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TRENDS IN THE DEVELOPMENT OF THE TUNGSTEN PRODUCTION

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ABSTRACT. Tungsten, as one of the "strategically important" metals, plays a key role in the contemporary development of the world industry and has specialised applications where it is currently impossible to replace it with other alternative materials. A study was carried out and data and information on the trends in the development of world resources, reserves and production of tungsten were analysed and summarised. Modern technologies and methods for obtaining concentrates, middlings or metal are presented. The trends concerning the changes in the production process have been identified and the forecast is for a steady low price trend over the next decade. New possibilities are presented for the production of metal of high purity by vacuum electrometallurgy methods - vacuum electric arc and electron beam melting. This enables both the production of metal of high purity and tungsten alloys and middlings with new or improved chemical composition, structure and properties.

Keywords: tungsten, primary production, processing, metal of high purity, electron beam melting, prices, markets

ТЕНДЕНЦИИ В РАЗВИТИЕТО НА ВОЛФРАМОВОТО ПРОИЗВОДСТВО

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РЕЗЮМЕ. Волфрамът, като един от „стратегически" важните метали, заема ключова роля в съвременното развитие на световната индустрия и има специализирани приложения, в които понастоящем е невъзможна замяната му с други алтернативни материали. Направено е проучване и са анализирани и обобщени данни и информация относно тенденциите в развитието на световните ресурси, запаси и производство на волфрам. Представени са съвременните технологии и методи за получаване на концентрати, междинни продукти или метал. Установени са тенденции относно промените в производствената активност и е прогнозиран устойчив нисък тренд на цените през следващото десетилетие. Представени са нови възможности при получаване на метал с висока чистота чрез методи на вакуумната електрометалургия - вакуумно електродъгово и електроннолъчево топене. Това дава възможност за получаване на метал с висока чистота и волфрамови сплави и полуфабрикати с нови или подобрени химичен състав, структура и свойства.

Ключови думи: волфрам, първично производство, преработка, метал с високо качество, електронно-лъчево топене, цени, пазари

Introduction

Tungsten (W) is a transition metal with the highest melting temperature (3422°C) in the group of refractory and alloying rare elements (B, Ti, Zr, Hf, Mo, Ta, Nb and V) and among all metals. The metal has a number of specific physical and mechanical properties: high density (19.3 g/cm^3), the lowest coefficient of thermal expansion (4.32-4.68.10^{-6}.K^{-1} at 25°C) and pressure of the vapour (8.15x10^{-8} Pa at 2000°C) among all metals, a high tensile strength (345-517 MPa at 1000°C), modulus of elasticity (390-410 GPa at 25°C), high heat (175 W/m.K at 25°C) and electrical conductivity (1.82x10^{7} S/m at 20°C) and high wear resistance. The tungsten is also characterised by high resistance to corrosion, water, inorganic (hydrochloric, sulfuric, nitric and hydrofluoric) and organic (formic, acetic, oxalic, tartaric) acids. Alkaline solutions do not act on tungsten but, when in contact with air, molten bases oxidise it to form tungstate. The tungsten is oxidised to tungsten trioxide at temperatures higher than 400-500°C. At temperatures ranging from 900 to 1200°C solid carbon and carbon-containing gases (CO, CH_4, etc.) together with the tungsten form very hard tungsten carbides (WC and W_2C), which are wear resistant and with high-melting point (the melting temperature of WC is 2900°C, of W_2C – 2750°C).

The properties of tungsten make it widely applicable in various fields of modern industry and machinery: automotive, steel, instrumental, mining, oil, gas, aerospace, chemical, construction, lighting industries, etc. Tungsten is used as a pure metal and an alloying component in steels, wear- and fire-resistant alloys, solid alloys based on tungsten carbide, as tungsten compounds, etc. Pure tungsten is used in electronics (cathode-ray tubes), X-ray technology (X-ray tubes), in electrical engineering (electric lighting, spotlights, electric heating elements in electric furnaces, microwave ovens, batteries, etc.), as well as in applications related to surfacing and welding in gas and tungsten (arc TIG welding). In metallurgy, tungsten is widely used in the production of special steels and alloys. Its content reaches up to 18-20% in the tool and high-speed steels. Tungsten alloys with molybdenum, tantalum, niobium and rhenium are used as refractories in aircraft and missile technology. Refractory and wear resistant alloys also include alloys containing tungsten (3-15%), cobalt (45-65%) and chromium (25-35%), which are used to cover heavy wear parts in machines (airplane engines, turbochargers jet engines, turbines, etc.). Nonferrous alloys based on Ni and Co with tungsten (Hastelloy® and Stellite®) are characterised by very high corrosion and wear resistance. Tungsten alloys of copper and silver and tungsten alloys of molybdenum are used in the preparation of high-temperature electrical sockets and thermocouples in electric arc furnaces and welding equipment. Tungsten alloys with copper and nickel (heavy alloys) are with high density (16.5-18 g/cm^3), which is used in the military industry to produce counterweights in aviation instruments, artillery parts, armour piercing bullets, super-fast gyro rotors for stabilising ballistic missiles, etc. They are also used in radiotherapy to protect against γ-rays and to produce containers for the storage of radioactive isotopes. An important area in the application of tungsten in the metallurgical industry is the production of solid alloys based on tungsten carbide (85-97% WC and 3-15% Co or Ni). Solid alloys are the highest quality tool alloys that retain their high hardness and wear resistance when heated to 1100°C. They have a wide range of industrial applications in the heavy machinery, mining and petroleum industries, etc., with some brands of these alloys containing titanium, tantalum and niobium carbide. Chemical compounds of tungsten are used in the production of catalysts, inorganic pigments and high temperature (up to 500°C) lubricants (based on tungsten disulphide). Tungsten oxides are used for the production of ceramic glazes, and "tungsten bronze" (named after the colour of the tungsten oxides) is used in the manufacture of paints. Tungstate (calcium and magnesium) is used in the production of luminescent luminaires. Crystalline tungstate is used as a scintillation detector in nuclear physics and medicine. Tungsten salts are applied in the chemical and tanning industries. A number of tungsten compounds are used in the textile industry for the aging of fabrics and the production of fire and waterproof fabrics.

