

Initial Stage of the Crack Formation in the Near-Surface Region of TiC and WC: Computer Experiment at the Atomic Level

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Abstract *Ab initio* methods of the density functional theory and pseudopotentials were used to study the crack formation on the surface of TiC and WC. The influences of surface oxidation and nitridization were studied. It is shown that the near-surface layer of pure tungsten carbide is more stable than the analogous layer of titanium carbide. Oxidation of WC (TiC) surfaces leads to easy formation of cracks, but nitridization makes surfaces stronger. The most stable for WC was found the case when the surface of WC was covered with the layer of TiN.

Keywords Modeling, Cracks, Surface, Tungsten carbide, Titanium carbide

1. Introduction

It is excessive to remind, how huge is influence of cracks in materials for mechanical characteristics of various products and tools. First it belongs to such fragile materials as carbides of transition metals. Many groups and labs are busy to study cracks, mechanisms of their creation and propagation, and ways of their healing and stabilization; and modeling at atomic level plays an important role in these investigations. Roughly, developing nanotechnologies stimulate researchers to pay a special attention to formation of cracks in nanoobjects because in this case the size of cracks may be comparable to the object size. For modeling of cracks of the macro and micro sizes the method of finite elements [1-5] and molecular dynamics [6, 7] are usually used. The first approach is based on the continual elasticity theory, the second one uses classical interatomic potentials. It is obvious that realistic modeling of nanoobjects should be carried out with use of quantum-mechanical methods, for example, with using the density functional theory (DFT) [8, 9].

The present work is devoted to simulation of initial stages of crack formation in the near-surface region of a TiC and WC nanowires under surface tension. The influence of oxygen and nitrogen is studied.

2. Methods and Approaches

All modeling was carried out using the density functional theory, the pseudopotential method [10] and the plane wave basis set for presentation of wave functions. This approach was rather fully described in our previous works therefore, we will describe it here very briefly.

The DFT is based on consequence of the Hohenberg-Kohn theorem [8] from which it is follows those one-particle electron energies ε_i and wave functions ψ_i may be found from a set of equations:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

where V_{eff} is an effective potential,

$$V_{\text{eff}} = V_{\text{ext}}(\mathbf{r}) + \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + V_{\text{XC}}(\mathbf{r})$$

and V_{XC} is the exchange-correlation potential for which a number of possible approximations may be made. Most popular of the approximations are the local density approximation (LDA) [11, 12] and the generalized gradient approximation (GGA) [13].

Pseudopotentials are intended to consider only valence electrons in calculations. A pseudopotential is constructed such that it matches the true potential outside a given radius, designated the core radius. Similarly, each pseudo wave function must match the corresponding true beyond this distance. In addition, the charge densities obtained outside the core region must be identical to the true charge density.

In this work, the pseudopotential of carbon was constructed with the FHI98PP package [14] in the scheme of Troullier-Martins [22], for titanium used the scheme of

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Hamann [16] for s -states, and the scheme of Troullier-Martins for d -states to avoid so called “ghost” states [17]. Pseudopotential for tungsten was calculated in the scheme of Hamann. For oxygen and nitrogen used Troullier-Martins pseudopotentials with the core correction. The parameters of pseudopotentials are listed in Table 1. For all main calculations used the FHI96md package [18] previously used with advantage for many systems, including transition metal compositions [19-23]. In all cases, the GGA approach to description of the exchange-correlation interactions has been chosen and the optimization of the atomic geometry has been performed.

Table 1. Critical radii of the s , p , and d components (r_s , r_p , r_d), the core correction radius (r_{core}), (all in Bohr, 1 Bohr=0.529 Å), and types of local parts (l_{loc}) of pseudopotentials

Element	r_s	r_p	r_d	r_{core}	l_{loc}
Ti	1.72	1.72	2.67	-	s
W	1.57	1.78	0.88	-	s
C	1.50	1.50	1.50	-	d
O	1.38	1.75	1.38	1.4	d
N	1.415	1.415	1.415	1.0	d

The purpose of the present work consisted in studying of cracks formation near the surface of hard material under extension of the surface. For carrying out this research as computer experiment, the model represented in Figure 1 was used.

