

# Cobalt layers crystallized on the WC(100) surface: Spin-polarized *ab initio* study

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## ABSTRACT

*Ab initio* methods of the density functional theory and pseudopotentials were used for studying the structure, electronic states, binding energy and separation energy of Co layers on the WC(100) surface. It has been found that the first monolayer repeats the geometry of the WC(100) surface with the same value of the lattice constant. Comparison of three cases – A) Co atoms are above C atoms; B) Co atoms are above W atoms; C) Co atoms are above the symmetry centers between WC pairs – shows that the A case is an energetically preferable one. The second Co monolayer also repeats the *fcc*-cubic WC geometry, however the distance between the first and second Co layers is less than the distance between planes in the WC cubic crystal. All Co layers are ferromagnetic ones with magnetic moments of 0.87–2.41  $\mu_B$  dependently on the case. The density of states (DOS) for the WC/Co system looks like the superposition of those for bulk *fcc*-WC and free Co layers.

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## 1. Introduction

The hard alloys based on tungsten carbide with cobalt cement interlayers are widely used as a material for cutting tools. Studying of atomic structure and energetics of the WC/Co interface is very important for understanding of properties of hard alloys especially for the cases when the sizes of WC crystallites aspire to 50–100 nm and the thickness of Co interlayers falls to 1–2 nm. It is known [1–4] that the smallest observed, 300–500 nm particles might have trigonal or cubic shapes with very sharp WC/Co interfaces: not larger than 1–2 nm. Quantitative analysis of the WC/Co interface for the *hex*-WC crystal boundaries was performed in some works [3,5–9], however there is a lack of information on the structure of the Co boundary with the *fcc*-cubic WC. The problem is strengthened by the fact that recent *ab initio* calculations [10] show that the atomic structure of small trigonal nanoparticles has much in common with structure of cubic particles. Namely, boundaries of the both types of particles contain W and C atoms in the same manner as NaCl(100) surface. Therefore, the present work is devoted for studying of the Co/WC(100) interface structure and energetics, using *ab initio* methods of quantum-mechanics simulation.

## 2. Methods and approaches

In this work, I used the same approach as in my previous paper [10]: namely, the density functional theory (DFT) [11,12] in the generalized gradient approximation (GGA) [13], the pseudopotential method [14] and the plane wave basis set. Because of cobalt magnetic

nature, I have used the spin-polarized version of DFT realized within the FHI96md package [15].

I used the same pseudopotentials for carbon and tungsten as in Ref. [10]. They were generated through the FHI98PP package [16] and were tested to describe lattice constants and bulk elastic modules for WC, the both hexagonal and cubic. For cobalt, I have constructed the pseudopotential with the following parameters:  $r_s = 2.18$ ,  $r_p = 2.92$ ,  $r_d = 2.18$ , and  $r_{core} = 1.0$ . Here  $r_s$ ,  $r_p$ , and  $r_d$  are the cutoff radii for *s*-, *p*-, and *d*-components and  $r_{core}$  is the radius of the nonlinear core-valence correction. All values are given in atomic units (a.u. = 0.0529 nm). The Co pseudopotential calculated in the scheme of Troullier–Martins [17], was checked for absence of ‘ghost’ states and was used for determining the equilibrium lattice parameter  $a_0$ , magnetic moment  $M$  and the bulk elastic modulus  $B$  of bulk *fcc*-Co. The values of  $a_0$  and  $B$  were found by using the Murnaghan’s equation [18], which shows the total energy  $E_{tot}(V)$  as a function of the cell volume  $V$  ( $V = a^3/4$ ):

$$E_{tot}(V) = E_{tot}(V_0) + \frac{BV}{B'(B'-1)} \left[ B' \left( 1 - \frac{V_0}{V} \right) + \left( \frac{V_0}{V} \right)^{B'} - 1 \right],$$

where  $V_0$  is the equilibrium value of  $V$ , and  $B'$  is the derivative of  $B$  on pressure.

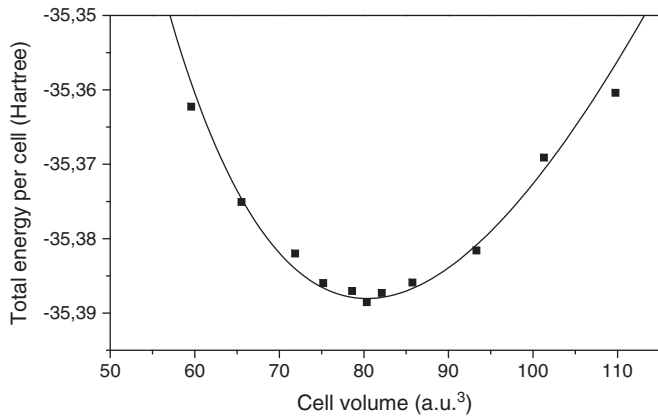
The calculated values of  $E_{tot}(V)$  are plotted in Fig. 1.

