A comparative study TiC/TiN and TiN/CN multilayers

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Abstract
We carried out a comparative study of TiC/TiN and TiN/CN multilayers using the linearized augmented plane wave (LAPW) scheme and density functional theory as implemented in the Wien2k code. Initially, we optimized the structural properties of the TiC/TiN and TiN/CN multilayers in the volume with NaCl structure, and the ground state energy, the bulk modulus, and the cohesive energy were determined. To determine the energy of formation, the total energy for TiN, TiC, and CN compounds was calculated. Finally, we determined the DOS (density of states) of the two multilayers. The analysis of the partial density of states reveals that multilayers has metallic behavior that can be explained by the strong p–d hybridization of N and Ti atoms.

Keywords: DFT, multilayers, electronic and structural properties.

Un estudio comparativo de las multicapas TIC/TiN y TiN/CN

Resumen
En este trabajo se hace un estudio comparativo de las multicapas TiN/CN y TiC/TiN usando el esquema ondas plana aumentadas y linealizadas y la teoría del funcional de la densidad tal como se halla implementado en el código WIEN2k. Inicialmente, se optimizaron las propiedades estructurales de las multicapas TiN/CN y TiC/TiN en volumen en la estructura NaCl y se obtuvo la energía de estado base, el módulo de volumen y la energía de cohesión. Para obtener la energía de formación, se calcula la energía total para los compuestos TiN, TiC, CN. Finalmente, se obtiene la densidad de estados los dos multicapas. El análisis de la densidad de estados revela que las multicapas poseen un comportamiento metálico que puede ser explicado por la fuerte hibridación entre los orbitales p-d de los átomos de N y Ti.

Palabras clave: DFT, multicapas, Propiedades electrónicas y estructurales.

1. Introduction

Because of its hardness, high chemical and thermal stability, and high resistance to wear, oxidation, and corrosion, both titanium nitride (TiN) and titanium carbide (TiC) have been widely used as hard coatings in high-speed cutting tools and in devices operating at high degrees of power and high temperatures [1-4]. Unfortunately, hard coatings based only on traditional TiN or TiC offer limited benefit in terms of prevention of rupture or adherence to the workpiece, which is one of the main problems associated with tribological applications [5-7]. For this reason, many studies have sought to improve the mechanical properties of thin films of these nitrides and carbides through the growth of multilayers or nanocomposites based on TiN or TiC [5, 8-11].

A TiN/CN multilayer grown via magnetron sputtering [5] has been found to possess a higher resistance to wear, oxidation, and corrosion than TiN or TiC [5]; therefore hard coatings based on a TiN/CN multilayer will have better mechanical and tribological properties than those based on traditional carbides or nitrides. Furthermore, a titanium carbide/titanium nitride (TiC/TiN) multilayer is a very interesting material, because it combines the high degree of hardness and the low friction coefficient of TiC with the high degree of wear resistance of TiN [12-16]. This unusual combination of properties makes the TiC/TiN multilayer a material with great chemical stability and excellent mechanical properties, such as extreme hardness, a low friction coefficient, a high melting point, high electrical conductivity and a high degree of wear resistance [17-23].

Due to this combination of properties, hard coatings based on a TiC/TiN multilayer improve the performance of high-speed cutting tools, since the high thermal conductivity of the new compound reduces thermal gradients and reduces stress cracks as a result of thermal shock in the tools [14,25], whereby the high-speed cutting tools have a longer lifespan [23,26]. Finally, we haven't found any scientific publications that compare the properties of these multilayers. For this reason, the main objective of this paper is do a comparative study of the structural and electronic properties of TiN/CN and TiC/TiN multilayers using calculations based on density functional theory.

2. Computational method

Calculations were performed within the framework of density functional theory (DFT) and using the full potential augmented plane wave (FP-LAPW) method implemented in the Wien2k package [27]. The correlation and exchange effects of electrons were dealt with using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [28]. In the LAPW method, the cell is divided into two types of regions, atomic spheres centered at nuclear sites and the interstitial region between the non-overlapping spheres. Within the atomic spheres, wave functions are linear combinations of products of radial and spherical harmonic functions, while in the interstitial region, the function expands as a linear combination of plane waves. The charge density and potentials are expanded in spherical harmonics up to $l_{max} = 10$ within the atomic spheres, and the wave function in the interstitial region is expanded in plane waves with a cutoff parameter of $R_{mt}K_{max} = 8$, where R_{mt} is the smallest radius of the atomic sphere in the unit cell and K_{max} limits the kinetic energy $\hbar^2 k^2 / 2m$ of the plane waves, where $|k| \leq k_{max}$. To ensure convergence in the integration of the first Brillouin zone, 54 points were used at the irreducible first Brillouin zone. The integrals over the Brillouin zone were solved using special Monkhorst-Pack alignment points [29]. Self-consistency was achieved by requiring that the convergence of the total energy be less than 10^{-4} Ry. For expanding the potential in the interstitial region, $G_{max} = 12$ was considered. Muffin-tin radii were 1.60 for N, 1.95 for Ti, and 1.60 bohr for C. Calculations were performed taking into account the spin polarization, in order to check possible magnetic properties of the compounds.

