

Review

Boron and tungsten carbides based and related nanodispersed composites— A review

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Abstract: Boron and tungsten carbides, B₄C and WC, are hard materials widely used in modern technologies. Further improvement of their performance characteristics involves the development of new B₄C and WC-based and/or related composites in a nanodispersed state. This article provides a review of available literature research on B-C-W systems, which would be useful in future studies in this direction.

Keywords: boron carbide; tungsten carbide; B-C-W system; composite; nanodispersed state

1. Introduction

Boron and tungsten carbides, B₄C and WC, are well-known hard materials widely used in modern technologies. Improvement of their performance characteristics involves the development of new composites with B₄C and WC matrices in a nanodispersed state. Good examples of this kind are the boron carbide-titanium diboride B₄C-TiB₂ quasieutectic and tungsten carbide-cobalt WC-Co ceramic alloys. In nanodispersed form, some additional attractive physical-mechanical properties are exhibited (for example, see the research of Chkhartishvili et al. [1,2] and Shabalin [3]) by more complex composites containing both boron and tungsten carbides, which serve as matrix and modifying components, respectively, or vice versa. This makes the development of newer boron and tungsten carbide-based and/or related composites very promising (for example, see the recent reviews of Manzar et al. [4] and Singh et al. [5] on various techniques for the development of hard boron carbon nitride nanoscale coatings on metal surfaces).

The present article aims to give only a short review of available in the literature research on B-C-W systems not illustrated with self-drawn or reproduced figures and tables and not provide criticism towards the described results. Authors are not claiming to provide exhaustive information about the huge number of publications in this field. Nevertheless, we believe that the data presented here are representative and thus will be useful in future studies on boron and tungsten carbide-based composite materials.

2. B-W systems

Using the tungsten coatings saturated with boron of compositions W-(13wt.-%-23wt.-%)B to substrates from austenitic steel was found [6] to be suitable. Obtained structures revealed much more resistance to corrosion and wear losses in material mass than uncoated steel. The beta-WB and W₂B (tungsten boride high-temperature phases) coatings of titanium Ti and steel surfaces containing tungsten can be formed [7]

applying the shaped charge explosion technique. Microhardness of coated material achieved 42 GPa. The hardness and stability of the highest tungsten borides, when they are built of tungsten atoms separated by borophene layers, were studied in the study of Gonzalez Szwacki [8].

Shift of so-called DBTT (Ductile-to-Brittle Transition Temperature) in tungsten foil was found by studying the neutron irradiation effect. Processing techniques, possible applications, as well as some physical characteristics of multilayered materials (ceramic-C and ceramic-metal structures) with an operating temperature higher than 1200 °C were considered in the study of Sorokin et al. [9]. This problem is of interest because of the applicability of boron compound-tungsten compound composites as effective neutron-shield materials.

Aiming to increase the physical-mechanical properties of tungsten tetraboride WB_4 (which is a lower-cost transition-metal boride), its solid solutions with metals, namely, chromium Cr, manganese Mn, and tantalum Ta, were synthesized and characterized [10]. And the concentrations of these transition metals up to 50.0at.% were tested. The listed solutions, which are the refractory compounds, were obtained from component elements by arc melting method. Samples chemical composition was examined using X-ray EDS (Energy-Dispersive Spectroscopy). The XRD (X-ray diffraction) results indicated that the solubility limits of Cr, Mn, and Ta in WB_4 are <10at.%, <20at.% and >20at.%, respectively. Vickers hardness optimized values measured by microindentation were of 53.5, 53.7, and 52.8 GPa when WB_4 was added with 10at.%, 4at.% and 2at.% of Cr, Mn, and Ta, respectively. It was also produced the tungsten tetraboride-based ternary solid solution with a Ta concentration fixed at 2at.%, while varying Mn and Cr concentrations. The values of hardness measured for $W_{0.93}Ta_{0.02}Cr_{0.05}B_4$ and $W_{0.94}Ta_{0.02}Mn_{0.04}B_4$ compositions equal to 57.3 and 55.8 GPa, respectively. According to the high-pressure (<65 GPa) in situ XRD measurements, for the hardest WB_4 -based solid solution, $W_{0.93}Ta_{0.02}Cr_{0.05}B_4$, the bulk modulus is 335 GPa, and a phase transition induced by pressure, which is observable in pure tungsten tetraboride, was suppressed.

Obtaining of powder tungsten tetraboride by reactive HPV (hot pressing in vacuum) method from powders of its component chemical elements (amorphous boron a-B and tungsten W) was systematically investigated [11] in dependence on temperature of synthesis, molar ratio between boron and tungsten in charge, applied pressure, and duration of phase formation. Metastable WB_4 was obtained at a molar ratio of B:W = 8:1 and a temperature of 1350 °C under uniaxial pressure of 30 MPa for 1 h. Both SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) studies revealed that particles of the obtained powder tend to agglomerate. Besides, a-B trace was detected in the product. At the same time, XRD pattern analysis of the as-synthesized powders conforms formation of the WB_4 crystalline phase.

3. C-W systems

In general, hard alloys are the wear-resistant metal materials that can retain their advanced properties at 900–1200 °C and are mainly made from carbides of tungsten, titanium, tantalum, or/and chromium and bonded with metal binders with varying

cobalt or nickel content. Hard alloys produced by industry can be divided into four groups according to the metal carbides present in them: tungsten, titanium-tungsten, titanium-tantalum-tungsten, and tungsten-free alloys [12]. One can see that the tungsten carbide presence is critical.

- The first group consists of alloys of the tungsten carbide-cobalt (WC-Co) system. They can be marked with the letters WCo and a number indicating the cobalt content as wt.%; for example, WCo10 alloy contains 10wt.% Co and the rest (up to 100wt.%) is WC. These alloys are characterized by maximum strength but reduced hardness. They are heat-resistant up to temperatures of 800 °C. As the content of cobalt increases, impact toughness increases as well, but wear resistance decreases. Alloys of the WCo-group are used for processing workpieces made of brittle metals such as cast iron, bronze, and other non-ferrous metals and alloys, as well as some non-metallic materials.
- The second group is formed by alloys of the tungsten carbide-titanium carbide-cobalt (WC-TiC-Co) system. They can be marked with the letters Ti and Co and numbers. The numbers after the letters Ti and Co mean the wt.% of TiC and Co, respectively, and the rest (up to 100wt.%) is WC. For example, the Ti5Co10 alloy contains 5wt.%, 10wt.% and 85wt.% of TiC, Co, and WC, respectively. Alloys in this group are more wear-resistant but less durable. As the TiC content increases, wear resistance increases, but strength decreases. The heat resistance of TiCo-group alloys is higher, about 900–1000 °C. The heat resistance performance increases as the amount of TiC increases. Tools made from alloys of this group provide higher cutting speeds. They are most often used for processing carbon and alloy steels.
- The third group is formed by alloys of the tungsten carbide-titanium carbide-tantalum carbide-cobalt (WC-TiC-TaC-Co) system. These alloys are usually marked with the letters TiTa and Co. The numbers after the letters TiTa and Co indicate the wt.% of titanium and tantalum carbides together, TiC-TaC and Co, and the rest (up to 100wt.%) is tungsten carbide WC. For example, the TiTa5Co15 alloy contains 5wt.%, 15wt.%, and 80wt.% TiC-TaC, Co, and WC, respectively. These alloys differ in greater strength and better resistance to vibration and chipping. Alloys of this group are used under the most severe cutting conditions—roughing of steel ingots, castings, and forgings.
- To rationally use scarce tungsten, a fourth group of tungsten-free hard alloys was developed. They contain titanium carbides (TiC) and titanium carbonitrides (TiCN) bonded with a nickel-molybdenum (NiMo) metallic alloy. Their manufacturing technologies are quite similar to the above-listed hard alloys containing tungsten; however, they have lower bending and impact strengths and, because of lower thermal conductivity, are more sensitive to changes in temperature. Their advantages are: higher (up to 1000 °C) heat resistance and lower adhesion during cutting and, consequently, not prone to buildup to materials being processed. This is why tools made from tungsten-free hard alloys are recommended for finishing turning and milling processes.