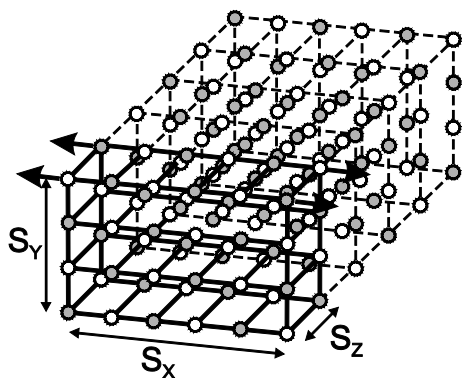


Figure 1. The perfect (ideal) scheme of the TiC (WC) nanowire. Grey circles present Ti (W) atoms, white circles show positions of C atoms. Solid lines correspond to the real $Ti_{24}C_{24}$ ($W_{24}C_{24}$) cell used for calculations; dashed lines link virtual atoms generated by the computer code to simulate the infinite periodic structure in the Z direction

The model represents a nanowire, infinite in the direction Z, and having rectangular section in the XY plane. The nanowire contains atoms of metal (Ti or W) and carbon and represents a cubic nanocrystallite of TiC or WC. The lower layer of a nanowire (in the direction Y) fixed, but the top layer exposed to step-by-step stretching both in the positive direction X, and in the negative direction. On each step the edge atoms of the top layer were fixed, and other atoms of model (except atoms of the lower layer) were spontaneously displaced in equilibrium positions as a result of quantum-mechanical calculations of forces and the total energy. In special cases the structure of the top layer can

differ from the main structure of the described nanowire. For example, atoms of carbon can be replaced with atoms of oxygen or nitrogen with formation of surface oxides and nitrides. Besides, we studied a case when the top layer of the WC-nanowire was replaced with a two-dimensional titanium nitride - TiN.

Apparently from Figure 1 the cell of our model consists of two atomic planes which are periodically translated in the direction Z. Each atomic plane contains 24 atoms. Thus, we can to use the following designations for difference of one studied case from another:

$Ti_{24}C_{24}$ – pure TiC;
 $W_{24}C_{24}$ – pure WC;
 $Ti_{24}C_{18}O_6$ – TiC with the oxidized surface (TiC-O);
 $W_{24}C_{18}O_6$ – WC with the oxidized surface (WC-O);
 $Ti_{24}C_{18}N_6$ – TiC with the nitridized surface (TiC-N);
 $W_{24}C_{18}N_6$ – WC with the nitridized surface (WC-N);
 $W_{18}C_{18}Ti_6N_6$ – WC with the surface covered with TiN (WC-TiN).

Our model allows us to simulate a long (infinite) crack of tiny depth. Each one-step shift for the surface extension was equal to 1.0 Bohr (0.5 Bohr left and 0.5 Bohr right). As the initial size of our nanowire in the direction X is about one nanometre, each step of our computer experiment corresponds to lengthening approximately for 5 percent.

3. Results and Discussions

3.1. Pure TiC and WC Surfaces

First we have studied formation of cracks in the pure TiC nanowire. Evolution of the system during the systematic linear extension of the surface layer is displayed in Fig. 2.

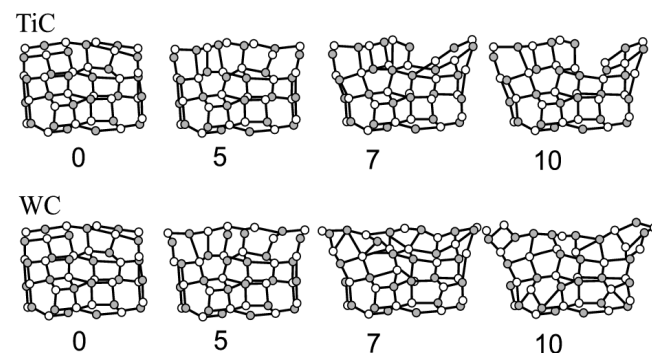


Figure 2. Evolution of the TiC and WC nanowires (two atomic planes in the XY plane) during the step-by-step linear extension of the surface layer. The numbers under the pictures are the numbers of steps of the surface linear extension in the X direction (0 means the initial relaxed configuration). Grey circles present metallic atoms, white circles show positions of C atoms

