronic structures and bonding characteristics. Therefore, we also investigate the electronic properties of the Ni/CrN interface models. The results demonstrate that the interface orientation has a significant effect on the mechanical properties of Ni/CrN interfaces, while the effect of stacking order is negligible. The Ni(111)/CrNi(111) interface is demonstrated to provide the greatest adhesion strength, interfacial stability, and fracture toughness among the Ni/CrN interfaces considered. In addition, the electronic properties of the Ni(111)/CrN(111) interface demonstrate that the high interfacial adhesion strength and fracture toughness of that interface are determined by its large number of N-Ni bonds with ionic and covalent features.

2. Methodology

First-principles calculations were performed using the Cambridge Serial Total Energy Package (CASTEP), which employs the plane-wave ultrasoft pseudopotential method based on DFT. The exchange-correlation energy was obtained using the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional. The GGA-PBE functional may underestimate the band gap of some complex materials [29, 30], however, it always yields excellent results for lattice constant and mechanical properties of transition metal and TMNs [26, 31–34]. Moreover, many studies have demonstrated that the GGA-PBE functional is reliable for the DFT calculations on cermet composite systems [20, 21, 23, 35]. The ground state was determined via electronic minimization conducted by solving the Kohn–Sham equation under a self-consistent field (SCF). Meanwhile, the atomic structure was relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The electronic configurations considered were Ni 3d84s2, Cr 3s23p63d44s1, and N 2s22p2. A plane-wave cutoff energy of 400 eV was used in all calculations. The convergence tolerances were set as 5.0 × 10−5 eV/atom for the energy, 0.1 eV/Å for the maximum force, and 0.005 Å for the maximum displacement.

2.1. Bulk properties

Both CrN and Ni have face centered cubic (FCC) structures with Fm 3 m space groups. Specifically, the stable configuration of CrN at room temperature is a paramagnetic (PM) NaCl structure [36–38]. The magnetic properties of CrN are induced by the asymmetric distribution of the Cr 3d spin-up and spin-down states in this compound [32, 39]. Therefore, the calculation of CrN should be conducted using spin-polarization. The k-point mesh of the Monkhorst-Pack grid was 12 × 12 × 12. The values of lattice constants (a), bulk modulus (B), elastic constants (Cij), and elastic compliances (Sij) calculated for Ni and CrN are listed in table 1 along with corresponding data obtained from other first-principles studies. The good agreement between the past and
Table 1. Calculated lattice constant (\(a\)), bulk modulus (\(B\)), elastic constants (\(C_{ij}\)), and elastic compliances (\(S_{ij}\)) of Ni and CrN.

| Phase | Data source | \(a\) (Å) | \(B\) (GPa) | \(C_{11}\) (GPa) | \(C_{12}\) (GPa) | \(C_{44}\) (GPa) | \(S_{11}\) (GPa\(^{-1}\)) | \(S_{12}\) (GPa\(^{-1}\)) | \(S_{44}\) (GPa\(^{-1}\)) |
|-------|-------------|------------|-------------|-----------------|-----------------|-----------------|-----------------------|-----------------------|-----------------------|
| Ni    | This work   | 3.548      | 173.79      | 227.35          | 147.02          | 120.08          | 0.00894               | 0.00351               | 0.00833               |
|       | [40]        | 3.511      | 200.59      | 260.15          | 170.81          | 118.59          | —                     | —                     | —                     |
|       | [41]        | 3.522      | 198         | 281             | 157             | 131             | —                     | —                     | —                     |
| CrN   | This work   | 4.176      | 230.45      | 389.14          | 151.10          | 106.84          | 0.00328               | 0.00092               | 0.00936               |
|       | [38]        | 4.164      | 209         | 386             | 120             | 111             | —                     | —                     | —                     |
|       | [42]        | 4.173      | 192         | 369             | 125             | 114             | —                     | —                     | —                     |

The lattice constant of CrN (4.176 Å) is much greater than that of Ni (3.548 Å). Therefore, a supercell approach with periodic boundary conditions was employed to obtain a perfect lattice match between Ni and CrN. As illustrated in figure 1, the interface models were built based on four types of interface orientations, including Ni(100)/CrN(100), Ni(110)/CrN(110), Ni(110)/CrN(111), and Ni(111)/CrN(111). All of the crystal orientations at the interfaces are the most common growth orientations of Ni and CrN materials according to standard XRD reflections (PDF#04-0850 of Ni, PDF#11-0065 of CrN), and these orientations are often detected in the experiments [5, 6, 15, 43].