Thus, according to the chemical composition, hard alloys are divided into tungsten-cobalt (WCo), titanium-tungsten-cobalt (TiCo), and titanium-tantalum-tungsten-cobalt (TiTaCo) alloys. As for the production method, such classification of

hard alloys divides them into two groups: sintered and casted alloys. Products from sintered hard alloys are manufactured by powder metallurgy, and they can be processed by physical or chemical methods (dispersing and grinding, treatment with US (UltraSound) and laser, etching in acids, etc.) and, most perfectly, by electrical erosion. Casted hard alloys intended for surfacing tools can be subjected to mechanical and thermal treatments (annealing, hardening, aging, etc.).

Finally, the ISO (International Organization for Standardization) standards classify the hard alloys according to their intended purpose:

- P: steel castings and materials, processing of which forms the drain chips;
- M: processing difficult-to-cut materials (for example, stainless steel);
- K: processing cast iron Fe;
- N: processing aluminum Al, other non-ferrous metals and metallic alloys;
- S: processing heat-resistant alloys and titanium-based alloys; and
- H: hardened steel.

In hard alloys, as a result of combining their matrix and reinforcing modifiers, a complex of properties of the composition is formed, which not only reflects the initial characteristics of components but also includes properties that the isolated components do not possess. In particular, the presence of interfaces between reinforcing components and matrix significantly increases the crack resistance of the material, and in hard composites, unlike homogeneous metals, an increase in static strength does not lead to a decrease but, as a rule, to an increase in fracture toughness characteristics.

Hard alloy tools have high hardness and heat resistance, typically of 80–90 HRA and 800–1000 °C, because of refractory metal carbide components. Products made from them can be processed at several times higher speeds in comparison with the characteristic speeds of cutting high-carbon steels. The main disadvantages of hard alloys are fragility and difficulty in machining their products. They have reduced bending strength, 1000–1500 MPa, and very low impact toughness. Due to their high hardness, hard alloys are low-tech. For example, it is impossible to shape tools from them. In addition, hard alloys can be ground to a limited extent—only with a diamond tool. In this regard, frequently there are used their plates, either soldered or fixed to the tool holders.

As entropy is a key characteristic of thermodynamic systems, its calculation allows studying the equilibrium state, in particular, component contact interaction, when the composite is formed. A study by Syrovatko [13] introduced such calculations for tungsten carbide phases WC-W₂C eutectic by statistically processing the digitalized photos of scanned component phases. Entropies of WC and W₂C phases were found to be 29.22 and 58.38 J/mol·K, respectively, which are in satisfactory agreement with reference data [14]: 32.21 and 56.28 J/mol·K, respectively. Ultrafast compacting possibility for tungsten carbide WC without adding any binder phase was explored [15] for a technology combining sintering processes assisted with uniaxial pressure and limited AC (alternating current).

In modern production, WC-Co hard alloy parts are mainly made either by casting or powder metallurgy methods. Therefore, details with complex geometry often require further mechanical processing, which is associated with difficulties due to the high hardness of the material. So-called additive manufacturing technology was proposed [16] for producing details of small dimensions and complex configurations.

It includes SLM (Selective Laser Melting), SEBM (Selective Electron Beam Melting), inkjet additive production of binder, gel 3D printing, and melting stages. Product properties depend on WC particle size and Co amount in the composite. Due to the uneven distribution of energy, the microstructures of samples obtained by SLM- and SEBM-methods are not uniform. For this reason, their properties are unstable. In addition, in the samples obtained by SLM, due to the high energy density, Co and C are burned. These losses lead to cracked and brittle samples, and if the energy density is reduced, the cobalt cannot melt completely and the samples turn out to be porous.

Using the method of obtaining nanocrystalline tungsten carbide with Co component developed in Gachechiladze et al.'s study [17], the ultradispersed WC-Co alloys were synthesized from the precursor in the form of a suspension of ethyl alcohol solution of tungsten chloride $WCl_6 \cdot 6H_2O$ and a mixture of aqueous solution of cobalt chloride $CoCl_2 \cdot 6H_2O$ and an alcohol solution of urotropin $C_6H_{12}N_4$. It is known that in the process of synthesizing tungsten carbide, the presence of some intermediate complex carbides, mainly W_3Co_3C and W_6Co_6C , in the final product is expected, which cause degradation of the material's physical-mechanical properties. However, optimizing the technological parameters made it possible to obtain the final product without these intermediate carbides.

A systematic analysis of WC-Co alloys was carried out [18] on samples obtained under identical conditions. Namely, the influences of WC matrix particle size, Co binder content, and temperature on their complex mechanical properties were studied. By determining the mechanical characteristics during bending tests, the three temperature intervals with different mechanisms of plastic deformation, temperatures of ductile-brittle transition, and strain hardening coefficients, as well as their indicators, were established. Impact toughness increases and hardness decreases with increasing both Co content and average WC grain size, with some exceptions, where impact toughness and, consequently, cracking resistance can be increased at hardness expense and, thus, wear resistance. The maximum strength limit is reached when the average WC grain size varies in the range of 1.4–5.3 μm , and the Co amount in the alloy is 6 wt.%. The maximum compressive strength is achieved when the average WC grain size changes in the range of 1.4–1.7 μm . As for the bending strength limit, it practically does not change with further reduction of the average grain size.

