

Tungsten as a critical element

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1. Introduction to Tungsten

Tungsten, the 74th element of the periodic table, is named after the Swedish word for *heavy stone*. The chemical symbol of Tungsten (W) stands for its German name *wolfram*, though. The origin of this name goes back to medieval German smelters who first found tungsten-containing tin ores show much lower yield (*History of Tungsten* 2011).

Historically, the pure tungsten metal was first produced in 1781-82 by two Spanish metallurgical chemists, de D'Elhuyar brothers, and then published in 1783. The main tungsten ore (scheelite) is named after Carl Wilhelm Scheele for his contribution in the discovery of tungsten. He actually first published (in 1781) the results of his experiments on tungsten ores which led to the formation of an unknown acid; the main contribution of the de D'Elhuyar brothers was to reduce this acid under an oxidant atmosphere made by charcoal (*History of Tungsten* 2011).

Back to the 20th century science, tungsten can be described with its electronic structure known to be $4f^{14}5d^46s^2$ giving this element the possibility to form various compounds with oxidation number of +4, e.g. WC (tungsten carbide) or +6, e.g. WO_3 (tungsten oxide) and H_2WO_4 (tungstic acid). Possessing the highest melting point (3422 ± 15 °C) together with the lowest thermal expansion coefficient (4.32 to $4.68 \times 10^{-6} K^{-1}$ at 25 °C) among metallic materials, and also a very low vapor pressure (8.15×10^{-8} at 2000 °C), tungsten is on the top list candidates of the engineering materials for high temperature applications (*Tungsten Properties* 2011).

Tungsten and its products are a collection of different superior physical and mechanical properties; one or more of the following strategies are determining in any material selection procedures:

- Thermal fatigue caused by non-uniform thermal expansion is considered to be one of the main failure mechanisms for multi-components systems; possessing very low thermal expansion coefficient, tungsten offers an excellent dimensional stability.
- Components intended to be used in high temperature applications are always susceptible to material loss due to the exponentially increased evaporation rate; due very low vapor pressure, tungsten is a promising candidate material for many high temperature applications.
- Together with the low vapor pressure, possessing uniquely low electrical resistivity ($5.28 \mu\Omega \cdot \text{cm}$ at 25 °C) makes tungsten an excellent current carrying material at elevated temperatures (*Tungsten Properties* 2011).
- Connected to the intrinsic physical properties of tungsten, and principally related to the high electrical conductivity of tungsten, tungsten offers excellent heat conductivity ($175 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25 °C). Owing such high conductivity together with its dimensional stability (due to low thermal expansion), tungsten is a promising material for heat sinking in integrated systems (*Tungsten Properties* 2011).
- Together with the superior mechanical properties, very high density is required for candidate materials for use in applications expecting to transfer the maximal momentum (or dissipate kinetic energy), such as anti-tank missiles. Tungsten possesses the highest density ($19.25 \text{ gr} \cdot \text{cm}^{-3}$ at 25 °C) among the engineering materials. (Iridium and Osmium are known to have even higher densities – about $22.50 \text{ gr} \cdot \text{cm}^{-3}$ at 25 °C – but are not as commonly used as tungsten due to their high price.) Basically, tungsten is the key element for the so-called heavy alloys (*Tungsten Properties* 2011) (Ho 2007).

Generally speaking, in any material selection strategy in which tungsten (but mostly its compounds or alloys) is selected, a combination of one or more physical properties of tungsten together with its superior high temperature mechanical properties pulled this element to the top of the list. Due to its relatively high price, tungsten is not the best choice for low temperature applications. Taking into account that tungsten compounds can offer a broad range of mechanical properties, they will be discussed separately for particular applications.



Figure 1: Kinetic Energy Penetrators; hard, dense and tough materials are required to transfer the maximum kinetic energy to a target. The rod-shaped penetrator and its carrier are illustrated in these pictures. Differently sized and shaped weapons are used for different purposes (Tanque Argentino (TAM) 2013)

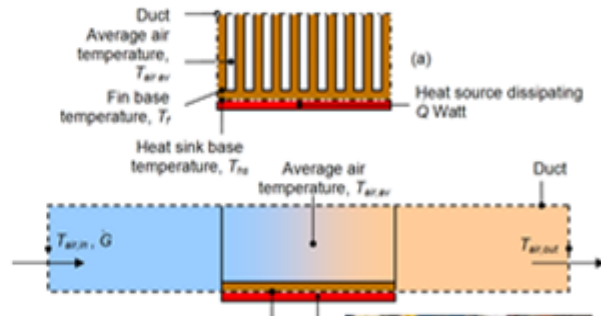


Figure 2: Heat Sinks in integrated systems require excellent heat conductivity as well as adequate dimensional stability. The mechanism of such cooling system is schematically shown (Intel GMA X3000 2014).

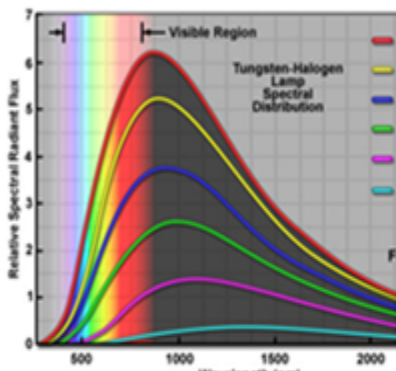


Figure 3: High melting temperature, low vapor pressure and low resistivity of tungsten has long made it an ideal material for light source in bulb lamps (Harris 2001), (Davidson).

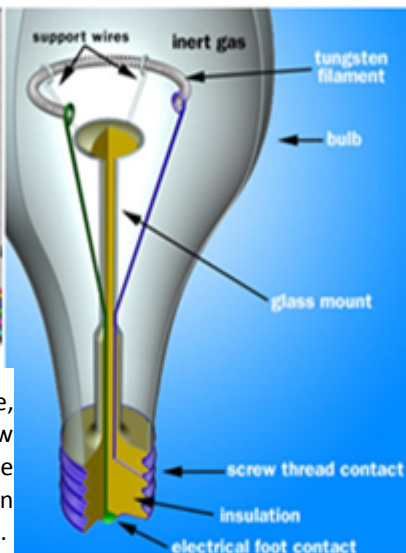


Figure 4: Tungsten compounds have long been found to significantly improve the mechanical properties of high speed steels; cemented carbides also provide a tough base for different tool (Tungsten in High Speed Steels).



Figure 5: High melting temperature, low vapor pressure, low electrical resistivity and superior mechanical properties at elevated temperatures ensure the adequate performance of tungsten compounds as welding tips (*TIG Welding 2014*).



Figure 6: Tungsten alloys are commonly used for electrical contacts due to their excellent conductivity together with sufficient endurance against arc friction (*Products: Electrical Contacts*).

Besides all conventional applications of tungsten (especially its compounds), new emerging high-tech applications mainly based on the intrinsic physical properties of tungsten, and in particular its electronic structure, have been developed strongly; in this context, critical catalysts for several important processes in refineries and full-cells can especially be highlighted. These applications will be discussed in details in the next chapters.

2. Tungsten Supply Chain

2.1 Geological Situation

World tungsten reserves in 2011 are estimated to be about 3'100'000 metric tons, with an annual production rate of about 73'000 metric tons (excluding US domestic production) (US Geological Survey: Mineral Commodities Summaries 2012). In contrast to 2010, when the total tungsten production increased for about 7 % (mainly due to the investments made on tungsten production in Canada in former years), no noticeable change in tungsten reserves and production states was reported in 2012 (US Geological Survey: Mineral Commodities Summaries 2011) (US Geological Survey: Mineral Commodities Summaries 2013).

