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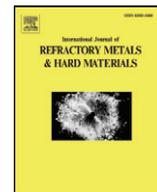
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## Ab initio study of inhibitors influence on growth of WC crystallites in WC/Co hard alloys

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## ABSTRACT

The density functional theory and pseudopotential method are used to study the energy barrier for migration of W and C atoms from one carbide grain to another through the cobalt binder. Calculations show that the pair WC migration is more preferable energetically than the separate migration of W and C atoms. Addition of metals (V, Cr, Ti) which segregate at the WC–Co interface, increases the energy barrier for the WC migration decreasing the WC flow responsible for growth of carbide grains. Vanadium was considered the most effective inhibitor of all atoms studied, titanium has proved as the worst one.

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### 1. Introduction

Hard alloys based on tungsten carbides (WC crystallites within a Co cement matrix) are widely used as a material for cutting tools. Recent investigations show that the work properties of hard alloys improve when crystallite sizes are decreasing to 300–500 nm or less [1–4]. However, the production of bulk nanocrystalline cemented tungsten carbide, is complicated by growth of WC crystallites during alloy sintering [5]. The results showed that the grain growth process consists of an initial stage of rapid growth which typically takes place during heat-up and the normal grain growth during isothermal holding. Recent studies on the sintering of nanosized WC–Co powders have shown that significant grain growth occurs during the early stages of sintering before the liquid phase sintering temperature is reached, suggesting a rapid grain growth process in the solid state [6,7].

For the reduction of WC grains, transition metals are doped into WC–Co based compounds. Vanadium proved to be by far the most effective grain growth inhibitor, followed by Ta, Cr, Ti and Zr. Quantitative comparison between V and Cr as WC grain refiners was studied by Luyckx and Alli [8]. Ab initio calculations predict submonolayer segregation of Ti, V, Cr, Mn, and Ta to WC boundaries [9–11]. Experiments verified segregation of V, Cr, Ti, Ta and Mn [12–16].

There is the opinion [12] that “the segregation layer would behave like a barrier to retard the process of solution/reprecipitation of WC to Co-phase”, however, the details for the retardation mechanism of carbide grains in doped compounds are still unclear. This problem is

complicated by the absence of a clear understanding of the nature and the structure of the WC–Co interface especially for nanosized WC crystallites.

The recent *ab initio* calculations [17] show that the atomic structure of small tungsten carbide nanoparticles might have trigonal or cubic types, and boundaries of both types of particles contain W and C atoms in the same manner as the NaCl(100) surface. The next work [18] demonstrates that cobalt layers crystallize hetero-epitaxially on the WC(100) surface. Namely, the first monolayer repeats the geometry of the WC(100) surface with the same value of the lattice constant. The placement of Co atoms just above carbon atoms has been found the most preferable. The second Co monolayer also repeats the *fcc*-WC plane geometry, however the distance between the first and second Co layers is less than the distance between planes in the WC cubic crystal. Results of [17,18] used here for construction of cobalt binder layers between WC crystallites and for the study of W and C migration through the WC–Co interface.

### 2. Methods and approaches

In this work, the same approach as in previous papers was used [18,19], namely, the density functional theory (DFT) [19,20] in the generalized gradient approximation (GGA) [21], the pseudopotential method [22] and the plane wave basis set. Because the magnetic nature of cobalt, the spin-polarized version of DFT was applied within the FHI96md package [23].

I used the same pseudopotentials for carbon, tungsten, and cobalt as in [18]. They were generated through the FHI98PP package [24] and were tested to describe lattice constants and bulk elastic moduli

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for WC, both hexagonal and cubic, and for *fcc*-cubic cobalt. Pseudopotentials for V, Cr, and Ti were constructed and tested in the same way.

For all calculations 12 *k*-points of the Brillouin zone were applied: namely, the special points for *fcc* lattice (0.25, 0.25, 0.75 and 0.25, 0.25, 0.25 [25]) were taken with the  $2 \times 2 \times 2$  Monkhorst-Pack scheme [26] and the energy cutoff of 50 Ry. The self-consistence convergence was provided by stabilizing the total energy with an accuracy of 0.05 eV per atom.