The structure of the world primary application (www.itia.info/tungsten) and the end use of tungsten in the industrial sectors (base 98 thousand t W; *ITIA*, 2017) is shown in Table 1 and 2.

Table 1. *World primary application of tungsten (Roskill – ITIA, 2010)*

Application	World, %		Countries,%					
			China	Europe		Japan	Russia	USA
Solid alloys (based on tungsten carbide and cemented carbides)	54	65*	54	72	66**	67	70	66
Steels/Alloys (high-speed, drilling, tool, refractor, heavy alloys, super alloys, etc.)	27	17*	28	9	11**	11	26	9
Middlings (wire, laminas, sheets, plates, etc.)	13	10*	11	8	10**	11	4	20
Other applications	6	8*	7	11	13**	11		5

Source: * ITIA, 2018; ** European Hard Materials Group (EuroHM), 2017

Table 2. *End use of tungsten worldwide*

Industrial sector	Usage, %
Energy	10
Transport	34
Industrial equipment	11
Mining and construction	21
Defence	8
Medicine, etc.	10
Consumer (household durable goods)	6

According to the British Geological Survey (2015) of chemical elements or groups of economic value, tungsten is defined with a high supply risk index with a value of 8.1 at a scale of one to ten.

Resources, reserves and mining production of tungsten

Identified tungsten resources worldwide have been estimated at around 13 million t W (16.34 million t WO_3) (Lapteva, 2018) and are available in 27 countries. Their distribution is characterised by a high degree of concentration in six countries (China, Kazakhstan, Russia, Canada, Australia and Vietnam), where over 80% of global resources are concentrated, Table 3.

Table 3. *Distribution of resources worldwide (base 2015)*

Countries	Resources, thousands t		
	W	WO_3	%
China	5713.6	7205.0	44.1
Kazakhstan	1590.0	2005.0	12.3
Russia	1576.5	1988.0	12.2
Canada	996.0	1256.0	7.7
Australia	644.8	813.1	5.0
Vietnam	225.8	284.7	1.7
Others	2210.8	2787.9	17.0
Overall	12957.5	16339.7	100.0

The proven tungsten reserves are estimated at about 3.345 million t W (base 2017). The development of the proven reserves and the mining production for the period 2002-2017 are presented in Figure 1 (*USGS*, 2002-2018). The increase of the mining reserves for the indicated period is 1.1 times and that of the production - 1.4 times. The reserves are characterised by a high degree of concentration in 13 countries, with around 90% in the world's top four (China, Russia, Canada and Australia). There is no published data about the US reserves. According to the used classification about the depletion rates of mineral reserves (Slastunov et al., 2001), the tungsten reserves for the period are characterised by a high rate of depletion, with a reserve life index of a resource (RLI, %) within the range of 2.0-3.0%. If global production is maintained at the level of 2016-2017, the reserves will ensure tungsten supply for no more than 35-40 years worldwide. The identified global tungsten resources may extend this period with about 80-85 years.

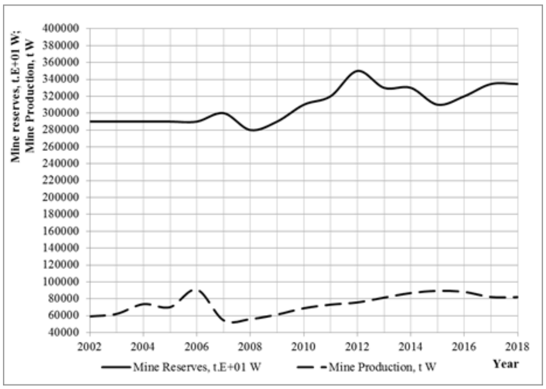


Fig. 1. World reserves and mining production of tungsten, 2002-2017

The main geological, genetic and industrial types of tungsten deposits (Vangelova, 2013) are presented in Table 4. Out of the 50 known minerals and mineral varieties of tungsten, only the minerals wolframite (Mn,Fe)WO_4 (with 74% W ± Nb, Sc, Ta, Y, In, Mo), ferberite $FeWO_4$, huebnerite $MnWO_4$ (with about 60.5% W) and scheelite $CaWO_4$ (~64% W) are of industrial importance. Wolframite and huebnerite cover about 75% of the world's yield, while the scheelite - about 25%.