Tungsten carbide compound produced by powder metallurgy methods, which is widely used to develop the tool materials necessary for high-speed processing, consists of carbide particles—usually tungsten carbide WC itself and a relatively soft metal binder. Currently, hundreds of WC-based alloys are known, most of which use cobalt Co, nickel Ni, and chromium Cr as binders, as well as other binders with various metallic and non-metallic additives. At room temperature, tungsten carbide WC is characterized by high hardness, which is largely maintained at higher temperatures. But it lacks sufficient high-temperature strength, the cutting tool's key property. To maintain the high hardness of tungsten carbide while increasing its toughness, the special metal binders should be used. The composite obtained in this way must have a much higher hardness than high-speed steel and a higher rate of service life as well. An increase in the amount of metal binder in the WC-Co alloy leads to a decrease in its hardness. The hardness of this material also depends on the size of the tungsten carbide particles; the hardness of the alloy decreases with the increase in the carbide

grain size [19].

The work of Pereira et al. [20] presents the WC-based composites with various binder metal systems: WC-Co, WC-CoNi, WC-Ni, WC-CoCr, WC-CoNiCr, WC-NiCr, and WC-NiCrMo. Wear in such samples was studied, and it has been determined that chromium-containing metal binders are characterized by higher wear resistance compared to other investigated composites.

The operational properties of hard alloys are improved not only by the influence of carbide additives but also by optimizing the composition of the cementing metal components. In this sense, the partial or complete replacement of cobalt in the WC-Co alloy still seems like a relevant task. Complex metal alloys have been proposed not only to replace cobalt but also to improve the high-temperature characteristics of the alloy. It is worth noting the creation of a cementitious multi-component metal alloy FeNiCoCr [21], in which the chromium content exceeds 8 wt.%. The characteristics of the WC-FeNiCoCr composite depend on the grain size of the matrix material, i.e., WC. In it, compared to WC-Co of the corresponding composition, the hardness value is essentially preserved and the toughness is reduced by 25%.

The WC-TiC-Co system alloys of various compositions are widely used in practice. Such compositions are characterized by high hardness, chemical stability at high temperatures, and wear resistance. It has been established that obtaining WC-TiC-Co systems in an ultradispersed state and maintaining such a state after compaction significantly improves the physical-mechanical and operational characteristics of the material. WC-TiC-Co systems can be obtained in a nanocrystalline state by sputtering liquid charge and chemical and mechanical methods. If the composition of the alloy is fixed, then the important factors that lead to the improvement of the material's mechanical characteristics are the size of the particles, the degree of homogeneity of the structure, and the purity of the initial powder. Thus, it is recommended that the sizes of the carbides, WC and TiC, which make up the WC-TiC-Co system, should be as small as possible—ultradispersed and their mixture—homogeneous. The sputtering method can be considered promising for obtaining high-purity nanopowders for industrial purposes. However, its application is hindered by the problem related to the titanium dioxide TiO₂ reduction in the WC-TiC-Co nanostructured system preparation process. A mechanical-chemical method was successfully used to obtain an ultra-dispersed WC-TiC-Co composite. In particular, its powder with 200 nm particle size was obtained [22] in this way.

The effect of TiC on WC-Co was studied [23], when it replaced WC by 5 wt.%–20 wt.%. This composite was consolidated by isostatic HTP (High-Temperature Pressing) at a temperature of 1350 °C and a pressure of 50–150 MPa. When replacing with 5wt.% and 20wt.% TiC, the required pressures were 50 and 150 MPa, respectively. It led hardness to increase from 1050 up to 1330 and 1600 HV. Such a high rate should be not only due to the addition of TiC but also to the reduction of porosity during high-pressure compaction. Young's modulus, on the contrary, decreases with the addition of TiC. When the Young's modulus of WC-Co was equal to 570 MPa, it became 420–490 MPa with the addition of TiC. The impact toughness and composite density also decrease slightly with the addition of TiC.

By discussing [24] the heat treatment processes in two-carbide, WC, and TiC alloys and the laser impulse effect on their structure, as well as operational mode

parameters, it has been established that the microcracks in the surface layers of Ti₁₅Co₆ alloy increase by 150–200 units due to laser-pulse impact. Such strengthening is associated with structural and phase transformations caused by electrical-physical effects: a new phase W₂C is formed in the surface layers, and the binding cobalt phase is saturated with tungsten and titanium carbides. In addition, laser heat treatment increases the operational characteristics of Ti₁₅Co₆ alloy by 2–3 times.

Physical-mechanical properties and structure of tungsten-cobalt WC-Co hardmetals, which contained different amounts of cobalt and alloyed tantalum and vanadium carbides (TaC and VC), were investigated in the work of Falkovsky et al. [25]. It was shown that the addition of 0.5 wt.%–2 wt.% TaC increases the hardness, while the bending strength remains practically unchanged. Then the content of TaC was kept at the constant level of 5 wt.%, while the VC amount changed from 0.4 wt.% to 10 wt.%. If the VC amount was less than its solubility in Co, the materials showed structure with basic carbide phase (WC) ultrafine grains: 0.2–0.5 μm. At 6 wt.% and 10 wt.% of Co, typical physical-mechanical parameters of these hardmetals were: hardness of 93.5 and 93.0 kgf/mm², bending strength of 1670 and 1870 MPa, cracking coefficient of 11 and 16 MPa·m^{1/2} and coercive force of 417 and 383 Oe, respectively. A process was developed [26] to produce WC in nanopowder form applying a plasma-chemical reduction method. The carbide grain size value was adjustable from 0.01 to 0.05 μm. Two more routes were suggested as alternatives to obtain WC-Co ultrafine-grade powder mixtures. Depending on the sintering mode variable parameters, the size of carbide phase grains was kept in ranges of 0.1–0.2 or 0.3–0.4 μm. The hardness of these hardmetals proved sharply increased, while their strength rose by 25%–30%.

It has been shown in the research of Ruziev et al. [27] that the addition of 1 wt.%–12 wt.% vanadium carbide VC in the WC-6 wt.%Co alloy slightly, no more than by 3%, increases the hardness of the material, but significantly, by 33%–50%, improves its wear resistance, compared to unmodified WC-6 wt.%Co. Also, properties and characteristics of WC-6 wt.%Co hard alloy separately modified with VC and rhenium carbide ReC were discussed. In particular, with the addition of ReC to 5 wt.%, the wear efficiency of WC-6 wt.%Co increases to 66.3%, while the working resource of the tool made from it increases to 35.0%.

The WC-13 wt.%Co composite with added iron Fe can be obtained [28] by pressureless sintering. Material structure, porosity, and size of grains, as well as mechanical properties, were studied using SEM, XRD, X-ray EDS, and Vickers hardness tests. The Fe atoms position, when they are added in component phases, was determined: in eutectic, at 2 wt.%–4 wt.%, it exists both in low-carbon eta- and binder phases. In the eta-phase lattice, Fe atoms occupy the Co sites, being uniformly distributed in the binder simple cubic lattice. Tungsten boride growth in melted iron was found to be strongly limited. In W-C-Co-Fe systems, WC grain size increases up to 1.14–1.21 μm, when iron content increases to 4 wt.%. Thus, the WC growth process in melted CoFe metallic alloy should differ from that in melted iron and be closer to that in melted cobalt. When both 2 wt.% Fe and 1 wt.% C are added, the sample possesses the optimal combination of hardness/toughness: hardness is increased up to 1070 HV (from 980 HV for the sample without Fe and C additives) at a slight increase in toughness.

