

Advanced tungsten-containing materials manufacturing from its scrap

Levan Chkhartishvili^{1,2,*}, Natia Barbakadze³, Otar Tsagareishvili², Archil Mikeladze², Tamaz Batsikadze⁴, Manana Buzariashvili³, Tamar Dgebuadze³, Roin Chedia^{2,3}

¹ Engineering Physics Department, Georgian Technical University, Tbilisi 0160, Georgia

² Semiconducting and Powder Composite Materials Laboratory, Ferdinand Tavadze Metallurgy and Materials Science Institute, Tbilisi 0186, Georgia

³ Petre Melikishvili Institute of Physical and Organic Chemistry, Ivane Javakhishvili Tbilisi State University, Tbilisi 0186, Georgia

⁴ Structural and Physical-Chemical Properties Research Laboratory, Ferdinand Tavadze Metallurgy and Materials Science Institute, Tbilisi 0186, Georgia

* **Corresponding author:** Levan Chkhartishvili, levanchkhartishvili@gtu.ge

CITATION

Chkhartishvili L, Barbakadze N, Tsagareishvili O, et al. Advanced tungsten-containing materials manufacturing from its scrap. *Characterization and Application of Nanomaterials*. 2025; 8(1): 9274. <https://doi.org/10.24294/can9274>

ARTICLE INFO

Received: 24 September 2024

Accepted: 5 November 2024

Available online: 22 November 2024

COPYRIGHT



Copyright © 2024 by author(s).

Characterization and Application of Nanomaterials published by

EnPress Publisher, LLC. This work is

licensed under the Creative

Commons Attribution (CC BY)

license.

<https://creativecommons.org/licenses/by/4.0/>

by/4.0/

Abstract: We develop a relatively cheap technology of processing a scrap in the form of already used tungsten-containing products (spirals, plates, wires, rods, etc.), as well not conditional tungsten powders. The main stages of the proposed W-scrap recycling method are its dispersing and subsequent dissolution under controlled conditions in hydrogen peroxide aqueous solution resulting in the PTA (Peroxopolytungstic Acid) formation. The filtered solution, as well as the solid acid obtained by its evaporation, are used to synthesize various tungsten compounds and composites. Good solubility of PTA in water and some other solvents allows preparing homogeneous liquid charges, heat treatment of which yield WC and WC–Co in form of ultradispersed powders. GO (Graphene Oxide) and PTA composite is obtained and its phase transition in vacuum and reducing atmosphere (H₂) is studied. By vacuum-thermal exfoliation of GO–PTA composite at 170–500 °C the rGO (reduced GO) and WO_{2.9} tungsten oxide are obtained, and at 700 °C—rGO–WO₂ composite. WC, W₂C and WC–Co are obtained from PTA at high temperature (900–1000 °C). By reducing PTA in a hydrogen atmosphere, metallic tungsten powder is obtained, which was used to obtain sandwich composites with boron carbide B₄C, W/B₄C, and W/(B₄C–W), as neutron shield materials. Composites of sandwich morphology are formed by SPS (Spark-Plasma Sintering) method.

Keywords: tungsten scrap; hydrogen peroxide; peroxopolytungstic acid; graphene oxides; composites; vacuum-thermal exfoliation; tungsten carbides and alloys; spark-plasma sintering; tungsten–boron carbide sandwich composites

1. Introduction

Modern technologies widely use the tungsten-containing alloys, compounds and composites to produce hard materials, cutting tools, drills, heating elements, weapons, electronics, catalysts, sensors, coatings, abrasives, dry lubricants, colorants, etc. This results in permanent increasing the demand for such class of materials. Tungsten W is a rare metal (it makes up just a miniscule of the Earth's crust). Usually, it is found in the form of ferberite and huebnerite minerals. The main industrial applications have scheelite and wolframite. Currently, China controlling 80% of tungsten world production partially restricts the export due to which the price of tungsten (as well as its compounds) on the world market has increased significantly. For example, metallic tungsten is separated from ore by turning it into ammonium paratungstate, the price of which increased 9 times from 2003 to 2011. At present, the development of economical and efficient technologies for the mining and processing of ores or scraps

is of great importance [1,2]. Unconditioned powders, plates, spirals, rods and other products of tungsten and its alloys are collected in various technological processes, which can be processed by various methods. Tungsten has a high melting temperature (3410 °C), so it is impossible to separate metallic tungsten from scrap by melting. For this purpose, chemical processes, which include several steps, are widely used. One commonly used method (in simplified scheme) is to obtain a tungsten compound from scrap, mainly WO_3 . Its reducing with hydrogen to metallic tungsten, adding other components, and sintering yield the final product. Therefore, the recycling and utilization of tungsten and its compounds from used materials, machine parts, or tools is of great importance [3–7]. In particular, cobalt-cemented tungsten carbide WC–Co is produced in large quantities and, therefore, a large amount of scrap is collected. Its processing methods (so-called direct and chemical recycling and melting metallurgical processes) are quite well optimized [1,8,9].

In the paper [10], the recycling of industrial scrap (i.e., new scrap) and used products (i.e. old scrap) was discussed. Because of tungsten's diverse uses, numerous types of scrap were available for recycling by a wide variety of processes. In 2000, around 46% of US tungsten supply was derived from scrap. The percentage ratio of tungsten consumed from new scrap to that consumed from old scrap was estimated to be of 20:80. Of all the tungsten in old scrap available for recycling, around 66% was either consumed in the US or exported to be recycled.

For last decades, to remove it from tool scrap and utilize by making the new hard instruments a number industrial technologies of tungsten extracting from tungsten-containing scrap have been developed. The methods implemented so far usually are characterized both by some examples of strengths and weaknesses. Generally, when selecting ways to recycle a tungsten waste, it is important to take into account technological process' simplicity, productivity, energy costs, and environmental friendliness [11–14].

The description of currently available ways of processing of tungsten-containing hard materials has been given in paper [15]. Here we list the main methods used to recycle such kind waste in the production of tungsten-containing hard alloys: (i) dispersion of sintered waste first with a crusher and then product grinding into fine fractions; (ii) waste decomposition by chemical-metallurgical methods with strong oxidizers, product pouring, crushing and leaching; (iii) waste chlorination in the presence of carbon dioxide to obtain tungsten chloride, product purification, conversion into tungsten oxides and reducing; (iv) waste heating to high temperature, product oxidizing in air and reducing WO_3 ; (v) first waste oxidizing and then product chlorinating to trap the tungsten chloride; (vi) electrochemical processing of waste solution in ammonia, alkaline or salts; (vii) hydro- or pyrometallurgical processing of sawdust; (viii) fine-grained grinding, quenching and crushing the forged mass; (ix) dissolution with sodium hydroxide, precipitation in hydrochloric acid, precipitation and purification of ammonium paratungstate with ammonia, and reduction to tungsten with hydrogen; (x) thermal regeneration in oxidation–reduction–carbide process; etc.

As mentioned, tungsten carbide–cobalt WC–Co hard alloy is widely used tool material. It is why frequently, tungsten-containing waste contains cobalt as well. Presence of cobalt makes a problem because forming the cobalt tungstate hampers the

complete removal of tungsten itself. Analysis of studies on the tungsten waste regeneration from hard alloys containing cobalt showed that selective extraction of cobalt could be done by chemical (chlorine and zinc) and thermochemical and hydro- and pyrometallurgical methods, as well as a technology based on explosive energy consumption.

Development in such industrial technologies solves the tungsten-containing superhard alloys and scrap materials recycling problem and, in this way, helps in their rehabilitation and, respectively, savings of these 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.

In our opinion, the processing of unconditioned tungsten powders by using spirals, plates and other products into tungsten compounds is best done by a relatively simple environmentally friendly technology, which involves obtaining of PTA (Peroxpolytungstic Acid) from scrap metal by reacting it with hydrogen peroxide. Unlike other methods, only oxygen is released in this process, which is not a harmful substance for the environment. By crushing tungsten spirals and dissolving the obtained powder in hydrogen peroxide solution (30%), PTA was obtained in [16]. The optimum dissolving temperature is 60 °C. The ability of W and Mo as well to dissolve in H₂O₂ solution was used to remove and separate them [17]. Investigation of thermal decomposition of peroxotungstic and peroxomolybdic acids confirmed that peroxomolybdic acid showed a preferable stability compared with PTA. This thermal stability difference can serve for the basic principle of the separation of W and Mo.

Method of dissolving tungsten in a solution of hydrogen peroxide and converting it into PTA is often used to deposit tungsten on various surfaces to obtain tungsten oxides. WO₃ obtained by this method has many applications in modern technologies as photocatalyst in water splitting, electrode materials for lithium-ion batteries, photochromic films and electrochromic displays [18–20].