Our calculations confirm that TiC is more fragile than WC. At the seventh step some surface interatomic bonds in TiC become broken and a crack core is created. The next extension of the surface layer (step 10) changes the picture a little. As for the WC case, we don't see any radical changes in the atomic structure of the nanowire. It behaves as quasi-elastic one.

To have additional information on processes in the studied materials we analyzed the changing of the total energy and the forces in the course of our computer experiments. Results are presented in Figure 3.

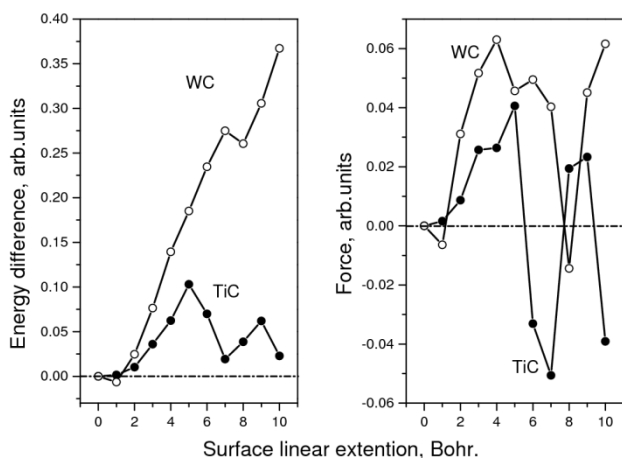


Figure 3. Changes of the total energy ΔE (left) and the force for the perfect TiC and WC nanowires as functions of the surface linear extension in the X direction

The energy of TiC grows until the fifth step of the process comes up. Then the energy goes down and has a minimum at the seventh step. At this stage the new surface bonds become formed instead of broken old bonds thus the energy decreases partially. Thus, we see that the moment of visible formation of a crack (the seventh step in Figure 2) coincides with the minimum on the energy curve. For WC we see more drastically growth of energy, which proceeds up to the seventh step. Then energy decreases a little that testifies to little changes of atomic structure, and again grows. In general, we can conclude that the course of energy curves correlates with change of atomic structure. In the both cases we see that the tensile force reaches a maximum near the fourth-fifth step (Figure 2, right), however the maximal force for the WC case is 1.5 time larger than that for the TiC case. The last result correlates with the known fact that the relation of the WC and TiC elastic modules is approximately 1.4.

3.2. Oxidized and Nitridized Surfaces

As the cutting tools containing carbides of transition metals are used as a rule in the air environment, it is very important to study influence of oxygen and nitrogen on formation of cracks. For this purpose atoms of carbon of the top layer of TiC (WC) were replaced with atoms of oxygen (nitrogen) then computer experiment on extension of a surface was made by the technique described above.

Let's firstly consider the energy changing for oxidized systems. Corresponding plots are presented in Figure 4.

We see that the oxidized WC surface layer stretches practically without resistance up to the third step (15 percent of lengthening). Then process is followed by almost constant stretching force (up to the eighth step), and after that goes again without resistance. Some signs the system destruction

are available, but they aren't too obviously expressed. In the TiC-O case we don't see strong indications of destruction; the energy grows monotonously. Plots of tensile forces (Figure 4, right) are more informative. One can see that in this computer experiment the real destruction begin at the fourth-fifth step (like in pure materials), however the maximal tensile forces are approximately the same for the both cases (TiC-O and WC-O).

