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Investigation of the Adhesion Strength, Fracture Toughness, and Stability of M/Cr₂N and M/V₂N (M = Ti, Ru, Ni, Pd, Al, Ag, and Cu) Interfaces Based on First-Principles Calculations

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Abstract: Obtaining detailed information regarding the interfacial characteristics of metal/hexagonal-TMN composites is imperative for developing these materials with optimal mechanical properties. To this end, we systematically investigate the work of adhesion, fracture toughness, and interfacial stability of M/Cr₂N and M/V₂N interfaces using first-principles calculations. The orientation (0001) of hexagonal phases and (111) of fcc phases are selected as the interface orientations. Accordingly, we construct M/Cr₂N interface models by considering 1N, 2N, and Cr terminations of Cr₂N(0001), as well as two stacking sequences (top and hollow sites) for the 1N- and 2N-terminated interface models, respectively. The M/V₂N interface models are constructed in the same way. The V-terminated Ni/V₂N interface is demonstrated to provide a good combination of the work of adhesion, fracture toughness, and interfacial stability. Therefore, the Ni/V₂N interface model can be regarded as the preferred configuration among the metal/hexagonal-TMN interface models considered. The present results offer a practical perspective for tailoring the interfaces in metal/hexagonal-TMN composite materials to obtain improved mechanical properties.

Keywords: adhesion strength; fracture toughness; hexagonal Cr₂N and V₂N; metals; interface; first-principles calculation

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1. Introduction

Metal/transition metal nitride (TMN) composite materials can have good mechanical and tribological properties, because they combine the ductility and hardness provided by soft metal and hard ceramic, respectively [1–3]. However, the strength and failure mechanisms of the interface between the two different phases also represent important factors when studying the mechanical properties of these composites. In this regard, studies have demonstrated that the enhanced toughness of these TMN composites is facilitated via various phenomena occurring at the interface, such as crack deflection, stress relaxation, and energy dissipation [4–8]. Therefore, obtaining detailed information regarding the interfacial characteristics is imperative for developing advanced metal/TMN composites with optimal mechanical properties.

TMNs that crystallize in hexagonal structures, such as Cr₂N and V₂N, which constitute a remarkable class of hard coating materials, have a wide range of potential scientific and industrial uses as protective materials [9–11]. Accordingly, metal/hexagonal-TMN coating composites have attracted considerable interest in recent decades [12–14]. Guan et al. [12] experimentally demonstrated that Cr/Cr₂N nano-multilayer coatings exhibited superior corrosion resistance and high load-bearing capacity. Li et al. [13] experimentally demonstrated that Cu/Cr₂N multilayered coatings showed a combination of high hardness, good wear and corrosion resistances. Bilek et al. [14] experimentally demonstrated that

Cr₂N-Ag nanocomposite thin films deposited on tool steel can have good tribological performances. However, the results of experimental methods lack important details regarding the interfacial molecular mechanisms leading to the phenomenon, and the results therefore tend to be limited.

First-principles calculations based on density functional theory (DFT) can provide a deep insight into the interfaces of composite systems [15–21]. Here, DFT calculation has been demonstrated to be a powerful method for revealing detailed information regarding atomic and electronic structures at the interfaces between two phases, thereby facilitating predictions regarding the stability, adhesion strength, and fracture toughness of interfaces [22–24]. Accordingly, first-principles calculation based on DFT has developed to become one of the most frequently used theoretical methods for revealing the interfacial properties of metal/ceramic composites. Its novelty is that it provides a quantitative evolution of the levels of interfacial properties for composite systems. Moreover, the theoretical results provide a strong reference for the proceeding of related experimental work. For example, Zhao et al. [15] demonstrated that the cohesion strength and fracture toughness of the Mo/TiC interface model were significantly affected by interface orientations, which could help explain the different mechanical properties of various Mo/TiC composites. Li et al. [22] studied the interfacial bonding mechanism and stability of Al(111)/Al₂MgC₂(0001) interface models by DFT calculations, which could explain the heterogeneous nucleation behaviors of Al crystallites on Al₂MgC₂ particles in Al/Al₂MgC₂ composites. Jin et al. [24] investigated the behaviors of He atoms and vacancies in TiO/V interface models, theoretically revealing the effect of He bubbles on TiO/V interfaces under radiation conditions. For the metal/TMN systems considered in this work, previous theoretical studies based on DFT focused their attention on interfacial configuration, stability and bonding strength of metals/cubic TMN interfaces, such as α -Fe/CrN [25], Ni/CrN [26], Cu/TiN [27], and Al/VN [28]. However, to the best of our knowledge, little research has been devoted to metal/hexagonal-TMN interfaces, except γ -Fe(111)/Cr₂N(0001) which is found in high-nitrogen steels [29,30]. Consequently, we confirm that, despite the considerable attention on the development of metal/hexagonal-TMNs composites, the interface properties of these composites remain relatively unexplored. The adhesion strength, electronic structure, fracture toughness, and stability at the interfaces between metal and hexagonal TMN materials remain poorly understood. Targeted research is needed, as it is highly conducive to understanding improvements to the mechanical properties of composites in the field of interface engineering.

The present work addresses this issue by systematically investigating the characteristics of M/Cr₂N and M/V₂N interfaces using first-principles calculations based on DFT. The (0001) orientation of hexagonal phases, including Cr₂N, V₂N, Ti, and Ru, and the (111) orientation of fcc phases, including Ni, Pd, Al, Ag, and Cu, are selected as the interface orientations because they are both the preferred orientations of the two types of crystals [12,13,29,30]. We constructed the M/Cr₂N and M/V₂N interface models by considering both the 1N, 2N, and metal terminations of the nitrides, as well as possible stacking sequences, including top and hollow sites. Convergence tests of the number of atomic layers and evaluation of interfacial lattice misfit were performed beforehand to ensure the validity of the configurations of the interface models. For every metal, we calculated interfacial work of adhesion of the M/Cr₂N and M/V₂N interface models, and determined the optimal one with the strongest bonding strength. The partial density of states (PDOS), charge density difference plots, and Mulliken charges were analyzed to reveal the strong bonding natures. We further calculated the interfacial fracture toughness of the optimal model for every metal, and ranked the interfacial mechanical properties of these models by considering both the interfacial work of adhesion and the fracture toughness. In addition, the interfacial energy of the optimal model for every metal was calculated for a criterion of the stability of these models from thermodynamics. Finally, we evaluated the interfacial properties of the models based on the combination results of interfacial mechanical properties and stability. We believe that this work can provide a

fundamental understanding of the interfacial properties of metal/hexagonal-TMN composites in order to develop advanced cermet materials with high mechanical properties and interfacial stability.