2.2. Interface models

As shown in figure 1, the interface models were built based on four types of interface orientations, including OT and HCP, where OT indicates that the interfacial N atoms sit directly above the interfacial Ni atoms, HCP indicates that the N atoms sit above the Ni atoms on the second layer. Therefore, seven Ni/CrN interface models in total were constructed. As shown in figures 1(i)–(k), we intentionally terminated the CrN(111) surfaces with N atoms rather than Cr atoms to facilitate covalent or ionic bonding between Ni and N atoms at the interface rather than metallic bonds between Ni and Cr atoms. Our rationality for doing so is that this will increase the adhesion strength and fracture toughness of the interfaces because covalent or ionic bonds appear to be much stronger than metallic bonds [27, 31]. The interface models were composed of Ni and CrN slabs with a sufficient number of layers to ensure a bulk-like structure in the interior, and vacuum spaces of 15 Å thickness were applied in the z direction above the Ni layer and below the CrN layer to avoid interactions between the periodic cells in that direction.

Interfacial mismatch rates \(\delta_U\) and \(\delta_V\) can be calculated according to the U and V directions shown in figures 1(e)–(h) and (l)–(n) as follows:

\[
\delta_U = \frac{|d_{U, \text{CrN}} - d_{U, \text{Ni}}|}{d_{U, \text{CrN}}} \times 100\%,
\]

\[
\delta_V = \frac{|d_{V, \text{CrN}} - d_{V, \text{Ni}}|}{d_{V, \text{CrN}}} \times 100\%,
\]

where \(d_{U, \text{CrN}}\) and \(d_{U, \text{Ni}}\) are the lengths of CrN and Ni surfaces along U, respectively, and \(d_{V, \text{CrN}}\) and \(d_{V, \text{Ni}}\) are the lengths of CrN and Ni surfaces along V, respectively. In addition, we calculate an angle difference \(d\theta\) (°) as follows:

\[
d\theta = |\theta_{\text{CrN}} - \theta_{\text{Ni}}|,
\]

where \(\theta_{\text{CrN}}\) is the angle between \(U_{\text{CrN}}\) and \(V_{\text{CrN}}\), and \(\theta_{\text{Ni}}\) is the angle between \(U_{\text{Ni}}\) and \(V_{\text{Ni}}\). The mismatches between the Ni and CrN surfaces obtained for the interface models are listed in table 2. It can be seen that the values of \(\delta_U\) and \(\delta_V\) are both less than 5%, and the values of \(d\theta\) are all less than 2°. Therefore, the interface models constructed in this work represent valid structures.

2.3. Surface convergence testing

We conducted convergence tests based on surface energy to determine the appropriate numbers of layers to apply in the interface models to ensure that they were sufficiently thick to exhibit bulk-like structures in the interiors. The surface energy \(\gamma_s\) for the non-polar Ni(100), Ni(110), Ni(111), CrN(100), and CrN(110) surfaces can be calculated as follows [31]:

\[
\gamma_s = \frac{(E_{\text{slab}} - nE_{\text{bulk}})}{2A},
\]

where \(E_{\text{slab}}\) is the total energy of the material slab, \(n\) is the total number of atoms (or chemical units) in the slab, \(E_{\text{bulk}}\) is the total energy per atom (or chemical unit) in the bulk material, \(A\) is the surface area, and the factor 2 represents two identical surfaces of the slab. However, this issue is more complicated for the N-terminated CrN (111) surfaces. Here, CrN(111) slab models with an even number of layers are stoichiometric, and the surface...
Table 2. Mismatch rates ($\delta_U$ and $\delta_V$) respectively calculated according to equations (1) and (2) and the angle difference ($\theta$) between Ni and CrN surfaces calculated according to equation (3) for different Ni/CrN interface models. Here, the $\delta_U$, $\delta_V$, and $\theta$ values obtained for interface models with different stacking orders are equivalent.