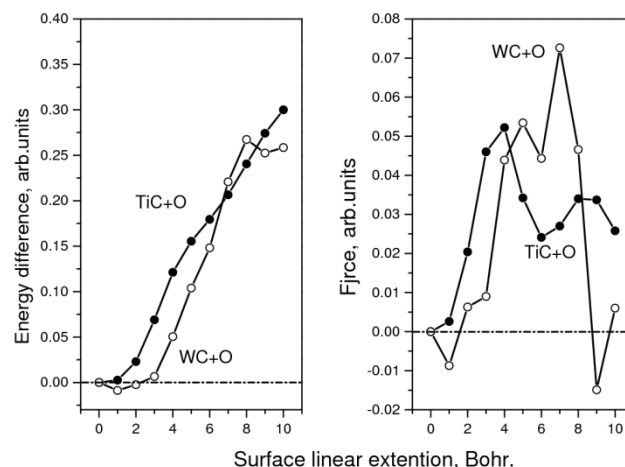


Figure 4. Changes of the total energy ΔE (left) and the tensile force for the oxidized TiC and WC nanowires as functions of the surface linear extension in the X direction

To obtain more information on the process we considered changes of atomic structure of the studied systems in the course of their surface stretching (Figure 5).

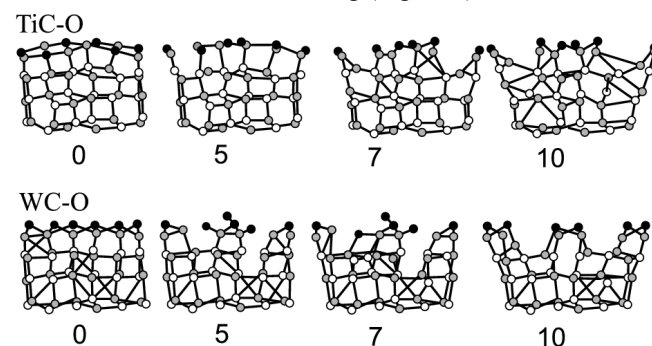


Figure 5. Evolution of the TiC and WC oxidized nanowires during the step-by-step linear extension of the surface layer. Grey circles present metallic atoms, white circles show positions of C atoms, black circles are oxygens

One can see that in the both cases (WC-O and TiC-O) the near-surface layer of the nanowire became considerably broken not only in case of WC-O, but also in case of TiC-O. Thus we can conclude that we need to compare in details the energy, forces and atomic structure data to judge the beginning destruction of a near-surface layer.

The same computer experiments were executed for nanowires, which surface carbon atoms were replaced with nitrogens. Looking at power curves (Figure 6, left) it is impossible to tell anything whether there are destructions in the studied systems. Both curves (TiC-N and WC-N) show

the monotonous growth of energy, and they differ from each other a little. However the plots of tensile forces (Figure 6, right) show that in the both cases destruction begin at the fifth step. At the same time, the pictures of atomic structure (Figure 7) demonstrate that destruction at the fifth step is visible for the WC-N case, but is invisible for the TiC-N case.

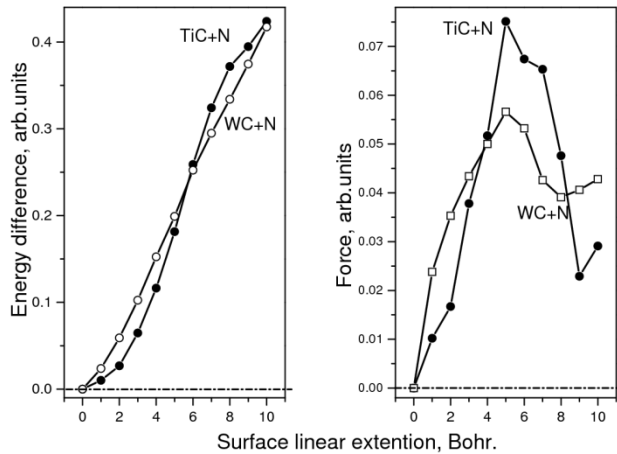


Figure 6. Changes of the total energy ΔE (left) and tensile forces (right) for the nitridized TiC and WC nanowires as functions of the surface linear extension in the X direction