Interface models of DCCC (Diamond-Coated Cemented Carbide) WC-Co, with

interface terminals TiC, TiN, CrN, and SiC but without intermediate layers, were suggested in Yang et al.'s study [29]. According to the conducted calculations, adding four corresponding intermediate layers increases the work of interface adhesion. Interface adhesion improvement of this DCCC could be ranked as: SiC > CrN > TiC > TiN. Adding the intermediate layer changes the interface junction charge distribution and forms a more stable chemical bond as a result of interface junction electron cloud overlapping. In the energy overlapping area, an additional intermediate layer increases the interface atoms DoS (density-of-states). And the DCCC interface bonding enhances as well. The most obvious should be diamond/SiC_{C-Si}/WC-Co interface interatomic electron cloud overlapping. Corresponding bond length was found to be the shortest: 1.62 Å, while the energy resonance peak-forming region was the largest, from -5 to +20 eV, and bonding was the strongest. At the diamond/TiN_{Ti}/WC-Co interface, on the contrary, these characteristics were the longest: 4.11 Å, the smallest from -5 to +16 eV, and the weakest, respectively. Among the considered intermediate layers, the best and the worst for improving the DCCC interface bonding were SiC and TiN, respectively.

4. B-C-W systems

WC tool cutting edges treated by LD (Laser Doping) of boron nitride BN revealed extra-long cutting distance. In view of this, WC-Co, the base material of the tool, was processed [30] similarly to the study, resulting in changes in crystal structure. X-ray and electron backscatter diffractions allow to observe the effect in the near-surface 50 nm thick LD: increased by ~11.7% strength at maintained WC structure.

Some physical-mechanical and tribological properties of WC-TiB₂ composites, as well as their microstructure, at sliding (against stainless steel-201) conditions were studied in Zhang et al.'s study [31]. Mechanical properties and relative density improved, while concentration of microstructural defects decreased when the TiB₂ component increased from 10 wt.% to 30 wt.%. As for the friction coefficient, it decreased both with increasing applied load and sliding speed. As the fracture effect is important for composite coatings contact surfaces, it led to the formation of abrasive and adhesive wear mechanisms. For WC-TiB₂ compositions, the rate of specific wear increased with increasing sliding velocity and normal load. In particular, the sample of intermediate composition WC-30wt.%TiB₂ possessed better tribological properties than WC-10 wt.%TiB₂ and WC-20 wt.%TiB₂ ones.

Tool materials from TiB₂-WC compositions can be produced [32] using the HPV technique with sintering additives such as Co and Ni metals and NiMo metallic alloys as well. SEM-, XRD-, and EDS analyses showed that TiB₂-WC ceramic composites microstructure consisted of TiB₂ uniform and WC fine grains. In composition TiB₂-WC-Ni, there are observed few pores and Ni₃B₄ brittle phase inclusions. As for the composition TiB₂-WC-Co, it contains a lot of pores and Co₂B and W₂CoB₂ brittle phases. Coarse-grained TiB₂ phase and pores are formed as a result of the reaction consuming the liquid cobalt. Coarse-grained components, brittle phase inclusions, and pores in significant volume fractions were harmful to the TiB₂-WC compositions mechanical properties and density. Using NiMo alloy as a sintering additive had significantly improved these characteristics. The accompanying process of MoNi₄

intermetallic compound formation not only inhibited NiMo liquid phase consumption and related coarse grains and pores growth but also strengthened the WC/TiB₂ interface interaction between grains of different components. As grains were fine, the relative density of TiB₂-WC-NiMo composite in average was up to 99.1%. Material Vickers hardness, flexural strength, and fracture toughness were of 22.7 GPa, 1307 MPa, and 8.2 MPa·m^{1/2}, respectively.

Boron carbide and its different nanocomposites manufacturing parameters were studied [33] for an effective two-stage technology. At the first stage, the combustion method is used to obtain boron carbide in nanopowder form, and then, at the second stage, metalceramic-ceramic nanocomposites on the basis of boron carbide are produced in the process of joint melting, milling, and sintering. At well-adjusted composition B₄C-25wt.%TiB₂-10wt.%(WC-10wt.%Co), the boron carbide-titanium diboride-tungsten carbide-cobalt nanocomposites powder morphology shows the reduction of B₄C particles in size from 500–5000 to 200–600 nm.

The synthesized composite powder XRD pattern proves the presence of all the target phases: B₄C, TiB₂, WC, and Co. WC peaks are of relatively low intensity, which can be explained by some transformations taking place in the WO₃ reagent phase. The obtained product may contain graphite with ultrafine grains, a mixture of various tungsten borides with “amorphous” structure, and trace phases as well. The different B:C:Ti:Co ratios according to the charge composition and experimentally obtained from the EDS spectra showed the combination of carbon reduction and cobalt evaporation yielding the ultrafine-grained tungsten borides formation. Such a mixture behaves as an amorphous-like inclusion. From XRD- and EDS-analyses, it can be concluded that the synthesized fine-grained powders contain both ceramic B₄C-TiB₂ and ceramic WC-Co components of the target composite; however, there are also some amorphous-like trace phases that are not visible on the XRD patterns. To find the sources, it is suitable to analyze chemical reactions taking place in the system at elevated, >1500 °C, temperatures. To examine the corresponding reaction, a test process was conducted with a powder mixture of B₄C-TiB₂-(WC-Co) at 1800 °C. The presence of crystalline B₄C, TiB₂, W₂B₅ and graphite traces is clearly visible on the product XRD pattern. Therefore, the sintering temperature of powders synthesized in this way should not exceed 1600 °C, as tungsten boride W₂B₅ is expected to form at higher temperatures.

A wet chemical method can be used [34] to prepare preceramic precursors for low-temperature synthesis of ultrafine powders of tungsten boride composite with boron carbide matrix ceramics. That technique includes the thermal treatment of ammonium paratungstate-zirconium oxide-cobalt acetate tetrahydrate-sucrose-amorphous boron mixture viscous paste in air at 200 °C and then in argon at 600 °C for 2 h, grinding of the intermediate powder product, and its additional thermal treatment at 800–1500 °C. These complex ceramic powders were pressed at 1000–1700 °C by using the SPS (Spark-Plasma Sintering). Phases WO_{3-x}, Co₃O₄, CoO, and amorphous carbon were formed at 600 °C. XRD-analysis data confirmed the relatively low-temperature (800–1000 °C) formation of WC-Co, B₄C, and metal boride (ZrB₂ and W₂B₅) phases. Finally, WC was completely converted into W₂B₅.