For the lattice constant, the minimum volume, the bulk modulus, and the cohesive energy of each structure studied, the calculated data were fit to the Murnaghan equation of state, Eq. (1)

$$E(V) = E(V) + \frac{B_0 V}{B_0'} \left[\frac{(V_0/v)}{B_0' - 1} + 1 \right] - \frac{B_0 V_0}{B_0' - 1} \qquad (1)$$

where B_0 is the bulk modulus, its first derivative is B'_0, V_0 is equilibrium volume of the cell, and E_0 is the cohesive energy.

In order to verify the thermodynamic stability of the

TiC/TiN and TiN/CN multilayers, with a concentration 50-50, we calculated the energy of formation of the multilayer in the rock salt structure. The energy of formation of a ternary (LMN) compound is defined as the difference between the total energy of the ternary $L_{1-x}M_xN$ phase and the total energy of the binary compounds in the ground states of LN and MN, E_{LN}^{fase} and E_{MN}^{fase} respectively; therefore, the energy of formation is given by Eq. (2) [30],

$$E_f = E_{L_{1-x}M_xN}^{fase} - (1-x)E_{LM}^{fase} - xE_{MN}^{fase} \qquad (2)$$

3. Results

3.1. Structural properties

We first optimized the structural parameters of the binary compounds TiN, TiC, and CN, because these parameters were used to model the TiN/CN and TiC/TiN multilayers. CN has two stable crystalline structures, one hexagonal-type graphite and the other cubical [31]. The lattice constant a, the bulk modulus (B_0), and the minimum energy (E_0) of the binary compounds are shown in Table 1, together with experimental and theoretical values reported by other authors. Note that the lattice constant and the bulk modulus B_0 calculated in this study agree well with the experimental values, which shows the reliability of the DFT-based computations.

Furthermore, it was found that both the TiN/CN multilayer modeled in the NaCl phase by inserting a layer of TiN and a layer of CN along the z axis as the TiC/TiN multilayer crystallize in a tetragonal structure with space

Table 1.
Lattice constant a and bulk modulus B_0 for the binary compounds, along with experimental and theoretical values, included for comparison. Also shown is the cohesion energy E_0.

	Parameter	This word	Exp.	Theoretical other works	E₀ (eV)
TiN	a (Å)	4.26	4.24[a]	4.249[b], 4.32[c]	- 14.55
	B_0 (GPa)	277.2	288[d], 320[a]	297[c], 317[f, g]	
TiC	a (Å)	4.336	4.33[a, e]	4.249[b], 4.32[c]	- 15.50
	B_0 (GPa)	250	252[h], 240[a]	267[c]	
CN cubic	a (Å)	3.620	-	-	- 8.43
	B_0 (GPa)	293.2	-	-	
CN graphite	a (Å)	6.542	6,44[i]	-	- 7.51
	B_0 (GPa)	412.3	-	427[j]	

Source: The Authors

[a] Reference [32]
[b] Reference [33]
[c] Reference [34]
[d] Reference [35]
[e] Reference [36]
[f] Reference [37]
[g] Reference [38]
[h] Reference [39]
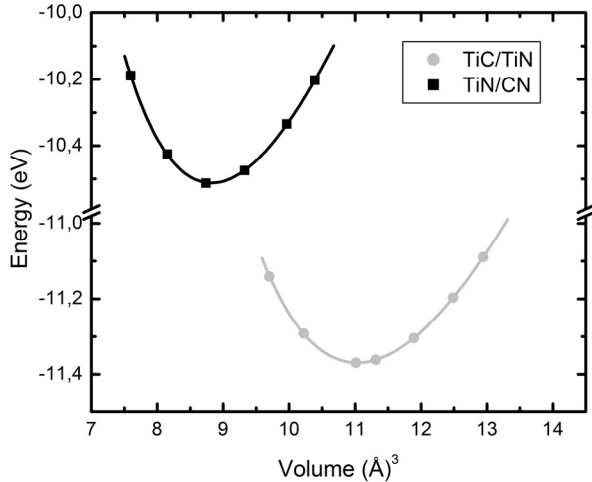[i] Reference [40]
[j] Reference [41]

Figure 1. Total energy as a function of volume and adjusted to the Murnaghan equation of state for the TiN/CN multilayer (black curve) and the TiC/TiN multilayer (gray curve). Energies and volumes are given by number of atoms in the cell.
Source: The Authors

Table 2.
Lattice constant *a* and bulk modulus B_0 for the binary compounds, along with experimental and theoretical values, included for comparison. Also are shown the values *c/a* and the cohesion energy E_0.