During the manufacturing the penetrators from fine powder of tungsten and some other metals (nickel, iron, cobalt, chromium, aluminum, etc.) three types of scraps are generated: compaction scrap (powder), machining scrap (turnings) and defective products (penetrators on form of solid rods), which may contain up to 90% W. Methods for the extraction of tungsten from this scrap developed in [21] include electrical leaching of turnings from solid rods, soda annealing and leaching of turnings/powder, impurity removal from powder scrap by acid leaching and physical enrichment of powder scrap. Copper was effectively removed from W–Cu scrap with increasing FeCl₃ concentration in dissolver. A weight ratio of FeCl₃ to scrap of 2:1 at room temperature for 24 h resulted in 97% copper removal and 75% tungsten recovery.

Complete removal of copper occurred at increased temperatures and acidic conditions, however, at the efficiency of direct tungsten reduction dropped to 50% [22].

On the one hand, metalperoxy compounds have the ability to form complex compounds with many organic compounds. For example, in work [23] is discussed synthesis of peroxotungstate (VI) complexes containing benzene core carboxylic, benzoic, 2-chlorobenzoic and 3-aminobenzoic acids. As GO (Graphene Oxide) may contain many oxygen functional groups (carboxyl, carbonyl, hydroxyl, peroxy groups, etc.), it can be considered as a macroligand and has to form complexes with metal compounds. On the second hand, the properties of hydrophilicity and hydrophobicity are combined in GO, therefore they will affect the adsorption ability of these composite materials toward both inorganic and organic species [24]. These properties can be used to obtain GO and PTA composites.

It is confirmed, that the oxide semiconductors can be strongly coupled with the GO sheets to form hybrid composites, which have to be promising platforms for the design of electronic devices. In particular, competition between the growth of tungsten oxide nanowires and the reduction of GO sheets leads to the formation of sandwich-structured tungsten oxide-rGO (reduced GO) composite [25,26]. G (Graphene) and its derivatives such as GO and chemically obtained rGO composites are promising materials for photocatalysis, making lithium battery electrodes, sensors, photocurrent generation, etc. In the paper solvothermal process simultaneously enables [27] the reduction of GO and the formation of tungsten oxide of composition $W_{18}O_{49}$ making it suitable for the preparation of other G-based composites. A systematic investigation on the incorporation of WO_3 nanorods and G for high-efficiency visible-light-driven photocatalysis and NO_2 gas sensing was given in paper [28].

Thus, by obtaining PTA from tungsten scrap it is possible to produce many tungsten compounds and composites that are now used in different fields. Among them, the composites of GO-PTA type are especially promising materials for modern developments in science and technology.

2. Experimental

2.1. Materials

Graphite flake (natural, 325 mesh, 99.98 % metals basis) used to obtain graphene oxide, reduced graphene oxide and graphene itself, and boron carbide powder (1–7 μm) were purchased from Alfa Aesar and used without prior purification. Reagents such as $KMnO_4$, H_2SO_4 (98%) and HCl (37%) were purchased from Sigma Aldrich and used without prior purification.

Organic compounds and polymers (carbohydrates, glucose, sucrose, cellulose, polyvinyl alcohol, polyvinylpyrrolidone, etc.) were used as a carbon source (for carbidization and as a reducing agent), which pyrolysis produces activated amorphous carbon, so-called carbon black. The purity of chemical reagents and solvents used for synthesis reached 99.00–99.99% purity.

Inert environment in the reaction area was created using nitrogen (99.95%) or argon (99.95%) gases. Hydrogen gas with purity of 99.95% was used to reduce the tungsten oxide and obtain WC-Co.

Tungsten scrap (unconditioned powders, plates, spirals, rods, etc.) was collected from the Ferdinand Tavadze Metallurgy and Materials Science Institute (Tbilisi, Georgia). It was crushed in a steel ball mill and sieved in a vibrating screen. For PTA syntheses, powders < 250 μm in size, as well powders with as larger grain sizes of 1–3 mm, were used.

2.2. Equipment

To grind the powders there was used planetary mill Pulverisette 7 Premium Line with grinding cup and balls made from WC–Co hard alloy. For the ultrasound treatment and homogenization of suspensions it was used an ultrasonic cleaner (45 kHz) and JY92–IIDN Touch Screen Ultrasonic Homogenizer (20–25 kHz, 900 W).

Thermal treatment (< 1500 °C) of samples was conducted in the high-temperature vacuum furnace Kejia. In the same furnace, metal oxides deposited on boron nitride were reduced in hydrogen flow. To obtain WC–Co, tungsten oxide also was reduced in the Kengo digital generator. Compaction of powder samples or simultaneous synthesis and compaction were carried out by using the SPS (Spark-Plasma Sintering) facility operating in DC (Direct Current), pulsed DC and pulsed AC (Alternating Current) modes, which was designed at the Georgian Technical University (Tbilisi, Georgia).

The morphology and microstructure of the powders were studied with SEM (Scanning Electron Microscope) JEOL–JSM 6510 LV equipped with energy dispersive analyzer: Dispersive Micro-X-ray Spectral Analyzer X-MaxN (Oxford Instruments). An EDS (Energy-Dispersive Spectrometer) and tabletop SEM TM3030 Plus (Hitachi) were be used to determine the samples elemental composition. XRD (X-Ray Diffraction) patterns were obtained with DRON–3M (Cu K_{α} , Ni filter, 2°/min) and XZG–4 (Cu K_{α} , $\lambda = 1.5418 \text{ \AA}$) diffractometers.

The powder particle sizes were determined by the Scherrer method. Particle sizes were also analyzed by photon correlation nanoparticle size analyzer Winner 802 DLS and Malvern Instruments Mastersizer. The powder specific surface area was measured on Micromeritics Gemini VII Instrument.

Samples FTIR (Fourier Transform InfraRed) spectra were recorded on Agilent Cary 630 Spectrometer (at 350–5000 cm^{-1}).

2.3. Chemical synthesis methods

The synthesis methods used in this study were previously used by authors to solve some other research tasks and are described in the papers [29–32]. Below are described their versions modified to fit the task of producing tungsten compounds and composites from its scrap.

Method 1: Synthesis of PTA

5.0 g of tungsten powder is slowly dissolved in 40 ml of 20%–25% H_2O_2 . The H_2O_2 solution is added to the tungsten powder in three portions during 2 h (Note that the reaction is very exothermic!). Then 15 ml of hydrogen peroxide solution is again added to the reaction mixture and stirred at room temperature for 5 h. The solution is left for 12 h and then filtered. A yellowish transparent solution is obtained. Excess H_2O_2 is decomposed using a platinum spiral and the solution is evaporated under

vacuum. An orange crystalline substance containing 85.4% WO_3 is obtained (at 600 °C for 4 h).

Method 2: Preparing PTA solution

To obtain different composite materials, it is convenient to use PTA solutions of a certain concentration. The production of PTA is carried out by the process described above with the difference that after filtering the obtained solution is diluted with distilled water and a solution with a W concentration of 50–100 mg/ml is prepared.

Method 3: Synthesis of GO

40 ml of 98% sulfuric acid and 1 g graphite powder (325 mesh) is added into a glass reactor. The mixture is stirred at 30–40 °C for 0.5 h and 3 g of KMnO_4 is added at 40–45 °C under 1 h (the temperature can reach 50 °C). The mixture is stirred for 3 h. A gray viscous mass is obtained, which is cooled to 10 °C and 100 ml of ice water is added to the reactor. The mixture is diluted to 500 ml and 2 ml of 30% of H_2O_2 solution is added. A yellowish suspension of graphite oxide is obtained. During the washing of the sediment, its color gradually changes to dark brown. 20 min later solution is removed by decantation. This process is repeated twice. For the rapid precipitation of graphite oxide from the suspension, a 5% solution of hydrochloric acid (500 ml) is added. Decantation is repeated 3 times in 10 min intervals. An aqueous gel-like mass is obtained. Washing of this precipitate is continued until the pH of the solution reached a value of 5–6. GO is separated from the obtained suspension by centrifugation and dried in a vacuum at 60 °C for 4 h. In many cases, to obtain composites containing PTA, it is more convenient to use GO suspension without separation from the reaction mixture. GO suspension with a GO concentration of 12 mg/ml is used in this process.

Method 4: Vacuum-thermal exfoliation of GO and obtaining of rGO

Vacuum exfoliation of GO temperature depends on its synthesis method, chemical composition, preparation time, heating rate and pressure. The vacuum exfoliation temperature range of GO obtained by methods known in the literature is of 150–250 °C. 0.5 g GO plates are cut into small pieces (2–4 mm) and placed in 1 l glass flask. After vacuuming the flask, it is heated at rate of 5 °C/min to 160–170 °C. In this temperature range, a volumetric exfoliation of the GO plates takes place and a fluffy black powder is formed. Vacuuming is continued for 1 h and then the flask is cooled under vacuum. The bulk density of the obtained powder reaches 20–30 mg/ml.

Method 5: Obtaining of GO–PTA composite

40 ml suspension containing 480 mg GO is sonicated for 1 h and placed in a 100 ml flask. The suspension is heated to 50 °C and 1 ml solution of PTA (50 mg W/ml) is added. The resulting suspension is stirred for 1 h at 50 °C. The obtained suspension is dried in air at 100 °C (3 h). Black plates (0.645 g) are obtained. It is kept in a desiccator. Carbon black–PTA composite can be obtained in a similar procedure.