Table 4. *Industrial types of tungsten deposits*

Type of deposit	Ore minerals		Known deposits
	Primary	Secondary	
Skarn	scheelite, sometimes molybdenite	cassiterite, bismuthinite, magnetite, pirrhotite, pyrite, arsenopyrite, wolframite, etc.	Vostok II, Turnaus (Russia); Chorukh-Dayron (Tajikistan); Ingichka (Uzbekistan); Sangdong (South Korea); Shizhuyuan, Huanpodi, Iliu (China); Emerald Fini, Mactung Cantung (Canada); Pine Creek, Osgood Range (USA); Salau (France); King Island, Moana (Australia) and others.
Greisen	wolframite, molybdenite, cassiterite	magnetite, bismuthinite, pirrhotite, pyrite, chalopyrite, galena and sphalerite	Akchatau, Kara-Oba (Kazakhstan); Yugodzyr, Bayamod (Mongolia); Piaotian, Xinhuangshin (China); Wolfram Camp, Torrington (Australia); Cornwall (United Kingdom); Altenberg (Germany); Cínovec, Krupka (Czech Republic); Zabaykalie (Russia) and others.
Veined (plutonogenic-hydrothermal)	wolframite, huebnerite, more rarely scheelite	cassiterite, molybdenite, bismuthinite, arsenopyrite, pyrite, pirrhotite, chalopyrite, galena, sphalerite, etc.	Panasqueira (Portugal); Iultin, Bom-Gorhon, Holtoson, Bukuka, Antonovogorskoe (Russia); Boguty, Verkneye Kairakty (Kazakhstan); Tumen-Tsogto (Mongolia); Red Rose (Canada); Herberton (Australia); Liandushan, Shanping (China); Belfort (France); Grancharitsa (Bulgaria) and others.
Epithermal (volcanogenic-hydrothermal) complex composition (Sn-Ag-W, Hg-Sb-W, Au-W, Mn-W)	Ore associations: (cinnabar) – antimonite-scheelite-ferberite; Ag-Au-scheelite; psilomelan-wolframite		Ascensión, Tazna (Bolivia); Tungsten Queen (Canada); Yellow, Boulder, Atolia, Golconda (USA); Gumusler (Turkey); Morococha (Peru); Akenobe, Ashio (Japan); Usin, Xian (China); Taskor (Kazakhstan), Ikar (Tajikistan) and others.
Orogenic	ferberite, antimonite, cinabar	pyrite, chalcopyrite, sphalerite, arsenopyrite, siderite	Felbertal, Kleinertal (Austria); Barun Shiveya, Olympiadinskoe (Russia); Hillgrove (Australia)
Placer (cassiterite-wolframite, wolframite, huebnerite, scheelite)	cassiterite, wolframite, huebnerite, scheelite		Iultin, Omchikandin, Sherlova Gora (Russia); Kara-Oba, Boguty (Kazakhstan); Bvabin, Heida (Myanmar), Atolia (USA), China, Indonesia, Thailand, Congo, Bolivia and others.

More than 98% of the world's tungsten reserves are concentrated in endogenous deposits, which according to their structural and morphological type are mainly stockwerk, layer- and lens-shaped and veined. The distribution of the world reserves and the production of tungsten in the main industrial deposits are shown in Table 5 (Vangelova, 2013; Starostin, 2016). The stockwerk deposits have a low WO_3 content (0.15-0.8%), but are of great importance because of their very large sizes and reserves. The skarn deposits are mainly represented by scheelite and molybdenite and are very important for the reserves and the tungsten yield. The veined deposits are small and medium in reserves, but have a high WO_3 content (0.5-2.0%) and are therefore also very important for tungsten yield.

Table 5. *Major industrial types of deposits and tungsten production*

Geological and industrial types of deposits	World reserves, %	World output, % WO_3
Stockwerk: Wolframite (hydrothermal and greisen) Scheelite	31 29	28
Skarn scheelite	23	25
Veined wolframite	12	43
Stratiform scheelite	4	-
Placer	>1	-

Global tungsten mining is about 82.1 thousands t W (base 2017) (*USGS*, 2002-2018) and it has grown 1.4 times over the period. There is no published output data about the United States. There is significant tungsten production in 10 countries, accounting for over 98% of the world output. China is an undisputed leader with a share of about 82%, followed by Vietnam (8%), Russia (2.5%), England (1.3%), Bolivia (1.2%), Austria (1.2%), Portugal (0.9%), Rwanda (0.9%), Spain (0.7%) and Mongolia (0.2%).

The modern development of the tungsten mineral resource base is related to the price of the metal. In 2006-2007 there was an increase in the reserves and the production of tungsten under the pressure of two major political and economic factors – the formation of a tungsten sector in China, leading to strict control and change in the structure of metal exports, and the growing demand for tungsten in China and globally. The rapid rise in the price of tungsten resumed the assessment and prospecting work and the introduction of new or recovery of existing productions in China and a number of countries (Australia, Vietnam, Canada, United Kingdom, Spain, South Korea, etc.) with a peak in the activity in 2011-2012 and at maximum prices of the metal. Over the next few years, due to the overproduction of tungsten, the price of the metal dropped down and a number of projects for the utilisation of economically viable deposits were discontinued or closed down. The rest of the projects could provide for a significant increase in the output of tungsten concentrate. The significant tungsten deposits ready for exploitation and processing are shown in Table 6.

Currently, mining production in Europe is carried out in several mining enterprises, accounting for about 3.6% of the world output. The main parameters and characteristics of the significant mines and mining projects are shown in Table 7.