In the current investigation, in order to construct a cobalt binder layer between two parallel WC(100) surfaces, I used the geometry of the WC/Co interface optimized in my previous work [19]. The WC(100) surface was taken as a surface that contacts with cobalt. A WC crystallite was modeled by a slab consisting of four atomic layers. The binder interlayer contained six cobalt monolayers. The supercell X-axis and Y-axis sizes were stated to be equal to five lattice constants of *fcc*-WC. The supercell Z-axis size was determined by the equilibrium geometry of the WC/Co system in this direction. Finally, the thickness of the Co binder layer was found to be 0.989 nm. Atomic schemes are presented in Fig. 1.

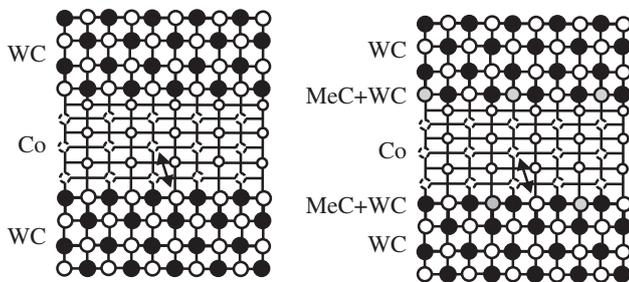
As it was shown experimentally [12,14,16], the contents of V, Cr and Ti atoms at the WC–Co interface are close to 50% relatively to W positions. Therefore, the Me/W relation of 50% was used for calculations in our work.

The difference of chemical potentials is a motive force for the transition of atoms from small crystalline particles to large ones. Certainly, many different variants of solid-phase diffusion may be realized for the WC migration from one grain to another. Only the simplest one will be considered here, namely: the exchange transpositions of W (and/or C) and Co atoms. Pair and separate movements of W and C atoms will be compared.

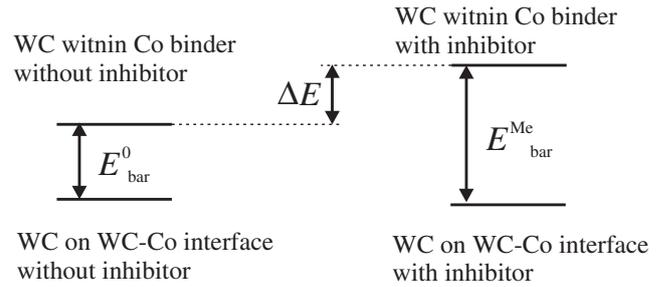
The basic idea of the given work consists in the following: when a W and C atom (pair or separate) pass from carbide into cobalt, their energy raises, and then, at joining to another grain, goes down again. In other words, they are overcoming some energy barrier  $E_{bar}^0$  (see Fig. 2). If presence of dopant metal atoms at the interface leads to increasing of this barrier ( $E_{bar}^{Me} > E_{bar}^0$ ), the given metal acts as an inhibitor of the grain growth. Thus, I studied the WC–Co and W(Me)C–Co systems shown in Fig. 1, calculated energy barriers for different Me (Me = V, Cr, Ti) and compared them.

### 3. Results and discussion

Firstly, I have calculated the total energy,  $E^0$ , for the WC–Co perfect hetero epitaxial system (without any inhibitors) in which all W, C, and Co atoms take their perfect positions. Secondly, I have found the energies,  $E_{bar}^0$ ,  $E_{bar}^0$ , for the cases when one of the Co atoms (in an internal layer of a binder) is replaced by W or C atom of the WC slab interface. Thirdly, I have calculated the energy,  $E_{bar}^{Me}$ , for the case



**Fig. 1.** Cobalt binder layers between WC(100) crystallite boundaries: A) a hetero epitaxial system without any dopants; B) a hetero epitaxial system with Me atoms (Me = V, Cr, Ti) substituted a part of the interface W atoms. Large open circles are tungsten atoms; large black circles are carbon atoms; gray circles are Me atoms. Cobalt atoms of the first plan are shown as solid small open circles; cobalt atoms of the second plan are presented as dotted small open circles. Two-side arrows demonstrate the exchange transpositions of W and Co atoms.