Method 6: Vacuum-thermal exfoliation of GO–PTA composite

0.315 g of GO–PTA composite is placed in a quartz flask. After vacuuming the flask, it is heated at a rate of 5 °C/min to 170–175 °C. In this temperature range, volumetric exfoliation of the composite powder takes place. Material heating at this temperature is continued for 1 h and then it is cooled in argon. The powder volume increases in 50–70 times. Black 164 mg composite – 1st Sample is formed: powder rGO–PTA-170. The 2nd Sample of the composite obtained by this method is heated at

500 °C in vacuum for 1 h and cooled to room temperature under argon: powder rGO–PTA-500.

Method 7: Reduction of powder rGO–PTA-170 with H₂ at 700 °C and obtaining of rGO–W composite

0.5 g of rGO–PTA-170 composite powder is placed in a quartz boat-like vessel and put in high temperature vacuum furnace. The sample is heated in argon flow at rate of 10 °C/min. At 400 °C, argon is replaced by hydrogen and the temperature is raised to 700 °C and kept under for 2 h. After that, the furnace is turned off and cooled in argon stream. To prevent oxidation of metallic tungsten, the sample is kept in an argon desiccator. As a result, the rGO–W composite is obtained.

Method 8: Obtaining of rGO–WO₂ composite

0.5 g of rGO–PTA-170 composite powder is placed in a quartz boat-like vessel and put in high temperature vacuum furnace. The sample is heated to 700 °C in an argon stream at a rate of 10 °C/min and kept for 2 h. After that, the furnace is turned off and cooled in argon stream. The sample is stored in an argon desiccator. rGO–WO₂ composite is obtained.

Method 9: Obtaining WC–W₂C composite from carbon black–PTA and rGO–PTA-170

WC–W₂C tungsten carbides are obtained by the interaction of acetylene carbon black and PTA solution, drying the obtained paste to 180–200 °C and sintering the obtained powder at 1000 °C in a hydrogen atmosphere for 1 h. WC–W₂C composite was obtained from rGO–PTA-170 powder in similar way.

Method 10: Obtaining WC–Co from PTA–Co(CH₃COO)₂·4H₂O–C₁₂H₂₂O₁₁ (sucrose).

A mixture of 2.65 g PTA, 2.1 g Co(CH₃COO)₂·4H₂O and 4 g C₁₂H₂₂O₁₁ (sucrose) is dissolved in 50 ml of water. The obtained solution is evaporated and the paste is dried at 180–200 °C for 2 h. The obtained black mass is ground, placed in a quartz tube and heated at 600 °C in an argon flow (30 ml/min) for 2 h. The obtained material is milled in nanomill. Then the pre-ceramic precursor powder is transferred into a quartz boat-like vessel, placed in muffle furnace tube, and thermally treated in H₂ flow (heating rate of 10 °C/min, holding time of 2 h at 1000 °C). The obtained powder of WC–Co is of a gray color.

Method 11: Preparation W–B₄C powder composite

1 g PTA is dissolved in 20 ml of 1% hydroxyl ethyl cellulose (HES 30000) aqueous solution, containing 5 ml of ethylene glycol. 6 g of boron carbide B₄C powder are added to the obtained solution. The suspension is evaporated under stirring and the obtained mass is burned in a high temperature furnace at 600 °C for 1 h in argon. The resulting WO₃/B₄C composite is reduced at 700 °C in H₂ flow for 2 h. A powder composite W/B₄C containing 9%–10% metallic tungsten is formed.

Method 12: Obtaining of sandwich-like W/(W–B₄C) composite by SPS method

12 mm diameter graphite press-form lined with graphite foil is placed together with a certain amount of W wet powder, which was obtained by heating PTA at 600 °C and then by the reduction of WO₃ at 700 °C in a H₂ stream for 2 h. Poured tungsten powder is pressed and wet W–B₄C powder obtained by the method described above is also poured on top. This surface is covered with graphite foil and a graphite punch is

placed on top. The press form is placed in the SPS facility, and after vacuuming its chamber, the powder is pressed at 30–50 MPa (holding at 1500–1700 °C for 10 min. Pulsed AC mode with pulse duration of 5 μ s and pause of 1 μ s is used to sinter these ceramics. The sample heating rate reaches 100–200 °C/min. The samples are cooled in vacuum. W/(W–B₄C) sandwich-like composite is obtained similarly.

3. Results and discussion

Tungsten scrap is a fragile material and it breaks easily under mechanical impact. In laboratory practice, it is possible to obtain powder from scrap (spirals, plates) using a steel mortar, and a steel ball mill was used to crush rods with large diameter. A fine fraction with a particle size of < 250 μ m and a relatively large fraction of 1–3 mm were obtained from the scrap. The interaction of the powders with the hydrogen peroxide solution takes place energetically resulting in the formation of a weak yellowish solution.

As a result of solution evaporation, an orange crystalline substance is obtained, the EDS analysis of which shows that it consists of tungsten and oxygen and does not contain other metals as impurities (**Figure 1**). For example, from ⁷⁴W L- and ⁸O K-series analysis in a point there are obtained: 21.16at.%W and 78.84at.%O.

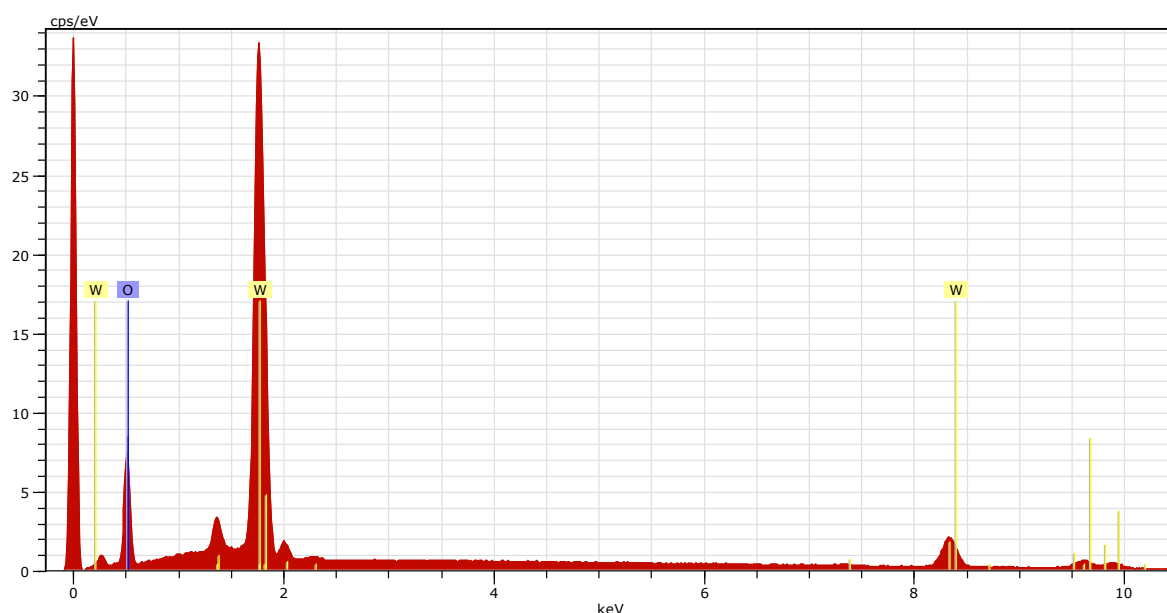


Figure 1. EDS spectrum of PTA obtained from tungsten scrap.

The main processes of scrap recycling are given in **Figure 2**. Obtaining PTA from tungsten scrap by this method is advantageous for several reasons. The simplicity of the method and the synthesis of a water-soluble substance, from which many promising and scarce materials or substances can be obtained are remarkable. For example, it is possible to obtain tungsten oxides (WO_x), metallic tungsten powder, carbides, borides, composites for various functional purposes, radiation-resistant metal ceramics, catalysts, metallized coatings, sensor materials and others.

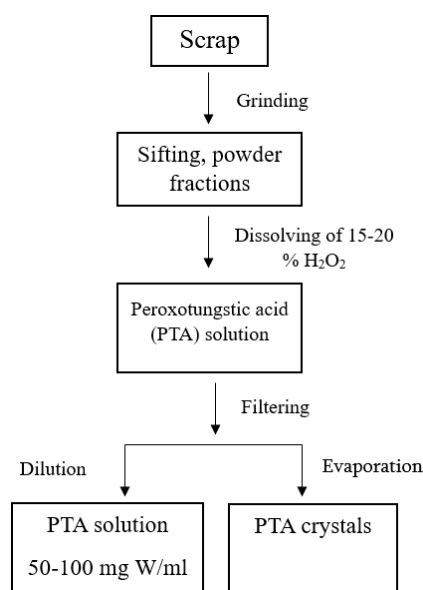


Figure 2. General scheme of technological route of obtaining PTA from tungsten scrap.