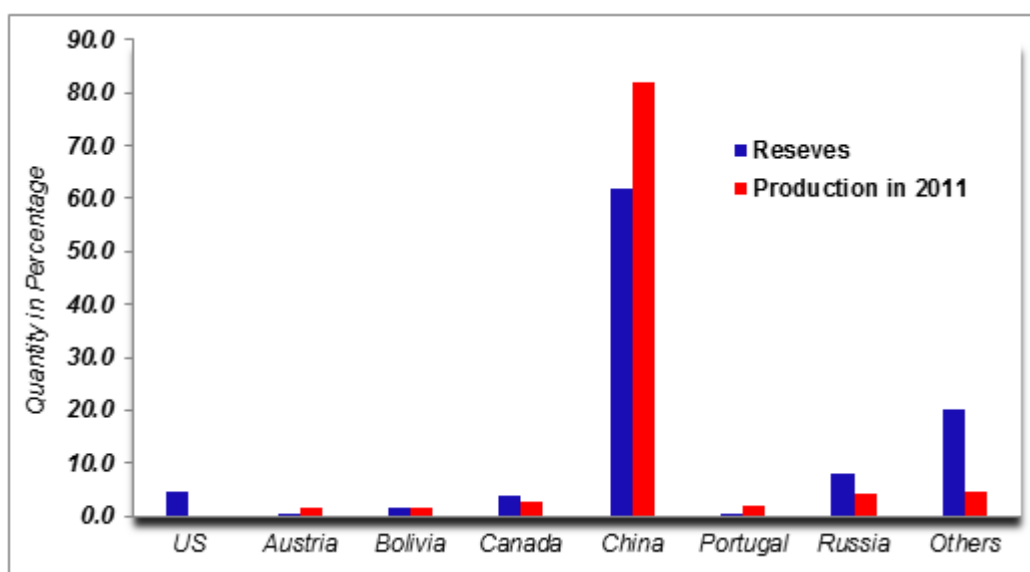


Figure 7: Tungsten market strongly relies on Chinese production and supply; China has approximately 62% of world tungsten reserves (out of 3'100'000 MT) and supplies 83% of world tungsten market (out of 73,000 MT). All related data is based on the tungsten content in the concentrates (US Geological Survey: Mineral Commodities Summaries 2012)

USA: The only tungsten producer in whole North America is North America Tungsten Corporation (NTC). Their mine, CanTung, was closed and reopened a few times since its discovery in 1954; it was last closed in 2009 for the maintenance due to the increased product inventory and the price fall resulting from the global economy recession. CanTung was reopened in late 2010 with the capacity of 1000 metric tons a day; Canada had then re-gained its share in the tungsten market in 2011 (Lifton 2006). There was no tungsten production in the United States in 2011; a tungsten mine in California produced concentrates in 2012 (US Geological Survey: Mineral Commodities Summaries 2011). Former operating sites were closed due to the environmentalists' activities or the low tungsten price in the market; the sites that were closed due to latter reason could not reopen because of the environmental concerns.

CHINA: China is placed as the largest tungsten consumer (with a consumption rate larger than the rest of the world in sum) – even more significantly after global economy recession, as result of its economy growth. The rate of tungsten consumption can be considered as an index representing the economy growth in the industrialized nations; tungsten products are known as the “teeth of the modern industry” (*China Tungsten Online*)

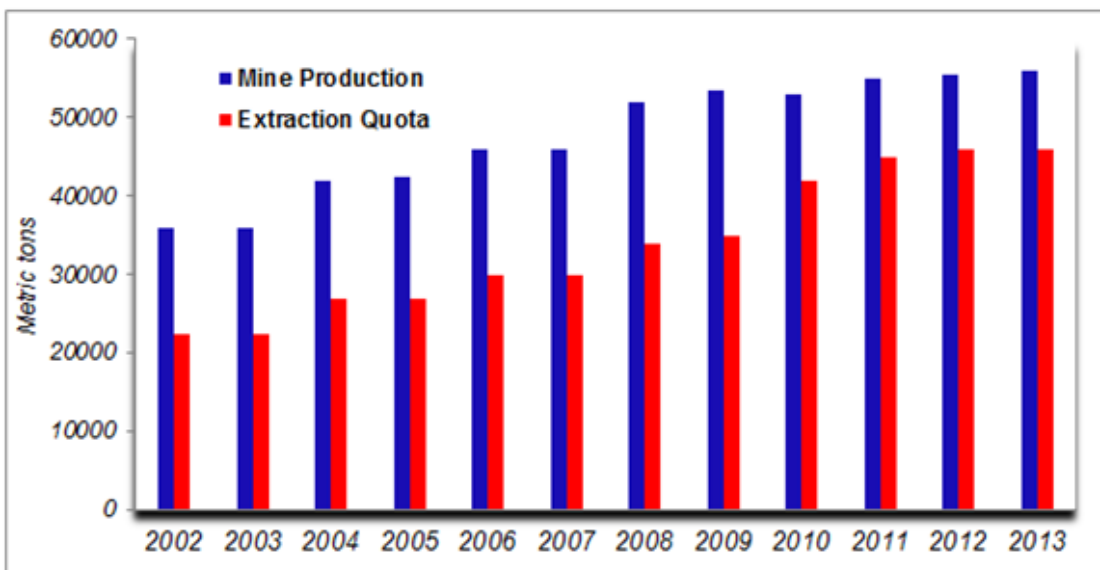
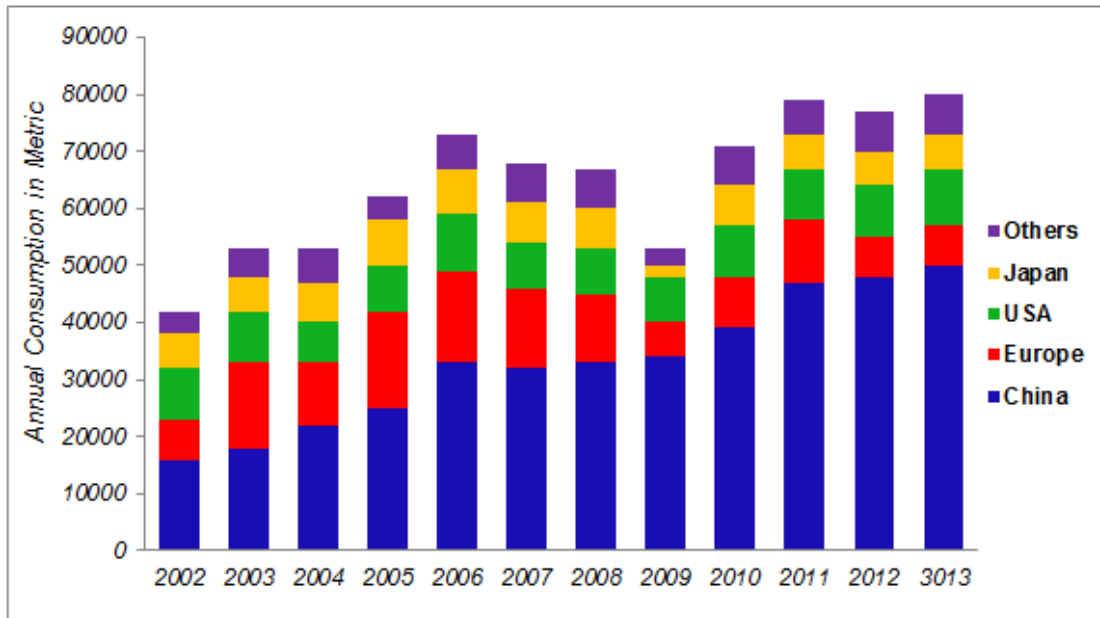