2. Mathematical and Computational Methods

2.1. 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 [31,32]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was chosen to describe the exchange correlation energy [33]. A plane-wave cutoff energy of 400 eV was used in all calculations. The convergence tolerances were set as 1.0×10^{-5} eV/atom for the energy, 0.03 eV/Å for the maximum force, and 0.001 Å for the maximum displacement.

2.2. Bulk Properties

Cr₂N and V₂N have hexagonal closed-packed (hcp) structures with $P\bar{3}1m$ space group. In the unit cell of Cr₂N (V₂N), there are three N atoms and six Cr (V) atoms. The N atoms occupy 1a (0, 0, 0) and 2d (0.333, 0.667, 0.5) Wyckoff sites, the Cr atoms occupy 6k (0.333, 0, 0.249), and the V atoms occupy 6k (0.323, 0, 0.272) sites [34–36]. The k-point mesh of the Monkhorst-Pack grid was set as $12 \times 12 \times 12$ for bulk Cr₂N, V₂N, Ni, Pd, Al, Ag, and Cu, and set as $16 \times 16 \times 9$ for bulk Ti and Ru. The values of lattice constants (a and c), bulk modulus (B), and elastic constants (C_{ij}) calculated for Cr₂N, V₂N, Ti, Ru, Ni, Pd, Al, Ag, and Cu are listed in Table 1 along with corresponding data obtained from other calculated and experimental results. The good agreement between the past and present calculation results indicates that our calculation parameters are available.

Table 1. Calculated lattice constant (a and c , in Å), bulk modulus (B , in GPa), and elastic constants (C_{ij} , in GPa) of Cr₂N, V₂N, Ti, Ru, Ni, Pd, Al, Ag, and Cu.

Phase	Space Group	Data Source	a	c	B	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Cr ₂ N	$P\bar{3}1m$ (162)	This work	4.773	4.406	288.9	476.7	157.5	230.6	409.0	169.2
		Ref. [37]	4.773	4.406	289.0	477.0	158.0	231.0	410.0	171.0
V ₂ N	$P\bar{3}1m$ (162)	This work	4.905	4.543	264.9	454.1	162.2	177.7	444.7	153.7
		Ref. [36]	4.917	4.568	—	—	—	—	—	—
Ti	$P63/mmc$ (194)	This work	2.940	4.649	111.6	174.5	83.9	76.2	182.5	43.6
		Ref. [38]	2.941	4.647	112.6	170.3	92.3	70.5	206.2	43.3
Ru	$P63/mmc$ (194)	This work	2.719	4.283	313.2	577.0	182.4	160.7	660.1	190.1
		Ref. [39]	2.720	4.292	329.9	577.4	176.7	170.9	644.2	190.4
Ni	$Fm\bar{3}m$ (225)	This work	3.536	—	200.4	281.8	159.7	—	—	130.5
		Ref. [40]	3.522	—	198.0	281.0	157.0	—	—	131.0
Pd	$Fm\bar{3}m$ (225)	This work	3.930	—	183.4	224.2	163.0	—	—	73.0
		Ref. [41]	3.890	—	195.0	230.0	177.0	—	—	78.1
Al	$Fm\bar{3}m$ (225)	This work	4.049	—	76.1	130.5	48.8	—	—	8.7
		Ref. [42]	4.000	—	73.4	123.8	48.6	—	—	21.4
Ag	$Fm\bar{3}m$ (225)	This work	4.138	—	98.0	114.9	89.6	—	—	54.5
		Ref. [43]	4.138	—	98.3	117.1	88.9	—	—	55.6
Cu	$Fm\bar{3}m$ (225)	This work	3.630	—	134.7	178.2	112.9	—	—	86.6
		Ref. [44]	3.631	—	137.4	162.1	125.1	—	—	84.1

2.3. Surface Convergence Test

To study the interfacial properties of the M/Cr₂N and M/V₂N models, we first investigated their surface structures. It is essential to ensure that both sides of the interface slabs used in calculations are thick enough to exhibit bulk-like interiors, as it is known that the binding property of thin film can differ significantly from that of thicker one. We conducted convergence tests based on the interlayer relaxation change Δ_{ij} (interlayer relaxation as the percentage of bulk interlayer distance) to determine the appropriate

numbers of layers to apply in the interface models to ensure that they were sufficiently thick. A uniform vacuum space of 15 Å thickness is applied in the *z* direction to separate the free surfaces. The Δ_{ij} can be calculated as follows:

$$\Delta_{ij} = (d_{ij} - d_{ij0})/d_{ij0} \times 100\% \quad (1)$$

where d_{ij} and d_{ij0} are the interlayer distances of neighboring layers after and before geometry optimization, respectively.

In general, the value of Δ_{ij} decreases with increasing thickness. For pure metal slabs, it has been widely demonstrated that the value of Δ_{ij} becomes low enough when the slab is thicker than 6 atomic layers [23,43,45,46]. For Cr₂N(0001) slabs, as shown in Figure 1, three terminations, including one-N-atom terminated (1N-T), two-N-atoms terminated (2N-T), and Cr terminated (Cr-T) are considered. The V₂N(0001) slabs have similar configurations. The interlayer distance changes for Cr₂N(0001) and V₂N(0001) surfaces after full relaxation are listed in Table 2. We can confirm that 9-layer Cr₂N(0001) and 7-layer V₂N(0001) are thick enough to exhibit bulk-like interior. In addition, these convergence results are consistent with the previous studies on Cr₂N(0001) [29,30]. Therefore, 7-layer metal, 9-layer Cr₂N(0001), and 9-layer V₂N(0001) slab models were employed in our subsequent calculations.

Table 2. Cr₂N(0001) and V₂N(0001) surface relaxations as a function of termination and slab thickness (change of the interlayer spacing Δ_{ij} as a percentage of the spacing in bulk).

Slab	Terminate	Interlayer	Atom Layers of Slab			Slab	Terminate	Interlayer	Atom Layers of Slab		
			7	9	11				7	9	11
Cr ₂ N(0001)	1N	Δ_{12}	−7.5	−8.0	−7.5	V ₂ N(0001)	1N	Δ_{12}	−14.7	−12.9	−13.8
		Δ_{23}	−8.9	−10.8	−9.8			Δ_{23}	−6.3	−5.1	−4.9
		Δ_{34}	2.9	4.9	4.3			Δ_{34}	−1.4	−1.7	−1.4
		Δ_{45}		−2.3	−0.6			Δ_{45}		1.3	0.4
		Δ_{56}			−2.5			Δ_{56}			−0.4
	2N	Δ_{12}	−15.2	−16.3	−16.2		2N	Δ_{12}	−27.0	−26.1	−25.4
		Δ_{23}	−11.5	−10.8	−9.9			Δ_{23}	−0.3	−1.1	0.2
		Δ_{34}	8.9	9.0	8.8			Δ_{34}	0.1	−0.8	0.1
		Δ_{45}		−0.9	−1.3			Δ_{45}		−0.2	−0.2
		Δ_{56}			1.5			Δ_{56}			−0.6
	Cr	Δ_{12}	−15.9	−21.9	−20.5		V	Δ_{12}	−6.2	−5.4	−5.6
		Δ_{23}	1.9	1.6	2.7			Δ_{23}	−0.3	0.6	0.2
		Δ_{34}	13.5	11.9	11.4			Δ_{34}	1.6	0.6	0.6
		Δ_{45}		2.7	3.6			Δ_{45}		1.4	1.0
		Δ_{56}			1.8			Δ_{56}			0

Figure 1. Three different terminations of Cr₂N(0001): (a) 1N-T, (b) 2N-T, and (c) Cr-T terminations. The V₂N(0001) surface has similar configurations.