| Interface model | Ni(100)/CrN(100) | Ni(110)/CrN(110) | Ni(100)/CrN(111) | Ni(111)/CrN(111) |
|-----------------|------------------|------------------|------------------|------------------|
| Matching plane  | Ni(100) | CrN(100) | Ni(110) | CrN(110) | Ni(110) | CrN(111) | Ni(111) | CrN(111) |
| $d_U$ (Å)       | 5.610  | 5.905  | 7.096  | 7.232  | 7.526  | 7.812  | 5.017  | 5.114  |
| $d_V$ (Å)       | 5.610  | 5.905  | 5.017  | 5.114  | 5.017  | 5.114  | 60     | 60     |
| $\theta$ (°)    | 90     | 90     | 90     | 90     | 70.529 | 70.893 | 60     | 60     |
| $\delta_U$ (%)  | 4.995  | 1.886  | 3.661  | 1.897  | 1.897  | 1.897  | 1.897  | 1.897  |
| $\delta_V$ (%)  | 4.995  | 1.897  | 1.897  | 1.897  | 1.897  | 1.897  | 1.897  | 1.897  |
| $\theta$ (°)    | 0      | 0      | 0.364  | 0      | 0      | 0      | 0      | 0      |
energy can be calculated using formula (4). However, the CrN(111) slab models with odd numbers of layers are non-stoichiometric. Therefore, we calculate the surface energy \( \gamma \) of these non-stoichiometric models as follows [44, 45]:

\[
\gamma = \frac{E_{\text{slab}}^N + E_{\text{slab}}^{CrN} - nE_{\text{bulk}}}{(4A)}
\]

(5)

where \( E_{\text{slab}}^N \) and \( E_{\text{slab}}^{CrN} \) are the total energies of the CrN(111) slabs with complementary N- and Cr- terminations, and the factor 4 comes from the fact that we create four slab surfaces. In fact, the surface energy calculated for the CrN(111) slab model is exactly the average value of slabs with the two terminations, namely, \( \gamma_{\text{CrN(111)}}(\gamma_{\text{CrN(111)-N}} + \gamma_{\text{CrN(111)-Cr}})/2 \).

The results of convergence testing demonstrate that the surface energies of the Ni and CrN slab models converge to stable values for slabs composed of 7 layers. Therefore, all interface models employed seven Ni layers and seven CrN layers. The surface energies obtained for the various 7-layer Ni and CrN slab models are listed in table 3. It is worth noting that the Ni(111) plane has the lowest surface energy of all Ni slab models considered, while the CrN(100) plane has the lowest surface energy of all CrN slab models considered. In fact, these results are consistent with corresponding experimental results [46]. In addition, the surface energies of these slab models are in good agreement with similarly calculated surface energy data in the literature, which are also listed in table 3. These results further verify the correctness of the calculation parameters employed in the present work. Finally, we note that the sum of the surface energies obtained for the combined Ni and CrN slab models follows the order: Ni(110)/CrN(111) (4.31 J m\(^{-2}\)) > Ni(110)/CrN(110) (4.07 J m\(^{-2}\)) > Ni(111)/CrN(111) (3.98 J m\(^{-2}\)) > Ni(100)/CrN(100) (3.3 J m\(^{-2}\)).

3. Results and discussion

3.1. Work of adhesion

The adhesion strength of the interface models was assessed according to the work of adhesion \( W_{\text{ad}} \), which can be calculated as follows [22]:

\[
W_{\text{ad}} = \frac{E_{\text{slab,Ni}} + E_{\text{slab,CrN}} - E_{\text{Ni/CrN}}}{A},
\]