Figure 8: (Top) The annual consumption rate of tungsten; Chinese industries demanded 61 % of the world tungsten production in 2013 (Seddon 2013). (Bottom) The yearly tungsten production rate in china and the corresponding quotas imposed by Chinese government (Seddon 2013) (Merriman 2013)

The increasing growth in China’s economy made the Chinese government to regulate the tungsten industry/market by limiting the number of exploration, mining and processing activities, imposing export taxes and establishing quotas on production and export (US Geological Survey: Mineral Commodities Summaries 2012). China’s Ministry of Land and Resources (MLR) increased the extraction quotas for 10 to 15 % annually (or at least every second year); it has not changed significantly since 2011, though. The extraction quotas for heavy rare earths and tungsten were not

modified for 2014 (Tanquintic-Misa 2014). The real tungsten production rate in China always exceeded the quotas released by MLR. This disparity has been decreased down since 2010 due to the introduction of an increased quota in this year.

Unlike many western companies, Chinese tungsten production is expected (controlled by the government) to first meet the domestic demands. Increased domestic consumption together with the constant annual production since 2011, therefore, directly affects the tungsten supply of China to the rest of the world. China has started to close inefficient tungsten producing sites since 2011 for environmental reasons; such policies were driven by the Chinese government to preserve their resources (Merriman 2013); Balanced with the increased productions of other operating sites and also new mines, the total annual tungsten production of China has not significantly changed.

Beside the mine production, recycling of tungsten-containing scraps (so-called secondary resources) has been in the focus for a long time. The net tungsten consumption is mainly driven by tungsten carbide and steel alloy end uses with 55 % and 25 % contribution, respectively, according to 2012 statistics (Merriman 2013). Tungsten carbide as an end use has much larger contribution in European, Japanese and the US's markets, due to well-established automotive industries in these regions, compared to Russian market.

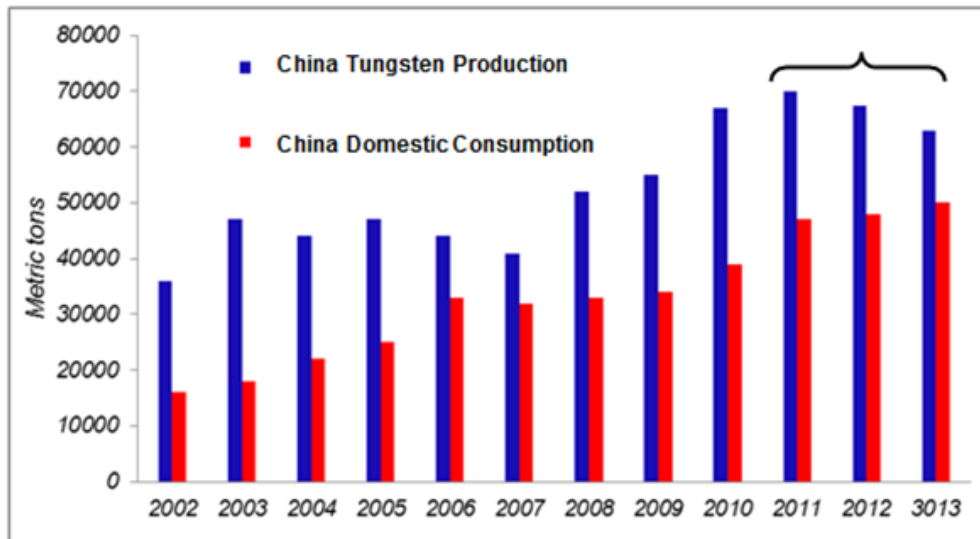


Figure 9: The tungsten market is dominated by Chinese producers. China first experienced a greater domestic use of tungsten compared to the exported quantity in 2005. The increasing demands of domestic market of china, combined with its decreasing production rate since 2011 has strongly influenced the tungsten supply to the rest of the world (Seddon 2013).

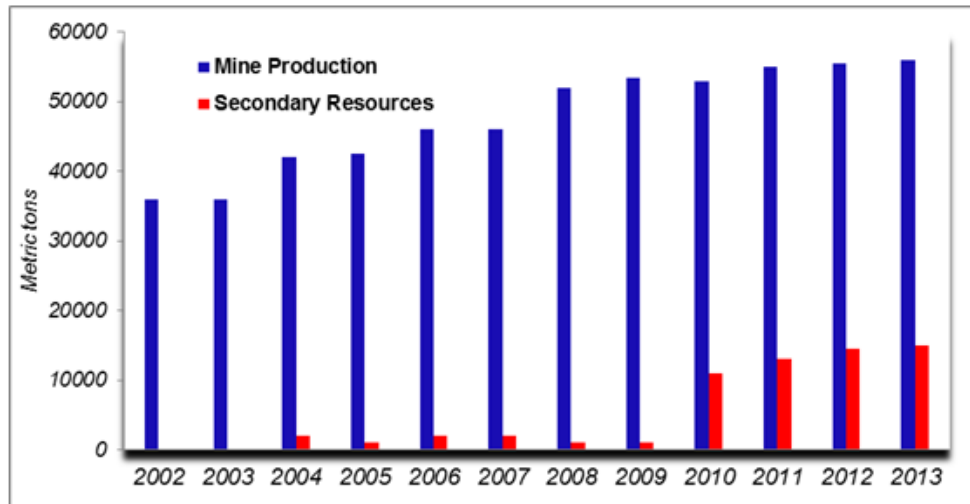


Figure 10: Secondary resources have found a significant importance particularly since 2010; the quotas on primary and secondary resources announced by Chinese government (Seddon 2013). The tungsten mines have faced troubles to keep their current outputs due to the reduction in the ore grades and lack of investment on new mining sites.

