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Structural, electronic and magnetic properties of η carbides (Fe_3W_3C, Fe_6W_6C, Co_3W_3C and Co_6W_6C) from first principles calculations

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ABSTRACT

First-principles FLAPW-GGA calculations have been performed with the purpose to determine the peculiarities of the structural, electronic, magnetic properties and stability for a family of related η carbides M_3W_3C and M_6W_6C (where M = Fe and Co). The geometries of all phases were optimized and their structural parameters, theoretical density, cohesive and formation energies, total and partial densities of states, atomic magnetic moments have been obtained and analyzed in comparison with available theoretical and experimental data.

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1. Introduction

Tungsten carbide WC attracts much attention thanks to its unique physical and chemical properties such as extreme hardness, high melting point, chemical inertness, interesting catalytic behavior, etc., and belongs to the most promising engineering materials with a wide range of industrial applications, for example in high-temperature tools and devices: high-speed tools, extrusion dies, rollers, drills, etc. Recent applications include their usage in catalysis industries and as aerospace coatings [1–8].

Simultaneously, significant attention is given to crystalline and nano-sized WC-based alloys and composites comprising other transition metals (WC-M, where M are d metals), which are suitable for many technological applications, see Refs. [8–12].

Today, a series of various materials has been prepared in the WC-M systems. One extensive group of such materials includes the above-mentioned composites (the so-called cemented carbides), i.e. heterogeneous WC-M systems, which consist of grains of tungsten carbide glued with a binder metal M to combine the hardness of the carbide and the toughness of the metal, see Ref. [8].

Another important group consists of double (M–W) carbides, which adopt individual crystal structures and properties. This group includes the so-called η carbides such as Fe_3W_3C or Co_6W_6C [1–3,8]. These phases may arise in heterogeneous composites in the interface region between WC and transition metals (or their alloys) [13–21] or may be prepared using special synthetic routes—for example, by mechanical alloying [22–24].

Today among the tungsten-containing η carbides several related phases with various M/W content are obtained (for example Co_2W_4C and Co_4W_2C, see Ref. [8]), but usually η carbides with stoichiometry M/W = 1, namely M_3W_3C and M_6W_6C, are found [1–3,8–24]. These η carbides possess interesting properties. For example, the bulk modulus for Co_6W_6C was found [25] to be 462 GPa, i.e. higher than that for diamond (~444 GPa, see Ref. [26]) and WC (~421, [27]). The Vickers microhardness (H_V) measurements for Fe_3W_3C and Fe_6W_6C show that they are hard phases with H_V~15.6 GPa [24]. These phases are of high technological importance: for example, the properties of widely used WC/M composite materials as well as tungsten-containing steels and heavy alloys are substantially determined by the formation of η carbides as secondary phases [8,13–21].

On the other hand, extensive theoretical studies have been performed for the electronic structure, stability and physical properties of binary tungsten carbides [28–36], whereas the data about the fundamental electronic properties of η carbides M_3W_3C and M_6W_6C are practically absent: to our knowledge, only in one earlier work [37] the electronic spectra for the non-magnetic Fe_3W_3C and Fe_6W_6C are discussed based on the cluster model.

In the present work, using the full-potential linearized augmented plane waves (FLAPW) method within the generalized gradient approximation (GGA) for the exchange-correlation

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Table 1
Atomic positions for the cubic η carbides M_3W_3C and M_6W_6C, where M = Fe or Co [1,38–40].

η carbides	W	M_1	M_2	C
M_3W_3C	48f (x_1;0.125;0.125)	32e (x_2; x_2; x_2)	16d (0.5;0.5;0.5)	16c (0;0;0)
M_6W_6C	48f (x_1;0.125;0.125)	32e (x_2; x_2; x_2)	16d (0.5; 0.5; 0.5)	8a (0.125;0.125;0.125)

potential we explore for the first time the structural, electronic, magnetic and cohesive characteristics of the double tungsten-containing η carbides Fe_3W_3C, Fe_6W_6C, Co_3W_3C and Co_6W_6C.

The choice of these four η phases allows us to compare the above properties of the related double carbides depending on the metal/carbon ratio ((M,W)/C = 6 versus (M,W)/C = 12), i.e. (Fe_3W_3C, Co_3W_3C)↔(Fe_6W_6C, Co_6W_6C), as well as on the transition 3d metal type (Fe versus Co, i.e. $Fe_3W_3C \leftrightarrow Co_3W_3C$ and $Fe_6W_6C \leftrightarrow Co_6W_6C$).

As a result, the optimized structural parameters, theoretical density, cohesive and formation energies, total and partial densities of states (DOS) and atomic magnetic moments for the η carbides M_3W_3C and M_6W_6C (where M = Fe and Co) have been obtained and analyzed in comparison with available theoretical and experimental data.