(6)

where \( E_{\text{slab,Ni}} \) and \( E_{\text{slab,CrN}} \) are the total energies of the fully relaxed surface slabs, \( E_{\text{Ni/CrN}} \) is the total energy of the interface model, and \( A \) is the area of the interface. The k-point meshes employed for the calculations involving the Ni(100)/CrN(100), Ni(110)/CrN(110), Ni(111)/CrN(111), and Ni(111)-CrN(111) interface models were 6 \times 6 \times 1, 5 \times 7 \times 1, 5 \times 8 \times 1, and 11 \times 11 \times 1, respectively. The values of \( W_{\text{ad}} \) can be calculated by two different methods. The first method is the universal binding energy relation (UBER) method [26, 31]. The values of \( W_{\text{ad}} \) obtained by this method versus the interfacial distance \( d_0 \) are shown in figure 2. The peaks of the curves represent the optimal values of \( d_0 \) and \( W_{\text{ad}} \). The second method adopts the optimal structures obtained from the UBER method, and relaxes the interface models fully. Four atomic layers at the top of the Ni slabs and three atomic layers at the bottom of the CrN slabs were fixed in their bulk positions, respectively. Then, the optimal values of \( d_0 \) and \( W_{\text{ad}} \) are obtained from the relaxed models. The values of \( d_0 \) and \( W_{\text{ad}} \) obtained for the different interface models using this second method are listed in table 4. We note from figure 2 and table 4 that the optimal \( W_{\text{ad}} \) values obtained for the Ni(110)/CrN(111) and Ni(111)/CrN(111) interface models are much greater than those obtained for the Ni(100)/CrN(100) and Ni(110)/CrN(110) interface models. This may be because the interfaces between the Ni slabs and the N-terminated CrN(111) slabs generate more polar covalent bonds with Ni, which, as discussed above, appear to be stronger than metallic bonds. In addition, we note that the Ni(111)/CrN(111) interface has the highest value of \( W_{\text{ad}} \) (3.54 J m\(^{-2}\)) among all the interfaces considered. Finally, the above results demonstrate that the interface orientation plays a predominant role in determining the value of \( W_{\text{ad}} \) obtained at Ni/CrN interfaces, while the stacking orders of the Ni or CrN surfaces have a relatively small influence on these values.

### Table 3. Calculated surface energies of Ni(100), Ni(110), Ni(111), CrN(100), CrN(110), and CrN(111) surfaces. The corresponding calculated data available in the literature are also included for comparison.

|                  | Surface energy (J m\(^{-2}\)) | This work | [47] | [48] | [49] |
|------------------|-------------------------------|----------|------|------|------|
|                  | Ni(100)                       | Ni(110)  | Ni(111)| CrN(100)| CrN(110)| CrN(111)|
| This work        | 2.27                          | 2.33     | 2.00  | 1.03  | 1.74  | 1.98   |
| [47]             | 2.24                          | 2.18     | 1.92  | ---   | ---   | ---    |
| [48]             | 2.426                         | 2.368    | 2.011 | ---   | ---   | ---    |
| [49]             | ---                           | ---      | 1.029 | 1.859 | ---   | ---    |
3.2. Interfacial energy

Interfacial energy $E_{\text{int}}$ is used to evaluate the thermodynamic stability of the interface. In general, the stability of the interface increases with decreasing $E_{\text{int}}$. Here, $E_{\text{int}}$ is calculated as follows:

$$E_{\text{int}} = \gamma_{\text{Ni}} + \gamma_{\text{CrN}} - W_{\text{ad}},$$

where $\gamma_{\text{Ni}}$ and $\gamma_{\text{CrN}}$ are the surface energies of the Ni and CrN surfaces, respectively, which are calculated according to equations (4) or (5) depending on the nature of the CrN slab model.

The calculated results are listed in Table 4. Again, we note that the interface orientation plays a predominant role in determining the value of $E_{\text{int}}$ obtained at Ni/CrN interfaces, while the stacking orders of the Ni or CrN surfaces have a relatively small influence on these values. The magnitude of $E_{\text{int}}$ follows the order: Ni(100)/CrN(100) > Ni(110)/CrN(100) > Ni(110)/CrN(111) > Ni(111)/CrN(111). Accordingly, the relatively large sum of $\gamma_{\text{Ni}} + \gamma_{\text{CrN}}$ obtained for the Ni(111)/CrN(111) interface model was compensated by its very large value of $W_{\text{ad}}$ to provide the lowest value of $E_{\text{int}}$ (0.44 J m$^{-2}$), indicating that this interface is more thermodynamically stable than the other interfaces.

