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# The Effect of Vanadium-Carbon Monolayer on the Adsorption of Tungsten and Carbon Atoms on Tungsten-Carbide (0001) Surface

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*Abstract:*

*We report a first-principles calculations to study the effect of a vanadium-carbon (VC) monolayer on the adsorption process of tungsten (W) and carbon (C) atoms onto tungsten-carbide (WC) (0001) surface. The essential configuration for the study is a supercell of hexagonal WC with a (0001) surface.  When adding the VC monolayer, we employed the lowest energy configuration by examining various configurations. The total energy of the system is computed as a function of the W or C adatoms' height from the surface. The adsorption of a W and C adatom on a clean WC (0001) surface is compared with that of a W and C adatom on a WC (0001) surface with VC monolayer. The calculations show that the adsorption energy increased for both W and C adatoms in presence of the VC monolayer. Our results provide a fundamental understanding that can explain the experimentally observed phenomena of inhibited grain growth during sintering of WC or WC-Co powders in presence of VC.*

*Keywords: Sintering; Tungsten carbide; Vanadium carbide; Grain growth inhibition.*

## 1. Introduction

Hardness and strength are the two most important properties for materials for mechanical machining tools, such as ceramics, high speed steel etc. But the hardness in high speed steel is less and the strength of ceramics is not very high. Instead of these intrinsic disadvantages of metals and ceramics, generally metals have high strength and ceramics have high hardness. To develop novel materials consisting of both the advantages many kinds of metal-ceramic composites have been fabricated intensively, largely by the powder metallurgical method. WC-Co is one of those cermets, which has much attention because their hardness, strength and wear resistance are well balanced at high level. The mechanical

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properties of WC-Co compounds are known to be dependent on the grain size of the carbides. Materials with smaller grain size have high mechanical properties [1]. Since WC-Co consists of WC grains with Co rich phase in between [2, 3], in order to improve the mechanical properties of WC-Co compounds, we need to obtain the microstructure with smaller carbide grain size [4, 5]. Among the various transition metal carbides as additives to control the grain growth of WC, VC is the most effective dopant to reduce the grain growth of WC [6]. It is known that a few % of VC addition is sufficient to inhibit the grain growth efficiently, but the inhibition mechanism is not so far clear [6, 7].

In the present study, we investigate the inhibition mechanism from a quantum mechanical view, using density functional theory. Adsorption and desorption are two mechanisms of sintering. The objective of the present work is to study the W and C adatom adsorption/desorption process on a clean WC (0001) surface and on a WC (0001) surface covered with a monolayer of VC. The structure of WC is hexagonal in base, and the (0001) surface could be either W or C terminated surface. Since it is reported [8] that WC (0001) surface is either purely W terminated or W terminated with 30% of available hcp hollow sites occupied by additional carbon atoms, we feel it will be reasonable to consider only W terminated WC (0001) surface for a simple approach that can provide a fundamental mechanism of inhibited grain growth of WC in presence of VC.


## 2. Methods

The adsorption energy of a single adatom $E_{ads}$ at height z is given by

$$E_{ads}(z) = E_{tot}(z) - E_{tot}(\infty) \qquad (1)$$

Where $E_{tot}(z)$ is the total energy of the structure with the adatom adsorbed at height z on the surface and $E_{tot}(\infty)$ is the total energy of the same surface with the adatom at an infinite distance.

All *ab initio* total-energy calculations and geometry optimizations are performed within density functional theory (DFT) using Blöchl's all-electron projector augmented wave (PAW) method [9] as implemented by Kresse et al. [10]. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) of Perdew et al.[11]. The Kohn-Sham equations are solved using a preconditioned band-by-band conjugate-gradient (CG) minimization [12]. The plane-wave cutoff energy is set to 400 eV in all calculations. Ionic relaxations are performed until the root-mean-square (rms) force is less than 0.001 eV/Å. The Brillouin zone is sampled with a density equivalent to 54 k-points in (1×1) surface Brillouin zone using the Monkhorst-Pack scheme [13]. A Fermi-level smearing of 0.2 eV was applied using the Methfessel-Paxton method [14]. We use a standard supercell technique in modeling the WC (0001) surface with (3×2) surface unit cell and the height (along Z direction) consists of three W and two C substrate layers. The unit cell maintains the periodic boundary condition in all three dimensions, and contains 15 Å of vacuum along the height (Z). In order to mimic a bulk like structure in the middle of the substrate, atoms at the bottom layers (one W and one C substrate layers) are fixed at their bulk positions, while all other atoms are allowed to relax.


