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First principle simulation of the Co layers behavior on a surface of hexagonal tungsten carbide

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Abstract

First principle calculations were performed for studying the structure, binding and separation energy of cobalt layers on the surfaces of hexagonal tungsten carbide WC – (0001), $(10\bar{1}0)$ and $(1\bar{2}10)$. It has been shown that Co layers with atom positions above the WC surface in accordance with the geometry of hexagonal lattice are preferable energetically. The binding and separation energies behavior at the transition from one- to two monolayer cobalt coverage depends strongly on the surface type. Comparison with the results of investigation of Co layers on the face centered cubic WC surface is also presented.

Keywords: first principles calculation; tungsten carbide; cobalt layers

1. Introduction

Owning to its high melting point and hardness, tungsten carbide (WC) is the most important material in industrial machinery as cutting tools and abrasives. The cobalt Co bonded WC is one of the most popular systems for cement carbides. Nanopowder of WC with grain sizes less than 100 nm has been the subject of active research in last years [1,2], due to the significant roles of grain-size reduction played in the enhancements of mechanical properties of WC-Co hard alloys. Studies of atomic structure and energetic characteristics of the WC/Co interface are very important for understanding of properties of hard alloys.

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Quantitative analysis of the WC/Co interface for the hexagonal tungsten carbide (hex-WC) was performed by Christensen *at al.* in series of works [3–5]. Study of Co layers on face centered cubic WC(100) surface was presented recently [6], but the complex investigation of Co monolayers behavior on hex-WC surface has not been performed up to date.

2. Methods and approach

Computer simulation package ABINIT [7] based on the density functional theory (DFT) [8,9] combined with the pseudopotential method was used in present work. Because of cobalt magnetic nature, all calculations were performed with taking into account spin-polarization. The pseudopotentials were generated by using the FHI98PP package [10] and were tested to describe lattice constants and bulk elastic modules for hexagonal WC and Co. The cutoff energy of 60 Ry was used in all calculations.

To investigate Co layers on the different hex-WC surfaces a periodic WC slabs were used, cobalt layers were placed simultaneously on both surfaces of the slab. The vacuum space between slabs has been established for at least 10 Å. For performing a WC/Co slab calculations the $6 \times 6 \times 1$ Monkhorst-Pack scheme was used for k-point set.

3. Results and discussions

The hexagonal WC structure is presented on Fig.1. At first the surface energies (E_{surf}) of clean WC surfaces was calculated. WC($1\,\bar{2}\,10$) surface contains both types of atoms (W and C) and E_{surf} is defined with the standard technique. Since the stoichiometric WC(0001) slab has two different surfaces–one C-terminated, and one W-terminated, for a non-stoichiometric model with identical surface the following approach [11] was used. The energy of WC($10\,\bar{1}\,0$) surfaces cannot be calculated using the standard slab model due to WC lattice has no mirror plane along this direction and we can get only estimated E_{surf} values for our case.

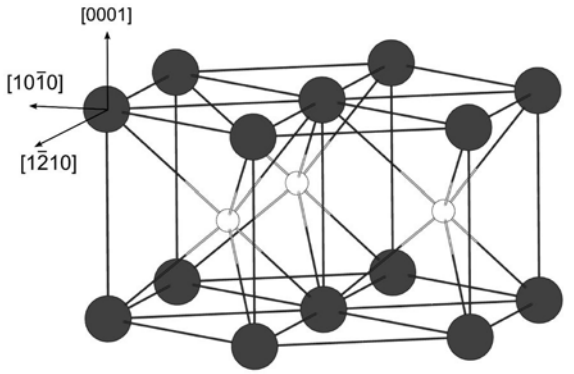

Fig. 1. Structure of hexagonal WC (W atoms are dark, C atoms – white).

Surface energies are presented in Table 1. They are in good agreement with a similar *ab initio* calculations. One can see that the most energetically preferable surface is a WC($10\,\bar{1}\,0$)-I, and the W-terminated surfaces are more stable compared with the C-terminated. Therefore for the investigation of Co layers on hex-WC surfaces we take into account only the WC($1\,\bar{2}\,10$) surface with a mixed spacing of W and C atoms in surface layer and W-terminated WC($10\,\bar{1}\,0$) and WC(0001) surfaces.