Table 6. *Basic parameters of the deposits ready for exploitation and processing (Lapteva, 2018)*

Deposit	Type	Mining method	Basic quantity		% WO_3 in the ore	Capacity according to	
			Ore, million t	WO_3, thou. t		Ore output, million t	WO_3 output in the product, thou. t
Sisson (Canada)	porphyry	opencast	334.4	220.7	0.07	11.05	5.9 (C); 5.5 (APT)
Sandong (South Korea)	skarn	underground	8.0	35.5	0.45	0.45–0.64	1.2–2.5 (C)
Mt Plesant, (Canada)	porphyry	underground	13.5	44.5	0.33	0.84	1.6 (APT)
La Parrilla, (Spain)	veined	opencast	46.9	42.2	0.09	3.5	3.4 (C)
Watershed, (Australia)	veined	opencast	21.3	31.4	0.15	2.5	2.7 (C)
Big Hill, (Australia)	veined	opencast	25.2	28.1	0.11	2.4	2 (C)
Barruecopardo, (Spain)	veined	opencast	8.7	26.1	0.30	1.1	2.3(C)
Mt Carbine, (Australia)	veined	opencast	18.0	25.2	0.14	1.5–3	1.6–3.2 (C)
Dolphin, (Australia)	skarn	opencast	3.1	22.9	0.73	0.45	3.5 (C)
Molyhil, (Australia)	skarn	opencast	3.0	9.2	0.31	0.5	1.3 (C)
Valtreixal, (Spain)	veined	opencast	2.5	6.4	0.25	0.5	0.7 (C)

Note: C – concentrate, APT – ammonium paratungstate

Table 7. *Parameters and characteristics of tungsten mines in Europe (Cuesta-López, 2016)*

Mine	Parameters							
	Company/Operator and stock exchange	Resources (assessed and identified), million t	Content WO_3, %	Operational costs, US$/mtu	Capital costs, US$	Annual output, mtu WO_3	Exploitation, years	Mining method
Panasqueira (Portugal)	Almonty Ind. Inc (TSX-V) 100%	9.54	0.22	160-170	-	85000–95000	10	underground
Los Santos (Spain)	Almonty Ind. Inc (TSX-V) 100%	2.21	0.29	88	80	65000-75000	4	opencast and underground
Drakelands–Hemerdon (UK)	Wolf Minerals Ltd (ASX) 100%	56.6	0.17	155	150	110000-120000 (in future up to 500000)	20	opencast
La Parilla (Spain)	W – Resources plc London AIM: WRES (100%)	51	0.096	95	52	250000 (2017) 500000 (2020)	15	opencast
Mittersill (Austria)	Sandvik AB (100%) (Wolfram Bergbau und Hutten AG)	6.1	0.2	-	-	85000	10	underground
Valtreixal (Spain)	Almonty Industries Corp. TSX-V: ATT (25%) и SIEMCALSA (75%)	2.83	0.34 (eqv. Sn)	80-90	45	90000	10	opencast
Barruecopardo (Spain)	Ormonde Mining plc LON: ORM (30%)	17.8	0.30	117	57.2	260000	7-10	opencast and underground
Regua (Portugal)	W – Resources plc London AIM: WRES (100%)	5.46	0.28-0.30	-	-	130000	5	underground

Note: mtu – 10 kg (100mtu – 1 t)

Data shows that Europe has sufficient tungsten resources, but due to the delicate balance between supply and demand and price fluctuations, some projects and mining might turn out to be economically not viable.

Tungsten production and tungsten intermediate compounds

The principle scheme for the tungsten production and intermediate tungsten compounds is shown on Figure 2 (*BGS*, 2011).

Due to the low content of tungsten in the mined ores (0.1-0.8% WO_3) and the high requirements for the quality of the commercial concentrates (65-75% WO_3), the beneficiation schemes usually include two cycles – the main cycle which produces a coarse tungsten concentrate and an additional beneficiation cycle to obtain a marketable concentrate. Tungsten ores are enriched by purely gravity, gravity-flotation and purely flotation schemes, depending on the dispersion of the tungsten minerals in the ore. The resulting concentrates are poor (5-20% WO_3) and besides tungsten they also contain other minerals - cassiterite, sulfides, tantalum, columbite, etc. The additional ore dressing cycle, depending on the mineral composition of the coarse concentrates, includes one or more of the following processes - magnetic and electrical separation, flotation, flotogravitation, roasting and hydrometallurgy. In some processing schemes a preliminary beneficiation cycle, which includes mechanical sorting of the ore prior to conventional beneficiation methods, is applied. Photometric sorting is applied for wolframite, and also for scheelite if it is contained in white quartzite veins. The preliminary beneficiation of the scheelite ore is performed by fluorescence sorting.

The wolframite concentrates are melted directly into electric arc furnaces to produce ferrotungsten (FeW), a widely used alloying component in the steel industry. The scheelite concentrates are also melted directly for the production of steel. Recycling of tungsten scrap (60 to 70% scrap) in the production of high-speed steel is widely used. In modern factories, the tungsten concentrates are subjected to hydrometallurgical processing to produce middlings – mainly ammonium paratungstate (APT). Important secondary raw materials for the production of tungsten intermediate compounds are the oxidised scrap and wastes (sludge, dust, precipitates, chips, etc.) containing from 40 to 95(99)% W. Innovative technologies for industrial hydrometallurgical recycling of scrap generating less toxic emissions (Takehiko, 2016) are currently being financed. The principal scheme of hydrometallurgical processing of tungsten concentrates, scrap and wastes is shown in Figure 3 (Lassner, Schubert, 1999).

