

Preface

Since the discovery of tungsten carbide in 1893 by Henri Moissan and the first using of WC for industrial production of hardmetals at the beginning of twentieth century, basic research on the chemistry and physics of high-melting tungsten carbides and wear-resistant hardmetals has been carried out for three decades mainly in Austria, Germany, USA and USSR. In the 1950s, 1960s the interest in research of WC-based hardmetals, however, relaxed somewhat. Scientific and technological results of first stage of research and production of tungsten carbide and WC-based hardmetals were generalized in two monographs: Kieffer and Benesovsky [1] and Samsonov et al. [2]. Also, the structure and properties of tungsten carbides were partially and very small discussed in the following books on transition metal carbides: Goldschmidt [3]; Storms [4]; Toth [5]; Upadhyaya [6]. Noted that these books contain the limited data on tungsten carbides, and the part of these data is specified repeatedly.

But this situation abruptly changed at the beginning of the 1980s when the first indication for possible creation of fine-grained and nanocrystalline hardmetals have appeared. This aspect immensely stimulated research of phase equilibria in the “tungsten-carbon” system and of new methods for producing fine tungsten carbide powders and fine-grained hardmetals. Thousands original studies and articles appeared in the literature dealing with phase equilibria and phase diagrams of the tungsten-carbide system, with the crystal and electronic structure and properties of tungsten carbides in different structural states. In the last 30 years, the most active efforts were made in synthesis and application of the nanocrystalline WC powders for the production of nanostructured hardmetals.

This prompted to publish a volume devoted to tungsten carbides in the series “Materials Science”. According to the purpose of this series, this volume must fill the gap between the scarce information about tungsten carbides in physicochemical textbooks and in monographs devoted to transition metal carbides and numerous review and original articles written for specialists. This monograph is the first work generalizing all up-to-date information about tungsten carbides.

The main subject of the monograph is comprehensive analysis of structure and properties of all stoichiometric and nonstoichiometric tungsten carbides including disordered and ordered phases. With this in mind, in [Chap. 2](#) we considered in detail the phase equilibria and crystal structure of phases of the binary W–C and ternary W–Co–C systems, as well as the electronic structure of these phases.

[Chapter 3](#) is devoted to discussing the phenomenon of ordering of tungsten carbides. Until now the literature data on the crystal structure of disordered and different ordered phases of W_2C_y carbide are limited and contradictory. In [Chap. 3](#) the symmetry analysis of all possible superstructures of lower tungsten carbide W_2C_y is performed and the physically possible sequence of phase transformations in this carbide is established. The obtained theoretical results are compared with the experimental data on the crystal structure and temperature-concentration regions of existence of ordered and disordered phases of tungsten carbides. On the basis of this comparison, the phase boundaries are determined and phase diagram of the W-C system is refined.

According to the modern concepts, tungsten carbides in the nanocrystalline state, i.e. carbides, whose grains or particles are less than 80 or 100 nm, show the most promise. Therefore in [Chap. 4](#) we described in detail the plasma-chemical and high-energy ball-milling methods for production of nanocrystalline tungsten carbide and consider the X-ray and electron microscopic methods for estimation of the average particle (grain) size. The model of mechanical grinding, which allows theoretical estimation of the ball-milling parameters necessary for production of powders with pre-assigned average particle size, is described for the first time. The application of this model is illustrated by the example of grinding of coarse-grained tungsten carbide powders.

Production of fine-grained WC–Co hardmetals has been examined repeatedly, but for a long time there were no available experimental data in the literature on the effect of particle size of tungsten carbide powders on the phase transformations taking place in hardmetals from the WC–Co system at different sintering temperature, on the peculiarities of interaction of nanocrystalline WC powders with cobalt, on thermal stability of phase and chemical composition, as well as on the particle size of nanocrystalline WC powders during their heating to 1400–1600 K in vacuum or in air. These problems as well as the peculiarities of sintering of WC–Co hardmetals with different cobalt content from nanocrystalline powders WC having different particle sizes, microstructure and mechanical properties of the sintered hardmetals are discussed in [Chap. 5](#).

We hope that this monograph will be useful to specialists in solid state physics, to materials science engineers, as well as to students of physical, chemical and materials science faculties.

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