Table 1. Surface energy (in J/m^2) for different orientations and termination of surface (W or C)

	WC(0001)	WC(10 $\bar{1}$ 0)	WC(1 $\bar{2}$ 10)
W-terminated	3.8	type I – 3.0 type II – 5.8	3.7
C-terminated	5.6	type I – 3.8 type II – 7.4	

The WC/Co interface was considered as the area between the two structures with a hexagonal type of crystal lattice which has the same orientation. Due to significant differences in lattice parameters of Co and WC hexagonal lattice, Co layers deformation takes place for receiving coherent periodic structure. For the one-monolayer coverage three configurations were studied, one corresponds to the Co atoms positioned above W atoms, and the other two correspond to Co atoms situated above the interstitial position of WC surface. Atoms of the second monolayer were placed above the first one in accordance with the symmetry of hex-Co geometry.

For the energetic characterization of the WC/Co system the binding energy E_{bind}, the separation energy E_{sep} and the binding energy in free cobalt film $E_{bind(Co)}$ are calculated as:

$$E_{bind} = (E_{slab} + n \cdot E_{Co1} - E_{WC/Co})/n \quad (1)$$

$$E_{sep} = (E_{slab} + E_{film} - E_{WC/Co})/2S \quad (2)$$

$$E_{bind(Co)} = (n \cdot E_{Co1} - E_{film})/n \quad (3)$$

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

Table 2. Energetic characteristics for one and two monolayers of cobalt coverage. 1, 2, 3 – different positions of the Co atoms above WC surface, 3* - case corresponding to the Co atom positions above the W atoms.

			1	2	3*
WC(0001)	E_{bind} (eV)	1 ML	4.89	4.99	4.18
		2 ML	4.63	4.69	4.24
	E_{sep} (J/m^2)	1 ML	3.95	4.17	2.41
		2 ML	8.53	8.78	6.85
	$E_{bind(Co)}$ (eV)	1 ML		3.07	
		2 ML		2.67	
WC(10 $\bar{1}$ 0)	E_{bind} (eV)	1 ML	4.54	5.30	3.96
		2 ML	4.50	4.97	4.10
	E_{sep} (J/m^2)	1 ML	3.00	4.48	1.87
		2 ML	7.20	9.02	5.67
	$E_{bind(Co)}$ (eV)	1 ML		2.99	
		2 ML		2.64	
WC(1 $\bar{2}$ 10)	E_{bind} (eV)	1 ML	4.70	4.48	-
		2 ML	4.53	4.36	-
	E_{sep} (J/m^2)	1 ML	6.13	5.63	-
		2 ML	3.61	2.84	-
	$E_{bind(Co)}$ (eV)	1 ML		1.96	
		2 ML		3.73	

Results of calculations are presented in table 2. From these data it is clear that Co layers with atoms positioned above W atoms are not preferable energetically, for a WC($1\bar{2}10$) surface there are no stable positions for the Co atoms to place above the W atoms. Comparing results obtained for the face centered cubic (100) surface [6] with ours we have the following conclusions. The binding energies of the cobalt layers with a hexagonal WC are in the range of 4-5 eV depending on the type of surface and location of cobalt atoms, while for the *fcc*-(100) surface this range is 3-4 eV.

Behaviors of binding and separation energies at the transition from 1 to 2 cobalt monolayer are different. The binding energy is reduced by a value from 0.1 to 0.3 eV, with the exception of the configuration with the cobalt atoms located over tungsten atoms. The separation energy values are also higher than the values obtained for the *fcc*-(001) surface. Its value increases by 2-3 times at the second cobalt layer formation for (0001) and ($10\bar{1}0$) surfaces. And in the case of ($1\bar{2}10$) surface, the behavior of the 2-monolayer coverage is qualitatively comparable with results obtained for the face-centered cubic (100) surface, the separation energy is reduced due to the increasing of free cobalt film binding energy.

4. Conclusion

Quantum-mechanical calculations showed that the behavior of cobalt monolayers on the hexagonal tungsten carbide surface is different from the results obtained for the face-centered cubic WC(100) surface. Calculated values of the separation energy for the (0001) and ($10\bar{1}0$) W-terminated surfaces indicate that the bonding between the cobalt layers and the WC surface becomes much stronger at the second cobalt monolayer formation. For the surface ($1\bar{2}10$) with a mixed arrangement of carbon and tungsten atoms in the surface layer coverage of 2 monolayers is less stable, the separation energy decreases to values comparable with results obtained for the fcc-WC (100) surface.

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