For boron carbide-based composites production, the ultradispersed powders of preceramic precursors were obtained [35] by their relatively low-temperature (200–

1000 °C) synthesis from liquid charge consisting of commercially available compounds (oxides and salts). These ceramics with boron carbide matrix were consolidated by their SPS at 1500–1700 °C. The XRD peaks of monoclinic zirconia ZrO_2 and WC phases visible in the preceramic precursors disappeared when the SPS process was conducted at 1500 °C. It was demonstrated that additive compounds of tungsten and cobalt promoted not only ceramic components low-temperature synthesis in powder form but also their sintering processes. According to the EDS analysis, the ceramic products contain a small amount of Co (0.8 wt%–2 wt%). The cobalt-containing ceramic B_4C - ZrB_2 - W_2B_5 -Co density exceeds that of Co-free ceramics (such as B_4C - ZrB_2 - W_2B_5).

5. B_4C -W systems

Compositions B_4C -W with 5 vol.%, 10 vol.%, 15 vol.%, and 20 vol.% W were synthesized [36] by SPS in vacuum at uniaxial pressure of 40 MPa and temperature of 1500–1600 °C for 4 min (at a heating rate of 100 °C/min). For initial materials served the commercial powders of B_4C and W with particle sizes of 0.7 and 60 μm and purity of 99.5% and 99.8%, respectively. The initial mixture of these powders was prepared by milling for 24 h in ethanol with WC balls. Tungsten pentaboride W_2B_5 formed as the result of a reaction between particles of the B_4C and W component phases. When the tungsten amount increased, part of the carbon remained unbound, forming the graphite phase inclusions. On the one hand, the free carbon presented in these composite materials deteriorated their physical-mechanical properties. But, on the other hand, metallic tungsten addition improved some technological properties of initial powder mixtures, in particular, their sinterability. Besides, it densifies the matrix like boron carbide samples with almost theoretical densities. Studies of neutron- and gamma-radiation attenuation by carbide-tungsten composites lead to the conclusion that increasing the tungsten concentration in the B_4C -W system yields the higher gamma-attenuation property of this composite, whereas it provides a lower neutron shielding capacity than that of pure B_4C .

For B_4C -based ceramics, pressureless sintering of powders can be considered an industry method. However, it possesses a disadvantage as well: the impossibility to sinter to high density without densification additives. Parts of sintering additives, tungsten among them, and appropriate methods of sintering are described in the review [37].

From B_4C -W-WC system powders, it was obtained [38] WC-WB- W_2B composites using reactive hot pressing, which initiated energization by a solid-state reaction between B_4C and W components. At 76.9 mol.% WC in the starting powder, phases of WB and WC were formed in the reaction $B_4C + 5W + xWC = WB + (1 + x)WC$. These two plus W_2B phases were produced at 85.4 mol.% WC. Pure WC in densely sintered state was not obtained. As for WC-WB- W_2B compositions obtained at (5.4 mol.%–95.6 mol.% WC), they were fully consolidated, having high mechanical characteristics (Young's modulus, Vickers hardness, and fracture toughness) comparable with pure WC.

Toughness, hardness, and crack density of fine-grained WC-Co compositions were investigated in Tamizifar et al.'s [39] work. Namely, about 30 experimental and

commercial hard metal grades with different additives, such as boron B_4C , vanadium VC, chromium Cr_3C_2 , and silicon carbides SiC, were obtained in an HPV commercial isostatic sintering furnace. Microstructural and physical-mechanical properties were investigated to construct a representative hardness/crack density measurement band useful to estimate the most effective temperature for sintering, as well as amounts of additives. Comparison of grain growth inhibitors effect in optimal conditions showed that B_4C - and VC-doped grades for growth inhibitors exhibit the maximal hardness. However, addition of Cr_3C_2 is found to favor the toughness improvement.

Boron carbide coatings can be synthesized using the method of an RF (Radio Frequency) plasma source and an external magnetic field [40]. The nanohardness of steel surfaces coated in this way was 14.0–16.6 GPa. Such B_4C coatings were found to have the hardness 1.73–3.89 times higher than uncoated (bare) steel surfaces served as targets. This technique would be useful for coating tungsten substrates with boron carbide.

Due to the high cross section of (epi)thermal neutrons captured by boron ^{10}B isotope nuclei, all-boron and boron-rich systems—compounds and composites—are widely used as materials that intensively interact with neutron radiation. In the fine-dispersive form, they have the improved performance characteristics. Preparation methods of some fine-dispersive important boron-containing B_4C -W composites useful in neutron shielding were reported in the studies of Chkhartishvili et al. [41,42].

Using the spin coating technique on the B_4C surface, first a WO_3 layer was deposited to reduce it to metallic α -W at a temperature of 600–800 °C under a hydrogen atmosphere. Usually, such α -W layer was weakly attached to the boron carbide. The sandwich composites can be effectively obtained by SPS at 1300–2000 °C. For this purpose, the method by which previously tungsten-contained multicomponent ceramics with boron carbide matrix were synthesized was modified. The substrates used were compacted by SPS at temperatures of 1500–2000 °C from ultradispersive boron carbide powders prepared from liquid charge systems like amorphous boron-carbohydrates-water and boron acid-organic compound-water. During heating at temperatures exceeding 1300 °C, in these sandwich structures, it starts the formation of tungsten pentaboride W_2B_5 , while at >1600 °C it converts into a new sandwich composite B_4C - W_2B_5 . From two-component sandwiches, applying the SPS, one is able to manufacture similar multicomponent structures: B_4C -W- B_4C -W, W- B_4C -W- B_4C , and the like.

Monolithic B_4C -W samples were obtained from B_4C and W powders in SPS processes as well. First, the powder of metallic W was compacted and placed in a graphite press mold with a graphitic foil lining. Then B_4C powder was sprinkled on the W layer. After leveling the surface, again the graphitic foil was placed on it. During the described method, including rapid heating together with applying a certain pressure, powder consolidates and a sandwich composite is obtained. The SEM and EDS investigations showed the presence of the fracturing on the contact interface between B_4C and W consolidated in the sandwich structure. There are the opposite directions of diffusion of B and W atoms, and an intermediate-phase W_2B_5 forms. The thickness of layers can be adjusted within wide limits. After removing metallic tungsten and tungsten boride layers, the sample sintered at 1600 °C revealed the relative density of boron carbide as 87%–92% of the theoretical value. XRD patterns

of the cleaned surface unambiguously confirmed boron carbide presence, as well as metallic tungsten removal from the sandwich surface. To obtain similar composites using tungsten plates instead of their powders, a new method was developed. Conclusion was made that heating and pressing of the boron carbide powder-metallic tungsten foil structure leads to the intermediate phase W_2B_5 formation and provides a strong bonding between these phases.