Calculated equilibrium values ( $a_0 = 0.362$  nm,  $B = 205$  GPa, and  $M = 1.65 \mu_B$ ) are close to experimental ones [19] (0.354 nm, 191 GPa, and  $1.72 \mu_B$ ). For these calculations I used 18 *k*-points of the Brillouin zone ( $\Gamma$ -point (0, 0, 0) with the  $3 \times 3 \times 3$  Monkhorst–Pack scheme [20]) and the energy cutoff of 50 Ry.

To investigate Co layers on the WC(100) surface I used a periodic WC slab contained seven WC layers with two WC pairs in the each layer (Fig. 2). The planar periodicity of the slab corresponded to the

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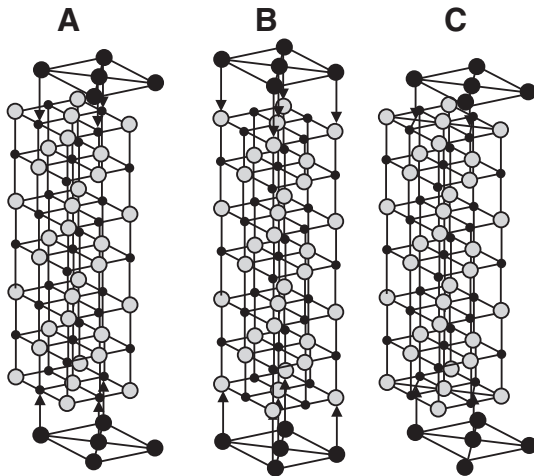
**Fig. 1.** Total energy  $E_{tot}(V)$  of *fcc*-cobalt as a function of the cell volume  $V$ . Black quadrates are calculated points; the solid curve is obtained following the Murnaghan's equation. Atomic units for energy are equal to Hartree (27.2 eV).

equilibrium *fcc*-WC lattice calculated previously with the  $a_0 = 0.439$  nm [10]. To eliminate possible artificial asymmetric effects, cobalt layers were placed simultaneously on the both surfaces of the slab. The vacuum space between slabs has been established, approximately 1 nm. In the majority of cases the WC-Co calculations were implemented with the  $k$ -points number of nine (the  $3 \times 3 \times 1$  Monkhorst-Pack scheme) and with the energy cutoff of 50 Ry, but in special tests the number of  $k$ -points has been increased up to 27. The special tests included studying of dependence of results on the slab thickness and on the energy cutoff. The self-consistence convergence was provided by stabilizing the total energy with an accuracy of 0.005 eV per atom. Electron densities of states were represented by superpositions of the Gaussian functions centered on each electron level.

### 3. Results and discussions

#### 3.1. Clean WC(100) surface

Because the cubic WC phase is unstable at room temperatures there are only few theoretical works devoted to studying its properties. Price and Cooper [21] have calculated the equilibrium lattice constant, the bulk modulus, and the bulk density of states; Hugosson et al. [22] have reported the calculated surface energy and the work function for the WC(100) surface; Vines et al. [23] have discussed the reasons of instability of cubic WC; Ilyasov et al. [24]



**Fig. 2.** Atomic scheme of WC slab with WC(100) surfaces. A, B, and C are different configurations in which atoms of the first Co monolayer were placed (as arrows show). Gray circles are W atoms, small black ones are C atoms, and large black circles represent Co atoms.

have modeled the WC-Fe-Ni hard materials based on cubic WC; Christensen et al. [25] have used cubic WC as a model to study the interaction of WC with cobalt. For my knowledge, there is no detailed information on the atomic structure (relaxation effects) and electronic states of the WC(100) surface. Therefore, my first task was to study the clean WC(100) surface. For this purpose I used the WC slab shown in Fig. 2. In this study as well as in all others only two WC layers (surface and undersurface) were relaxed but internal layers were kept in their bulk positions.

Calculations have shown that surface and undersurface atoms moved from their bulk positions. Namely, carbon atoms moved outward, while tungsten atoms moved inward. Vines et al. [23] observed the same behavior of the (100) surface in the case of cubic carbides of some transition metals (MeC) and reported the values of the vertical Me-C separations ( $d_1 = 0.009$ – $0.025$  nm for the surface layer and  $d_2 = 0.004$ – $0.08$  nm for the undersurface layer, dependently on metal kind), however, they did not provide such calculations for cubic WC. My calculations give  $d_1 = 0.030$  nm and  $d_2 = 0.006$  nm.