Besides its domestic production, China is one the main costumers for tungsten ores and concentrates; in September 2013, the imports reached 960 t mainly from Russia, Canada and Rwanda. The export of down-stream tungsten products (ores and concentrates) from China is banned, though. Such policies that conflict with free circulations of goods in the world have raised serious international reactions. The World Trading Organization (WTO) acted multiple times against these restrictions, but the Chinese government does not seem to stop or change the long-term plans for their resources.¹

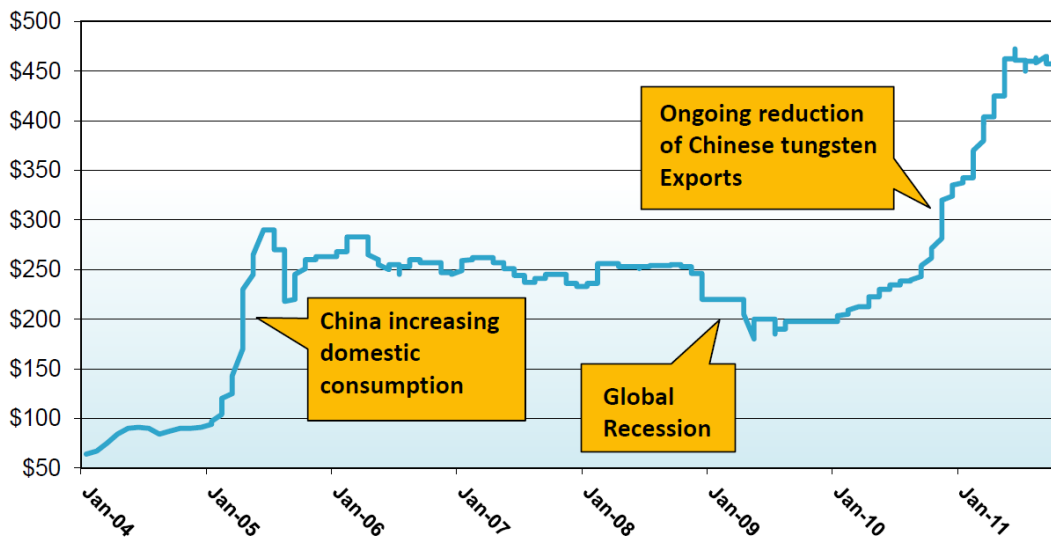


Figure 11: The price figure of Ammonium Paratungstate (APT) in the time span from 2004 to 2011 (Near Term Tungsten Producer with Exciting Copper/Gold Exploration). APT is the most frequent tungsten product on the market; note that prices are in unit of metric tons (10 Kgs) of APT.

¹ In March 2012, the EU requested the WTO to solve China's violation of its commitments, which distorted the global markets. Thus, a consultation was carried out on 25 and 26 of April in Geneva, in which the U.S and Japan also attended. However, no progress was made as China did not give any positive signals to the international concerns on shortage of rare earth metals (China — Measures Related to the Exportation of Various Raw Materials 2012)

2.2. Trends for extraction and prices for W

The key point in making a material critical/strategic is the balance between demand and supply. The rate of tungsten consumption is closely related to industrial activities which accelerate in growing economies. The significant fall of the tungsten price in 2008/2009 implies the strong influence of economic stability on the tungsten markets, and consequently tungsten producers.

The reason for the sharp increase of the tungsten intermediate price in 2011 and 2012 can be found in previous figures comparing Chinese tungsten production and their domestic demands; ammonium para-tungstate (APT) price reached the record of 43 to 44 USD/kg in February 2012. Upon such increase of tungsten price in market over these years, tungsten production outside China has become economic. Due to the restart of inactive mines in other countries and efforts to develop tungsten deposits, the world tungsten market became more stable, and is expected to experience further price decrease in coming years; the APT price decreased to 35 to 36 USD/kg in February 2013. The latest figures on tungsten price in October 2014 shows further decrease to about 32 USD/Kg of APT on the European markets.

The trend of a decreasing tungsten intermediates price in metal markets shows the decreasing reliance of world tungsten demands on Chinese supply. Mine CanTung in Canada, owned by NTC, is one of the largest tungsten producer outside China and produces with its full capacity since its re-opening in 2010; exploration for new mines are in parallel under progress. ORMONDE MINING LPC has invested in the Barruecopardo Tungsten Project located in Salamanca province in the West of Spain with a start-up production of about 8 % of the world (exploding Chinese production) tungsten production in 2012 that makes it the largest non-Chinese tungsten producer (*Near Term Tungsten Producer with Exciting Copper/Gold Exploration*).

Tungsten production in Austria and Portugal has declined over the last decades due to mines end of life; production in Russia showed no considerable change (about 3000 tons W per year). A new emerging tungsten producer is Vietnam with 1635 tons in 2011 (according to ITIA reports). The opening of a new mine (Nui Phau) owned by Masan Recourses in 2013 has further increased the productions; once the full capacity is reached, a yearly production of 4-5000 tons is expected. Another tungsten production project under development is Wolf Minerals' Hemerdon which is expected to produce up to 2750 tons tungsten in early 2015; this project still requires an environmental permit in the UK.

The increased demands on tungsten after 2009 together with the new exportation restrictions of the Chinese government on tungsten, as well as many other materials, led to material shortage on the free markets. Europe is still a significant market for tungsten having share of world tungsten consumption has been as high as 30% in the last 10 years especially for the European consumption of products that use tungsten like e.g. cutting tools, drill bits, light bulbs etc. (Seddon 2013).

Due to the strong impact of critical elements like tungsten, the European Union created an Ad-Hoc Working Group on Defining Critical Raw Materials, a subgroup to the Raw Materials Supply Group, which is an expert group of the European Commission. In 2010 this group published a first report on 14 critical elements from a candidate list of 41 non-energy, non-food materials regarding their use and difficulties for substitution and supply risk (Report on Critical Materials for the EU 2010). In 2014 a second report was published (Report on Critical Materials for the EU 2014). Tungsten, together with rare earths, is in the top list of *relative risk of supply* with an index of 9.5 out of 10 in the 2012 report of the British Geological Survey (BGS) (Risk list 2012) Besides investing in explorations of new tungsten deposits and re-developing the current mines, governmental organizations in China, Russia and the US directly control the collection of tungsten-containing scraps for recycling purpose.

Table 1: New tungsten production projects; mines start-ups in Australia, Vietnam has already influenced tungsten market in 2012 and 2013 (Seddon 2013). Note this table was last updated in 2012; e.g. the Hemerdon project in the UK will start production in 2015.

Project	Company	Planned output	Start-up	Remarks
Currais Novos	Largo Resources	180tpy W in 2012 330tpy W from 2013	Q3 2011	Commercial production of tungsten in December 2011
Wolfram Camp, Australia	Deutsche Rohstoff	1,250tpy W	Q4 2011	In production, first concentrates shipped in March 2012.
Mt. Carbine, Australia	Carbine Tungsten Ltd.	520tpy W from 2012 1,980 tpy W from 2014	Q1 2012	First shipment of concentrates in July 2012 from tailings. Hard rock mining from 2014
Nui Phao, Vietnam	Masan Group	3,800tpy W	Q2 2013	New investment certificate and mining licence secured
Sangdong, South Korea	Woulfe Mininig	3,150tpy W	Q3/4 2013	Feasibility study completed in April 2012
Barruecopardo, Spain	Ormonde Mining	1,800tpy W	Q4 2013	DFS completed February 2012
Hemerdon, UK	Wolf Minerals	2,750 tpy W	Q4 2013	Approx. 70% of funding secured
Molyhil, Australia	Thor Mining	1,750tpy W	Q4 2013	Updated DFS published in June 2012
Cookes Creek/Big Hill, Australia	Hazlewood Resources	1,600tpy W	2014	
Sisson, Canada	Northcliff Resources	3,500tpy W	2014	Feasibility study due for completion Q3 2012
Watershed, Australia	Vital Metals	1,000tpy W	2014	DFS in progress
Springer, USA	EMC Metals	1,100tpy W	2013/2014	Working towards strategic restart
Mt. Lindsay, Australia	Venture Minerals	1,500tpy W	2014	Pre-feasibility study completed Mar 2011
King Island, Australia	King Island Scheelite	800tpy W from tailings 2,750tpy W hard rock (+3 years)	2014/15	DFS completed February 2012, funding to be secured
O'Callaghans, Australia	Newcrest	3,800tpy W	?	
Mactung, Canada	N. American Tungsten	7,000tpy W	?	NI 43-101 technical report completed April 2009
Northern Dancer, Canada	Largo Resources	6,500tpy W	?	Pre-feasibility study under way
Sautbay, Uzbekistan	Uzbek-Korean JV	1,200tpy W	?	JV signed in August 2011 for US\$120M project

2.3 Mining and Beneficiation

2.3.1 Tungsten Minerals

The average tungsten concentration in the earth's crust is about 1.5 ppm, much smaller than most of the rare earths. Among various tungsten minerals, scheelite (CaWO_3) and Wolframite ($(\text{Fe, Mn})\text{WO}_4$) have significant economic importance. Hydration or other alternative processes, however, lead to whitish to yellowish masses, such as $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ and $\text{CeW}_2\text{O}_6(\text{OH})_3$, so-called tungstic ochre.