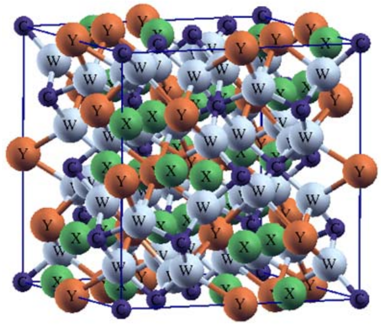
2. Models and method of calculations

According to available crystallographic data [1,3,38–40], all the examined η carbides Fe_3W_3C, Fe_6W_6C, Co_3W_3C and Co_6W_6C adopt the cubic symmetry with the space group Fd3m (no. 227) and $Z = 16$ (for Fe_3W_3C and Co_3W_3C) and $Z = 8$ (for Fe_6W_6C and Co_6W_6C). In both crystal structures (M_3W_3C and M_6W_6C, where M = Fe or Co), the tungsten atoms occupy the 48f sites; Fe and Co are placed in two non-equivalent 32e (M_1) and 16d (M_2) sites, whereas the carbon is located in the 16c (for M_3W_3C) or the 8a sites—for M_6W_6C, Table 1.

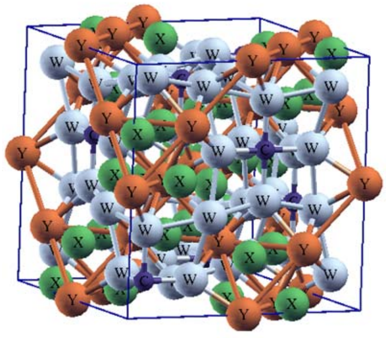
The ideal structure of the cubic η carbides M_3W_3C is quite complicated and consists of eight regular octahedra of tungsten atoms centered in a diamond cubic lattice and eight regular tetrahedra of Fe(Co) atoms centered in the second diamond cubic lattice that interpenetrates the first through the 1/2, 1/2, 1/2 unit cell translation. Sixteen additional Fe(Co) atoms are tetrahedrally coordinated around the Fe(Co) tetrahedra and 16 carbon atoms surround the tungsten octahedra in tetrahedral coordination.

The only difference between the above M_3W_3C and M_6W_6C is that these phases contain 16 and 8 carbon atoms (per cell), respectively, and for M_6W_6C, the carbon atoms occupy the 8a sites in the octahedral coordination [1,38,40], see Fig. 1.

Our band structure calculations for all η carbides M_3W_3C and M_6W_6C were performed within the full-potential method with mixed basis APW+lo (LAPW) implemented in the WIEN2k suite of programs [41]. The generalized gradient correction (GGA) to exchange-correlation potential of Perdew, Burke and Ernzerhof [42] was used. The electronic configurations were taken to be [Xe] $6s^2 5d^4$ for W, [Ar] $4s^2 3d^6$ for Fe, [Ar] $4s^2 3d^7$ for Co and [He] $2s^2 2p^2$ for carbon. Here, the noble gas cores were distinguished from the sub-shells of valence electrons. The basis set inside each muffin-tin (MT) sphere was split into core and valence subsets. The core states were treated within the spherical part of the potential only, and were assumed to have a spherically symmetric charge density in MT spheres. The valence part was treated with the potential expanded into spherical harmonics to $l = 4$. The valence wave functions inside the spheres were expanded to $l = 12$. The plane-wave expansion with $R_{MT} \times K_{MAX}$ was equal to 7, and k sampling with $5 \times 5 \times 5$ k-points mesh in the Brillouin zone was used. Relativistic effects were taken into account within the scalar–relativistic approximation. The MT atomic radii were 1.97 a.u. for W, Fe, Co, and 1.75 a.u. for carbon.



M_3W_3C



M_6W_6C

Fig. 1. The models of crystal structures for the ternary η carbides M_3W_3C and M_6W_6C. Here, X = M_1 and Y = M_2 depict two different types of 3d-metal atoms placed in the 32(e) and the 16(d) positions.

The self-consistent calculations were considered to have converged when the difference in the total energy of the crystal did not exceed 0.01 mRy as calculated at consecutive steps. In this way we used the optimization regime as was described in the original version WIEN2k [41]; this means minimization of the total energy by variation of the lattice parameters (a) and minimization of the atomic forces (<1 mRy/a.u.). The density of states (DOS) was obtained using the modified tetrahedron method [43]. Finally, to examine the magnetic properties of the η carbides, our calculations were carried out for non-magnetic and magnetic variants. In the latter case the ferromagnetic ordering (FM) was assumed.

3. Results and discussion

3.1. Structural properties and density

At the first step, the equilibrium lattice constants (a) and cell volumes (V) for the ideal stoichiometric η carbides Fe_3W_3C, Fe_6W_6C, Co_3W_3C and Co_6W_6C were calculated. The results are presented in Table 2. As can be seen, $a(Fe_3W_3C) > a(Co_3W_3C)$ and $a(Fe_6W_6C) > a(Co_6W_6C)$; this result can be easily explained by the

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