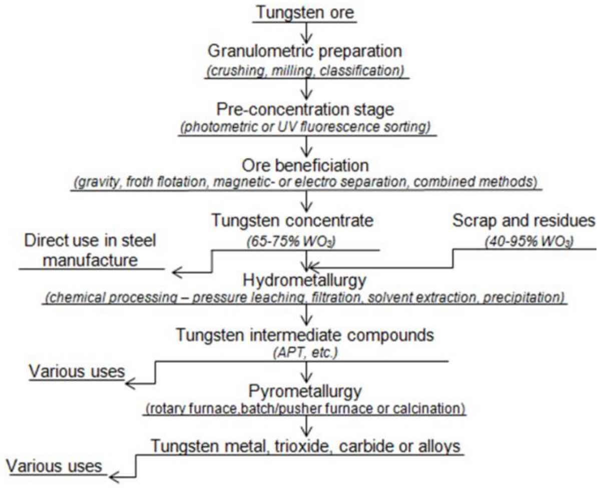


Fig. 2. Simplified flow sheet showing generic steps in processing tungsten

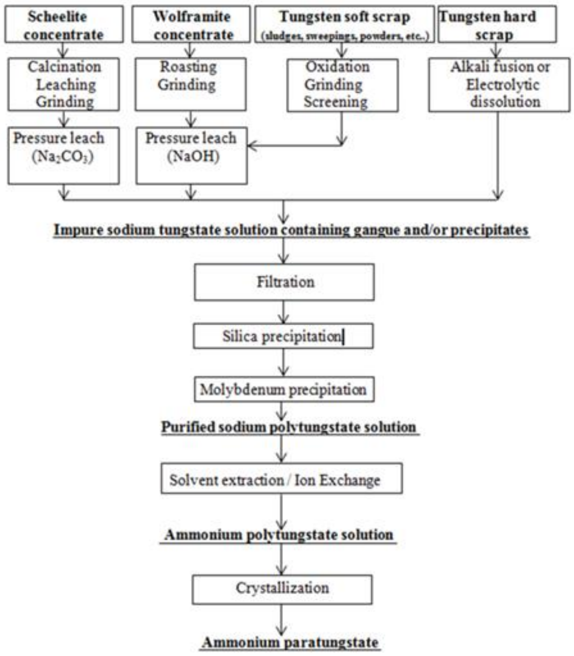


Fig. 3. Simplified flow sheet of hydrometallurgical processing of tungsten concentrates and wastes

The tungsten concentrates are decomposed under pressure – the scheelite with Na_2CO_3 and the wolframite with NaOH. Mechanical activation is required in parallel with the leaching for both types of concentrates to avoid formation of insoluble particles on the minerals' surface. Tungsten scrap is easier to process than ore concentrates due to the absence of impurities such as P, As and Si. Prior to the alkali leaching process, the scrap is subjected to oxidation in oxygen-containing environments in furnaces. The decomposition is achieved by one of the processes – leaching under pressure with NaOH, oxidative alkaline melting (Na_2Co_3 with the addition of $NaNO_3$ and $NaNO_2$) or electrolysis. The residues undissolved after the decomposition are removed by filtration. The impurities (silicates, molybdenum, etc.) in the sodium tungstate solution are removed using precipitation under strictly controlled conditions of the environment. By applying liquid extraction or ion exchange, the solution of sodium tungstate is converted to ammonium isopolytungstate. The solution obtained by the two processes is subjected to heating to evaporate water and ammonia, where the ammonia concentration decreases compared to that of WO_3 and the paratungstate, whose ammonium salts have low solubility and crystallise. Depending on the conditions of the environment, the APT reaches a purity of 90-99%. The ammonium paratungstate $(NH_4)_{10}(W_{12}O_{41}).5H_2O$ is the major precursor used to produce various tungsten middlings (tungsten "yellow" trioxide (WO_3), tungsten "blue" oxide ($WO_{2,97}$), tungstic acid (H_2WO_4) and ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}.xH_2O$) by partial or total thermal or chemical decomposition.

The pyrometallurgical processing of APT involves calcination under oxidative conditions until its conversion into WO_3. By maintaining low reduction conditions, calcination results in the formation of tungsten "blue" oxide. The treatment of both oxides in furnaces turns them into a tungsten metal powder that is used in the production of WC and a number of tungsten alloys. Globally, 70-80% of tungsten is produced by powder metallurgy.

Methods for obtaining tungsten of high purity and tungsten super alloys

On the basis the analysis of the world and Bulgarian experience to obtain tungsten of high purity and properties, which meet the high requirements for many of its applications, the following modern methods have been accepted as sufficiently effective: powder metallurgy (PM), electrolysis of salts, metallothermic refining, and some of the special electrometallurgical methods such as chemical vapour deposition (CVD), plasma arc melting (PAM), spark plasma sintering (SPS), vacuum induction melting (VIM), electron beam melting (EBM), hot isostatic processing (HIP) and thermoplastic routes that are successfully applied in metallurgical and metalworking practices around the world.

It has been found that an established method for the preparation of a technically pure metallic tungsten and for the production of solid alloys on its basis is the powder metallurgical method – the metallic powders are initially obtained by reduction of their compound, usually an oxide, in an atmosphere of hydrogen or carbon. The reduction occurs at relatively low temperatures (800-1200°C). The reduction processes, occurring in the reactions presented in Table 8, are the most widely used in the practice.