2.4. Surface Energy

The surface energy is the energy required to split the crystal into two parts along a specific plane and then to form two new surfaces per unit area, which is used to describe the surface stability. The surface energy γ_M^{slab} of a pure metal slab can be calculated as follows [38]:

$$\gamma_M^{\text{slab}} = (E_M^{\text{slab}} - n_M^{\text{slab}} E_M^{\text{bulk}}) / (2A) \quad (2)$$

where E_M^{slab} is the total energy of the metal slab; n_M^{slab} is the total number of atoms in the slab; E_M^{bulk} is the total energy per atom in the bulk material; A is the corresponding surface area, and the factor 2 represents two identical surfaces of the slab, respectively. The surface energies obtained for the 7-layer metal slab models are listed in Table 3. The surface energies of these slab models are in good agreement with other calculated and experimental surface energy data in the literature, which are also listed in Table 3. These results further verify the reliability of the present DFT calculations.

Table 3. Calculated surface energies of Ti(0001), Ru(0001), Ni(111), Pd(111), Al(111), Ag(111), and Cu(111) surfaces. The corresponding data available in the literature are also included for comparison.

Metal Slab	Surface Energy (J/m ²)		
	This Work	Other Calculations	Experiment
Ti(0001)	1.99	1.99 [47], 1.96 [48]	1.99 [49]
Ru(0001)	2.70	2.31 [50]	3.04 [49]
Ni(111)	1.91	1.93 [23], 1.92 [51]	2.38 [49]
Pd(111)	1.47	1.54 [23], 1.31 [48]	2.00 [49]
Al(111)	0.81	0.829 [45], 0.83 [52]	1.14 [49]
Ag(111)	0.79	0.80 [43], 0.75 [23]	1.25 [49]
Cu(111)	1.33	1.322 [46], 1.41 [47]	1.79 [49]

The Cr₂N(0001) and V₂N(0001) planes are both polar surfaces, and they have the similar configurations. Take the case of Cr₂N, the surface energy of the Cr₂N(0001) slab $\gamma_{\text{Cr}_2\text{N}}^{\text{slab}}$ can be calculated as follows [38]:

$$\gamma_{\text{Cr}_2\text{N}}^{\text{slab}} = \frac{1}{2A} (E_{\text{Cr}_2\text{N}}^{\text{slab}} - n_{\text{Cr}}^{\text{slab}} \mu_{\text{Cr}}^{\text{slab}} - n_{\text{N}}^{\text{slab}} \mu_{\text{N}}^{\text{slab}}) \quad (3)$$

where A is the corresponding surface area; $E_{\text{Cr}_2\text{N}}^{\text{slab}}$ is the total energy of the Cr₂N(0001) slab; $n_{\text{Cr}}^{\text{slab}}$ and $n_{\text{N}}^{\text{slab}}$ are the number of Cr and N atoms in the Cr₂N(0001) slab, respectively; $\mu_{\text{Cr}}^{\text{slab}}$ and $\mu_{\text{N}}^{\text{slab}}$ are chemical potential of Cr and N atoms in the slabs, respectively.

The Cr₂N unit cell has six Cr and three N atoms. When the surface is assumed to be in equilibrium with the bulk, the total energy $\mu_{\text{Cr}_2\text{N}}^{\text{bulk}}$ of the Cr₂N unit cell is expressed as follows:

$$\mu_{\text{Cr}_2\text{N}}^{\text{bulk}} = 6\mu_{\text{Cr}}^{\text{slab}} + 3\mu_{\text{N}}^{\text{slab}} \quad (4)$$

By combining Equations (3) and (4), the $\gamma_{\text{Cr}_2\text{N}}^{\text{slab}}$ expression with only one variable $\mu_{\text{Cr}}^{\text{slab}}$ can be calculated as follows:

$$\gamma_{\text{Cr}_2\text{N}}^{\text{slab}} = \frac{1}{2A} \left(E_{\text{Cr}_2\text{N}}^{\text{slab}} - n_{\text{N}}^{\text{slab}} \frac{\mu_{\text{Cr}_2\text{N}}^{\text{bulk}}}{3} - (n_{\text{Cr}}^{\text{slab}} - 2n_{\text{N}}^{\text{slab}}) \mu_{\text{Cr}}^{\text{slab}} \right) \quad (5)$$

According to the thermodynamic theories, $\mu_{\text{Cr}_2\text{N}}^{\text{bulk}}$ also equals the sum of bulk Cr₂N formation heat $\Delta H_f^0(\text{Cr}_2\text{N})$ and Cr₂N chemical potentials of Cr and N ($\mu_{\text{Cr}}^{\text{bulk}}$ and $\mu_{\text{N}}^{\text{gas}}$). Thus, the following equation can be obtained:

$$\mu_{\text{Cr}_2\text{N}}^{\text{bulk}} = 6\mu_{\text{Cr}}^{\text{bulk}} + 3\mu_{\text{N}}^{\text{gas}} + \Delta H_f^0(\text{Cr}_2\text{N}) \quad (6)$$

The $\mu_{\text{Cr}}^{\text{bulk}}$ is calculated as $E_{\text{Cr}}^{\text{bulk}}$, the energy of per Cr atom in bulk Cr. The $\mu_{\text{N}}^{\text{gas}}$ is calculated as $\mu_{\text{N}}^{\text{gas}}$, the energy of N atom with gaseous N₂ structure (one N₂ molecule in the center of a fixed cubic lattice).