Based on theoretical simulations [43–45], B_4C -W thin-layered sandwich compositions are considered effective shield materials containing both low- and high- Z atoms (here Z denotes the atomic number), boron and tungsten, serving as effective absorbers for, respectively, (epi)thermal neutrons and secondary gamma-quanta, which accompany the neutrons captured by ^{10}B nuclei.

The thin film materials based on W and B and including B_4C , WC, and WB_3 phases can display too high a hardness. Compounds of composition WB_{3+x} were shown to have Vickers hardness approaching 40 GPa for relatively small x . Thin film materials based on W and B and including B_4C , WC, and WB_3 display very high hardness. Also, borophene doped with W was found to exhibit superior hardness. In Martin's [46] study, $W_{1-y}B_{3+x}$ structures elastic properties were summarized. Among them, only the stoichiometric WB_3 phase can be considered as superhard material. Contamination with extra B-atoms is energetically unfavorable and affects the hardness: it lowers the shear modulus while maintaining the bulk modulus, effectively leading to a softer material. The W-vacancies, e.g., in $W_{0.75}B_{3+x}$ composition, form structures with hardness less sensitive to variations in boron content.

Interface roughness influences the B_4C -W multilayer reflectivity and varies with bilayer number N [47]. In particular, multilayers of B_4C -W composition with equal design period thickness (2.5 nm), a real-structure model can be used to calculate the variation of reflectivity with N ($N = 50, 100, 150,$ and 200). DC (Direct Current) magnetron sputtering system was used to fabricate such multilayers. The XRD measurement of their reflectivity and scattering intensity indicates that the reflectivity is a function of bilayer number, and interface roughness slightly increases from layer to layer during the growth of the multilayer.

6. B_4C - WB_2 systems

From B_4C and WB_2 as initial raw materials, the densified compositions B_4C - WB_2 were produced by the HPV method at a temperature of 1950 °C [48]. The B_4C -68.7 vol.% WB_2 composition obtained in this way demonstrated a quite good set of physical-mechanical properties such as superior hardness of 34.8 GPa, high flexural strength of 696 MPa, acceptable fracture toughness of $3.3 \text{ MPa}\cdot\text{m}^{1/2}$ and low density of 5.59 g/cm^3 . These compositions, in addition, showed good electrical conductivity of $3.3 \times 10^5 \text{ S/m}$, which, together with the above mechanical properties, make them interesting for various applications, e.g., as armor protection and cutting tool materials.

Based on the explored B_4C - TiB_2 compositions fine microstructure, it was proposed [49] an overall evolution picture of their microstructure, starting from the processing of raw powders to sintering and compacting. It was found that structures with small-scale grain and their local mechanical properties (measured applying the nanoindentation method) are correlated and thus provide a trend in their mechanical

behavior. In particular, dense ceramics can be typified by the core-shell structure development in titanium boride grains, where shells comprise two-component solid solution $\text{TiB}_2\text{-WB}_2$ with different assemblage and variable (in dependence on the technological route) content of tungsten atoms, i.e., guest cations. Analyses conducted by TEM revealed some morphological and chemical differences that can be related to the densification mechanisms. To extract the composite and component phases (core TiB_2 , shell WB_2 , and matrix B_4C) properties, it was used the nanoindentation highlighting modulus and hardness variations as functions of lattice perturbation from nominally pure boride coarse to shell regions.

7. $\text{B}_4\text{C-W}_2\text{B}_5$ systems

To understand the WC and TiC additions effect on mixtures of compositions $\text{B}_4\text{C-B-Si}$ on the sintering process and final product mechanical properties, a special investigation was undertaken [50]. In the process of milling in attrition, the starting component powders are alloyed with WC, TiC, and Co phases by the hard metal spheres. In the case of long milling, the rate of material wear decreased strongly. Powder products milled for 2 and 4 h, respectively, contained 39 wt.% and 47 wt.% WC-TiC. During the heating, the components of the starting powder milled for 2 h (B, B_4C , Si, Co, WC, and TiC) reacted to form B_4C , TiB_2 , and W_2B_5 . Some chemical reactions took place in the temperature range of 800–1500 °C.

The W_2B_5 boride phase started formation at 1100 °C and its maximum amount is reached at 1600–1800 °C. The content of W_2B_5 phase very strongly decreases at higher temperatures. The TiB_2 phase started its formation at 1050 °C and at further heating the system up to a temperature of 1200 °C its content increased. Within the temperature range of 1200–1800 °C, the TiB_2 phase amount remains almost unchanged, and when temperature is higher than 1800 °C, a strong increase in the TiB_2 amount takes place.

Increasing in TiB_2 amount and decreasing in W_2B_5 amount at same temperatures lead to the conclusion that the solubility of W in TiB_2 increases with temperature. It is why the three different phases in form of boron compounds are observable. These are boron carbide, tungsten pentaboride, and titanium diboride. The grain size of these boron compounds is about 1 μm .

The 72 vol.%, 20 vol.% and 8 vol.% of component phases B_4C , TiB_2 and W_2B_5 , respectively, contained the alloy compositions prepared by powder attrition milling for 2 h. The material porosity was less than 3 vol.%. The increase in temperature causes the decrease in density because of W_2B_5 dissolution and subsequent formation of the diboride system $\text{TiB}_2\text{-WB}_2$. This reaction lowers both the hardness and bending strength of the material after its compacting. The above-presented observations can be summarized as follows: Attrition milling of mixtures containing B_4C , B, and Si powders with WC-TiC-Co spheres decreases the hot-pressing temperature and increases the strength of boron-carbide-based hard material. During heating, the starting components reacted and formed boron carbide and TiB_2 and W_2B_5 boride phases, which are more stable than corresponding carbides.

Pure boron carbide and boron carbide-based composite ceramics $\text{B}_4\text{C-W}_2\text{B}_5$ were prepared [51] by the hot-pressing method. Their microstructure and chemical and phase compositions were characterized by means of XRD, TEM, and EPMA (Electron

Probe MicroAnalysis). Measuring results of their electrical conductivity and Seebeck coefficient temperature dependences in the range of 300–1500 K showed that the B_4C - W_2B_5 composite electrical conductivity strongly exceeds that for pure boron carbide, while the composite Seebeck coefficient is somewhat lower if compared with that for the B_4C ceramic. Note that both of these characteristics increase with temperature. The figure-of-merit of this composite ceramic was found to be higher than that of the B_4C , though its thermal conductivity is somewhat higher in comparison with that of boron carbide.