	Parameter	This Word	Other works	c/a	E_0 (eV)
TiC/TiN	*a* (Å)	4.343	4.30[k], 4.27[l]	1.412	- 11.37
	B_0(GPa)	269.7	283[k], 325[l]		
TiN/CN	*a* (Å)	2.923	-	1.413	- 10.51
	B_0(GPa)	236.8	-		

Source: The Authors

[k] Reference [42]
[l] Reference [43]

group 123 (P4=mmm). Fig. 1 shows the total energy curves as a function of volume and fitted to the Murnaghan equation of state (Eq. 1) for the TiN/CN multilayer (black curve) and the TiC/TiN multilayer (gray curve).

We have taken as zero the sum of the energies of neutral atoms of isolated Ti, C, and N. Therefore, the absolute value of the minimum energy of each curve is the cohesive energy of the TiN/CN and TiC/TiN multilayers in the NaCl phase. Fig. 1 shows that each structure is considered metastable, since there is a minimum of energy in the corresponding curve. The lattice constant, the bulk modulus (B_0), and the minimum energy (E_0) of the TiN/CN and TiC/TiN multilayers calculated in the NaCl structure are shown in Table 2.

We note that the lattice constants calculated in this paper are in good agreement with the experimental and theoretical results reported by other authors. Additionally, we see that the values of the volume modules of the TiN/CN and TiC/TiN multilayers are quite high, confirming the hardness of these materials and making them ideal candidates for hard coatings on high-speed cutting tools and devices that must operate at a high degree of power and at high temperatures.

Table 3.
Energy of formation

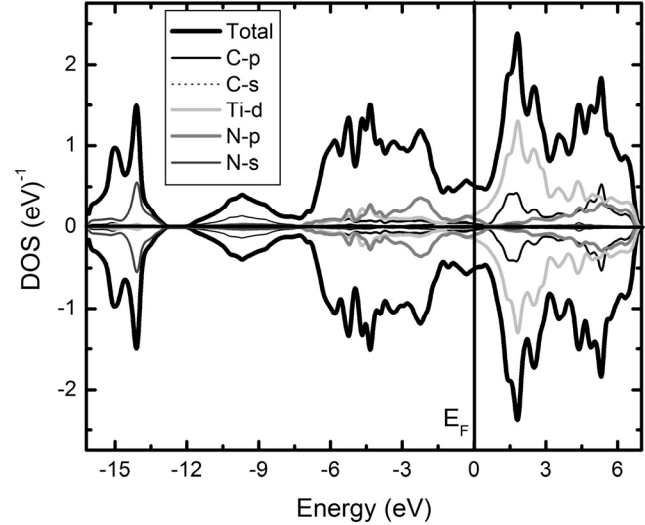| Multilayer	E_0 (eV)	E_f (eV)
TiC/TiN	- 11.37	3.69
TiN/CN	- 10.51	5.22

Source: The Authors

Figure 2. Total density of states (TDOS) and partial density of states (PDOS) of the TiN/CN multilayer in the NaCl phase at the equilibrium volume.
Source: The Authors

As a next step, we calculated the formation energy _E_f of the TiC/TiN and TiN/CN multilayers, with a 50-50concentration, that is, *x* = 50% TiC molecules, *x* = 50% TiN molecules, and x = 50% NC molecules. For this, we calculated the cohesive energy of the binary compounds TiC, TiN, and CN in their ground states, $E_{TiN}^{NaCl} = -14.63\ eV$, $E_{TiC}^{NaCl} = -15.50\ eV$, and $E_{CN}^{NaCl} = -15.97\ eV$. Table 3 shows the values of the energy of formation that we calculated using Eq. (2)

The energy of formation of the TiC/TiN and TiN/CN multilayers was calculated to be 3.69 and 5.22 eV, respectively. Because these values are positive as compared with the reference state for both multilayers, these TiC/TiN and TiN/CN multilayers are thermodynamically unstable, i.e. they cannot be formed under equilibrium conditions. Therefore, only when kinetic constrains prevent the system from reaching the equilibrium state, as found e.g. in plasma-induced physical and chemical vapor deposition (PVD and PCVD) at relatively low temperatures, can the metastable phase of TiC/TiN and TiN/CN multilayers in the rock salt structure be obtained, similar to the result predicted by Zhang and Veprek [30] for the ternary $Ti_{0,5}Al_{0,5}N$ phase.