Table 2: Tungsten Minerals

Tungsten Minerals			
Economic Minerals	Scheelite, CaWO_3	Wolframite, $(\text{Fe, Mn})\text{WO}_4$	
Non-economic Minerals	$\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$	$\text{CeW}_2\text{O}_6(\text{OH})_3$	$\text{AlWO}_3(\text{OH})_3$

Table 3: Physical properties of two main tungsten minerals

	Density (g/cm^3)	Hardness (Mohs)	Crystal System	Color
Scheelite	5.9-6.1	4.5-5	Tetragonal	colorless, whitish, ochre, yellow, grey
Wolframite	7-7.5	4-4.5	Monoclinic	Grayish, black, brownish to reddish black

SCHEELITE

Its color is highly dependent of the Mo content, varies from whitish blue to yellow as increasing Molybdenum content; Mo exists in tungsten minerals as a substitutional solid solution. Scheelite is a fluorescent material. Other Characteristics are:

1. *High density*; capable of being enriched by gravitational methods
2. *Brittleness*; risk of being over-grinded during comminution
3. *Mo impurity*; not suitable for certain downstream processes

WOLFRAMITE

Wolframite is a Fe/Mn-tungstate; thus containing less theoretical tungsten content, about 76.5% WO_3 while Scheelite contains 85.5% WO_3 . Its characteristics are the following:

1. *High density*; capable of being enriched by gravitational methods
2. *Brittleness*; risk of being over-grinded during comminution
3. Paramagnetic; capable of being concentrated by high-intensity magnetic fields
4. Not amenable to flotation

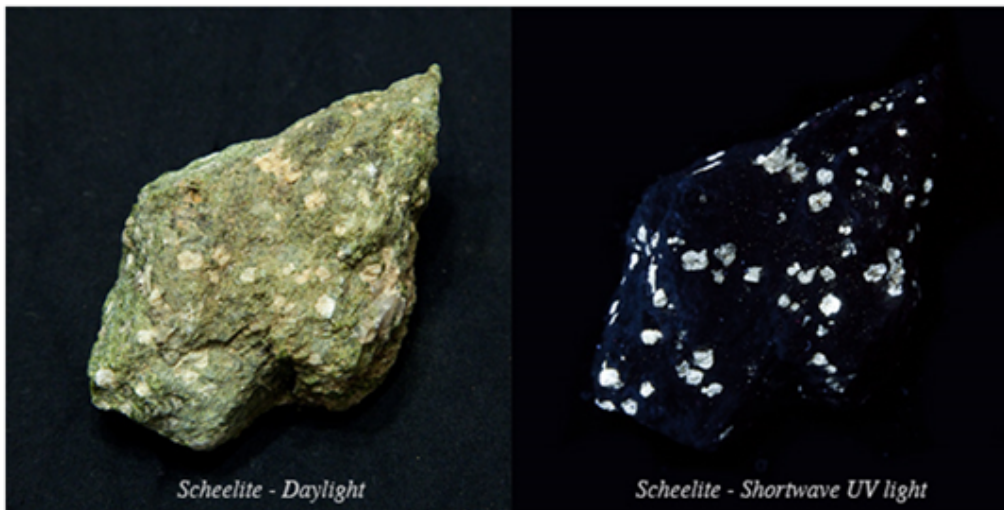


Figure 12: Scheelite is a fluorescent material that is highly excited by UV light ; this is actually the main strategy for exploration of tungsten deposits (van Breugel 2010)

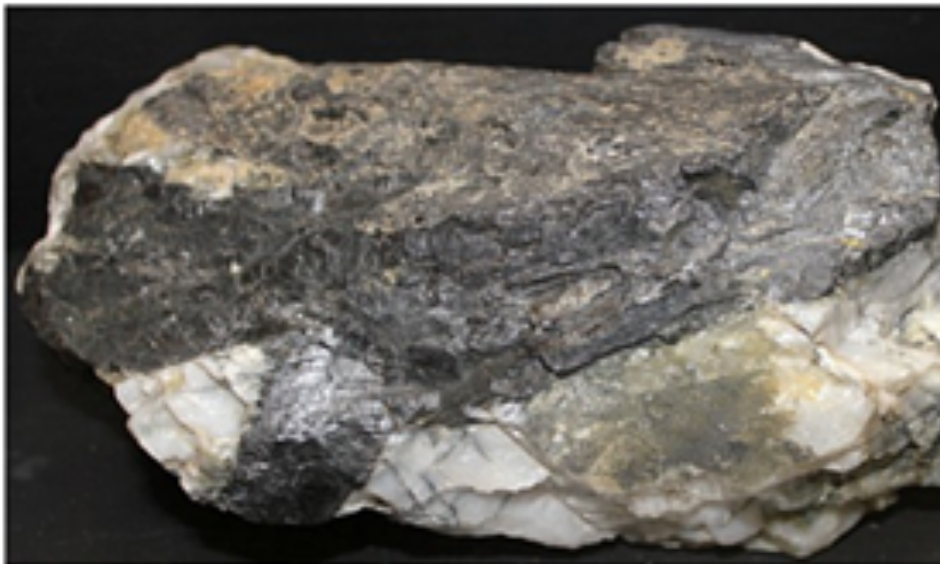


Figure 13: Wolframite is the second important tungsten mineral which possesses magnetic property due its iron content (*Wolfram Mineral Facts*).

2.3.2 Tungsten Deposits

Tungsten deposits can be found worldwide. Considerable clusters occurred on some places, though; e.g. scheelite sharn deposits in the North America and wolframite-quartz vein in the South America (mainly in Bolivia and Peru). However, the largest tungsten resources occurred in Eastern Asia, extending from North Korea, Japan and China into Vietnam and Thailand.



Figure 14: The Jiangxi province in china, the location for the largest tungsten deposits accumulation

CLASSICAL VEIN DEPOSITS

These deposits are more or less continuous veins of decimeters to meters in thickness. Most deposits have wolframite, but scheelite vein deposits also occur. They usually found with quartz (Schmidt 2012).

1. *Typical tonnages:* few 10s to few 100,000 of tons of ore
2. *Typical grades:* 0.5-5%
3. *Typical bi-product:* Sn

SKARN DEPOSITS

The mineralization in this class of deposits can be either as mono-metallic tungsten (exclusively as scheelite) or polymetallic (often with Mo or base metals such as Pb, Zn and Cu), or together with gold, fluorite or magnetite. In some cases, tungsten is only the by-product (Schmidt 2012).