Table 8. *Reduction metallurgical methods for the preparation of pure tungsten from its oxides*

Reducer	Metal	Reaction	Technological conditions
C	W	$2WO_3 + 3C = 2W + 3CO_2$	800 – 1200°C
H_2	W	$WO_3 + 3H_2 = W + 3H_2O$	800 – 1200°C

The behaviour and properties of the compact metal in the subsequent processing steps are highly dependent on the chemical composition and structure (including particle size and shape, size distribution) of the resulting metal powders. The structure of the metal powders depends on the structure of the parent compounds and the reduction regime. The powder metallurgical method, used to process the resulting metal powder to a compact metal, comprises of the following steps:

- Compacting metal powders as briquettes, washers or moulds close to the type and dimensions of the metal products after the sintering process;
- Sintering the blanks by heating to a specific temperature;
- Additional processing (forging, drawing, rolling) of the sintered blank to a final product.

This tungsten processing technology does not provide the metal with sufficient plasticity and weldability. The physical and mechanical properties of tungsten produced by sintering are too anisotropic and depend on the initial state, purity and structure of the powders prior to sintering (Mushegyan, 2009). The metal produced after the reduction has a high percentage of metallic and gas impurities. It needs to be further refined as the requirements to the chemical composition, structure and quality of the final product are constantly increasing.

Tungsten displays brittle behaviour at ambient temperatures limiting the use of some conventional processing methods. Additive manufacturing (AM) also has unique features to produce components of high melting point refractory alloys that are difficult to process using conventional methods (DebRoy, 2018). By utilising AM techniques such as selective laser melting (SLM), complex geometries of even refractory metals like tungsten can be realised. SLM of tungsten remains a challenging task due to the high melting point, high viscosity, high thermal conductivity, its affinity for oxygen at high temperatures and brittle nature at room temperature, resulting in parts with cracked and porous microstructure (Iveković et al., 2018; Tan et al., 2018).

So far the world production of tungsten has been achieved mainly by conventional metallurgical processes and, as a final phase of refining, the top refineries mainly use hydrometallurgical and electrolytic processes. Another possibility to improve the quality of the obtained refined metal can be the application of vacuum metallurgy as part of the special electrometallurgy. The development of effective methods for the production of metals and alloys with a low content of metallic, non-metallic and gas impurities and the preservation of the achieved chemical composition during further processing are important problems that modern metallurgy has successfully solved. Vacuum metallurgy occupies a leading position among the industrial methods for the production of metals and high purity alloys.

As part of the vacuum metallurgy, the electron beam (EB) refining method achieved significant success in scientific research in the last decades of the last century, and the development of electron beam technologies as high-performance aggregates has also established it in the industry as a promising method for obtaining high-purity metals and alloys in vacuum (Vassileva et al., 2005; Vutova et al., 2010; Mladenov et al., 2011; Oh et al., 2013; Tan, Shi, 2013; You et al., 2018; Vutova et al., 2019).

Methods such as vacuum arc melting (VAM) and electron beam melting (EBM) are required for further refining in the industrial production of pure tungsten and its alloys in countries such as the United States, Ukraine, Russia, etc. In VAM, the starting materials are melted in electric arc furnaces with consumable electrode in vacuum or in argon medium, in copper water-cooled crucible or in melting furnaces with a copper or graphite melting-pots.

Electron beam melting (EBM) technology has been considered as one of the key steps for preparing high purity tungsten and its alloys, and reasonable setting of process parameters is the premise. The EBM yields the metal with the lowest impurity content, there is a possibility to obtain large ingots and the melted tungsten ingot consists of well-collimated long columnar crystal grains (Takaai, 1966; Tan, Shi, 2013; Long et al., 2015;).

The electron beam method is suitable both as a final step in the production of tungsten with improved chemical composition and structure using metallic concentrate obtained after thermal reduction, and for the recycling of waste materials from tungsten or its alloys and compounds (Mladenov et al., 2011; Vutova et al., 2018). The method combines two main advantages –

achieving a very high temperature and vacuum environment in which the hot molten metal cannot be oxidised. The EBM method does not have special requirements for the type of initial material, there is economical feedstock preparation, and yet it provides for good refining from gases, non-metallic and metallic impurities that are more volatile than the refined metal.

With the electron beam melting, the possibility of uncontrollable side reactions is excluded as there is no direct contact between the molten metal and the fire-proof lining or the atmospheric gases. In the refining process, favourable conditions are created for the reactions and processes, in which the gas phase is involved, to continue till the end, as it is possible to displace their thermodynamic equilibrium in the desired direction. Under the conditions of electron beam refining certain reactions can take place - degassing, reduction of oxides, reduction and evaporation of volatile impurities that cannot be used in case of atmospheric pressure. Refining takes place at the boundary surface between superheated liquid metal and vacuum in several reaction zones. In each of them, processes such as mass transfer (from the volume to the boundary surface and vice versa), chemical interactions between components present in the surface area (elements and chemical compounds) and evaporation from the boundary surface of impurities in the form of atoms or connected as compounds, take place simultaneously.

To summarise, based on the characteristics and advantages of the EB method, the following options can be realised:

(a) in the established metallurgical scheme for the production of tungsten, the EB method can be applied as:

• final stage – to use tungsten powder prepared by reduction of tungsten oxide as an initial material for the EB refining.

(b) in secondary recycling processes for:

• tungsten scrap

• waste tungsten carbide products.