## 3. Results and Discussion

Tungsten carbide is related to hcp lattice with space group P6m2. From the full relaxation of lattice parameters, we found that a = 2.905 Å and c = 2.836 Å that are very close to the reported value of hexagonal WC (a = 2.906 Å, c = 2.837 Å) [15]. We also have found that the lattice parameter of VC in NaCl structure is 4.159 Å which is again very close to the reported value of 4.16 Å [16].

To prepare the foundation to study the adsorption of W and C atoms on top of the WC (0001) surface with VC monolayer, we construct three different models for vanadium carbide (VC) monolayer on top of the WC substrate. Fig. 1 shows the three different models we considered. We compare these three different models of VC on top of WC (0001) surface to determine the minimum energy configuration. The minimum energy configuration corresponds to the most sTab. structure of VC monolayer on top of WC (0001) surface. Model 1 (Fig. 1a) is constructed in such a way that all the V and C atoms lay on the same plane. The V and C atoms are alternatively arranged, such that it has the same structure of a (001) plane of VC in NaCl structure. In model 2 and 3 we place V and C atoms in separate planes. In model 2 (Fig. 1b), V atoms form the terminating surface while C atoms form the terminating surface for model 3 (Fig. 1c). Out of the three different models, we found that the model 1 is energetically the most favorable configuration. Tab. 1 shows the comparison of the three different models. Our study of adsorption process is continued with model 1 consists of VC monolayer on top of the WC (0001) surface.

**Tab. I**. Comparison of total energies of three models of vanadium-carbon on top of the tungsten-carbide (0001) surface. Total energies of Model 2 and 3 are given with reference to Model 1.

| Model 1 (eV) | Model 2 (eV) | Model 3 (eV) |
|---|---|---|
| 0.00 | 38.2129 | 99.1189 |



(a)                                        (b)                                        (c)
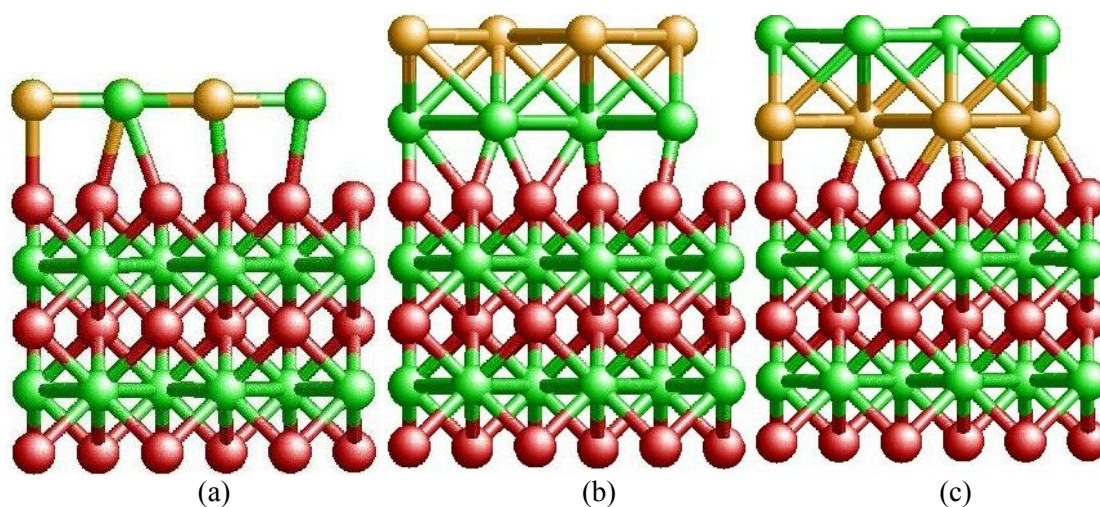
**Fig. 1.** (Color online) Three different models of vanadium-carbon (VC) monolayer on top of the tungsten-carbide. (Red spheres are tungsten (W) atoms, green spheres are carbon (C) atoms, and gold spheres are vanadium (V) atoms). In model 1 (a) V and C atoms lie on same plane. In model 2 (b) and model 3 (c) V and C atoms are staggered. In (b) the plane of V atoms is above that of the plane of C atoms, and in (c) the plane of C atoms is above that of the V atoms.