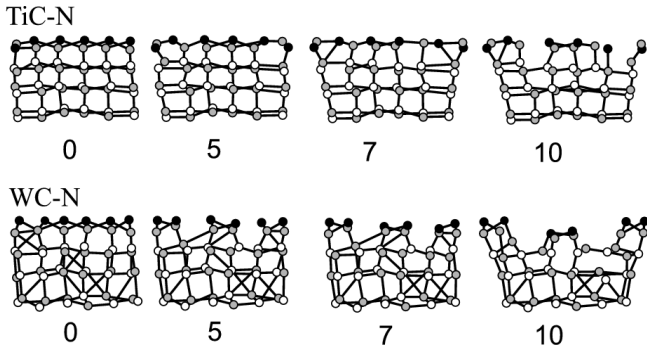


Figure 7. Evolution of the TiC and WC nitridized nanowires during the step-by-step linear extension of the surface layer. Grey circles present metallic atoms, white circles show positions of C atoms, black circles are nitrogens

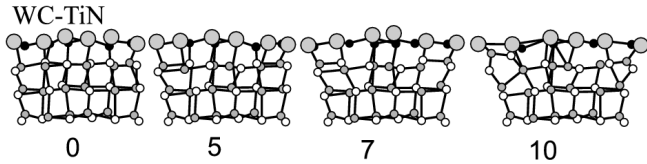


Figure 8. Evolution of the WC nanowire covered with a TiN layer during the step-by-step linear extension of the surface. Small grey circles present W atoms, white circles show positions of C atoms, black circles are nitrogens, big grey circles are Ti atoms

Composites based on WC are widely used as a material for cutting tools. For increase of performance characteristics of these tools, they are often covered with various coverings, for example with TiN. Below we consider how a TiN layer protects the WC nanowire from formation of cracks. Let's firstly consider the evolution of atomic structure

(Figure 8). We see that in this case stretching of the top layer (i.e. the TiN layer) doesn't lead to dramatic changes of near-surface atomic structure of a nanowire. Let's look now at Figure 9 where changing of energy and tensile force for the nanowire of WC covered with a thin TiN layer on the surface are shown.

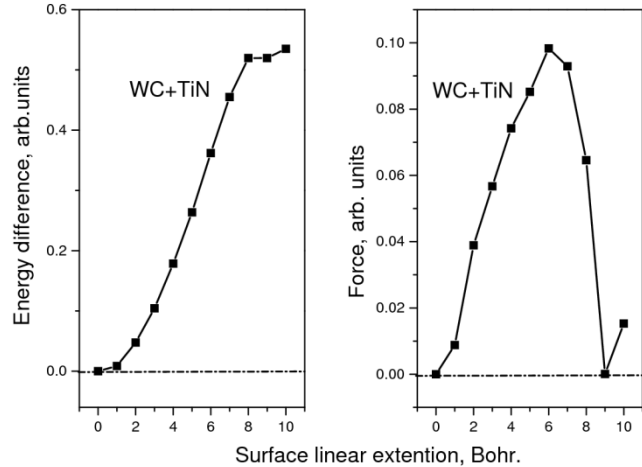


Figure 9. Changing of the total energy ΔE (left) and forces (right) for the WC nanowire covered with a TiN layer as function of the surface linear extension in the X direction

We see that the both plots in Figure 9 (left and right) demonstrate destruction signs after the eight step of stretching: the value of the tensile force is going to zero. Before the eight step the WC-TiN system behaves as elastic.

3.3. Relaxation of Stretched Systems

There is a very important question: how stable are changes of atomic structure caused by surface stretching? What happens with the system after disappearance of forces stretching a surface?