Two, WB and W_2B_5 , tungsten borides, were experimentally prepared [52] by the SHS (self-propagating high-temperature synthesis) process, during which borothermic reduction of tungsten oxide WO_3 and interaction between B and W proceeded concurrently. Two series of molar proportions, $WO_3:B:W = 1:5.5:x$ with $x = 1.16$ – 2.50 and $1:7.5:y$ with $y = 0.50$ – 1.33 , were adopted for powder mixtures to produce WB and W_2B_5 phases, respectively. The reactants compact starting stoichiometry substantially affected the combustion regime and the final product composition. Increasing in tungsten and boron contents reduced the overall exothermicity of the reaction, which leads to some decrease in both reaction front velocity and combustion temperature. The initial composition of the reactant compact should be optimized for the predominant synthesis of WB or W_2B_5 . The compact WO_3 -5.50B-2.00W powder system dominantly produced WB together with small amounts of W_2B and W_2B_5 additive phases. As for the W_2B_5 phase optimal formation, it was observed from the initial system of WO_3 -7.50B-0.85W composition. Excess in boron amount about 10 mol.%–13 mol.% was experimentally found to be favorable for the formation of mentioned WB and W_2B_5 trace phases.

Pressureless sintering at 2150 °C can be used [53] to compact boron carbide-based ceramic powders to a relative density of 96.1% with the co-incorporation of tungsten carbide WC and pyrolytic carbon C phases. The specific surface of as-batched boron carbide powder was 7.89 m²/g. In the BW-6C composite, the fracture toughness value of 5.80 MPa·m^{1/2} was achieved. As for the sintering aids for tungsten boride and carbon, they were formed in an in-situ reaction. The observed improvement in material toughness should be attributed to the residual thermal stresses as well as the presence of W_2B_5 phase platelets. Thus, B_4C - W_2B_5 composites have the potential to be used as structural materials.

Boron carbide matrix graphite-containing composites and in situ-formed W_2B_5 were obtained [54] by the SPS method. Starting powders of B_4C containing 5 vol.%W were shaped into the composite bulk. The sintering was conducted under vacuum at 1500, 1550, and 1600 °C. Sintering temperature and tungsten addition influences on material microstructural and phase properties, densification degree, hardness, and fracture toughness were examined by XRD and SEM in-Lens mode, as well as Vickers indentation technique and Palmqvist method. Results showed that these composites possess high hardness and improved fracture toughness.

The ceramic compositions B_4C -(WC-TiC) containing different amounts of WC-TiC solid solution were obtained in the work of Deng et al. [55] by the hot-pressing method. A chemical reaction taking place during the process resulted in B_4C -TiB₂- W_2B_5 composite with high density and mechanical properties improved in comparison with monolithic boron carbide. Addition of WC-TiC solution affects the rates of

densification of the composite. Increasing in WC-TiC content increased the densification rate, while the B₄C-(WC-TiC)C composites sintering temperature was lowered to 1850 °C from that of 2150 °C for monolithic boron carbide. With an increase in WC-TiC content up to 50 wt.%, the composite material's hardness decreased while its flexural strength and fracture toughness increased continuously.

The boron carbide matrix composites B₄C-(TiB₂-ZrB₂)-W₂B₅ and their cobalt Co additive can be obtained from commercially available initial compounds on the basis of preparing corresponding precursor pastes and their processing in controlled thermal regimes [56]. All the component phases (B₄C, TiB₂, ZrB₂, W₂B₅ and Co) can be synthesized at relatively low temperatures (around 1000 °C) from cobalt-containing liquid charges. Note that from cobalt-free precursors only zirconium diboride formation can be observed under the same conditions. Maintaining the initial grain size by inhibiting their SPS growth in boron carbide matrix composite powders with cobalt additive is one more advantage of this approach.

8. W layers

Surfaces of different types coated with metallic tungsten are widely used in DRA (Dynamic Random Access) and flash memories, microprocessors, image sensors, and a number of other modern technologies. The thin-layer coatings of semiconducting surfaces with W are mainly carried out applying CVD (Chemical Vapor Deposition) technique using for precursor materials WF₆, SiH₄ and H₂. Maintaining the vacuum in the reaction chamber at pressure within the range of 20–760 Torr increases both the tungsten deposition rate and reflectivity of the produced W-surface [57].

Using the LPCVD (Low Pressure CVD) method, thin W film was deposited [58] (see Plyushcheva et al.'s [59] work as well) on Si(100) substrate. WF₆ and SiH₄ were used for source and tungsten-reducing (from WF₆) gases, respectively. The deposited tungsten thin film was formed either on SiH₄ or Si substrates by the WF₆ reduction in cold wall conditions and by the SiH₄ reduction under the hot wall conditions. The nm-layer tungsten silicide W₅Si₃ was formed at the W-Si interface only during the gas phase deposition. Growth of other tungsten silicide WSi₂ layers commences at 700 °C for CVD layers and above 750 °C for plasma-chemically deposited films. This drastic increase increases the material's electrical resistance: under optimal conditions, W-films with a resistivity of 8×10^{-6} Ohm·cm can be obtained.

Dissolving of tungsten in hydrogen peroxide and subsequent evaporating the residual solvent yielded [60] the water-soluble powder of tungsten-IPA (Inorganic Peroxopolytungstic Acid). The obtained W-IPA solution was mixed with organic solvent and spin-coated on wafer. Films of metallic tungsten were formed by the reduction process. Appropriate selection of organic solvent and UV (ultraviolet) irradiating leads to the film with remarkably decreased sheet resistance.

Frequently obtained tungsten powders are nanosizes. Reduction of WO₃ at 600 °C by using in situ produced hydrogen gas [61] could be considered for a W nanopowder production route. According to the XRD patterns, the final product's alpha- and beta-W phases are presented in nanostructured form. DTA (Differential Thermal Analysis) showed that phase transition from beta-W to alpha-W takes place at a temperature of 435 °C. Pastes and suspensions of powders of this type were used for coating various

surfaces. Tungsten alpha-W layer can be formed by reducing WO_3 oxide layer preliminary formed by spin coating in hydrogen at a temperature of 600–800 °C [62]. Applying the $WO_x(OH)_y$ chemical vapor transport, the morphology of the tungsten surface can be transformed into star-shaped cracking, floret, irregularly fibrous, rod-like, and spherical particles.

Technologies of tungsten deposition on different metal substrates are also used [63]. Commonly applied metals are aluminum, copper, and titanium. PNL (Pulsed Nucleation Layer) and ALD (Atomic Layer Deposition) methods can be used to grow layers of tungsten nucleation. The ultrafine tungsten powder reduction industrial process evolution is described in Gao et al.'s [64] study. In industrial push furnaces, the blue oxides of tungsten were used for reduction in hydrogen counter-current flow. Reduction was carried out according to the following scheme: $WO_{2.9} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$. Quite often, the pure tungsten films are deposited using PVD (Physical Vapor Deposition) or evaporation/sputtering and CVD. The HWALD (Hot Wire-assisted ALD) method, which was developed in Yang et al.'s [65] work, forms a tungsten layer from W-filament heated up to a temperature of 1700–2000 °C. Atomic hydrogen generated by molecular hydrogen dissociation can react with WF_6 at the substrate to form the deposit. Typically, nucleation CVD layers are deposited in argon carrier gas from SiH_4 and WF_6 . A cheap and, at the same time, practical method is the metallic tungsten coating on the ceramic surface, which uses the applicability of chemical solution deposition to form films on the alumina tubules inner surfaces. This approach includes the tungsten oxide layer preparation from PTA (PeroxoTungstic Acid) precursor solutions and subsequent reduction to tungsten under hydrogen [66].