1. *Typical tonnage:* few million tones, but larger deposits are known.
2. *Typical grades:* 0.3-1% WO_3

BULK MINEABLE

This is a mining term; it means that a large volume of low-grade material can be mined instead of following complex contacts of the individual mineralized structures. *Greisen* and *porphyry* deposits are generally located in the apical parts of felsic intrusions, while stock-work vein deposits can be found either in the intrusions itself or in the surrounding country rock. Technically, some skarn deposits are also bulk mineable (Schmidt 2012).

1. *Typical tonnage:* dozens of millions tones.
2. *Typical grades:* 0.1-0.3% WO_3

- Object of mining is not the individual mineralized vein but the entire rock mass including the quartz or greisen veins.

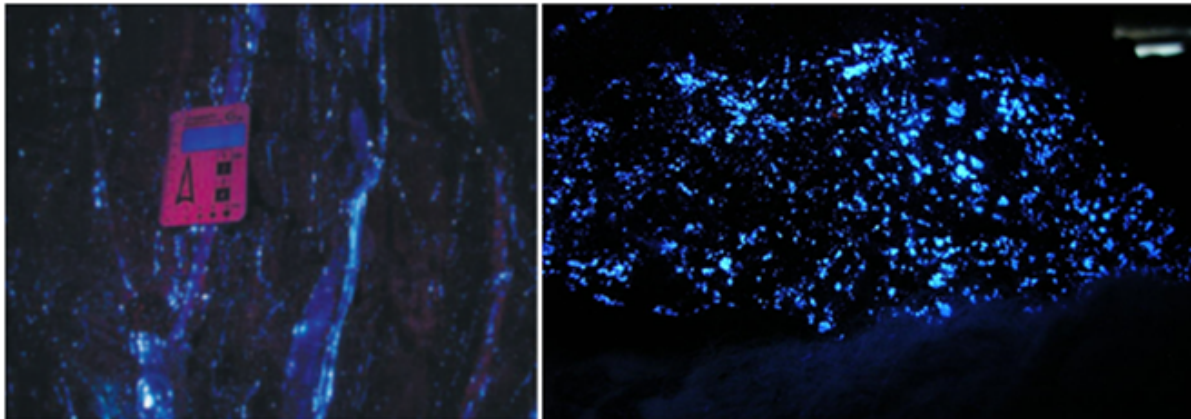


Figure 15: There are various types of tungsten deposits among which the vein deposits and skarn are the most popular. A typical scheelite vein deposit (Schmidt 2012) and skarn (*High grade Scheelite under ultraviolet light in skarn Nightcrawler Zone* 2005) under UV light are shown.

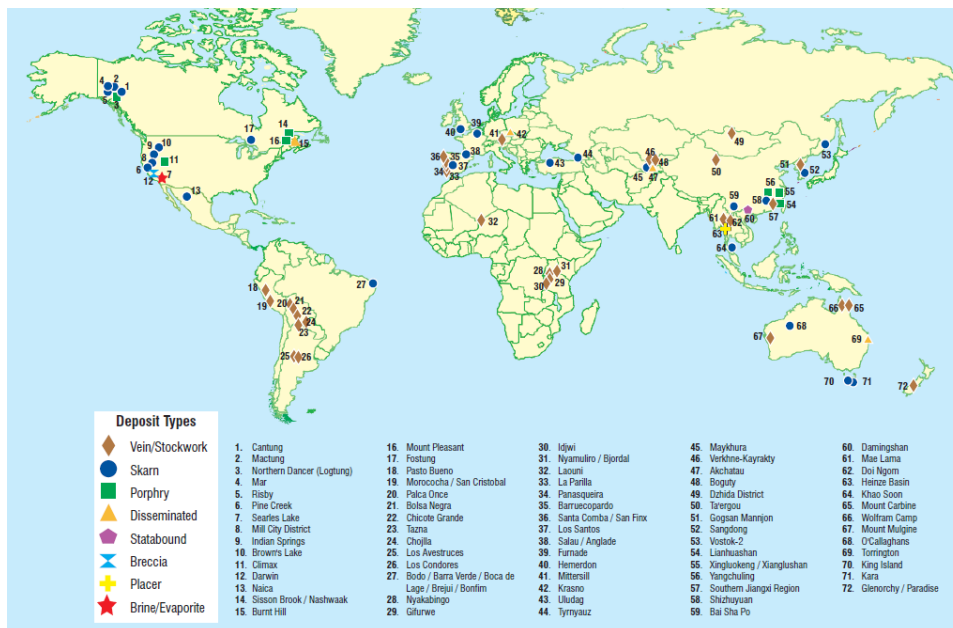


Figure 16: Location and type of major tungsten deposits (Schmidt 2012).

2.3.4 Mining Technologies

There are two types of mining methods: *Open pit* mining and *underground* mining. Many factors are definitive for selecting the adequate method for a given mine. Hereunder is a list of the most important ones:

- Size of deposit and expected annual production
- Ground condition and physical properties of ore
- Ore value (deposit grade)
- Economic, environmental, legal and regulatory considerations

Typical procedure for open pit mining is drilling, charging the hole with explosive materials, blasting, loading on a truck and finally hauling to the processing plant. Figure 17-left shows the drilling machine making a hole in the ground. Examples of important open pit tungsten mines are Barruecopardo (skarn, Spain), Kara (skarn, tungsten is by-product, Australia), part of CanTung (skarn, Canada) and multiple Chinese producers (Schmidt 2012)



Figure 17: Barruecopardo tungsten mine in Salamanca, Spain. The huge open pit tungsten mine was under develops since 2009 with start-up in 2012. The historic pit in 1980 is marked in the top picture and showed on the right (*Barruecopardo tungsten project*)

Over the centuries, many different underground mining methods have been developed to overcome different problems arising from the highly variable ground conditions, geometry and production rate. The basic infrastructure of a typical mine is illustrated in Figure 18.