Market price characteristics of the tungsten production

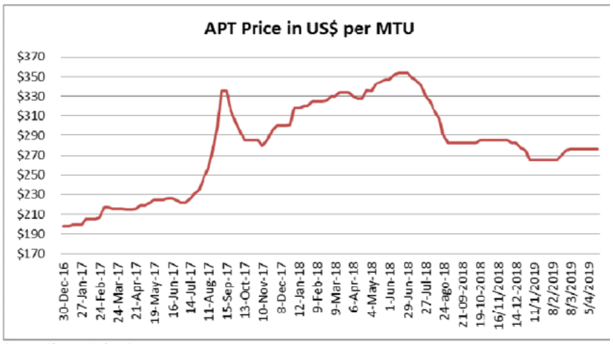
The market-price parameters for tungsten ore extraction and subsequent processing are determined by the behaviour of two main factors and their interdependence.

First, this is the state and behaviour of the world economy, its cyclicality and the associated fluctuations in the quantities of the extracted primary tungsten, the products produced and consumed and, of course, the prices at which these processes take place. For the sake of clarity, we will point out that, unlike the predominant part of the mineral resources where market-pricing procedures are specific and very often standardised products (e.g. the base metals at the London Metal Stock Exchange, noble metals, etc.), the tungsten range is very wide, and the variety in the product nomenclature depends on the vertical development of the production and includes *tungsten ores, tungsten concentrates (scheelite and wolframite), paratungstate, tungsten anhydride, ferro-tungsten, metallic tungsten*. This makes the economic feasibility assessment of the development of a particular tungsten deposit quite specific, the most important being the type of final output to be produced, i.e. concentrates or subsequent industrial products.

The genesis of the second factor emerged in the 1990s and is based on the tungsten production in China. According to information from (INFOMINE Research Group, 2017), China owns the largest tungsten ore reserves and produces the largest quantities of tungsten concentrates and end products, which contain tungsten in various forms. These estimates do not account for the US reserves about which no official information is available. In fact, the world market is monopolised by China, which is both the largest consumer and exporter of tungsten concentrates and products. There is a hybrid political-economic approach in this process in which the Chinese government plays an important role and has a strong influence on the world market by imposing export duties and quotas.

As a result of the interaction between these key factors, the prices of tungsten concentrates and products are subject to sensitive fluctuations, which have been particularly high during the last decade. Since 2011, there has been a tendency for a dramatic decrease in the price of tungsten concentrates. For example, for a period of five and a half years, the price has fallen about 3.5 times (from 415 USD/MTU WO_3 to 140 USD/MTU WO_3). The main reason for this price collapse is the presence of oversupply as a result of unsold final production and the accumulation of huge quantities of waste products containing tungsten. In order to get a clear idea of the parameters of this collapse, we will point out that at the beginning of 2015 the price fell below the average world production cost of 195 USD/MTU WO_3 and in the second half it became even lower than the average production costs in the Chinese enterprises - 165 USD/MTU WO_3. These processes resulted either in the closure of a number of tungsten mining enterprises or in sharp reduction of the production.

The price bottom was reached in the beginning of 2016 when the price fell to 120 USD/MTU WO_3, which caused a lot of losses to a number of companies. Naturally, analysts' forecasts for a recent price backlash came true and at the end of 2016 they reached 150USD/MTU WO_3, which is seen as a threshold for the profitability of a large number of enterprises. Since then, there has been a tendency for relative retention, even reduction of the price. According to the latest data of April 2019 (price.metal.com), the price of 65% tungstate concentrate on the Chinese market was around 135 USD/MTU, which indicates stability of the price at a low level. The trends with respect to the ammonium paratungstate are similar, the values and price trends are presented in Figure 4.



Source: Almonty Industries

Fig.4. Price dynamics of ammonium paratungstate, 2016-2019

As a general conclusion it can be stated that the market environment is dynamic and unpredictable for the products from primary tungsten. It is obvious that there are a number of factors which influence it and they have maintained relatively low price levels over the last ten years. As it is quite safe to state that the

Chinese producers will have a major influence on the market, it can be concluded that the launch of new tungsten production is justified only in the case of presence of mining and geological characteristics similar to those of the major world producer.

Conclusion

Based on the above, the following main conclusions can be made for the future development of tungsten mining and processing, which can be useful for elaborating the company policies in our country:

- Firstly, the tendency for retention and slight increase of the world consumption of tungsten will remain stable in the next one to two decades as a response to the technological development and new areas of application;
- Secondly, the presence of significant quantities of tungsten scrap suppresses the growth of prices, which poses serious problems to the investments in new deposits and to the ongoing development of those with low quality indicators and difficult mining and geological conditions;
- Thirdly, the above estimates suggest that tungsten prices in the next decade will have a sustained but low upward trend, offsetting inflation pressure;
- Fourthly, the new applications of tungsten and its alloys in modern technologies and directions imply higher requirements for its composition, structure and technological properties, which can only be achieved by the application of modern metallurgical methods. One good option is the electron beam melting method that combines the advantages of vacuum metallurgy and high energy special electrometallurgy.
- Fifthly, the integration of these conclusions makes it possible to conclude that investing in new and developing existing mining capacities for extraction and processing of tungsten ores with low quality indicators has an increased component of market risk.

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References

British Geological Survey. 2011. Tungsten; www.itia.info/tungsten.

British Geological Survey. 2015. Risk list; www.bgs.ac.uk/downloads/start.cfm?id=3075.

Cuesta-López, G. S., R. B. García, M. M. Arragonés, M. G. Moya, Q. Monge, N. Maund. 2016. Report on balance between demand and supply of refractory metals in the EU. – MSP-REFRAM, D1.3, November 2016.

DebRoy, T., H. L. Wei, J. S. Zuback, T. Mukherjee, J. W. Elmer, J. O. Milewski, A. M. Beese, A. Wilson-Heid, A. Ded, W. Zhang. 2018. Additive manufacturing of metallic components – process, structure and properties. – *Progress in Materials Science, 92*, 112–224.