**Fig. 2.** Scheme of barrier increasing for WC migration from one WC crystallite to another through cobalt binder in presence of metal inhibitors.

when a Co atom is replaced by a WC pair. This procedure was repeated for the W(Me)C–Co system where a half of the W atoms of the WC surface were replaced by atoms of V, Cr, or Ti, obtaining the values  $E_{bar}^{Me}$ ,  $E_{bar}^{Me}$ ,  $E_{bar}^{Me}$ , and  $E_{bar}^{Me}$ . Finally, I have calculated energy barriers:

Barriers for W migration:

$$E_{bar(W)}^0 = E_{bar(W)}^0 - E^0 \quad \text{and} \quad E_{bar(W)}^{Me} = E_{bar(W)}^{Me} - E^{Me};$$

Barriers for C migration:

$$E_{bar(C)}^0 = E_{bar(C)}^0 - E^0 \quad \text{and} \quad E_{bar(C)}^{Me} = E_{bar(C)}^{Me} - E^{Me};$$

Total barriers for separate W and C migration:

$$E_{bar(W+C)}^0 = E_{bar(W)}^0 + E_{bar(C)}^0 \quad \text{and} \quad E_{bar(W+C)}^{Me} = E_{bar(W)}^{Me} + E_{bar(C)}^{Me};$$

Total barriers for pair WC migration:

$$E_{bar(WC)}^0 = E_{bar(WC)}^0 - E^0 \quad \text{and} \quad E_{bar(WC)}^{Me} = E_{bar(WC)}^{Me} - E^{Me};$$

Barrier growth forced by inhibitor for separate W and C migrations:

$$\Delta E_{sep} = E_{bar(W+C)}^{Me} - E_{bar(W+C)}^0;$$

Barrier growth forced by inhibitor for pair WC migration:

$$\Delta E_{pair} = E_{bar(WC)}^{Me} - E_{bar(WC)}^0.$$

Results of all calculations are listed in Table 1. First of all, one can see that the pair WC migration is more preferable energetically than the separate migration of W and C atoms. Next, one can conclude that in both cases the presence of inhibitors increases the energy barrier for the WC transfer from one carbide grain to another through a cobalt binder. The sequence of inhibitors (V, Cr, Ti) by their efficiency correlates with known experimental data. Namely,  $\Delta E(V) > \Delta E(Cr) > \Delta E(Ti)$  in accordance with the inhibitor efficiency decrease in the row V, Cr, Ti.

**Table 1**

Energetic parameters for the W and C migration from one carbide grain to another through a cobalt binder.

	WC–Co without Me	Me = V	Me = Cr	Me = Ti
$E_{bar(W)}^0$ or $E_{bar(W)}^{Me}$ , eV	1.38	1.73	1.63	1.41
$E_{bar(C)}^0$ or $E_{bar(C)}^{Me}$ , eV	1.51	1.53	1.52	1.56
$E_{bar(W+C)}^0$ or $E_{bar(W+C)}^{Me}$ , eV	2.89	3.26	3.15	2.97
$\Delta E_{sep}$ , eV	–	0.37	0.26	0.08
$E_{bar(WC)}^0$ or $E_{bar(WC)}^{Me}$ , eV	2.17	2.50	2.37	2.22
$\Delta E_{pair}$ , eV	–	0.33	0.21	0.05

#### 4. Conclusions

Quantum-mechanical calculations show that the increasing of the energy barrier for migration of W and C atoms from one carbide grain to another through the cobalt binder may be one of the possible mechanisms of the retardation of grain growth in the WC–Co alloys doped by transition metals. The pair WC migration is more preferable energetically than the separate migration of W and C atoms. The effect of inhibitors (V, Cr, Ti) on the increase of the energy barrier correlates with known experimental data on the decrease of carbide grains. Certainly, there may be other mechanisms retarding the growth of grains (for example, agglomeration). However, it seems to me that the above mechanism plays an important role at a stage of the solid phase sintering of hard alloys.

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