To answer this question, we made a special computer experiment: for the WC based nanowires (WC, WC-O, WC-N, and WC-TiN) we took the stretched systems (5 and 10 steps) and relaxed them as much as they were possible to relax. Then we compared their electronic structures (Figure 10) and energies (Table 2) with those of initial states (0 step).

Table 2. Energy difference (ΔE) between stretched system and its initial state. ΔE . Data are presented after relaxation procedure and before this procedure (in brackets)

	The number of steps of stretching before relaxation	Studied system			
		WC	WC-O	WC-N	WC-TiN
ΔE , eV/atom	5	0.00 (0.10)	-0.09 (0.06)	0.00 (0.11)	0.00 (0.15)
	10	0.11 (0.21)	-0.08 (0.15)	-0.10 (0.24)	0.01 (0.30)

Analysis of Figure 10 and Table 2 shows that practically all systems stretched up to the fifth step (≈ 25 percent of surface lengthening) relax to their initial state energetically

and structurally. The exception is made by the WC-O system where oxygen atoms enter chemical bonds with atoms of tungsten and carry out irreversible reorganization of structure. A large stretching of a surface (up to the ten step, or 50 percent of surface lengthening) leads to changes of atomic structure in all cases. However in the WC-TiN case these changes are practically invisible and energetically are very small. Thus we can suppose that WC crystallites covered with TiN can be stretched and relaxed many times without noticeable destruction at the atomic level. It justifies use of titanium nitride coverings for protection of the cutting tools based on tungsten carbide.

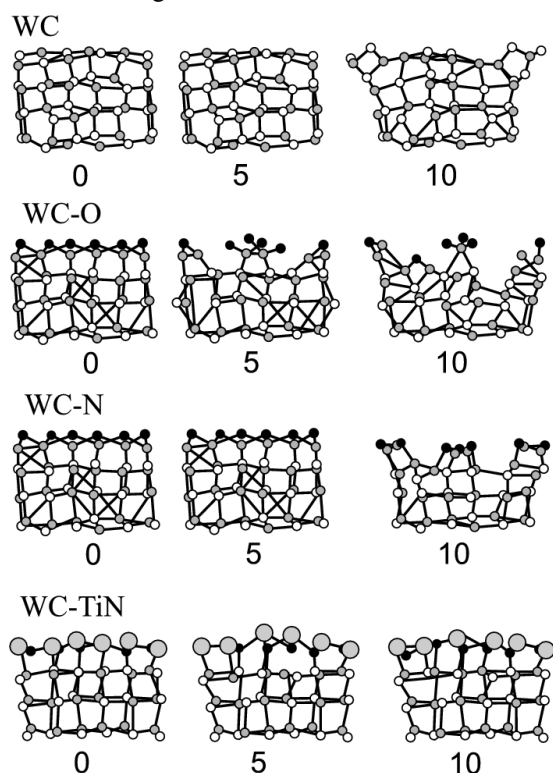


Figure 10. Relaxation of WC, WC-O, WC-N, and WC-TiN nanowires after their linear surface extensions. Small grey circles present W atoms, white circles show positions of C atoms, black circles are oxygens or nitrogens, big grey circles are Ti atoms. The numbers under the pictures are the numbers of steps of the surface linear extension, after which relaxation procedure began (0 means the initial configuration)

4. Conclusions

Quantum-mechanical calculations show that details of the initial stage of crack formation can be studied using computer modeling. It was found that the force to start destruction of a near-surface layer of WC is 1.5 times more than in case of the TiC. Oxidation of WC (TiC) surfaces leads to easy formation of cracks, but nitridization makes surfaces stronger.

One can see that in the both cases (WC-O and TiC-O) the near-surface layer of the nanowire became considerably broken not only in case of WC-O, but also in case of TiC-O.

WC crystallites covered with TiN can be stretched and relaxed many times without noticeable destruction at the

atomic level. It justifies use of titanium nitride coverings for protection of the cutting tools based on tungsten carbide.

In general, we can conclude that comparison in details the energy, forces and data on the atomic structure allows us to study the initial stage of crack formation in the near-surface layer of solids.

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