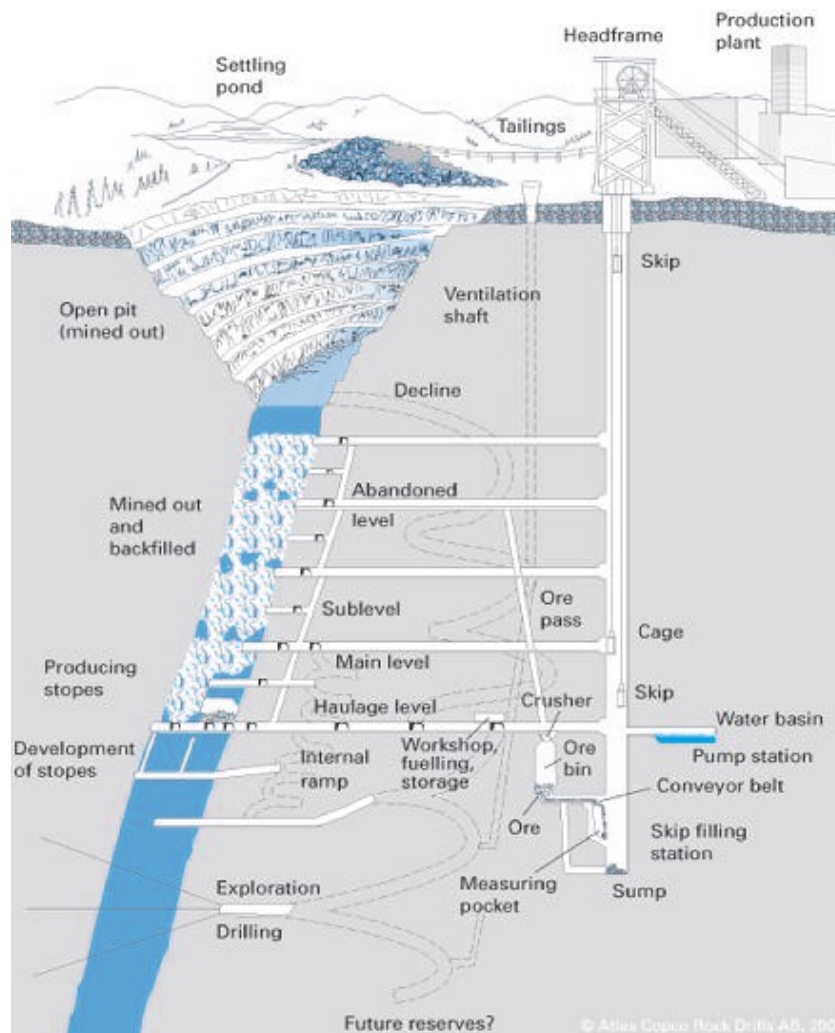


Figure 18: Schematic illustration of the main infrastructures for the underground tungsten mining; note that tungsten ores are mined out by open pitting followed by underground mining (Schmidt 2012)

BENEFICIATION (ORE DRESSING)

The selection of the beneficiation technique(s) depends on type and grade of ores. Both scheelite and wolframite are dense and brittle. Scheelite is sufficiently amenable to flotation, but not as much as common sulfides; wolframite is paramagnetic, though. In the following, various steps for ore dressing are briefly reviewed:

Comminution (Crushing & milling)

Due to the brittle nature of the tungsten minerals, comminution must be completely under control to avoid over-grinding the minerals. A series of milling steps are generally used. Pre-concentration

can then be done via various methods which are classified into four categories: *sorting*, *gravitational enrichment*, *flotation* and *magnetic separation*.



Figure 19: (left) the staged rod and mill, and spiral classifier at the Vostok-II mine, Russia (Schmidt 2012); (top) grinded tungsten ore stock (*Tungsten ore beneficiation process in Russia*)

Pre-Concentrating I; Sorting

At some tungsten projects, pre-concentration methods are used to discard a portion of the run-of-mine ore to increase the head grade prior to traditional beneficiation methods.

- 2 *Hand-picking*; this method is very effective for large grade contrasts, and in countries with low labor costs.
- 3 *Optical Sorters*; this method may be used when strong optical contrast exists between high-grade portions of the overall run-of-mine ore.
- 4 *X-ray Sorter*; this method is the most advanced as it looks inside the individual rock fragments. Tungsten minerals have large X-ray absorption coefficient; hence, they are observed black.

Pre-Concentrating II; Gravitational Enrichment

This concentration strategy is based on weight/density differences between particles in the milled ore. It can be practical, with efficiencies as large as 90 %, for ores with narrow particle size distributions and large density contrast between intended particles and wastes.

1. *Dense-media Separation (DMS)*: a dense medium is a thick suspension of para-magnetic particles in water, which behaves like a heavy liquid with a well-defined density. Ore particles with lower densities will then float on the surface and can be removed. DMS concentrates are usually only pre-concentrates, which require further comminution and upgrading.
2. *Spiral Concentrator*; in this technique, the ore particles flow spirally down-wards, and denser/heavier and less dense/lighter particles are separated by the combined effect of centrifugal force and differential settling rates. Since the grain size and density effect compensate each other, the spiral separation is the most effective if used for ores with narrow size distributions.
3. *Jig*: the idea behind a jig is that particles are introduced to a jig bed (usually a screen) and then thrust upward with a water column; the particles are then suspended within the water. Once the

pulse dissipates, the particles settle again, but those with higher densities are quicker than the ones with low densities.

4. *Shaking Tables*: are probably the metallurgically most efficient means of density separation. The sorting method combines a water film and rapid strokes, which make the particles crawl along the surface of the table and then separate into coarser/low density and finer/high density grains.

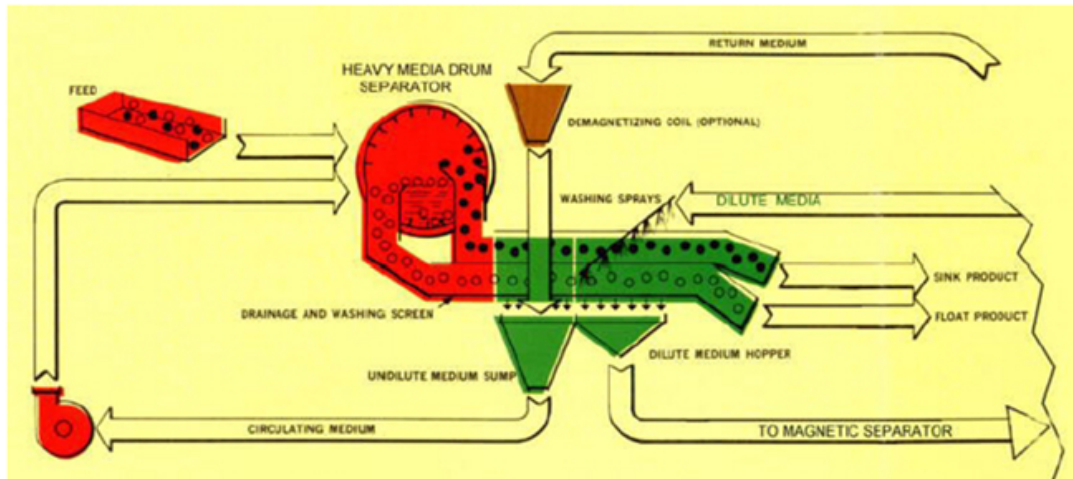
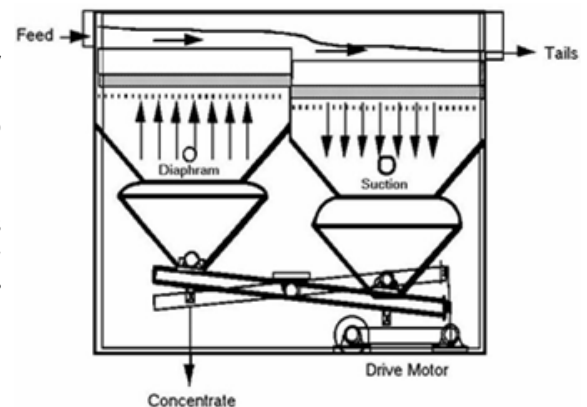


Figure 20: Any ore beneficiation method is based on a given property of the intended mineral(s). Density contrast is the core idea in gravitational separation methods which must be optimized by taking into account the size effect; for example, the spiral separation efficiency is less influenced by ore particles size distribution than the other methods such as (top) DMS and (right) Jigs (*Heavy Media Gravity Separation*) (*Jigging Machine for Iron Ore Benefication*).



Pre-Concentrating III; Flotation

Froth flotation is a common beneficiation method on differences in hydrophilic/hydrophobic properties of the individual ore particles, which depends on volume fraction of the intended mineral(s). The ore is finely grinded and mixed with the water and selected reagents; the mixture is then aerated to form bubbles. The hydrophobic minerals attach to the bubbles and can be skimmed off, while hydrophilic particles remain in the liquid phase and are discharged as tailings. Flotation reagents are used to selectively enhance or decrease the hydrophobic properties of the minerals.