A schematic one dimensional energy landscape for adsorbed atom is shown in Fig.2a, in the vicinity of the W terminated WC surface. Far from the surface, the interaction of the adsorbed atom with the WC substrate is minimum and considered as the reference. The energy while the adsorbed atom is at the sTab. position near the surface is known as the adsorption energy ($E_{ads}$). The adsorbed atom must overcome the penetration energy barrier ($E_p$) in order to be located within the bulk site. Finally in order to diffuse within the bulk site, adsorbed atom needs to overcome the bulk diffusion energy barrier ($E_{mB}$). However, for the

reverse migration of the adsorbed atom from the bulk site to surface site, the required energy barrier is $(E_p\text{-}\chi)$. On the other hand, if an extra plane of atoms is placed on top of the host surface, the energy barrier for the adsorbed atom to penetrate the extra plane of atoms and adsorbed on the host surface is shown in Fig.2b. This energy barrier will be different depending on the nature of the interaction of adsorbed atom with the extra plane of atoms, as shown in the Fig.2b. In our previous study [17], we have shown that an extra plane of Fe atoms on W (100) surface introduces a small energy barrier of 0.53 eV, and the W adsorbed atom can easily penetrate that much of energy barrier and be adsorbed on the W (100) surface.
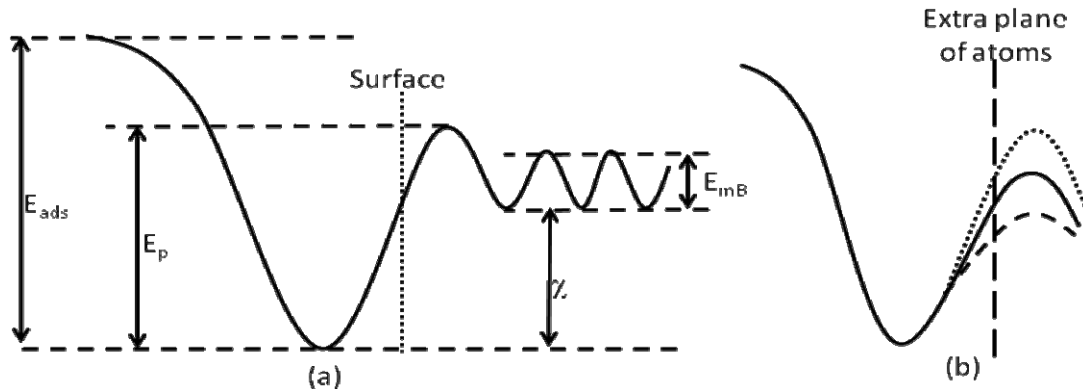