3.3. Interfacial fracture toughness

The fracture toughness of an interface represents its strength to resist the development of a fracture along the interface. According to Griffith crack theory, the interfacial fracture toughness $K_{\text{IC}}$ along a specific direction [hkl] can be calculated as follows:

$$K_{\text{IC}} = \sqrt{\frac{4W_{\text{ad}}}{d_{\text{hkl}}}} E_{\text{hkl}},$$

where $E_{\text{hkl}}$ is the Young's modulus of bulk Ni or CrN along the [hkl] direction. For the cubic Ni and CrN crystals, $E_{\text{hkl}}$ can be calculated in the [100], [110], and [111] directions as follows:

$$E_{100} = \frac{1}{S_{11}},$$
The values of $E_{hkl}$ obtained for bulk Ni along the $[100]$, $[110]$, and $[111]$ directions are 111.88, 208.51, and 292.80 GPa, respectively, while those obtained for bulk CrN along the $[100]$, $[110]$, and $[111]$ directions are 304.62, 283.91, and 277.62 GPa, respectively.

The values of $K_{hklIC}$ obtained for the Ni/CrN interface models are listed in Table 4. Here, the values are given as a range because they include two fracture toughness values indicative of fracture along the Ni surface and along the CrN surface. We again note that the interface orientation plays a predominant role in determining the fracture toughness of the Ni/CrN interface models, while the stacking orders of the Ni or CrN surfaces have a relatively small influence on these values. The magnitudes of $K_{hklIC}$ obtained for the Ni/CrN interface models follow the order: Ni$(111)$/CrN$(111)$ > Ni$(110)$/CrN$(111)$ > Ni$(110)$/CrN$(110)$ > Ni$(111)$/CrN$(110)$.

Accordingly, the relatively high values of $E_{111}$ obtained for bulk Ni and CrN combined with the very large value of $W_{ad}$ obtained for the Ni$(111)$/CrN$(111)$ model ensured that the Ni$(111)$/CrN$(111)$ interface model obtained the largest value of $K_{hklIC}$ for all models considered.

### 3.4. Electronic structure

The electronic structure and bonding characteristics of the Ni/CrN interface models were evaluated according to the charge density, charge density difference, Mulliken population analysis, and partial density of states (PDOS).

The charge density and charge density difference plots of the Ni$(100)$/CrN$(100)$-OT, Ni$(110)$/CrN$(110)$-OT, and Ni$(111)$/CrN$(111)$ interface models are presented in Figures 3(a), (d), (b), (e), and (c), (f), respectively. Here, the dashed lines represent the positions of the interfaces. We note that the interface adhesion of Ni/CrN interfaces depends mainly on bonding between the N and Ni atoms. In addition, charge accumulation occurs between the interfacial N and Ni atoms in Figures 3(a)–(c), indicating that N-Ni covalent bonds are formed at the interfaces. Furthermore, as shown in Figures 3(d)–(f), electron depletion occurs mainly around the Cr atoms and Ni atoms.
interfacial Ni atoms, and electron accumulation occurs mainly in the vicinity of N atoms. This indicates that electrons are transferred from Ni to N atoms, and N-Ni ionic bonds are formed at the interfaces. Finally, the density of the N-Ni bonds decreases in the order of Ni\(111\)/CrN\(111\)-OT > Ni\(110\)/CrN\(110\)-OT > Ni\(100\)/CrN\(100\)-OT, which follows the trends observed in Table 4 for the values of \(W_{ad}\) and \(K_{hklIC}\). Therefore, these results illustrate the bonding mechanism responsible for the observed trends in \(W_{ad}\) and \(K_{hklIC}\) obtained for the seven Ni/CrN interfaces.