Comparing the total energies of bulk crystal WC ( $E_{\text{bulk}}$ ) and of the WC slab ( $E_{\text{slab}}$ ) it is possible to find surface energy  $E_{\text{surf}}$ :

$$E_{\text{surf}} = \frac{(E_{\text{slab}}(N) - E_{\text{bulk}}(N))}{2 \cdot S},$$

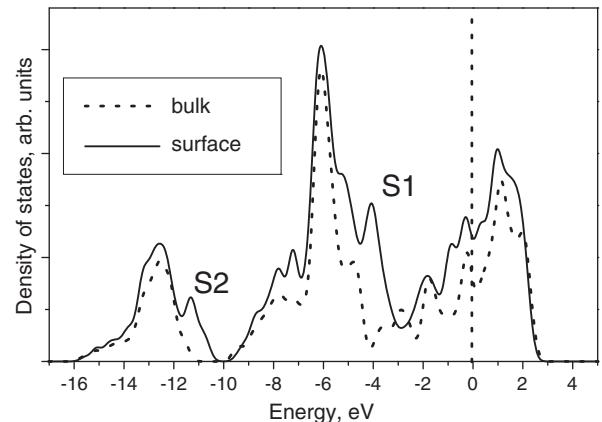
where  $N$  symbolizes that  $E_{\text{bulk}}$  and  $E_{\text{slab}}$  correspond to the same number  $N$  of WC pairs,  $S$  is the one-side surface square of the slab.

My calculations give the WC(100) surface energy of  $2.14$  J/m<sup>2</sup>. Known reported values are  $2.64$  J/m<sup>2</sup> for relaxed surface [22] and  $1.6$  J/m<sup>2</sup> for unrelaxed [26].

Besides, I have calculated the density of electronic states (DOS) for the slab and have plotted them in Fig. 3 in comparison with the bulk data. Because the thin structure of calculated DOS depends on the size of used cell and on the number of  $k$ -points, the bulk DOS calculations were performed here by using the same cell and  $k$ -points as in the slab calculations. One can see that DOS for the slab differs from DOS for the bulk crystal mainly by two surface peaks: namely, S1 and S2 at  $-4$  eV and  $-11$  eV under the Fermi level.

#### 3.2. Layers of cobalt on WC(100) surface

Energetics and electronic states of the WC(100)/Co interface was studied by Christensen et al. [6], however they ignored ferromagnetic properties of cobalt and considered only layered WC/Co systems without free surfaces. In present work I take into account spin-polarization effects and study one-monolayer and two-monolayer films in contact with free WC(100) surface. I believe that my results



**Fig. 3.** Densities of states for the tungsten carbide slab with the (100) surface and for the bulk cubic WC. Vertical dotted line shows the Fermi level.

will be useful for understanding of crystallization processes in nanostructured WC/Co alloys.

Like Christensen et al. [6] I considered the Co/WC(100) interface as a hetero epitaxial boundary between two *fcc*-structures. As the *fcc*-WC lattice constant is larger than the cobalt lattice constant, the cobalt layers must be stretched to obtain coherent periodic structures. For the one-monolayer film I have studied three configurations (see Fig. 2): A) Co atoms are above C atoms; B) Co atoms are above W atoms; C) Co atoms are above the symmetry centers between WC pairs. Atoms of the second monolayer were placed above the first one in accordance with the *fcc*-symmetry. However, calculations show that the equilibrium distance between the first and second Co layers is less than the distance between planes in the WC and Co cubic crystals. Namely, these distances are equal to 0.107 nm, 0.075 nm, and 0.111 nm for the A, B, and C cases, respectively. For comparison, they are 0.220 nm for WC and 0.181 nm for Co.

For the energetic characterization of the Co/WC system I calculated the binding energy  $E_{\text{bind}}$  and the separation energy  $E_{\text{sep}}$ :

$$E_{\text{bind}}(\text{in total}) = (E_{\text{tot}} - E_{\text{slab}} - n \cdot E_{\text{Co1}}) / n,$$

$$E_{\text{bind}}(\text{in layer}) = (E_{\text{film}} - n \cdot E_{\text{Co1}}) / n$$

$$E_{\text{sep}} = (E_{\text{tot}} - E_{\text{slab}} - E_{\text{film}}) / 2S,$$

where  $n$  is the number of Co atoms,  $E_{\text{tot}}$ ,  $E_{\text{slab}}$ ,  $E_{\text{Co1}}$ , and  $E_{\text{film}}$  are respectively energies for the Co/WC system, the WC slab, one free Co atom, and the unsupported cobalt film with the geometry corresponding to the relaxed cobalt film on the WC surface.