**Fig. 2.** One dimensional energy landscape for an adsorbed atom on a surface (a), and on an extra plane of atoms (b) on top of the surface. $E_{ads}$, $E_p$, and $E_{mB}$ are the adsorption, penetration and bulk diffusion energy barrier for the adsorbed atom, respectively. Depending on the nature of the interaction of an adsorbed atom and the extra plane of atoms, the energy barrier to penetrate the extra plane of atoms and to be located on the host surface changes. Once the adsorbed atom penetrates the extra plane of atoms in (b), the energy landscape is similar to the adsorbtion of the adatom on the host surface in (a).
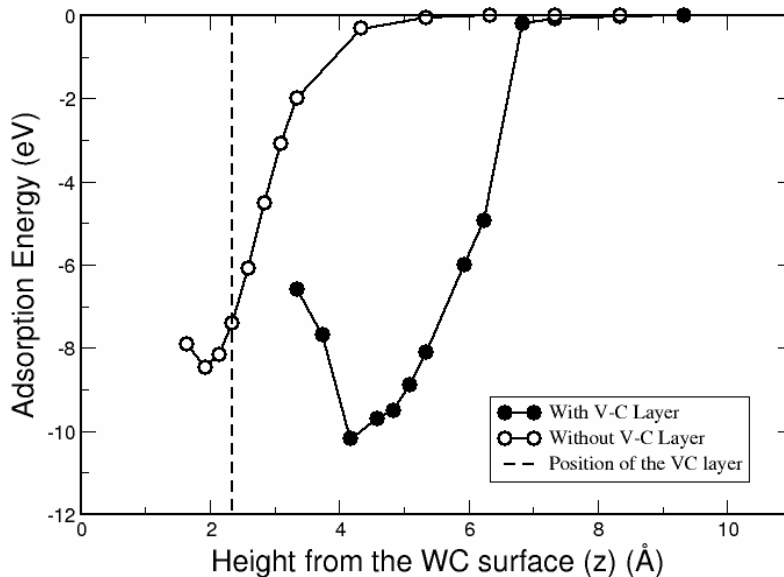


**Fig. 3.** The adsorption energy $E_{ads}$ (z) of a tungsten adatom on a clean tungsten-carbide (WC) (0001) (open circles) surface and on a vanadium-carbon (VC) monolayer on a WC (0001) surface (filled circles) as a function of the height from the surface. The position of the VC monolayer is shown by a dashed line.

Fig. 3 shows the adsorption energy of a W adatom on two different surfaces of W terminated WC, a clean WC (0001) and a VC monolayer on top of the WC (0001), as a function of the height. The position of the VC monolayer is depicted by a dotted line in the figure. In order to get the lowest energy points for both of the cases, only two bottom layers are fixed and all other atom positions are fully relaxed. Other points in Fig 3 are generated by additionally fixing the height of the W adatom. It is clear from Fig. 2 that a W atom needs more energy to be adsorbed on the WC surface covered with a VC monolayer, compared to a clean WC surface. The depth of the adsorption well is a measure of the strength of binding to the surface, where minimum on the horizontal axis corresponds to the equilibrium distance for the adsorbed W atom on the WC (0001) surface with or without VC monolayer. Compared to the direct adsorption to the WC (0001) surface in absence of VC monolayer, adsorption through VC monolayer is much more incompetent because the adsorption energy of W atom through VC monolayer is significantly higher (1.73 eV). We found that the energy barrier for the W adatom to penetrate the VC monolayer on top of the WC (0001) surface and to be located on the WC host surface is significantly high (> 4 eV) and it is very unlikely for that W adatom to penetrate the VC monolayer. The W and C adsorption energies and the corresponding heights are listed in Tab. II. Tab. II also shows the difference between the adsorption energies for a W adatom on a clean WC (0001) surface and on a WC (0001) surface covered with VC monolayer.
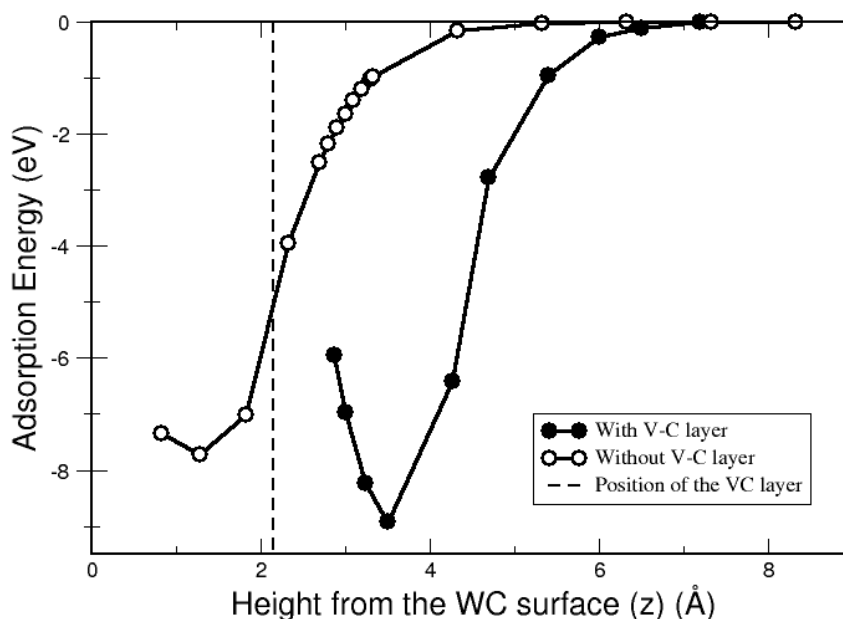