3.1. Phase transitions in GO–PTA composite

It is very promising to obtain composites containing tungsten compounds from G and its oxides—GOs. This needs studying the phase transitions in GO–PTA composite due to the interaction of GO with PTA in different environments and temperature regimes. Corresponding results are summarized in **Figure 3**.

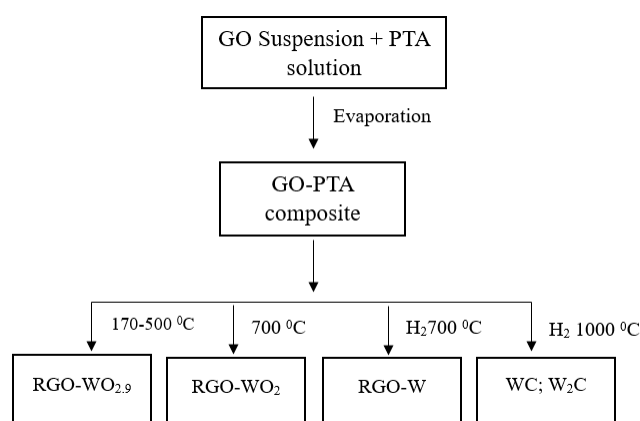


Figure 3. Scheme of obtaining different materials from GO–PTA composite.

At the initial stage, GO–PTA composite was obtained. The formation of this composite is easy because the components consist of many oxygen-containing functional groups, which interact with each other and form a stable homogeneous suspension, by drying of which, the polymer films are obtained. They are flexible and can be used to coat various surfaces with tungsten oxides.

We aimed to study the effect of temperature increase on the synthesized composite under vacuum, inert and reducing atmospheres. It should be noted that the process of vacuum-thermal exfoliation of composites GO–Me compounds was previously studied by authors and in this way, it was obtained rGO–Me (Me = Ag, Pt and Pd) and rGO–Me_xO_y (Me_xO_y = CuO, Cu₂O, TiO₂, Fe₂O₃, Fe₃O₄, CoO, etc.)

composites. Their biocidal (rGO–Ag, rGO–CuO, rGO–TiO₂, rGO–Fe₂O₃) and magnetic properties, as well as effects of G on morphology, fracture toughness and electrical conductivity of titanium dioxide composite (G–TiO₂), were studied [32–35].

The developed methods were used for vacuum-thermal exfoliation of GO–PTA composite. It is determined that the exfoliation temperature of the composite, when using newly synthesized GO, is 170–175 °C and practically coincides with the temperature of vacuum exfoliation of GO (160–170 °C). Because of exfoliation, a fluffy powder is obtained, the volume of which is in 200–300 times greater, than the volume of the initial composite. For comparison, we present the corresponding images in **Figure 4**.

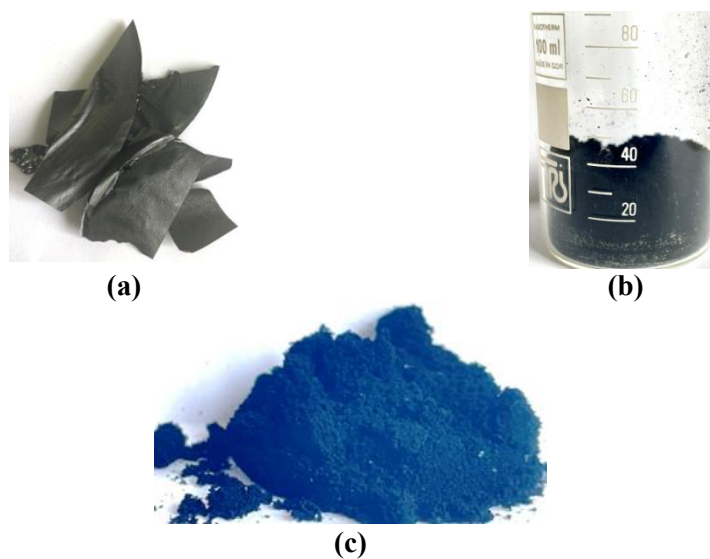


Figure 4. (a) GO–PTA composite; (b) and (c) composite rGO–PTA-170 obtained from it by vacuum-thermal method.

It is confirmed that the volume of the rGO–PTA-170 powder composite depends on several factors. For example, if the drying temperature of the initial rGO–PTA composite is increased to 150 °C, the volume of the obtained powder decreases by 5–7 times. Also, the volume of the rGO–PTA-170 powder composite depends on the GO: PTA mass ratio. The maximum volume of powdered rGO–PTA-170 is obtained when the amount of PTA in the GO–PTA composite is in the range of 8–20% of GO.

When obtaining similar powders by vacuum-thermal exfoliation, the preparation time of the GO suspension sample should be taken into account. In the case of using a suspension made 3 months earlier or more, powders of a significantly smaller volume are obtained from the GO–PTA composite. A similar result was obtained when obtaining composites of compounds of other elements, with the difference that the vacuum exfoliation of the composite of GO–metal nitrates actually takes place by explosion. This is caused by the presence of nitrate ions in the system, which with any organic compound produces explosive materials. Exfoliation of non-nitrate systems is safe and easy to do even in glassware.

We note here that the separation of the matrix (GO) is caused by the decomposition of the oxygen-containing functional groups contained in it, the generation of gases (CO₂, H₂O and vapors of organic compounds) and the

development of a certain pressure between the layers of GO, which causes the exfoliation of the layers. Without vacuum, i.e. in air or any gas flow the films of GO itself or its composites do not change their geometric shape and remain in the form of plates. Thus, the method of vacuum-thermal exfoliation can be considered as a new method for obtaining composites of tungsten compounds and GOs.

Further heating of the rGO-PTA-170 composite up to 500 °C literally does not change the phase composition and the rGO-WO_{2.9} composite is obtained, which transforms into the rGO-WO₂ composite at 700 °C (Figures 5 and 6).

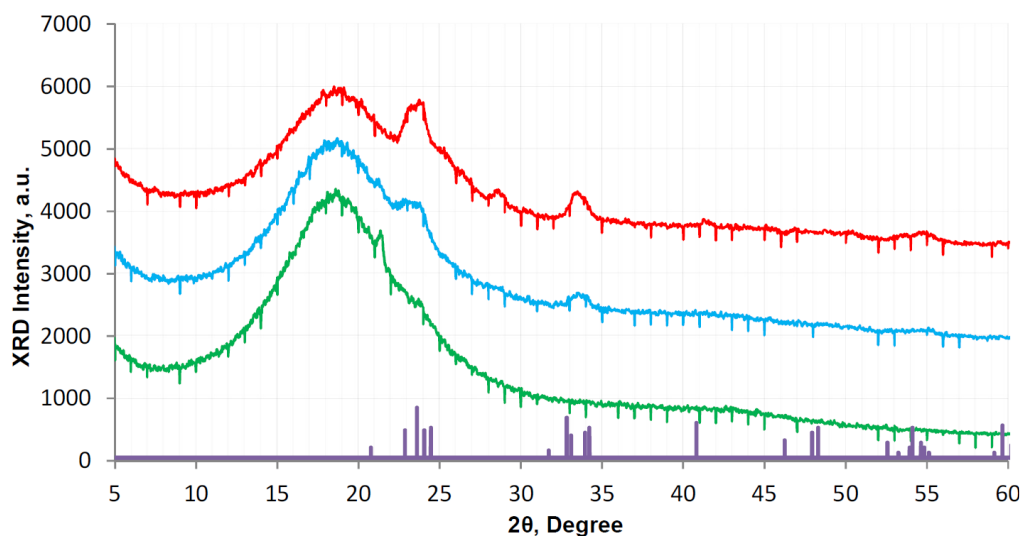


Figure 5. XRD patterns of rGO (green) and composites rGO-(rGO-WO_{2.9}-170) (blue) and rGO-(rGO-WO_{2.9}-500) (red).

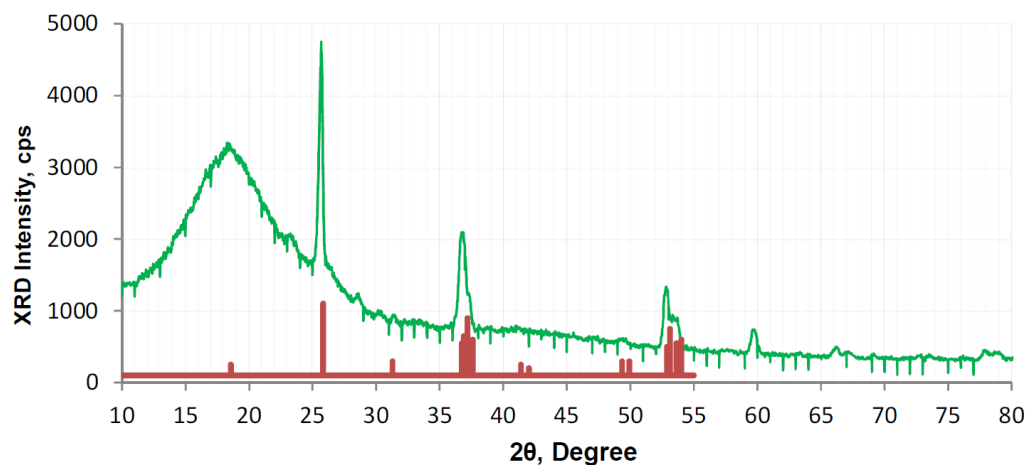


Figure 6. XRD patterns of rGO-WO₂-700 composite (green) and WO₂ phase (red).