The patent [67] proposes a technological route of formation of the sandwich structures, namely, a method of metallization of boron carbide ceramics. This invention describes the four-step process: Step 1: Mixing of metal powder containing 10 wt.%–40 wt.% Mo, Ni, and W (according to wt.% ratio) during ball milling and 300-mesh sieving; Step 2: Mixing the obtained in the Step 1 metal powder with 5 wt.% ethylcellulose solution in wt.% ratios of (100–120):30 to prepare the metalized paste; Step 3: Printing the obtained in the Step 2 metalized paste on the boron carbide ceramic part to be metalized to a layer of thickness of 20–30 μm and its drying; and Step 4: Metalizing the obtained in the Step 3 dried boron carbide part by its placement for metallization into a sintering furnace and for 30–35 min at temperature from the range of 1650–1680 °C in hydrogen, keeping the dew point at 0–10 °C and cooling along with the furnace. The proportioned MoNiW metallic alloy layer is close to the boron carbide thermal expansion system. Its bonding strength is high, while the metalized stress is small. Due to the sub- μm network structure, the formed metal layer is not prone to falling off after brazing.

The spin coating allows to reduce the previously formed WO_3 tungsten oxide layer to an alpha-W layer at a temperature of 600–800 °C in hydrogen [68]. Hardness and wear resistance of such tungsten layers, when they are sequentially implanted with boron B (and carbon C as well) 60 keV ions at temperatures of 300–350 K, were investigated. For sample hardness testing, they were modified by fluences of 1×10^{15} – 3×10^{15} and 1×10^{16} – 3×10^{17} ion/cm². Nano- and micro-indentations showed that hardness and wear resistance of obtained composites are improved with 1.3–4.5- and 2.0–6.7-times, respectively.

The superior mechanical properties characteristic of tungsten foils at room temperature can be expanded [69] by fabricating the metallic laminate composites containing tungsten.

9. Utilization of W-containing waste

As mentioned, tungsten-containing alloys are widely used in modern technologies. For this reason, the demand for this type of material is increasing day by day. The scarcity of tungsten led to its removal from tool scrap and reuse to make hard instruments. Methods for extracting tungsten from tungsten-containing scrap have been developed for decades. A number of methods implemented in practice have certain strengths and weaknesses. In general, when selecting ways to process such waste, it is important to take into account the productivity and simplicity of the technological process, its environmental friendliness, and also low energy costs. The description of main ways of processing wastes of tungsten-containing hard materials is given in the book of Panov and Chuvilin [70].

Here are listed the main methods used to recycle such kind of waste in the production of tungsten-containing hard alloys.

- Crude dispersion of sintered waste with different types of crushers and then grinding of the obtained mixtures into finely dispersed fractions (a version of this method is to extract cobalt from waste by heating it to 2300–2500 °C and dispersing the rest material);
- Complete decomposition of waste by chemical-metallurgical methods in a special furnace with strong oxidizers—alkaline nitrates and nitrites, product pouring, crushing, and leaching in hot water;
- Selective separation of cobalt from the solution by heating and treating it with acid or alkali;
- Multistep chlorination in the presence of carbon dioxide to obtain tungsten and cobalt chlorides and their separation in distillation columns, purification, conversion into oxides, and reducing;
- Heating to 1100 °C, oxidizing it in air, and reducing WO_3 together with forming cobalt tungstate hampering complete removal of tungsten;
- Oxidizing and then chlorinating to trap the tungsten chloride and leave the cobalt dioxide in the chlorinator;
- Electrochemical processing of solutions of ammonia, alkaline, and salts;
- Hydro-/pyrometallurgical sawdust processing;
- Processing with regenerators, including fine-grained grinding with a high-energy air stream, quenching of hard alloys in ice water at 1300–1400 °C and crushing the forged mass;
- Dissolution with sodium hydroxide, precipitation in hydrochloric acid, precipitation and purification of ammonium paratungstate with ammonia, and reduction to tungsten with hydrogen;
- Thermal regeneration as an oxidation-reduction-carbidization process; and
- Cobalt extraction with zinc and vacuum distillation.

A comparative economic analysis [71] of different regeneration technologies of producing the metalceramic alloys demonstrated the ability of shock-wave processing

as a stimulating factor for powder products (of any configuration) destruction to obtain high-quality powder for further molding and sintering to produce tools of various purposes, eco-friendly technology of processing superhard materials, as well as metalceramic components of obsolete military equipment. Industrial tests of rock destroying tool batches, die-blanks for non-ferrous metallic drawing pipes, and mandrel-blanks confirmed the high quality, effectiveness, and feasibility of the developed technology.

An analysis of available methods to study the tungsten waste regeneration from hard alloys containing cobalt was conducted. These are chemical (chlorine and zinc) and thermochemical and hydro- and pyrometallurgical methods, as well as technology based on explosive energy consumption. Metalceramic solid alloys are heterogeneous mixtures, in bulk of which there are surfaces with gaps in any microscopic parameter values.

Industrial technology development solves the superhard alloys and scrap materials recycling problem and also helps in their subsequent rehabilitation and, respectively, significant savings of expensive raw materials.

The regeneration process of hard alloys under the influence of shock waves is also processed. Through the direct regeneration of secondary raw materials, this highly efficient production technology allows, without thermochemical and metallurgical processes, obtaining the powders of hard alloys useful to create the tools. This technology differs from the existing ones in terms of high technical and economic indicators, high performance, low energy consumption, and environmental friendliness. The recovery of the tungsten-containing mixture is carried out under conditions of high-pressure gradients and delivery velocities in cylindrical reaction ampoules subjected to the impact caused by the detonation of an axially symmetric explosive charge.

10. Conclusions

In summary, there is a review of scientific publications on boron and tungsten carbide-based and related nanodispersed composites, the hard materials, with a perspective of wide technological applications. It covers a class of hard materials such as boron-tungsten B-W, carbon-tungsten C-W, boron-carbon-tungsten B-C-W, boron carbide-tungsten B_4C-W , boron carbide-tungsten diboride B_4C-WB_2 and boron carbide-tungsten pentaboride $B_4C-W_2B_5$ systems, as well as tungsten W layers. Especially is discussed one of the related important tasks: utilization of the W-containing waste to reduce tungsten, an expensive metal, for its reusing in hard instrument production.

Conflict of interest: The authors declare no conflict of interest.

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