**Fig. 4.** The adsorption energy $E_{ads}$ (z) of a carbon adatom on a clean tungsten-carbide (WC) (0001) (open circles) surface and on a vanadium-carbon (VC) monolayer on a (WC) (0001) surface (filled circles) as a function of height from the surface. The position of the VC monolayer is shown by a dashed line.

Fig.4 shows the variation of adsorption energy with respect to height from the WC (0001) surface for a C adatom, as similar to Fig. 3. Fig. 4 also shows the C adatom adsorption on two different surfaces of W terminated WC, a clean WC (0001) and a VC monolayer on top of the WC (0001). Position of the VC monolayer is also shown in the Fig. 4. Using the similar procedure as described for W adatom adsorption, we found that C atom needs more energy to be adsorbed on the WC surface covered with a VC monolayer, compared to a clean WC surface. A C atom adsorption through VC monolayer is much more incompetent because

the energy barrier for C atom to penetrate the VC monolayer is significantly high (> 3.2) and it is very improbable to get that much of energy from the applied heating source (furnace). It is worthwhile to mention here that the probability for the adatom to penetrate the VC monolayer and to be located on the WC surface site increases with the increase of system temperature with $\Gamma = 10^{13} \exp(-E_b/k_B T)$, where the phonon frequency is typically considered to be $10^{13}$/Sec (Energy barrier $E_b$, Boltzmann Constant $k_B$, and absolute temperature is T.)

**Tab. II.** Tungsten and carbon adsorption energies along with their adsorbed heights (z) from the tungsten-carbide surface covered with and without vanadium-carbide monolayer

| Adatom | Configuration | $E_{ads}$ (eV) | Z (Å) | $\Delta E$ (eV) |
|--------|---------------|----------------|-------|-----------------|
| W      | Without VC    | -8.46          | 1.93  | -1.732          |
|        | With VC       | -10.192        | 4.18  |                 |
|        | Without VC    | -7.726         | 1.282 | -1.206          |
| C      | With VC       | -8.932         | 3.5   |                 |

Tab. II shows the difference between the adsorption energies for a C adatom on a clean WC (0001) surface and on a WC (0001) surface covered with VC monolayer. This adsorption energy of C atom on VC monolayer on top of the WC surface is 1.21 eV higher than the adsorption of C atom on clean WC surface. This energy difference also indicates that the growth of WC surface is inhibited when there is a VC layer on top of the WC surface. We also found that the C adatom interact strongly with the VC monolayer on top of the WC surface due to C-C interaction. A further detailed investigation will be required to elucidate the chemistry of C adatom interaction with the VC layer of atoms. It is evident from the Tab. 2, and Figs. 3 and 4 that the W and C adatom needs much energy (~4 eV) to overcome the barrier height generated by VC monolayer, and it is barely possible for the adatoms to cross the barrier and adsorbed on WC surface. The larger adsorption energy of W or C atom on a VC monolayer-covered WC suggests that the VC retard the grain growth of WC. Our result is consistent with the experimental observation that an addition of a small amount of VC inhibits the WC growth in sintering mechanism.