Due to the compound Cr₂N being more stable compared to both elementary substances, the $\mu_{\text{Cr}}^{\text{slab}}$ and $\mu_{\text{N}}^{\text{slab}}$ have to be less than $\mu_{\text{Cr}}^{\text{bulk}}$ and $\mu_{\text{N}}^{\text{gas}}$, respectively. Accordingly, the following inequation can be obtained by combining Equations (4) and (6):

$$\frac{\Delta H_f^0(\text{Cr}_2\text{N})}{6} \leq \mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}} \leq 0 \quad (7)$$

The value of $\Delta H_f^0(\text{Cr}_2\text{N})$ can be obtained by Equation (6). Our calculation result of $\Delta H_f^0(\text{Cr}_2\text{N})$ is -4.97 eV. This value is in agreement with previous theoretical data of -5.59 eV [30]. The value of $\Delta H_f^0(\text{V}_2\text{N})$ can be obtained using the same method, and the result is -10.18 eV. Accordingly, the ΔH_f^0 (eV/atom) obtained for Cr₂N and V₂N are -0.55 eV/atom and -1.13 eV/atom, respectively. The two values are consistent with the data of -0.506 eV/atom for Cr₂N and -1.090 eV/atom for V₂N in the Materials Data by Materials Project, respectively.

Consequently, we calculate the surface energies of 1N, 2N, and Cr terminations of Cr₂N(0001), and 1N, 2N, and V terminations of V₂N(0001), and the results are illustrated in Figure 2a,b, respectively. For 1N, 2N, and Cr terminations of Cr₂N(0001), the values of $\gamma_{\text{Cr}_2\text{N}}^{\text{slab}}$ are in the ranges of 1.25–1.92 J/m², 0.90–2.24 J/m², and 3.32–4.37 J/m², respectively. For 1N, 2N, and V terminations of V₂N(0001), the values of $\gamma_{\text{V}_2\text{N}}^{\text{slab}}$ are in the ranges of 1.97–3.27 J/m², 0.82–3.37 J/m², and 3.13–5.13 J/m², respectively. It can be concluded that 1N- and 2N-terminated Cr₂N(0001) have lower surface energies, which indicates that they are more thermodynamically stable than the Cr-terminated slab. Similarly, the 1N and 2N-terminated V₂N(0001) are demonstrated to be more thermodynamically stable than the V-terminated slab. However, for a comprehensive investigation, 1N, 2N, and Cr or V terminations are all considered in the following studies.

2.5. Interface Models

We constructed the M/Cr₂N models considering 1N, 2N, and Cr terminations of Cr₂N(0001), respectively. Two stacking sequences, including top and hollow sites, were considered for the 1N-T and 2N-T interface models, respectively. Here, the top site indicates that the interfacial M atoms sit above the interfacial N atoms, and the hollow site indicates that the interfacial M atoms sit above Cr atoms at the fourth layer. Figure 3 illustrated five types of configurations for the M/Cr₂N interface model for every metal considered. Accordingly, the interfacial orientation relationship of the M/Cr₂N interface model for every metal are listed in Table 4, which are intentionally constructed to minimize the interfacial mismatch rate.

Figure 2. (a) Cr₂N(0001) and (b) V₂N(0001) surface energy as a function of chromium chemical potential $(\mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}})$ and vanadium chemical potential $(\mu_{\text{V}}^{\text{slab}} - \mu_{\text{V}}^{\text{bulk}})$, respectively.

The M/Cr₂N and M/V₂N interface models were built in the same way because the lattice constants of Cr₂N and V₂N are approximate. Here, the softer M slabs are stretched to align with Cr₂N and V₂N slabs. Interfacial mismatch rates are calculated according to the change of lattice constant of the M slabs [26]. The calculated results of interfacial mismatch rates for the M/Cr₂N and M/V₂N interface models are illustrated in Figure 4, and they are unanimously less than 7%. Therefore, the interface models constructed in this work represent valid structures.

Figure 3. Interface models of $M/\text{Cr}_2\text{N}$ interfaces, including (a–e) $M_1(0001)/\text{Cr}_2\text{N}(0001)$ ($M_1 = \text{Ti}$ and Ru), (f–j) $M_2(111)/\text{Cr}_2\text{N}(0001)$ ($M_2 = \text{Pd}, \text{Al}, \text{Ag},$ and Cu), and (k–o) $\text{Ni}(111)/\text{Cr}_2\text{N}(0001)$. The orientation relationships of the interface models are $(0001)_{M_1}[2\bar{1}\bar{1}0]_{M_1} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$, $(111)_{M_2}[10\bar{1}]_{M_2} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$, and $(111)_{\text{Ni}}[2\bar{1}\bar{1}]_{\text{Ni}} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$, respectively. There are five atom layers in the top views of (a₁–e₁), (f₁–j₁) and (k₁–o₁). The smallest spheres denote interfacial atoms of metal phases, from the second smallest to largest spheres are atoms from the first to fourth layers of $\text{Cr}_2\text{N}(0001)$. Five interface models for each $M/\text{Cr}_2\text{N}$ are considered: (a₁,f₁,k₁) 1N-T top, (b₁,g₁,l₁) 1N-T hollow, (c₁,h₁,m₁) 2N-T top, (d₁,i₁,n₁) 2N-T hollow, and (e₁,j₁,o₁) Cr-T.

Table 4. The interface orientations of $M_1/\text{Cr}_2\text{N}$ ($M_1 = \text{Ti}$ and Ru), $M_2/\text{Cr}_2\text{N}$ ($M_2 = \text{Pd}, \text{Al}, \text{Ag},$ and Cu), and $\text{Ni}/\text{Cr}_2\text{N}$ interface models.

$M/\text{Cr}_2\text{N}$	Interfacial Orientation Relationship
$M_1/\text{Cr}_2\text{N}$ ($M_1 = \text{Ti}$ and Ru)	$(0001)_{M_1}[2\bar{1}\bar{1}0]_{M_1} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$
$M_2/\text{Cr}_2\text{N}$ ($M_2 = \text{Pd}, \text{Al}, \text{Ag},$ and Cu)	$(111)_{M_2}[10\bar{1}]_{M_2} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$
$\text{Ni}/\text{Cr}_2\text{N}$	$(111)_{\text{Ni}}[2\bar{1}\bar{1}]_{\text{Ni}} // (0001)_{\text{Cr}_2\text{N}}[1\bar{1}00]_{\text{Cr}_2\text{N}}$

Figure 4. Interfacial mismatch rates calculated for the interface models constructed in this work.

3. Results and Discussion

The calculations on interfacial work of adhesion, electronic structure, interfacial fracture toughness, weak point, and interfacial energy are performed in this section. Interfacial mechanical properties are assessed by the results of work of adhesion and fracture toughness. PDOS, charge density difference plots, and Mulliken charges are used to analyze interfacial bonding natures. Interfacial energies are provided to assess the interfacial stability. The interfacial properties are evaluated based on the combination of interfacial mechanical properties and stability.

3.1. Work of Adhesion

The work of adhesion W_{ad} is defined as the reversible work to separate a unit area interface of two condensed phases α and β . The value of W_{ad} can be calculated as follows [53]:

$$W_{ad} = (E_{slab,\alpha} + E_{slab,\beta} - E_{\alpha/\beta}) / A \quad (8)$$

where $E_{slab,\alpha}$ and $E_{slab,\beta}$ are the total energies of the fully relaxed surface slabs, $E_{\alpha/\beta}$ is the total energy of the α/β interface model, and A is the interface area. The k-point meshes employed for the calculations of the interface models are $8 \times 8 \times 1$. Larger values of W_{ad} imply larger bonding strength in the interface model [54,55].

