Chapter 1
Introduction

Carbides of Group IV-VI transition \(d\)-metals belong to strongly nonstoichiometric interstitial compounds [1–5]. Transition metals of subgroups IVA and VA (Ti, Zr, Hf, V, Nb, Ta) form cubic carbides \(MC_y\) with carbon with the \(B1\)-type (NaCl) structure, while the metals of subgroups VA and VIA (V, Nb, Ta, Cr, Mo, W) form in addition lower hexagonal carbides \(M_2C_y\) with the \(L'3\) (\(W_2C\)) structure (hereinafter in this book, the crystal lattice types of inorganic compounds are shown according to the handbook [6]).

A characteristic feature of the structures of these compounds is the presence of the face-centered cubic (fcc) or hexagonal (simple or closely-packed (hcp)) metallic lattice. Carbon atoms are located in the center of octahedral or trigonal interstitials of the metallic lattice. However, in carbides, the metallic sublattice symmetry differs from that of transition metallic lattices. Thus, the crystal structure of metals changes with the formation of carbides. Group IV metals (Ti, Zr, Hf), which have the hcp structure, form carbides with the fcc metallic sublattices. Metals with the body-centred cubic (bcc) structure (V, Nb, Ta, Cr, Mo, W) form carbides with the cubic or hexagonal metallic sublattices. The changeover of the crystal structure of metals upon formation of carbides suggests strong metal—carbon interactions while direct interactions between carbon atoms are negligibly small [5].

In carbides, the carbon atoms that are located in the interstitial voids of the metallic sublattice form a nonmetallic sublattice. Unoccupied interstitials are called structural vacancies and designated as □. Together with carbon atoms, they form an interstitial solution in the nonmetallic sublattice. The presence of structural vacancies is a characteristic feature of carbides that belong to the group of nonstoichiometric compounds. The concentration of vacancies and their disordered or ordered distribution in a crystal lattice have a strong effect on the properties of such carbides. The results of experimental and theoretical studies on how the distribution of atoms and vacancies affects the structure and properties of strongly nonstoichiometric compounds are generalized in monographs [1–5, 7, 8] and review article [9].

Carbides of Group IV-VI transition \(d\)-metals have the highest melting points and are the hardest among all the compounds known [3–5, 7–14]. Therefore, these
Carbides are used in manufacturing structural and tool materials capable of operating at elevated temperatures, in aggressive media and under heavy loads. Carbides are used for deposition of protective and hard coatings, etc. Tungsten carbide WC is not the hardest and the most refractory compound, viz., its melting point (≈3060 K) is low as compared with nonstoichiometric carbides TiC_y, ZrC_y, HfC_y, VC_y, NbC_y, TaC_y and its hardness (18–22 GPa at 300 K) is also low as compared with these carbides [3–5]. However, the hardness of WC is sufficiently stable and decreases relatively slightly with the increase in temperature from 300 to 1200–1300 K [15]. Moreover, as compared with carbides of other transition metals, tungsten carbide WC has a higher Young’s modulus of elasticity $E \approx 700$ GPa which is twice as large as Young’s modulus of other carbides. A thermal expansion coefficient of WC is equal to $\sim 5.5 \times 10^{-6}$ K$^{-1}$ and is half as much as that of other transition metal carbides.

The mentioned properties of WC and especially their thermal stability during the heating up to 1000–1200 K determine the use of WC in the production of wear-resistant hardmetals, which form the major part of all tool materials. The direct use of WC carbide as cutting tool material is impossible because of its brittleness and sintering at very high temperatures.

Tungsten carbide was first synthesized by H. Moissan in 1893 [16]. Later, in 1897, Moissan managed to produce fused tungsten metal by the electrothermal way (earlier tungsten metal produced only in the form of a powder). The synthesis of high-melting carbides including WC from oxides, in which calcium carbide is used as the reactant, was described in work [17]. The industrial production of hardmetals based on WC started 20–25 years after discovery of tungsten carbide WC and goes on at present. The first period (1918–1923) of development of hardmetals on the basis of tungsten carbide was described in work [18] and the first patent for these hardmetals was received by K. Schrüter in the USA in 1925.

The practical interest in tungsten carbide determines the active fundamental investigations of its crystal and electronic structure and also of the physicochemical properties of both WC as such and related compounds and systems that contain it. In the past 20 years, the most active studies were associated with the synthesis and application of nanocrystalline tungsten carbide.

The studies of tungsten carbide [19] and WC-based hardmetals began at the Institute of Solid State Chemistry of the Ural Division of the RAS (ISSC UrD RAS) after 1992 on the initiative and with immediate participation of Prof. A. A. Rempel. He also took the lead in the research of nanocrystalline materials including nanocrystalline powders of tungsten carbide and nanostructured hardmetals WC-Co [20–23]. Earlier, tungsten carbide and nanocrystalline materials have not been studied at the Institute of Solid State Chemistry UD RAS.

The main aim of this book is to generalize the modern experimental and theoretical findings on tungsten carbide, including the results obtained at the ISSC UrD RAS under the direction of A. A. Rempel, and to promote the application of tungsten carbide for the production of nanostructured hardmetals.
References

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