Comparing these diffractograms, it can be concluded that in the rGO-WO_{2.9}-170 and rGO-(rGO-WO_{2.9}-500) composites, the WO_{2.9} phase is not fully formed, while in the rGO-WO₂-700 composite, the WO₂ phase is well defined (Figure 6). In general, PTA gradually undergoes dehydration and deoxygenation during heat treatment, and at 600 °C the WO₃ phase is obtained and metallic tungsten is obtained in hydrogen environment [18–20]. It is also known that in a reducing environment WO₃ reduces to metallic W. In our case, rGO-PTA-170, as well as rGO-WO_{2.9}-170 composites in a reducing atmosphere (H₂) are reduced to metallic tungsten and rGO-W is obtained.

It is known [8] that in the temperature range of 700–1000 °C the W–C system produces tungsten carbides. Different types of organic compounds are often used for carbon sources, which, when the temperature rises, produce active carbon, both carbonizing and reducing agent in the carbonizing process. Using organic reagents, we have obtained nanopowders of many metal carbides and multicomponent metal-ceramics – see the earlier papers [36–38]. In general, the GO–PTA composite is a W–C type system containing a tungsten compound and a carbonizing agent (carbon source) in the form of GO. By their heating to 900 °C in hydrogen (or argon) flow tungsten carbides WC and W₂C are obtained (**Figure 7**).

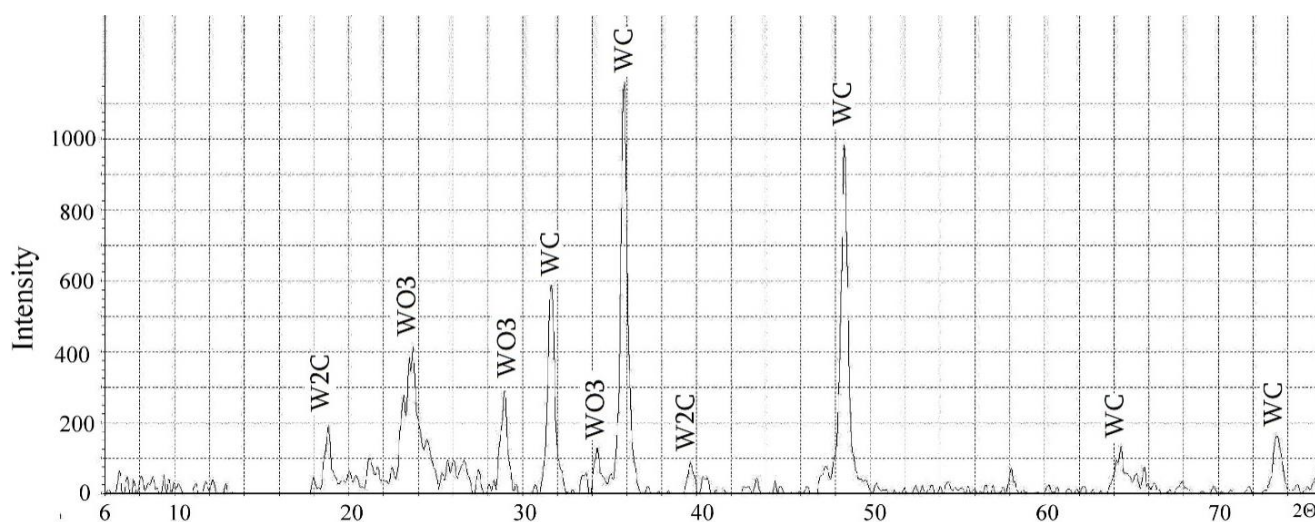


Figure 7. XRD patterns of WC and W₂C phases obtained from GO–PTA composite at 900 °C in H₂ flow.

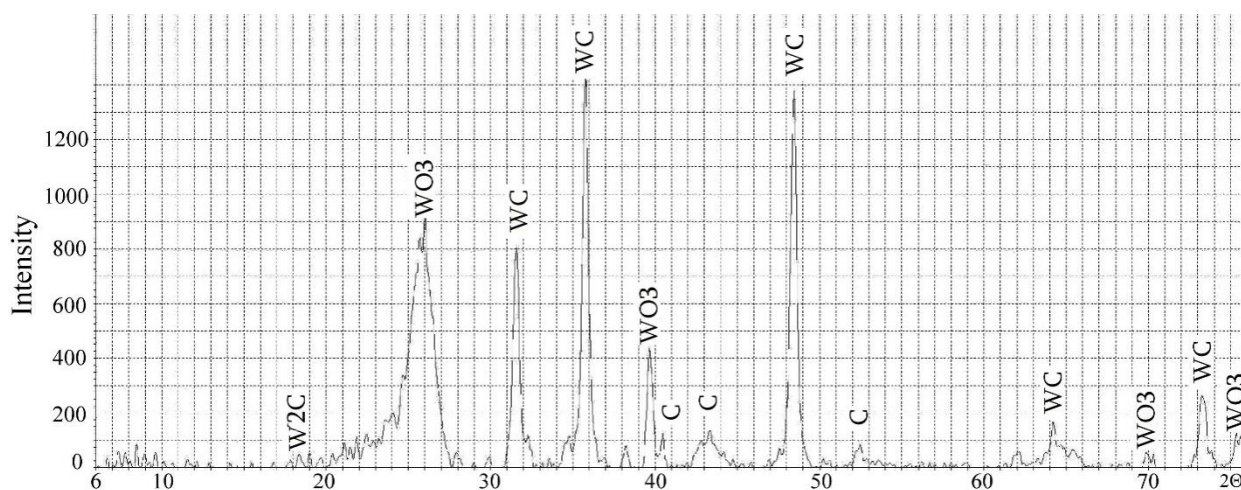


Figure 8. XRD patterns of WC and W₂C phases obtained from carbon black–PTA mixture at 900 °C in H₂ flow.

For comparison, we carried out carbon black–PTA mixture carbonization at 900 °C in H₂ flow. As can be seen from the XRD patterns, as it was expected WC and W₂C phases are also obtained in this case (**Figure 8**). The diffractogram also shows the peak of excess carbon. In the case of GO–PTA, a carbon low intensity peak is visible. Such a difference is due to the fact that GO forms G with a defective structure at high temperature (a chemical method of graphene synthesis) because the oxygen-containing groups are removed from it. Therefore, the carbon present in GO is spent

both on carbonization and formation of low-molecular carbon-containing compounds. In the case of carbon black, the oxygen content is low (1%–3%), while the oxygen content in GO is in the range of 20%–34%. These results are presented in our previous works [33,35,39].

3.2. Preparation WC–Co from PTA

With the proposed method, it is possible to transform tungsten scrap into WC–Co, which is an important metal-ceramic in metalworking technology (drills, cutters, abrasives, coatings, etc.). Carbothermic process is mainly used to obtain the mentioned material, which involves the carbonization of a mixture of tungsten powder, cobalt and carbonaceous material (amorphous coal, black carbon obtained by various methods) in a hydrogen environment at 900–1000 °C. The technological process requires dispersed tungsten powder, which is obtained by long grinding in mills, due to which the target product is contaminated with wear materials of the mill and balls. Besides, the grain size of the WC–Co powder obtained by the traditional method is several micrometers.

Currently, much attention is being paid to the technologies that lead to obtaining ultradisperse (nanosize) powders of hard materials [36,40]. Using traditional methods, it is impossible to achieve the goal, because it is practically impossible to grind the components of the starting material down to the nanosize. One of the ways to solve this problem is to obtain pre-ceramic precursors from liquid charge, where the components are broken down into molecules and ions [37,38,41].