The values of W_{ad} can be obtained by two different methods. The first method is the universal binding energy relation (UBER) method [22]. Figure 5 displays the values of W_{ad} obtained by the UBER method versus the interfacial distance d_0 . The peak of the curve represents the optimal values of d_0 and W_{ad} . Therefore, we can have a preliminary evaluation on the optimal configuration among the M/Cr₂N and M/V₂N interface models for every metal considered. The results show that: (i) the Ti/Cr₂N-2N(hol) interface model has the largest value of W_{ad} among the Ti/Cr₂N interface models; (ii) the M'/Cr₂N-Cr (M' = Ru, Ni, Pd, Al, Ag, and Cu) interface model has the largest value of W_{ad} among the M'/Cr₂N interface models. In addition, the M/V₂N interface models have similar results to those of the M/Cr₂N interface models for every metal considered. Accordingly, the optimal M/Cr₂N and M/V₂N interface models for every metal are determined, respectively. The second method adopts the optimal structures obtained from the UBER method, and relaxes the interface models fully. Three atomic layers at the top of the M slabs and four atomic layers at the bottom of the Cr₂N(0001) and V₂N(0001) slabs were fixed in their bulk positions. Then, the d_0 and W_{ad} values of the optimal M/Cr₂N and M/V₂N interface models for every metal after relaxation are obtained. Figure 6 displays both the values of W_{ad} for the optimal interface models before and after relaxation. The values of W_{ad} change a little during the relaxation processes, indicating that the interface models we constructed are stable. In addition, the value of W_{ad} after relaxation for the optimal M/Cr₂N interface model follows the order: Ru/Cr₂N-Cr > Pd/Cr₂N-Cr > Ti/Cr₂N-2N(hol) > Ni/Cr₂N-Cr > Al/Cr₂N-Cr > Cu/Cr₂N-Cr > Ag/Cr₂N-Cr. Meanwhile, the value of W_{ad} after relaxation

for the optimal M/V₂N interface model follows the order: Ti/V₂N-2N(hol) > Ni/V₂N-V > Pd/V₂N-V > Al/V₂N-V > Ru/V₂N-V > Cu/V₂N-V > Ag/V₂N-V. The Ti/V₂N-2N(hol), Ni/V₂N-V, and Ru/Cr₂N-Cr interface models exhibit the largest, second largest, and third largest value of W_{ad} , 5.73, 5.30, and 5.05 J/m², among all the optimal interface models considered, respectively.

Figure 5. Relationship between the work of adhesion W_{ad} and the interfacial distance d_0 obtained using the UBER method for every metal considered: (a) Ti, (b) Ru, (c) Ni, (d) Pd, (e) Al, (f) Ag, (g) Cu.

Figure 6. The work of adhesion W_{ad} obtained for the interface models before and after full relaxation.

In addition, we performed test calculations for the verification on the reliability of the selected crystallographic interfaces in present work. We built other low-index crystallographic interface models as much as possible, and evaluated their interfacial bonding strengths by the values of W_{ad} using UBER method. The calculation results are presented in the Supplementary Materials. It follows that other crystallographic interfaces have lower or negative values of W_{ad} than the crystallographic interfaces we chose for this work. Therefore, we can confirm that the present crystallographic interfaces are preferred because of the enhanced interfacial bonding strength. This result makes sense for the coating applications motivating these composites. As we know, crystalline orientation is an important characteristic of coating growth. Interface orientation, which is constructed by crystalline orientation of each layer, have an important role in the interfacial mechanisms [15,26]. Therefore, the control of interface orientation may serve as a promising way to affect overall properties of the composites. For example, Wang et al. [26] theoretically demonstrated that the Ni(111)/CrN(111) interface orientation provides the greatest adhesion strength among the Ni/CrN interfaces, so the development of Ni(111)/CrN(111) interfaces is preferred in actual Ni/CrN coating applications. Toshihiko et al. [56] reported that the improvement of mechanical properties of Ti/TiN Multilayer coatings with increasing layer number could be explained by the evolution of preferred orientation from (111) to (100). With respect to the concerned M/Cr₂N and M/V₂N systems, the enhanced cohesion of their coating composites greatly associates with tailoring of special crystalline orientation of each component. Therefore, it can be inferred that the relations between deposition process and interface orientation are a great issue for the preparation of these coating composites.

3.2. Electronic Structure

The information about electronic orbitals can be helpful for evaluating the nature of bonding interactions at the interfaces. Figures 7 and 8 illustrate the PDOS and charge density difference plots of the Ti/V₂N-2N(hol), Ni/V₂N-V, and Ru/Cr₂N-Cr interface models after relaxation, respectively. The Mulliken charge is labeled beside the atoms in Figure 8.

Figure 7. PDOS for selected atoms in the (a) Ti(0001)/V₂N(0001)-2N(hol), (b) Ni(111)/V₂N(0001)-V, and (c) Ru(0001)/Cr₂N(0001)-Cr interface models. The vertical dashed line indicates the Fermi level.

Figure 8. Charge density difference plots of (a) Ti(0001)/V₂N(0001)-2N(hol), (b) Ni(111)/V₂N(0001)-V, and (c) Ru(0001)/Cr₂N(0001)-Cr interface models. Mulliken charge (unit: e) is labeled beside the atoms. The dashed lines represent the positions of the interfaces.

Figure 7a shows that the 3d orbital of the interfacial Ti atom interacts and hybridizes with the 2p orbital of the interfacial N atom at the energy of -5.0 and -6.5 eV in the Ti/V₂N-2N(hol) interface model. Similarly, Figure 7b shows the Ni/V₂N-V interface model exhibits the interaction and hybridization behaviors between interfacial Ni-3d and V-3d orbitals at the energy of -1.6 , -2.3 , and -3.3 eV, respectively. It can also be seen from Figure 7c that interfacial Ru-3d orbital interacts and hybridizes with the interfacial Cr-3d orbital for the Ru/Cr₂N-Cr interface model at the energy of -1.2 , -2.1 , and -3.1 eV, respectively. These orbital hybridization behaviors imply the formation of covalent bonding between the atoms [38,57]. Therefore, the Ti/V₂N-2N(hol), Ni/V₂N-V, and Ru/Cr₂N-Cr interface models all have interfacial covalent natures.