European Hard Materials Group (EuroHM). 2017. Wolfram-Mining&Refining: Raw Materials in Cemented Carbide, 02.06.2017, www.epma.com.

INFOMINE Research Group. 2017. Tungsten Production, Market and Forecast in the CIS. 12th Edition, Moscow, 2017.

ITIA. 2017. Tungsten End Use Analysys.

ITIA. 2018. Tungsten. Newsletter May.

Iveković, A., N. Omidvari, B. Vrancken, K. Lietaert, L. Thijs, K. Vanmeensel, J. Vleugels, J-P. Kruth. 2018. Selective laser melting of tungsten and tungsten alloys. – *International Journal of Refractory Metals & Hard Materials, 72*, 27–32.

Lapteva, A. M. 2018. Situatsiya na mirovom volframovom ryinke i vozmojnosti rossiyskoy syirevoy bazyi volframa. – *Otechestvennaya geologiya*, 1, 29–39 (in Russian).

Lassner, E., W.-D. Schubert. 1999. *Tungsten – Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds*. Kluwer Academic; Plenum Publishers, New York.

Long, L., W. Liu, Y. Ma, Y. Liu, S. Liu. 2015. Refining tungsten purification by electron beam melting based on the thermal equilibrium calculation and tungsten loss control. – *High Temp. Mater. Process, 34*, 605–610.

Ma, Y., Y. Liu, W. Liu, L. Long. 2014. Preparation procedure of high purity tungsten via electron beam side surface melting. – *Mater. Sci. Technol., 22*, 30–35.

Mladenov, G., E. Koleva, K. Vutova, V. Vasileva. 2011. Experimental and theoretical studies of electron beam melting and refining. – In: *Practical Aspects and Applications of Electron Beam Irradiation (Eds. M. Nemtanu, M. Brasoveanu).* Research Signpost/Transworld Research Network, 43–93.

Mushegyan, V. O. 2009. Elektronno-luchevaya plavka vosstanovlennogo kontsentrata molibdena. – *Sovremennaya elektrometallurgiya*, 4(97), 26-28 (in Russian).

Oh, J. M., B .K. Lee, G. S. Choi, H. S. Kim, J. W. Lim. 2013. Preparation of ultrahigh purity cylindrical tantalum ingot by electron beam drip melting without sintering process. – *Mater. Sci. Technol., 29*, 542–546.

www.price.metal.com/Tungsten-Cobalt-Antimon.

Slastunov, S. V., V. N. Koroleva, K. S. Kolikov, E. Yu. Kulikova, A. E. Vorobev, V. V. Kachak, V. I. Babkov-Esterkin, A. T. Ayruni, A. S. Batugin, A. A. SHilov. 2001. *Gornoe delo i okrujayuschaya sreda.* Logos, Moskva, 192 p. (in Russian)

Starostin, V. I. 2016. Volframovyie rudyi. – In: *Bolshaya rossiyskaya entsiklopediya, Elektronnaya versiya*; https://bigenc.ru/geology/text/3472803 (in Russian)

Takaai, T. 1966. The electron beam melting of tungsten. The Electron Beam Melting of Refractory Metals (VIII). – *Journal of the Japan Institute of Metals and Materials, 30*, 11, 1027–1031.

Takehiko, H., F. Sato, K. Sasaya, A. Ikegaya. 2016. Industrialization of tungsten recovering from used cemented carbide tools. – *SEI Technical Review*, 82, April.

Tan, C., K. Zhou, W. Ma, B. Attard, P. Zhang, T. Kuang. 2018. Selective laser melting of high-performance pure tungsten: parameter design, densification behaviour and mechanical properties. – *Science and Technology of Advanced Materials, 19*, 1, 370–380.

Tan, Y., S. Shi. 2013. Progress in research and development of electron beam technology in metallurgy refining field. – *J. Mater. Eng*., 8, 92–100.

USGS. 2002-2018. Mineral Commodity Summaries.

Vangelova, V. 2013. Nahodishta na metalni polezni izkopaemi, SU „Sv. Kliment Ohridski", 142-148 (in Bulgarian).

Vassileva, V., G. Mladenov, K. Vutova, T. Nikolov, E. Georgieva. 2005. Oxygen removal during electron beam drip melting and refining. – *Vacuum, 77*, 429–436.

Vutova, K., V. Vassileva, E. Koleva, E. Georgieva, G. Mladenov, D. Mollov, M. Kardjiev. 2010. Investigation of electron beam melting and refining of titanium and tantalum scrap. – *J. Mater. Process. Technol., 210*, 1089–1094.

Vutova, K., V. Vassileva, E. Koleva, V. Stefanova, D. P Amalnerkar. 2018. Effects of process parameters on electron beam melting technogenic materials for obtaining rare metals. – *IOP Conf. Series: Journal of Physics: Conference Series,* 1089 (1), 012013.

Vutova, K., V. Vassileva, V. Stefanova, D. Amalnerkar, T. Tanaka. 2019. Effect of electron beam method on processing of titanium technogenic material. – *Metals*, 9, 683.

www.itia.info/tungsten.

You, Q., H. Yuan, L. Zhao, J. Li, X. You, S. Shi, Y. Tan, X. Ding. 2018. Removal inclusions from nickel-based superalloy by induced directional solidification during electron beam smelting. – *Vacuum, 156*, 39–47.