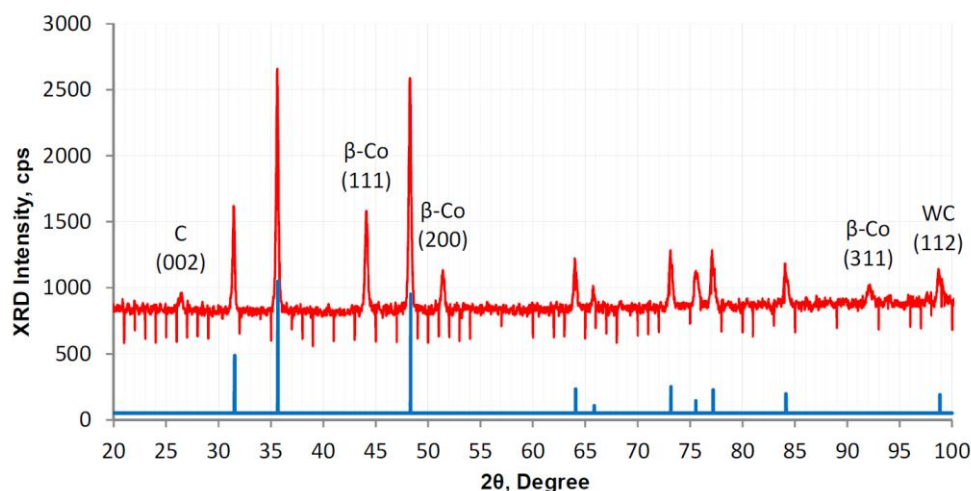


Figure 9. XRD pattern of WC–Co obtained from PTA–Co(CH₃COO)₂·4H₂O–C₁₂H₂₂O₁₁ (sucrose) precursors at 1000 °C in H₂ flow.

To obtain WC–Co, we selected the system PTA–Co(CH₃COO)₂·4H₂O–C₁₂H₂₂O₁₁ (sucrose), which contains water-soluble components. Specifically, PTA is an ideal precursor candidate for obtaining WC–Co as it is highly soluble in water and can be obtained as a solution up to 50%. Cobalt acetate (or cobalt nitrate and chloride) is also soluble in water. It is possible to use water-soluble synthetic and natural polymers, carbohydrates, alcohols and other organic compounds as carbonizing agents. By mixing the component solutions and drying them by vaporization at 300–400 °C, a preceramic precursor is obtained, in which tungsten, cobalt and carbon compounds are

homogeneously distributed, and WC–Co is obtained by their carbonization in a hydrogen atmosphere. This technology does not require scarce metal powders: the target product is obtained from available reagents. The WC–Co diffractogram obtained by heating the preceramic precursor obtained from PTA–Co(CH₃COO)₂·4H₂O–C₁₂H₂₂O₁₁ (sucrose) at 1000 °C in the hydrogen environment is shown in **Figure 9**.

3.3. Obtaining of radiation resistant sandwich-like composites W/B₄C and W/(W–B₄C)

Boron carbide–tungsten B₄C–W thin-layered sandwich structures are known as effective shield composite materials, in which low- and high-Z atoms (Z is the atomic number), B and W, serve as effective absorbers for, respectively, (epi)thermal neutrons and secondary gamma-quanta accompanying the neutrons capture by ¹⁰B nuclei [42–44]. To obtain them, first note that WO₃ is obtained from tungsten scrap by heating of PTA, which is reduced above > 500 °C to metallic tungsten in H₂ flow [19,45,46]. PTA solutions are also used for tungstenizing (metallizing with tungsten) of various surfaces [47,48].

We obtained both metallic tungsten powder and powder of composite W–B₄C containing 8–10% tungsten from PTA using a similar method. The obtained powders were used to obtain W/B₄C and W/(W–B₄C) sandwiches. It is known that boron carbide reacts with metals at high temperatures and forms borides, which are also binding (cement) phases of composites. Many composites were obtained by this method, which found use in obtaining radiation resistant materials [49]. Thus, the W–B₄C powder composite obtained by us from PTA is a promising material for making radiation-resistant sandwiches. Sintered composites of WC–WB–W₂B were prepared from B₄C–W–WC powders using a reactive energization hot-pressing technique that initiated a solid state reaction between B₄C and W [50]. It is established that the resulting sandwiches do not undergo exfoliation because at the contact boundary between the metal and boron carbide, a transitional bonding phase W₂B₅ is formed, which is also the best neutron absorber compound [51].

When tungsten and boron carbide powders are sintered by SPS method, actually a three-layer sandwich W/W₂B₅/B₄C is formed. If we selectively remove the tungsten layer with a hydrogen peroxide solution, the sandwich W₂B₅/B₄C will remain. XRD analysis of such composition detects both W₂B₅ phase and B₄C. For XRD analysis, half the surface of the W₂B₅/B₄C cylindrical sample was peeled off at an angle of approximately 40–45 degrees to expose the B₄C layer [31]. W/B₄C and W/(W–B₄C) sandwiches were made by SPS method, in which tungsten powder was obtained by reduction of PTA separated from scrap (in H₂ flow at 700 °C). In this case, the sintering method was partially changed. In the SEM image of the W/B₄C sample fragment, the separation boundary between tungsten and boron carbide is clearly seen in **Figure 10**. It seems that there is a mutual diffusion of tungsten and boron carbide, as a result of which the W₂B₅ phase is formed, whose irregular layer is well separated between the white and black layers. **Figure 11** shows the EDX (Energy Dispersive X-ray) mapping images and distributions of each element in the sandwich structure. W/(W–B₄C) sandwiches were obtained by a similar method.

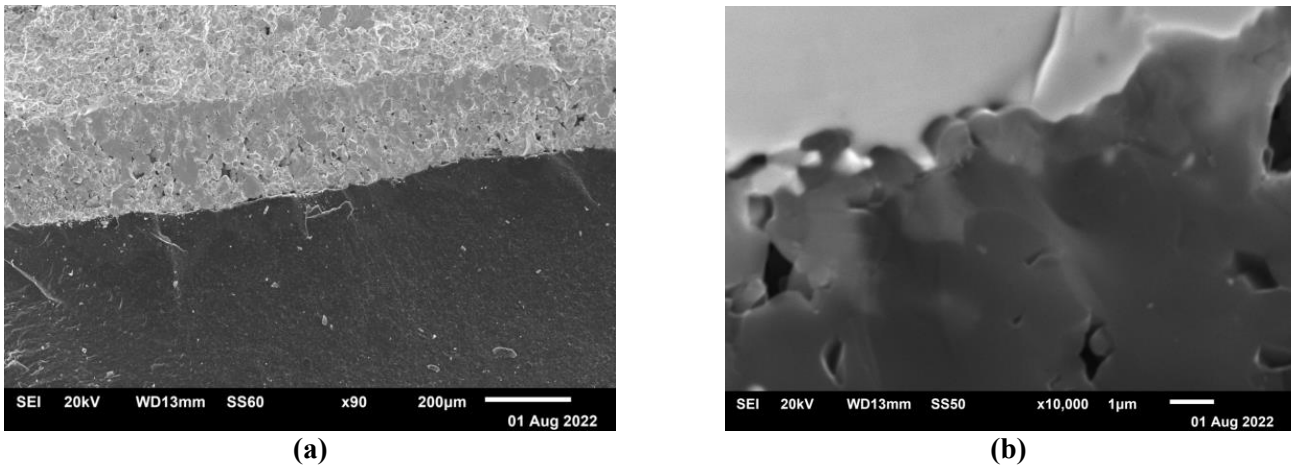


Figure 10. SEM images of composite B₄C–W obtained by SPS from B₄C and W powders at 1500 °C: fracture surfaces with different magnifications. (a) × 90; (b) × 10,000.