Figure 8 shows that the interfacial total charge transfer for the Ti/V₂N-2N(hol), Ni/V₂N-V, and Ru/Cr₂N-Cr interface models are approximately 0.90, 0.46, and 0.17 e, which are mainly contributed from Ti-N, Ni-V, and Ru-Cr atom pairs, respectively. The larger charge transfer means larger electronic interactions at the interfaces. Accordingly, the interfacial strength of these interface models follows the order: Ti/V₂N-2N(hol) > Ni/V₂N-V > Ru/Cr₂N-Cr. This tendency is consistent with the observed trends in the W_{ad} results, where the Ti/V₂N-2N(hol) interface model has the largest value of W_{ad} among the three interface models.

3.3. Interfacial Fracture Toughness

The fracture toughness K_{IC} of an interface represents its strength to resist the development of a fracture along the interface. According to Griffith crack theory, the value of K_{IC} along a specific direction [hkl] can be calculated as follows [58]:

$$K_{IC} = \sqrt{4W_{ad}E_{hkl}} \quad (9)$$

where E_{hkl} is the Young's modulus of bulk materials in the direction of unit vector [hkl]. For the hexagonal crystal, E_{hkl} can be calculated as follows [59]:

$$\frac{1}{E_{hkl}} = S_{11} \left(h^2 + k^2 \right)^2 + S_{33} l^4 + (2S_{13} + S_{44}) \left(k^2 l^2 + h^2 l^2 \right) \quad (10)$$

Accordingly, the E_{0001} of hexagonal phases can be calculated as follows:

$$E_{0001} = \frac{1}{S_{33}} \quad (11)$$

Meanwhile, for the cubic crystal, E_{hkl} can be calculated as follows [60]:

$$\frac{1}{E_{hkl}} = S_{11} - 2 \left(S_{11} - S_{12} - \frac{S_{44}}{2} \right) (h^2 k^2 + k^2 l^2 + l^2 h^2) \quad (12)$$

Thus, the E_{111} of fcc metals can be calculated as follows:

$$E_{111} = \frac{1}{S_{11} - \frac{2}{3}(S_{11} - S_{12} - \frac{1}{2}S_{44})} \quad (13)$$

where S_{ij} are elastic compliance constants.

The values of elastic compliances S_{ij} and Young's moduli E_{0001} obtained for hcp-TMNs (Cr_2N , V_2N) and hcp-metals (Ti, Ru), and elastic compliances S_{ij} and Young's moduli E_{111} obtained for fcc-metals (Ni, Pd, Al, Ag, and Cu), are listed in Table 5. We note that Ru exhibits the larger value of E_{0001} (592.10 GPa) in the hcp-metal group, and Ni exhibits the largest value of E_{111} (321.70 GPa) in the fcc-metal group.

Table 5. Calculated elastic compliances (S_{ij} , in GPa^{-1}), Young's moduli (E , in GPa) along [0001] direction for Cr_2N , V_2N , Ti, and Ru, and along [111] direction for Ni, Pd, Al, Ag, and Cu.

Lattice	Phase	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	E_{0001}	E_{111}
hcp-TMN	Cr_2N	0.00292	−0.00024	−0.00151	0.00415	0.00596	241.20	—
	V_2N	0.00282	−0.00071	−0.00084	0.00292	0.00669	342.18	—
hcp-M	Ti	0.00809	−0.00296	−0.00214	0.00727	0.02292	137.55	—
	Ru	0.00200	−0.00053	−0.00036	0.00169	0.00526	592.10	—
	Pd	0.01150	−0.00484	—	—	0.01370	—	193.35
	Al	0.00962	−0.00262	—	—	0.11494	—	25.14
fcc-M	Ag	0.02756	−0.01208	—	—	0.01835	—	137.93
	Cu	0.01103	−0.00428	—	—	0.01155	—	213.89
	Ni	0.00601	−0.00218	—	—	0.00766	—	321.70

The values of K_{IC} obtained for the optimal M/ Cr_2N and M/ V_2N interface models for every metal after relaxation are illustrated in Figure 9. Here, the values of K_{IC} are given as a range, because they include two fracture toughness values indicative of fracture along the metal surface ($K_{IC\text{-metal}}$) and along the ceramic surface ($K_{IC\text{-ceramic}}$). The results show that: (i) both the Ru/ Cr_2N -Cr and Ru/ V_2N -V interface models have larger values of $K_{IC\text{-metal}}$ than the values of $K_{IC\text{-ceramic}}$, which is determined by the considerably large value of E_{0001} obtained for Ru; (ii) the Ni/ Cr_2N -Cr interface model has a larger value of $K_{IC\text{-metal}}$ than the value of $K_{IC\text{-ceramic}}$, which is because the value of E_{111} obtained for Ni is larger than the value of E_{0001} obtained for V_2N ; (iii) except Ru/ Cr_2N -Cr, Ni/ Cr_2N -Cr, and Ru/ V_2N -V, the other interface models have the larger value of $K_{IC\text{-ceramic}}$ than the value of $K_{IC\text{-metal}}$. We rank the interfacial fracture toughness K_{IC} of the interface models in term of the lower value between $K_{IC\text{-metal}}$ and $K_{IC\text{-ceramic}}$. Accordingly, the K_{IC} of M/ Cr_2N interface models follows the order: Ru/ Cr_2N -Cr > Ni/ Cr_2N -Cr > Pd/ Cr_2N -Cr > Ti/ Cr_2N -2N > Cu/ Cr_2N -Cr > Ag/ Cr_2N -Cr > Al/ Cr_2N -Cr. Similarly, the K_{IC} of M/ V_2N interface models follows the order: Ni/ V_2N -V > Ru/ V_2N -V > Pd/ V_2N -V > Ti/ V_2N -2N > Cu/ V_2N -V > Ag/ V_2N -V > Al/ V_2N -V. In addition, the Ni/ V_2N -V, Ru/ V_2N -V, and Ru/ Cr_2N -Cr interface models exhibit the largest, second largest, and third largest value of K_{IC} , 2.61, 2.26, and 2.21 $\text{MPa} \cdot \text{m}^{1/2}$, among all the interface models considered, respectively.

Figure 9. The K_{IC} -metal and K_{IC} -ceramic obtained for the interface models after full relaxation.

Figure 10a,b show a combination of the W_{ad} and K_{IC} of the M/Cr₂N and M/V₂N interface models, respectively. Here, the K_{IC} is the lower value between K_{IC} -metal and K_{IC} -ceramic. We note from Figure 10a that the Ru/Cr₂N-Cr interface model has the largest values of W_{ad} and K_{IC} among the seven M/Cr₂N interface models. In addition, from Figure 10b, we can see that the Ni/V₂N-V interface model not only has a considerably large value of W_{ad} , but also possesses the largest value of K_{IC} among the seven M/V₂N interface models. As to the Ti/V₂N-2N(hol) interface model, despite having the largest value of W_{ad} , it is not the perfect model, because of its relatively low value of K_{IC} . Therefore, we can confirm that the Ru/Cr₂N-Cr interface model has the best interfacial mechanical properties in the M/Cr₂N group, and the Ni/V₂N-V interface models has the best interfacial mechanical properties in the M/V₂N group. Furthermore, the Ni/V₂N-V interface model can be regarded as the best interface configuration among all the interface models considered because of its having the largest value of K_{IC} and a larger value of W_{ad} than the Ru/Cr₂N-Cr interface model.