Mulliken population analysis provides a semi-quantitative evaluation of charge transfer and ionicity. Therefore, Mulliken population analysis was applied to the interfacial N, Cr, and Ni atoms of the Ni\(110\)/CrN\(110\)-OT and Ni\(111\)/CrN\(111\) interface models given in Figures 4(a) and (b), respectively, and the results are listed in Table 5. We note that the charges of the N and Ni atoms in the interfacial N-Ni bonds are in the ranges of \(-0.49\) e to \(-0.57\) e and \(0.03\) to \(0.20\) e, respectively, which indicates that electrons transfer from Ni atoms to N atoms, and an ionic bond is formed. In addition, we also conducted a semi-quantitative bond population analysis to shed more light on the relative strength between ionic and covalent bonding for a given pair of atoms. Here, a high bond population value indicates a covalent bond, while a low value indicates an ionic interaction. The relatively high bond population values \((0.23\text{ to } 0.45)\) of the N-Ni bonds for the Ni\(110\)/CrN\(110\)-OT and Ni\(111\)/CrN\(111\) interface models given in Figures 4(a) and (b), respectively, and the atoms are also labeled.

**Table 5.** Mulliken population analysis of the interfacial N, Cr, and Ni atoms in the Ni\(110\)/CrN\(110\)-OT and Ni\(111\)/CrN\(111\) interface models given in figures 4(a) and (b), respectively.

| Interface model               | Atom  | s   | p   | d   | Total | Charge (e) | Bond   | Population | Length (Å) |
|------------------------------|-------|-----|-----|-----|-------|------------|--------|------------|------------|
| Ni\(110\)/CrN\(110\)-OT     | N8    | 1.68| 3.84| —   | 5.52  | -0.52      | N8-Ni2 | 0.41       | 1.78       |
|                              | N7    | 1.68| 3.85| —   | 5.53  | -0.53      | N7-N22 | 0.24       | 2.01       |
|                              | N21   | 1.68| 3.85| —   | 5.53  | -0.53      | N21-N22| 0.24       | 2.01       |
|                              | Ni2   | 0.49| 0.66| 8.65| 9.80  | 0.20       | Cr8-Ni9| 0.14       | 2.33       |
|                              | Ni22  | 0.41| 0.72| 8.68| 9.81  | 0.19       | Cr7-Ni15| 0.24       | 2.48       |
|                              | Ni9   | 0.56| 0.67| 8.70| 9.93  | 0.07       | Cr21-Ni15| 0.24      | 2.48       |
|                              | Ni15  | 0.55| 0.78| 8.69| 10.02 | -0.02      | —       | —          | —          |
|                              | Cr8   | 2.33| 6.55| 4.89| 13.77 | 0.23       | —       | —          | —          |
|                              | Cr7   | 2.30| 6.53| 4.88| 13.72 | 0.28       | —       | —          | —          |
|                              | Cr21  | 2.30| 6.53| 4.88| 13.72 | 0.28       | —       | —          | —          |
| Ni\(111\)/CrN\(111\)        | N8    | 1.68| 3.81| —   | 5.49  | -0.49      | N8-Ni2 | 0.45       | 1.83       |
|                              | N7    | 1.66| 3.91| —   | 5.57  | -0.57      | N7-N8  | 0.24       | 1.96       |
|                              | N12   | 1.68| 3.89| —   | 5.57  | -0.57      | N7-N15 | 0.24       | 1.96       |
|                              | Ni2   | 0.50| 0.81| 8.66| 9.97  | 0.03       | N7-N22 | 0.24       | 1.97       |
|                              | Ni8   | 0.45| 0.72| 8.67| 9.83  | 0.17       | N12-N22| 0.25       | 2.05       |
|                              | Ni15  | 0.45| 0.72| 8.67| 9.83  | 0.17       | N12-N15| 0.25       | 2.05       |
|                              | Ni22  | 0.45| 0.72| 8.67| 9.83  | 0.17       | N12-N18| 0.23       | 2.07       |

Figure 4. Atomic configurations of fully-relaxed (a) Ni\(110\)/CrN\(110\)-OT and (b) Ni\(111\)/CrN\(111\) interface models. Interfacial bonds are denoted with dashed lines, and the atoms are also labeled.
Ni(111)/CrN(111) interface models in table 5 indicate that the N-Ni bonds exhibit some degree of covalence. Moreover, the bond population obtained for the N-Ni bonds in the Ni(111)/CrN(111) interface model is greater than that obtained for the Ni(110)/CrN(110)-OT interface model. Furthermore, more N-Ni bonds are formed in the Ni(111)/CrN(111) interface model than those formed in the Ni(110)/CrN(110)-OT interface model. Therefore, the N-Ni bonds are stronger in the Ni(111)/CrN(111) interface. This tendency is also consistent with the observed trends in the $W_{ad}$ results, where the Ni(111)/CrN(111) interface model has a larger value of $W_{ad}$ than the Ni(110)/CrN(110)-OT interface model.