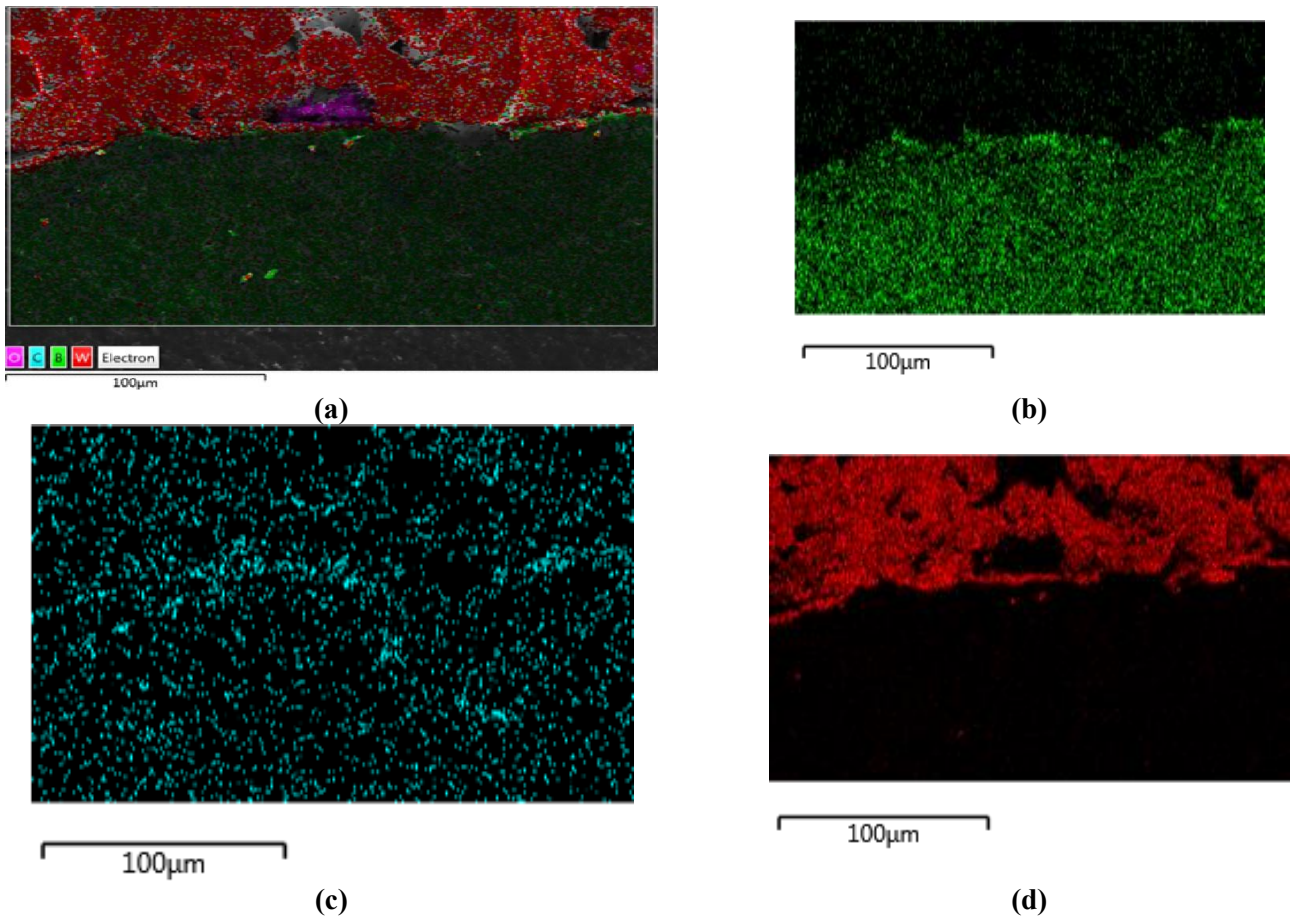


Figure 11. EDX mapping of all elements (a) and separately B (b) C (c) and W (d) distributions in B₄C and W phases contact regions.

If we consider these processes, it can be concluded that the W₂B₅ phase, which is a powder binder, is formed on the contact surface of the W–B₄C composite powder particles. This is important because it allows pressure-free sintering of pressed composites (green products) at relatively low temperatures (1400–1500 °C). Thus,

PTA is a necessary component for obtaining W–B₄C powder composites, so its obtaining from tungsten scrap is a promising direction.

4. Conclusions

Methods for obtaining solution and crystalline PTA from tungsten scrap are developed. By mechanically crushing tungsten scrap and dissolving the resulting powder in hydrogen peroxide solution, a PTA solution is obtained. In addition, by its evaporating a crystalline PTA is formed. They are used in the preparation of metallic tungsten W powder; tungsten–boron carbide composite W–B₄C powder, GOs containing composites GO–PTA, rGO–WO_{2.9}, rGO–WO₂, and rGO–W; tungsten carbides W₂C, WC, and WC–Co; and sandwich composites W/B₄C and W/(W–B₄C). It is established that by thermal treatment of PTA in the hydrogen environment at 600–700 °C, metallic tungsten W powder is obtained, which has many applications.

Phase transitions of GO–PTA composite in vacuum and hydrogen atmosphere at 170–900 °C is studied. By the interaction of PTA solution and GO suspension, an amorphous GO–PTA composite is obtained. In addition, rGO–WO_{2.9} composite powder is formed by their vacuum thermal explosion at 170–500 °C. It is determined that WO_{2.9} phase transforms into WO₂ at 700 °C and rGO–WO₂ composite is formed. By reduction the latter in a hydrogen atmosphere (700 °C), rGO–W composite containing metallic tungsten is obtained.

Using the PTA solution, a liquid charge containing the PTA–Co(CH₃COO)₂·4H₂O–C₁₂H₂₂O₁₁ (sucrose) system is prepared. A preceramic precursor powder is obtained from this charge. It is determined by XRD analysis that through carbonization in hydrogen atmosphere at 1000 °C WC–Co is obtained, in which cobalt content reaches 6–20wt.%.

Obtaining possibilities of sandwich composites containing boron carbide and metallic tungsten layer using metallic tungsten powder obtained from PTA also are studied. It is confirmed that by SPS process it is possible to obtain sandwich-like W/B₄C and W/(W–B₄C) composites at 1500–1700 °C. On the contacting surface of tungsten and boron carbide, formation of the W₂B₅ intermediate phase is detected, which serves for an additional binder phase.

Thus, from the point of view of implementing environmentally friendly technologies, replacing commercial tungsten powder with tungsten scrap obtained from PTA and processing with appropriate methods, it is possible to obtain many scarce and widely used tungsten-containing composites and materials. We note here that when tungsten scrap is dissolved in an aqueous solution of hydrogen peroxide, oxygen is formed as a by-product, which is not an environmental pollutant.

Author contributions: Conceptualization, LC and RC; methodology, LC, NB, OT, AM and RC; software, TB, MB and TD; validation, TB, MB and TD; formal analysis, OT and TB; investigation, LC, NB, OT, AM and RC; resources, OT and RC; data curation, TB, MB and TD; writing—original draft preparation, LC, NB and RC; writing—review and editing, LC; visualization, TB, MB and TD; supervision, LC and RC; project administration, OT and RC; funding acquisition, OT and RC. All authors have read and agreed to the published version of the manuscript.

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

References

1. MTS (Midwest Tungsten Service). Tungsten and Costs. Available online: <https://www.tungsten.com/asset/61bbda640726d> (accessed on 1 September 2024).
2. Yang X. Beneficiation studies of tungsten ores—A review. *Minerals Engineering*. 2018; 125: 111-119. doi: 10.1016/j.mineng.2018.06.001
3. Kumar R, Kariminejad A, Antonov M, et al. Progress in sustainable recycling and circular economy of tungsten carbide hard metal scraps for Industry 5.0 and onwards. *Sustainability*. 2023; 15(16): 12249. doi: 10.3390/su151612249
4. ITIA (International Tungsten Industry Association). Tungsten Processing. Available online: <https://www.itia.info/tungstenprocessing.html> (accessed on 1 September 2024).
5. Lin JC, Lin JY, Lee SL. Process for recovering tungsten carbide from cemented tungsten carbide scraps by selective electrolysis. Available online: <https://patents.google.com/patent/US5384016A/en> (accessed on 1 September 2024).
6. Katiyar PK, Randhawa NS, Hait J, et al. Anodic Dissolution behaviour of Tungsten Carbide scraps in ammoniacal media. *Advanced Materials Research*. 2013; 828: 11-20. doi: 10.4028/www.scientific.net/amr.828.11
7. Furberg A, Arvidsson R, Molander S. Environmental life cycle assessment of cemented carbide (WC-Co) production. *Journal of Cleaner Production*. 2019; 209: 1126-1138. doi: 10.1016/j.jclepro.2018.10.272
8. Lassner E, Schubert WD. *Tungsten*. Springer US; 1999. doi: 10.1007/978-1-4615-4907-9
9. Schubert WD, Zeiler B. Recycling of Tungsten. *The Technology—History, State of the Art and Peculiarities*. Available online: https://www.itia.info/assets/files/newsletters/Newsletter_2019_08.pdf (accessed on 1 September 2024).
10. Shedd KB. *Tungsten recycling in the United States in 2000*. USGS; 2005.
11. Xia X, Zhang G, Guan W, et al. A novel method for preparing tungsten and molybdenum peroxy complex solution and its application to tungsten-molybdenum separation. *Hydrometallurgy*. 2023; 215: 105974. doi: 10.1016/j.hydromet.2022.105974
12. Asher A, Borukhin L, Ruhr M. Applications of chemically recycled tungsten powder in heavy metal products. In: *Tungsten and Refractory Metals*. Princeton, Metal Powder Industries Federation; 1994. pp. 337-344.
13. Berrebi G, Dufresne P, Jacquier Y. Recycling of spent hydroprocessing catalysts: EURECAT technology. *Resources, Conservation and Recycling*. 1994; 10(1-2), 1-9. doi: 10.1016/0921-3449(94)90032-9
14. Kurylak W, Retegan T, Bru K, et al. State of the Art on the Recovery of Refractory Metals from Urban Mines. Available online: <https://prometia.eu/wp-content/uploads/2020/12/MSP-REFRAM-D4.2-State-of-the-art-on-the-recovery-of-refractory-metals-from-urban-mines.pdf> (accessed on 1 September 2024).
15. Tsagareishvili O, Chkhartishvili L, Matcharashvili M, et al. Boron and tungsten carbides based and related nanodispersed composites—A review. *Characterization and Application of Nanomaterials*. 2024; 7(2): 5454. doi: 10.24294/can.v7i2.5454
16. Murau PC. Dissolution of tungsten by hydrogen peroxide. *Analytical Chemistry*. 1961; 33(8): 1125-1126. doi: 10.1021/ac60176a021
17. Zhang W, Li J, Zhao Z, et al. Separation of W and Mo from their peroxyacids solutions by thermal decomposition. *Transactions of Nonferrous Metals Society of China*. 2016; 26(10): 2731-2737. doi: 10.1016/S1003-6326(16)64402-3
18. Kudo T, Okamoto H, Matsumoto K, et al. Peroxopolytungstic acids synthesized by direct reaction of tungsten or tungsten carbide with hydrogen peroxide. *Inorganica Chimica Acta*. 1986; 111(2): L27-L28. [https://doi.org/10.1016/S0020-1693\(00\)84626-5](https://doi.org/10.1016/S0020-1693(00)84626-5)
19. Kim H, Lee J, Sohn I, et al. Preparation of tungsten metal film by spin coating method. *Korea-Australia Rheology Journal*. 2002; 14(2): 71-76.
20. Tsuyumoto I. Facile synthesis of nanocrystalline hexagonal tungsten trioxide from metallic tungsten powder and hydrogen peroxide. *Journal of the American Ceramic Society*. 2017; 101(2): 509-514. doi: 10.1111/jace.15250
21. Jana RK, Kumar V, Saha AK, et al. Processing of tungsten alloy scrap for the recovery of tungsten metal. In: *Proceedings of the National Seminar on Environmental & Waste Management in Metallurgical Industries*. National Metallurgical Laboratory-Jamshedpur; 1996. pp. 94-98.
22. Masoudi A, Abbaszadeh H. Tungsten direct recovery from W-Cu alloy scrap by selective digestion via FeCl₃ aqueous solution. *American Journal of Materials Science and Engineering*. 2013; 1(1): 1-5.