Figure 10. The combination of the interfacial work of adhesion W_{ad} and the interfacial fracture toughness K_{IC} of the (a) M/Cr₂N and (b) M/V₂N interface models considered, respectively.

Previous studies [13,14] have experimentally demonstrated the excellent mechanical and tribological properties of Ag/Cr₂N and Cu/Cr₂N coating composite systems. However, from the perspective of first-principles study, the Ag/Cr₂N-Cr and Cu/Cr₂N-Cr interfaces have the minimum interfacial mechanical properties among all the models, as shown in

Figure 10a. This indicates relatively weak load capacities at the interfaces, which may limit the overall mechanical properties of the composites. This result is satisfactory. It is doubtless that thermal effect will play an important role in the interfacial bonding strength of Ag/Cr₂N and Cu/Cr₂N composites. Further discussions of the thermal effect on the composites are beyond the scope of the present work.

3.4. Interfacial Weak Point

To achieve further understanding of the mechanical strength of the Ru/Cr₂N-Cr and Ni/V₂N-V interfaces, the interfacial weak point is investigated for the two interface models [53]. We assume that both interface models are to be cleaved along six different planes. Cleavage energies are related to the number of bonds broken; therefore, all the cleavage planes are selected by considering the minimum bonds to be cut along these planes. For the Ru/Cr₂N-Cr interface model, the cleavage planes are between the 1st and 1st layers of Ru(0001) and Cr₂N (0001), the 1st and 2nd and 2nd and 3rd layers of Ru(0001), and the 1st and 2nd, 2nd and 3rd, and 3rd and 4th layers of Cr₂N (0001). For the Ni/V₂N-V interface model, the cleavage planes are between the 1st and 1st layers of Ni(111) and V₂N (0001), the 1st and 2nd and 2nd and 3rd layers of Ni(111), and the 1st and 2nd, 2nd and 3rd, and 3rd and 4th layers of V₂N (0001). For simplicity, these cleavage planes are denoted as cp1~cp6, respectively (as shown in Figure 11).

To estimate the reversible work needed to separate the interfaces, the W_{ad} are calculated along different cleavage planes, and the results are labeled in Figure 11. For the Ru/Cr₂N-Cr interface model, the minimum W_{ad} (4.35 J/m²) is generated by cleaving along the cp2 plane (between the 1st and 2nd layers of Ru(0001)); for the Ni/V₂N-V interface model, the minimum W_{ad} (3.44 J/m²) is generated by cleaving along cp2 plane (between the 1st and 2nd layers of Ni(111)). The results demonstrate that the weak point always lies on the metal side for both the Ru/Cr₂N-Cr and Ni/V₂N-V interface models. However, the Ni/V₂N-V interface model, despite its better interfacial mechanical properties, is more likely to separate because of the cracking of the Ni side under external stress.

Figure 11. Different cleavage planes (cp1~cp6) for the (a) Ru(0001)/Cr₂N(0001)-Cr and (b) Ni(111)/V₂N(0001)-V interface models. Here, the values of W_{ad} (unit: J/m²) obtained for the models along cp1~p6 cleavage planes are also labeled.

3.5. Interfacial Energy

Another quantity usually associated with interface stability is the interfacial energy γ_{int} . In general, the thermodynamic stability of the interface increases with decreasing γ_{int} . When both materials are similar, a tiny value of γ_{int} ($\gamma_{int} \approx 0$ J/m²) is acceptable. When both materials are completely different, a positive value of γ_{int} should be obtained, and the magnitude is determined by the interfacial strain caused by the lattice misfit. In

particular, the interface with a negative value of γ_{int} is thermodynamically unstable. It will provide the driving force to push interfacial atoms to diffuse across the interface, resulting in interfacial alloying behavior, or even forming a new interfacial phase [38]. Negative interfacial energies have been reported for some interface systems, in which interfacial alloying occurred through the inter-diffusion of metal atoms [61–63].

Figure 12a shows the values of γ_{int} for the M/Cr₂N group as a function of the chromium chemical potential ($\mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}}$). Here, the values of γ_{int} are calculated as follows [25,64–66]:

$$\gamma_{\text{int}} = \gamma_{\text{M}}^{\text{slab}} + \gamma_{\text{Cr}_2\text{N}}^{\text{slab}} - W_{\text{ad}} \quad (14)$$

where $\gamma_{\text{M}}^{\text{slab}}$ and $\gamma_{\text{Cr}_2\text{N}}^{\text{slab}}$ are the surface energies of the M and Cr₂N slabs, which are calculated according to Equations (2) and (3), respectively. Similarly, the values of γ_{int} for the M/V₂N group are calculated, and the results are presented in Figure 12b. Accordingly, the thermodynamic stability of the M/Cr₂N interface models follows the order: Pd/Cr₂N-Cr > Ru/Cr₂N-Cr > Al/Cr₂N-Cr > Ni/Cr₂N-Cr > Ag/Cr₂N-Cr > Cu/Cr₂N-Cr, and the thermodynamic stability of the M/V₂N interface models follows the order: Al/V₂N-V > Pd/V₂N-V > Ni/V₂N-V > Ag/V₂N-V > Cu/V₂N-V > Ru/V₂N-V, respectively.

Figure 12. Interfacial energies of the (a) M/Cr₂N and (b) M/V₂N interface models as a function of chromium chemical potential ($\mu_{\text{Cr}}^{\text{slab}} - \mu_{\text{Cr}}^{\text{bulk}}$) and vanadium chemical potential ($\mu_{\text{V}}^{\text{slab}} - \mu_{\text{V}}^{\text{bulk}}$), respectively.