## 4. Conclusions

We presented a first principles DFT investigation of the structure and energetic of W and C adatom on WC (0001) surface with and without a VC monolayer. We found that W and C adsorption energy increases significantly in presence of VC. W or C adatom needs much energy (~4 eV) to overcome the barrier height generated by VC monolayer, and it is improbable for the adatoms to cross the barrier generated by VC monolayer and adsorbed on WC surface. In conclusion, observing the adsorption mechanism, it is evident that VC monolayer retards the process of grain growth mechanism of WC system.

## Acknowledgement

## 5. References

1.  J. Gurland, Trans Met. Soc. AIME 227, (1963) 1146
2.  J. Vicens, M. Benjdir, G. Nouet, J. Mater. Sci. 29 (1994) 987
3.  B. K. Kim, G. H. Ha, D. W. Lee, J. Mater. Proc./Tech. 63 (1997) 317
4.  W. D. Schubert, A. Bock, B. Lux, Int. J. Refractory Metals and Hard Mater. 13 (199) 281
5.  G. E. Springgs, Int. J. Refractory Metals and Hard Mater 13 (1995) 241
6.  T. Yamamoto, Y. Ikuhara, T. Sakuma, Sci. and Tech. of Adv. Mater 1, (2000) 97
7.  S. Lay, M. Loubradou, P. Donnadieu, Adv. Eng. Mater. 6, 10 (2004) 811
8.  J. Brilo, A. Hammoudeh, H. Kuhlenbeck, N. Panagiotides, S. Schwegmann, H. Over, H. –J. Freund, Jrnl. of Electron Micros. And relat. Phenm. 96 (1998) 53
9.  P. E. Blöchl, Phys. Rev. B 50, 17953 (1994)
10. G. Kresse and D. Joubert, Phys. Rev. B. 59, 1758 (1999)
11. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
12. G. Kresse and J. Hafner, Phys. Rev. B. 47, 558 (1993)
13. H. J. Monkhorst and J. D. Pack, Phys. Rev. B. 13, 5188 (1976)
14. M. Methfessel and A. T. Paxton, Phys. Rev. B. 40, 3616 (1989)
15. C. Guo, Y. Liu, X. Ma, Y. Qian, and L. Xu, Chem. Lett. 35, 11, (2006)
16. S. Lay, S. Hamar-Thibault and M. Loubradou, Interface SCIENCE 12, 187–195, 2004
17. J. Houze, Sungho Kim, Seong-Gon Kim, Seong-Jin Park, Randall M. German, and M. F. Horstemeyer, Jrnl. Of Appl. Phys. 103, 106103 (2008)

**Садржај:** *У овом раду проучавани су рви прорачуни и ефекат ванадијум-карбонског монослоја на процес адсорпције атома волфрама и угљеника на волфрам-карбидну површину.. Почетна конфигурација за ово проучавање је суперћелија хексагоналног ванадијум-карбида са (0001) површином. Са додатком ванадијум-карбонског монослоја, користили смо конфигурацију са најнижом енергијом. Укупна енергија система је посматрана као функција волфрамових и угљеничних ад-атома. Адсорпција волфрамових и угљеничних атома на чисту волфрам-карбидну (0001) површину упоређивана је са адсорпцијом истих на волфрам-карбидну (0001) површину са ванадијум-карбидним монослојем. Наши прорачуни указују на пораст енергије адсорпције у присуству монослоја. Наши резултати, такође, пружају фундаментално разумевање феномена инхибиције раста зрна током синтеровања волфрам-карбида или кобалт-волфрам-карбида у присуству ванадијум-карбидног монослоја*
**Кључне речи:** *синтеровање; волфрам-карбид; ванадијум карбид; инхибиција раста зрна.*