23. Das N, Chowdhury S, Purkayastha RND. Peroxo–tungstate(VI) complexes: Syntheses, characterization, reactivity, and DFT studies. *Monatshefte für Chemie—Chemical Monthly*. 2019; 150(7): 1255-1266. doi: 10.1007/s00706-019-02435-1
24. Dzyazko YS, Volfkovich YM, Chaban MO. Composites containing inorganic ion exchangers and graphene oxide: Hydrophilic–hydrophobic and sorption properties (Review). Cham, Springer; 2021. pp. 93-110.
25. Fu C, Foo C, Lee PS. One-step facile electrochemical preparation of WO₃/graphene nanocomposites with improved electrochromic properties. *Electrochimica Acta*. 2014; 117: 139-144. doi: 10.1016/j.electacta.2013.11.123
26. Chang X, Sun S, Dong L, et al. Tungsten oxide nanowires grown on graphene oxide sheets as high-performance electrochromic material. *Electrochimica Acta*. 2014; 129: 40-46. doi: 10.1016/j.electacta.2014.02.065
27. Chang X, Dong L, Yin Y, et al. A novel composite photocatalyst based on in situ growth of ultrathin tungsten oxide nanowires on graphene oxide sheets. *RSC Advances*. 2013; 3(35): 15005. doi: 10.1039/c3ra41109e
28. An X, Yu JC, Wang Y, et al. WO₃ nanorods/graphene nanocomposites for high-efficiency visible-light-driven photocatalysis and NO₂ gas sensing. *Journal of Materials Chemistry*. 2012; 22(17): 8525. doi: 10.1039/c2jm16709c
29. Makatsaria S, Kekutia S, Markhulia J, et al. Magnetic properties of nanopowder h-BN doped with Fe and Fe₃O₄ nanoclusters. *Nano Studies*. 2021–2022; 21/2: 287-292. doi: 10.52340/ns.2022.08
30. Chkhartishvili L, Chedia R, Tsagareishvili O, et al. Preparation of neutron-capturing boron-containing nanosystems. In: *Proceedings of the 9th International Conference and Exhibition on Advanced and Nano Materials*; 2022; Victoria, IAEMM. pp. 1-15.
31. Chkhartishvili L, Makatsaria S, Gogolidze N, et al. Obtaining boron carbide and nitride matrix nanocomposites for neutron-shielding and therapy applications. *Condensed Matter*. 2023; 8(4): 92. doi: 10.3390/condmat8040092
32. Chkhartishvili L, Makatsaria S, Barbakadze N, et al. Synthesis of 2D-material(G,GO,rGO,h-BN)–magnetic(Fe,Fe₃O₄) nanocomposites. *Nano Hybrids and Composites*. 2024; 43: 23-37. doi: 10.4028/p-momlh1
33. Nadaraia L, Dundua T, Gamkrelidze N, et al. Graphite foil waste to graphene: New carbon precursors for synthesis of graphene and its oxides. *Key Engineering Materials*. 2021; 891: 68-74. doi: 10.4028/www.scientific.net/kem.891.68
34. Nadaraia L, Jalabadze N, Khundadze L, et al. Effects of graphene on morphology, fracture toughness, and electrical conductivity of titanium dioxide. *Diamond and Related Materials*. 2021; 114: 108319. doi: 10.1016/j.diamond.2021.108319
35. Dundua T. Preparation of graphene oxide composites containing nanometals and oxides from graphite foil wastes and study of their biocidal activity. *Nano Studies*. 2021–2022; 21/22: 91-110. doi: 10.52340/ns.2022.06
36. Barbakadze N, Sarajishvili K, Chedia R, et al. Obtaining of ultrafine powders of some boron carbide based nanocomposites using liquid precursors. *Nanotechnology Perceptions*. 2019; 15(3): 243-256. doi: 10.4024/N27BA19A.ntp.15.03
37. Mikeladze A, Tsagareishvili O, Chkhartishvili L, Chedia R. Obtaining of some boron-containing and related nanocrystalline systems from solutions and suspensions. Available online: https://www.researchgate.net/publication/334964450_Obtaining_of_Some_Boron-Containing_and_Related_Nanocrystalline_Systems_from_Solutions_and_Suspensions (accessed on 1 September 2024).
38. Chkhartishvili L, Mikeladze A, Tsagareishvili O, et al. Advanced boron carbide matrix nanocomposites obtained from liquid-charge: Focused review. *Condensed Matter*. 2023; 8(2): 37. doi: 10.3390/condmat8020037
39. Barbakadze NG, Tsitsishvili VG, Korkia TV, et al. Synthesis of graphene oxide and reduced graphene oxide from graphite foil industrial wastes. *European Chemical Bulletin*. 2019; 7(11-12): 329. doi: 10.17628/ecb.2018.7.329-333
40. Peng Y, Wang H, Zhao C, et al. Nanocrystalline WC-Co composite with ultrahigh hardness and toughness. *Composites Part B: Engineering*. 2020; 197: 108161. doi: 10.1016/j.compositesb.2020.108161
41. Shawgi N, Li S, Wang S, et al. Towards a large-scale production of boron carbide nano particles from poly (vinyl alcohol) and boric acid by a solid-state reaction-pyrolysis process (SRPP). *Ceramics International*. 2018; 44(1): 774-778. doi: 10.1016/j.ceramint.2017.09.246
42. Nabakhtiani G, Chkhartishvili L, Gigineishvili A, et al. Dekanosidze. Attenuation of gamma-radiation concomitant neutron-absorption in boron-tungsten composite shields. *Nano Studies*. 2013; 8: 259-266.
43. Evans BR, Lian J, Ji W. Evaluation of shielding performance for newly developed composite materials. *Annals of Nuclear Energy*. 2018; 116: 1-9. doi: 10.1016/j.anucene.2018.01.022
44. Chkhartishvili L. Boron-contained nanostructured materials for neutron-shields. Springer Science; 2018. pp. 133-154.
45. Singla G, Singh K, Pandey OP. Structural and thermal properties of in-situ reduced WO₃ to W powder. *Powder Technology*. 2013; 237: 9-13. doi: 10.1016/j.powtec.2013.01.008

46. Wang Y, Long BF, Liu CY, et al. Evolution of reduction process from tungsten oxide to ultrafine tungsten powder via hydrogen. *High Temperature Materials and Processes*. 2021; 40(1): 171-177. doi: 10.1515/htmp-2021-0017
47. Dippel AC, Schneller T, Lehmann W, et al. Tungsten coatings by chemical solution deposition for ceramic electrodes in fluorescent tubes. *Journal of Materials Chemistry*. 2008; 18(29): 3501. doi: 10.1039/b802686f
48. Cao P, Cao JP, Cao JH. Boron carbide ceramic metallization preparation method. Available online: <https://eureka.patsnap.com/pdfnew/> (accessed on 1 September 2024).
49. Ozer SC, Buyuk B, Tugrul AB, et al. Gamma and neutron shielding behavior of spark-plasma sintered boron carbide-tungsten based composites. Cham, Springer International Publishing; 2016. pp. 449-456.
50. Sugiyama S, Taimatsu H. Preparation of WC-WB-W₂B composites from B₄C-W-WC powders and their mechanical properties. *Materials Transactions*. 2002; 43(5): 1197-1201.
51. Martini F. Preparation and Characterization of Uranium and Tungsten Borides for Applications in the Nuclear Industry [PhD Theses]. Bangor University; 2023.