Calculated values of energies  $E_{\text{bind}}$ ,  $E_{\text{sep}}$ , and the magnetic moment  $M$ , as well as the distance  $d$  between a Co atom and a nearest atom of the WC surface, are listed in Table 1. From these data it is clear that epitaxial layers of cobalt with atoms positioned above carbon atoms are preferable energetically. The Co binding energies,  $E_{\text{bind}}$  (in total) and  $E_{\text{bind}}$  (in layer), grow when going from 1 to 2 ML, while the separation energy ( $E_{\text{sep}}$ ) decreases. The reason of decreasing of the separation energy is as follows: with the advent of the second monolayer the bonding abilities of atoms of the first monolayer become partially switched from atoms of a substrate to atoms of the second layer. This explanation proves to be true that  $E_{\text{bind}}$ (in layer) increases faster than  $E_{\text{bind}}$ (in total). It is remarkable that the results for the separation energy and cobalt-surface distances obtained in the spin-polarization approach are rather close to corresponding spin-restricted data [6]. It means that spin-restricted calculations can give us a correct enough information about WC/Co systems.

The density of electronic states (DOS) for the 1 ML cobalt film with Co atoms placed above C atoms is plotted in Fig. 4. As it is shown in this Figure, the shape of this DOS may be obtained in the whole as a sum of DOSes for bulk *fcc*-WC and Co layer. The main distinction consists in the sharp peak lying at 1.7 eV below the Fermi level. This peak has the same position as the position of a corresponding peak in

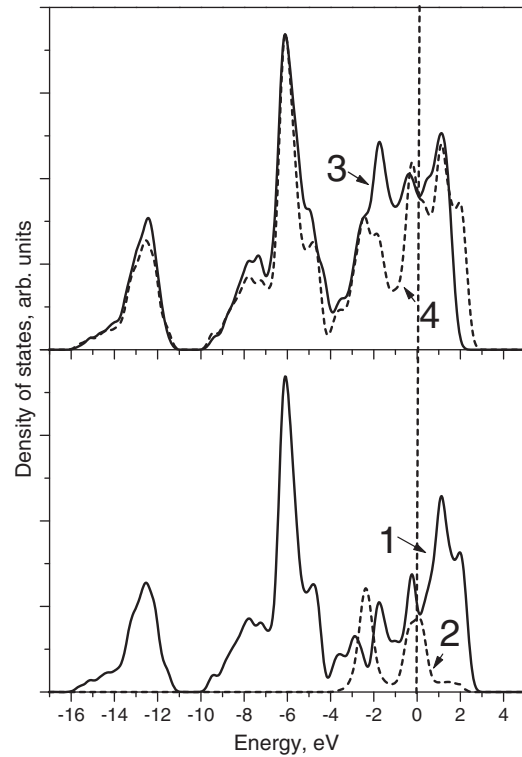


Fig. 4. Density of states for 1 ML Co layer with Co atoms above C atoms. 1) bulk *fcc*-WC; 2) free Co layer; 3) Co layer on WC(100) slab; 4) WC(100) slab + free Co layer. Vertical dotted line represents the Fermi level.

the bulk states but its intensity is larger. The 2 ML DOS looks like the 1 ML one, and is not presented here.

#### 4. Conclusions

Quantum-mechanics calculations show that epitaxial layers of cobalt with atoms positioned above carbon atoms are preferable energetically. The second Co monolayer repeats the *fcc* geometry, however the distance between the first and second Co layers is less than the distance between planes in the WC and Co cubic crystals. The binding energy grows while the separation energy decreases, when going from 1 ML to 2 ML of cobalt covering. The density of states for the WC/Co system looks like the superposition of DOSes for bulk *fcc*-WC and Co layers. All Co layers are ferromagnetic ones, however, the magnetization does not influence essentially on their energies and geometries.

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Table 1

The binding  $E_{\text{bind}}$  (in total and in layer) and separation  $E_{\text{sep}}$  energies, the magnetic moment  $M$  and the distance  $d$  from a Co atom and a surface atom, calculated for 1 ML and 2 ML Co film on the WC(100) surface. The data of Ref. [6] are shown in parentheses.

		Interface configurations		
		A	B	C
$E_{\text{bind}}$ , eV	1 ML	4.05	3.04	3.69
	(in total)	2 ML 4.54	3.95	4.30
$E_{\text{bind}}$ , eV	1 ML	1.53	2.13	1.62
	(in layer)	2 ML 3.45	3.40	3.44
$E_{\text{sep}}$ , J/m <sup>2</sup>	1 ML	4.18 (4.50)	1.52 (1.58)	3.43
	2 ML	3.61	1.82	2.89
$d$ , nm	1 ML	0.184 <sub>Co-C</sub> (0.180)	0.235 <sub>Co-W</sub> (0.237)	0.202 <sub>Co-C</sub> ; 0.250 <sub>Co-W</sub>
	2 ML	0.185 <sub>Co-C</sub>	0.233 <sub>Co-W</sub>	0.202 <sub>Co-C</sub> ; 0.251 <sub>Co-W</sub>
$M$ , $\mu_B$	1 ML	1.37	1.55	0.87
	2 ML	2.14	2.25	2.41

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