The Pd/Cr₂N-Cr interface model exhibits the lowest value of γ_{int} , from 0.08 to 1.13 J/m², in the M/Cr₂N models. The Al/V₂N-Cr interface model exhibits the lowest value of γ_{int} , from −0.38 to 1.66 J/m², in the M/Cr₂N models. Thus, the Pd/Cr₂N-Cr and Al/V₂N-Cr interface models have the most stable configurations among the models considered. However, the mechanical properties of Pd/Cr₂N and Al/V₂N composites are not so good. As shown in Sections 3.1 and 3.3, they are limited by the relatively low interfacial work of adhesion and fracture toughness. The Ti/Cr₂N-2N(hol) and Ti/V₂N-2N(hol) interfaces have negative values of γ_{int} throughout the whole range. Thus, they are thermodynamically unstable. The interfacial Ti-N distances of Ti/Cr₂N-2N(hol) and Ti/V₂N-2N(hol) after relaxation are 2.045 and 2.060 Å, respectively. These values are very close to the length of Ti-N bond (2.090 Å) [67]. Thus, it can be inferred that the Ti/Cr₂N-2N(hol) and Ti/V₂N-2N(hol) interfaces strongly tend to form Ti-N interfacial phases. In fact, the interfacial productions of Ti nitrides have been frequently observed in previous composites systems [68–72]. These results are reasonable because Ti is the only strong nitride-forming element in the metals we considered. The Ni/V₂N-V interface model exhibits a low value of γ_{int} (1.74 J/m²) at the N-rich side. As the V chemical potential increases, the value of γ_{int} decreases to −0.25 J/m², which is very close to zero. Thus, it follows that the Ni/V₂N-V interface model has good thermodynamic stability. Moreover, based on the results in Sections 3.3 and 3.5, an important conclusion that can be drawn is that the Ni/V₂N-V interface model not only has the best interfacial mechanical properties, but also exhibits the superior stability compared to most of the other interface models.

In sum, the interfacial properties of the considered M/Cr₂N and M/V₂N interface models were compared and discussed in a theoretical way using the first-principles method. The results demonstrated that the Ni/V₂N-V interface model is prominent among all the models considered. Therefore, Ni additives can be regarded a good choice for achieving enhanced mechanical properties in V₂N phase. These results also serve as the motivation for a noteworthy attempt to explore the structure and properties of Ni/V₂N composite materials in our future work.

4. Conclusions

The incorporation of ductile metal within hexagonal-TMNs, such as Cr₂N and V₂N, is a promising approach for the enhancement of mechanical properties. However, interfacial mechanisms at metal/hexagonal-TMN interfaces, which are the key features leading to enhanced mechanical properties of the composites, remain poorly understood. The first-principles method based on DFT could reveal interfacial mechanisms at the atomic and electronic levels, and evaluate interfacial properties quantitatively by figuring out the values of work of adhesion, fracture toughness, and interfacial energy. Thus, we conducted a systematic investigation on M/Cr₂N and M/V₂N (M = Ti, Ru, Ni, Pd, Al, Ag, and Cu) interfaces using the first-principles method in this work. (0001) of hexagonal phases and (111) of fcc phases were selected as the interface orientations. The M/Cr₂N interface models were built by considering 1N, 2N, and Cr terminations of Cr₂N(0001), and two stacking methods, including top and hollow sites. The M/V₂N interface models were built in the same way. The main calculation results are given as follows:

- (1) The Ti/V₂N-2N(hol), Ni/V₂N-V, and Ru/Cr₂N-Cr interface models exhibit the first, second, and third largest values of W_{ad} , 5.73, 5.30, and 5.05 J/m², among all the interface models considered, respectively.
- (2) The analyses of partial density of states (PDOS), charge density difference, and Mulliken charge are in good agreement with the observed trends in the W_{ad} results.
- (3) The Ni/V₂N-V, Ru/V₂N-V, and Ru/Cr₂N-Cr interface models exhibit the first, second, and third largest values of fracture toughness, 2.61, 2.26, and 2.21 MPa·m^{1/2}, among all the interface models considered, respectively.
- (4) The Ni/V₂N-V interface model has a relatively low value range of γ_{int} from −0.25 to 1.74 J/m², suggesting considerably high thermal stability compared to most of the other interface models.

According to above results, it can be concluded that the Ni/V₂N-V interface model exhibits a good combination of work of adhesion, fracture toughness, and interfacial stability, and thus provides the preferred configuration among the metal/hexagonal-TMN interface models considered. Therefore, the Ni/V₂N composite system is considered to be exploitable for metal/hexagonal-TMN materials with enhanced mechanical properties. This work reveals a fundamental understanding of developing advanced metal/hexagonal-TMN composites with respect to optimizing interfacial properties.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12010066/s1>, Figure S1: Interface models of M/Cr₂N interfaces, including (a)–(c) M1(10 $\bar{1}$ 0)/Cr₂N(0001) (M1 = Ti and Ru), (d)–(f) M2(100)/Cr₂N(0001), and (g)–(i) M2(110)/Cr₂N(0001) (M2 = Ni, Pd, Al, Ag, and Cu). The orientation relationships of the interface models are (10 $\bar{1}$ 0)_{M1}[[1 $\bar{2}$ 1]]_{M1}//(0001)_{Cr₂N}[[1 $\bar{1}$ 0]]_{Cr₂N}, (100)_{M2}[[011]]_{M2}//(0001)_{Cr₂N}[[1 $\bar{1}$ 0]]_{Cr₂N}, and (110)_{M2}[[001]]_{M2}//(0001)_{Cr₂N}[[1 $\bar{1}$ 0]]_{Cr₂N}, respectively. There are five atom layers in the top views of (a₁)–(c₁), (d₁)–(f₁) and (g₁)–(i₁). The smallest spheres denote interfacial atoms of metal phases, from the second smallest to largest spheres are atoms from the first to fourth layers of Cr₂N(0001). Three interface models for each M/Cr₂N are considered: (a₁, d₁, g₁) 1N-terminated, (b₁, e₁, h₁) 2N-terminated, and (c₁, f₁, i₁) Cr-terminated, Table S1: Mismatch rates (δ_U and δ_V) of the M1(10 $\bar{1}$ 0)/Cr₂N(0001) and M1(10 $\bar{1}$ 0)/V₂N(0001) interface models (M1 = Ti and Ru), Table S2: Interfacial distance (d_0) and work of adhesion (W_{ad}) of the M1(10 $\bar{1}$ 0)/Cr₂N(0001) and M1(10 $\bar{1}$ 0)/V₂N(0001) interface models with different terminations (M1 = Ti and Ru), Table S3: Mismatch rates (δ_U and δ_V) of the M2(100)/Cr₂N(0001), and M2(100)/V₂N(0001) interface models (M2 = Ni, Pd, Al, Ag, and Cu), Table S4: Interfacial distance (d_0) and work of adhesion (W_{ad}) of the M2(100)/Cr₂N(0001) and M2(100)/V₂N(0001) interface models with different terminations (M2 = Ni, Pd, Al, Ag, and Cu), Table S5: Mismatch rates (δ_U and δ_V) of the M2(110)/Cr₂N(0001) and M2(110)/V₂N(0001) interface models (M2 = Ni, Pd, Al, Ag, and Cu), Table S6: Interfacial distance (d_0) and work of adhesion (W_{ad}) of the M2(110)/Cr₂N(0001), and M2(110)/V₂N(0001) interface models with different terminations (M2 = Ni, Pd, Al, Ag, and Cu).

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