3.2. Electronic Properties

The total density of states (TDOS) and partial density of states (PDOS) for TiN/CN and TiC/TiN multilayers in the NaCl phase are shown in Figs. 2 and 3, respectively.
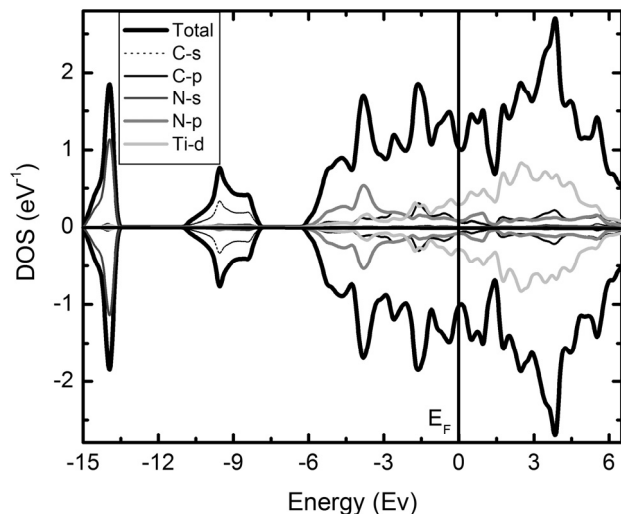
Figure 3. Total density of states (TDOS) and partial density of states (PDOS) of the TiC/TiN multilayer in the NaCl phase at the equilibrium volume.
Source: The Authors

It can be observed that both TiC/TiN and TiN/CN multilayers exhibit a metallic behavior, determined by the Ti-*d*, C-*p*, and N-*p* hybrid states that cross the Fermi level. Moreover, according to the theory proposed by Jhi et al. [44], the highly directional coupling between metal *d* and non-metal *p* electrons results in covalent bonding, and this bonding makes a positive contribution to the hardness, which is responsible for the high degree of hardness of the TiC/CN and TiC/TiN multilayers. A similar result was found by Restrepo, Parra et al. [45] in their study of TIN and TiC. Additionally, it can be seen that the DOS of the TiC/CN multilayer at the Fermi level, mainly dominated by Ti-*d* states, is smaller than total density of states when compared with TiC/TiN. This may be caused by the metallic *d–d* interactions, which make a negative contribution to the bulk modulus [44]. This might be the cause of the low degree of hardness of TiN/CN [43]. Similar behavior was reported for the binary compounds TiC and TiN [46], and NbC and NbN [47].

For the total density of states of the TiN/CN multilayer, it can be observed that the valence band is divided into two regions. The first one, between ~ - 16.0 eV and ~ -13.0 eV, is mainly governed by the N-s states, with a small contribution from C-s states. The region between ~ -11.6 eV and the Fermi level is in great part composed of the N-p states, with a small contribution of Ti-d and C-p electrons. Between ~ -13.0 eV and ~ -11.6 eV, an intraband gap of ~ -1.4 eV is present. The multilayer does not exhibit magnetic properties, because the total density of spin up is fully offset by the total density of spin down.

In the total density of states of the multilayer it can be observed that valence band is divided into three regions. The first, between ~ -15.0 eV and -13.0 eV, is mainly governed by the N-s states, with a small contribution from C-s states. The region between ~ -10.8 eV and ~ -7.7 eV is mainly dominated by C-s states, with a small contribution of N-p electrons. The region between ~ -6.3 eV and the Fermi level is governed by the Ti-*d*, C-*p*, and N-*p* states. The TiCN compound has two

intraband gaps, one in the region between ~-13.0 eV and ~ -10.8 eV and the other in the region between ~ -7.7 eV and ~ -6.3 eV, with widths of ~ -2.2 eV and ~ -1.4 eV, respectively. As before, the multilayer does not exhibit magnetic properties, because the total density of spin up is fully offset by the total density of spin down.

Conclusions

We reported first-principles calculations to determine the structural and electronic properties of TiN/CN and TiC/TiN multilayers and carried out a comparative study of them. The calculated lattice constants are in good agreement with experimental data. The calculated values of bulk modulus are quite high, which means that these materials are very rigid. This property is due to the strong covalent bonds that exist between the metallic Ti-*d* and the nonmetallic C-*p* and N-*p* states. This confirms that these materials exhibit a high degree of hardness, which makes them attractive for potential applications at high temperature and for hard coatings. However, we found that the bulk modulus of the TiC/TiN multilayer was larger than that of the TiN/CN multilayer.

From the density of states it was found that the compounds exhibit metallic behavior, because of the Ti-*d*, C-*p*, and N-*p* hybrid orbitals traversing the Fermi level.

Acknowledgements

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