According to the preceding discussion, the Ni(111)/CrN(111) interface model provided the strongest adhesion, largest thermodynamic stability, and largest interfacial fracture toughness among the seven interface models considered. Therefore, we evaluated the nature of bonding interactions in the Ni(111)/CrN(111) interface further by calculating the PDOS for the selected N, Cr, and Ni atoms in the different layers (as labeled in figure 4(b)) of the Ni(111)/CrN(111) interface model, which are presented in figure 5, where the Fermi level is marked by a dashed line at an energy of zero. We note that states are observed at the Fermi level for all atomic layers, implying that both Ni and CrN have a metallic nature. In addition, the electron density values of the Ni-3d orbital for Ni4, Ni16, and Ni2 atoms at the Fermi level are 2.8, 2.8, and 1.6 eV$^{-1}$, respectively. The large decrease in the electron density of the Ni-3d state for the Ni2 atom at the Fermi level indicates that electrons in the Ni-3d orbital of the Ni2 atom take part in the covalent bonding between Ni2 and N8 atoms or electron transfer from Ni2 to N8 atoms. Furthermore, a comparison of the PDOS obtained for the Ni2 atom with those of the Ni4 and Ni16 atoms indicates that the d orbital in the PDOS of the Ni2 atom shifts toward more negative energy levels. Meanwhile, the p orbital in the PDOS of the N8 atom shifts toward more positive energy levels compared to that orbital in the PDOS of the N2 atom. These results indicate that the 3d orbital of the Ni2 atom interacts and hybridizes with the 2p orbital of the N8 atom at the energy of $-3.9$ eV, as shown by the arrows in figure 5. Therefore, we can conclude that a covalent bond is formed between Ni2 and N8 atoms in the Ni(111)/CrN(111) interface model. Finally, the PDOS obtained for the Ni2 atom is lower in height compared to those obtained for the Ni4 and Ni16 atoms, indicating that electrons transfer from Ni2 to N8 atoms. The above analysis demonstrates that the high interfacial adhesion strength and fracture toughness of the Ni(111)/CrN(111) interface model are determined by its large number of N-Ni bonds with ionic and covalent features.
4. Conclusions

Conditions at Ni/CrN interfaces, which are the key features leading to the enhanced toughness of Ni/CrN composites, remain poorly understood. In this regard, the condition of crystal orientation at the interface is a critical factor that should be considered. Therefore, the present work systematically investigated the effect of interface orientation on the adhesion strength and fracture toughness of Ni/CrN interfaces using first-principles calculations based on DFT. We constructed seven Ni/CrN interface models in total by considering both interface orientations and stacking orders. The work of adhesion, interfacial energy, fracture toughness, and electronic properties of the seven Ni/CrN interfaces were evaluated and compared. The results demonstrated that the interface orientation plays a predominant role in determining the mechanical properties of the Ni/CrN interfaces, while the effect of the stacking order is negligible. In addition, the Ni(111)/CrN(111) interface model was demonstrated to provide the greatest adhesion strength, thermodynamic stability, and fracture toughness of all models considered. Accordingly, the development of Ni(111)/CrN(111) interfaces are preferred in actual Ni/CrN coating applications. Furthermore, the electronic properties of the Ni(111)/CrN(111) interface demonstrate that the high interfacial adhesion strength and fracture toughness of this interface are determined by its large number of N-Ni bonds with ionic and covalent features. Accordingly, we can conclude that the present study provides a practical perspective for tailoring the interfaces in Ni/CrN materials to obtain improved mechanical properties.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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