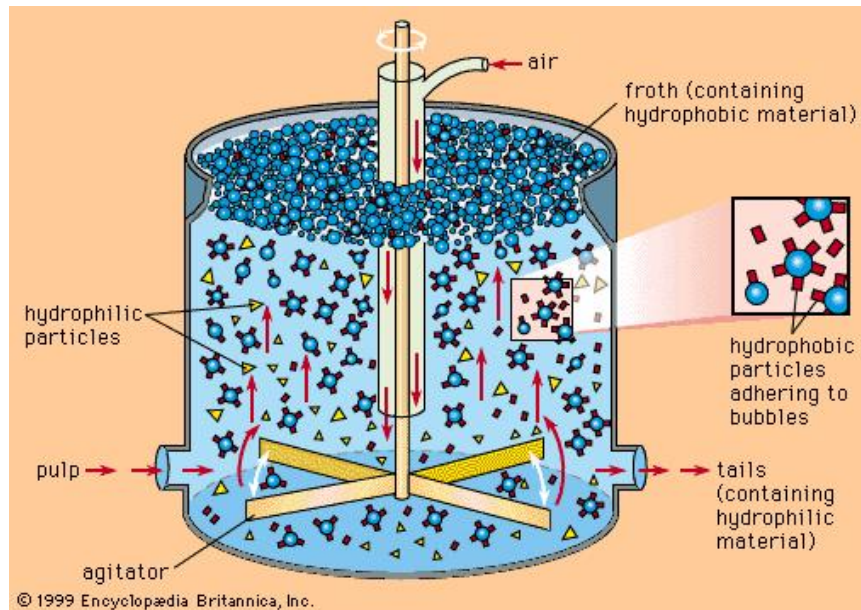


Figure 21: The schematic illustration on ore particles separation based on their difference in hydrophilic properties (Lorig and Gruner 2006).

Pre-Concentrating VI; Magnetic Separation

Difference in *magnetic susceptibility* is often used to clean concentrates. Low-intensity magnetic separation is capable of removing magnetite and other ferromagnetic impurities, while high-intensity magnetic separation allows collecting of wolframite and its separation from cassiterite (tin impurity).

Impurities

Common contaminants and deleterious elements in tungsten mining are radiation, arsenic, lead, molybdenum and fluoride among which the first three are of particular attention as they have legal implications. For example, allowable radiation levels for imports of tungsten concentrates into the EU are far lower than those naturally found in many commercially available ores. Critical levels of radiation are caused by U and/or Th content in the range of a few tens of ppm, and it is often difficult to detect and separate. Similar regulations are also imposed on Pb and As content; usually 0.25 % and 0.1 %, respectively (Schmidt 2012)

Secondary Tungsten Minerals

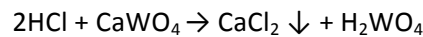
In general, scheelite and wolframite are fairly resistant to chemical weathering. However, in tropical climates or during hydrothermal alteration, secondary tungsten minerals can partly replace the primary scheelite or wolframite minerals; see Table 3. Most secondary tungsten minerals have extremely friable (powdery) nature and are easily washed out during the traditional ore dressing process, leading to reduced yield.

3. Extraction (Hydro-Metallurgy)

As previously explained in chapter 2, the two main tungsten minerals are either in calcium tungstate (scheelite) form or in iron-manganese tungstate (wolframite). The basic idea to extract tungsten from the corresponding minerals is their dissolution in a solvent in such a way that tungsten content is separated from the residues in second phase. More precisely, tungsten is converted to tungstate form (WO_4^{2-}); the subsequent steps are the same in all methods. In this section, chemistry (not technologies!) behind the most common processes is reviewed.

3.1 Acidic Decomposition

In this method, hydrochloric acid (HCl) is employed to react with calcium tungstate (scheelite) to form tungstic acid and insoluble calcium chloride. This process is not applicable on wolframite, though; it is due to the partial solubility of Iron/Manganese tungstate in the solution. The net reaction is formulated as below:



The tungstic acid then separately precipitates by reducing the temperature. To remove impurity, it is re-dissolved in ammonium hydroxide (NH_4OH); APT is finally crystallized.

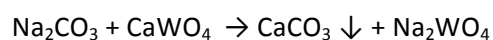
DISADVANTAGES:

4. Only applicable on scheelite
5. High consumption rate of HCl, more than its stoichiometric ratio
6. Maximum yield only up to about 95%
7. Disability for removal of molybdenum as an impurity; a subsequent basic treatment is required. This is a big drawback of the acidic decomposition process because it cannot be employed for ores high (and undesirable!) molybdenum contents. Furthermore, it cannot be used for recycling of hard metals (WC composite in Mo matrix) (Tungsten recovery from tungsten ore concentrates by caustic digestion 1981)

To overcome the first three drawbacks of acidic decomposition with HCl, dissolution of tungsten-bearing ores in nitric acid at elevated temperature is proposed to form tungstic acid and calcium nitride. At reduced temperatures, tungstic acid crystals are filtered out from the solution; they are then re-dissolved in ammonium hydroxide to produce APT followed by final re-crystallization. The last two steps are then repeated several times to further remove the impurities (Quatrini, Vogt, and Martin 1981).

3.2 Autoclave Sodium Carbonate Digestion

Sodium carbonate digestion in an autoclave produces soluble sodium tungstate and insoluble calcium carbonate (from scheelite), or iron/manganese carbonate (from wolframite). The excess sodium carbonate is subsequently neutralized with acid and the tungsten in solution converted to iron tungstate by the addition of ferrous sulfate.



The yields of over 98 % are applicable even for low grade concentrates. The obtained sodium tungstate solution is purified (by subsequent precipitation and dissolution in water) and then dissolved in ammonium hydroxide for further purification; APT is finally crystallized (Queneau, Huggins, and Beckstead 1981).

ADVANTAGES

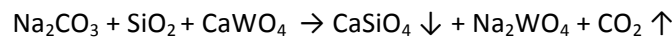
1. Applicable for various tungsten minerals (scheelite, wolframite, etc.)
2. Applicable for both low- and high grades tungsten ores, as well as tungsten-containing scraps

DISADVANTAGES

1. Relatively high consumption rate of sodium carbonate ($\text{Na}_2\text{CO}_3/\text{WO}_3$ ratio of over 1.8:1)
2. High temperature operation together with high pressure (typically from 180°C to 200°C at 15 atmospheres)
3. Undesired leach of silica (from quartz impurity) in strong basic pH results from high sodium carbonate concentration (Queneau, Huggins, and Beckstead 1981).

3.3 Fusion with Sodium Carbonate

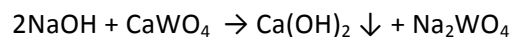
Fusion with sodium carbonate involves the addition of sodium carbonate and silicon dioxide to the scheelite ore concentrate, and reaction to produce soluble sodium tungstate, insoluble calcium silicate and carbon dioxide gas. The subsequent steps are similar to autoclave sodium carbonate digestion process.



Disadvantages of this technique are a large consumption of sodium carbonate, very high temperatures (above 1,000 expensive refractory materials), and the necessity for close control of the blend and temperature of reactants to obtain molten material which will flow from the reaction vessel.

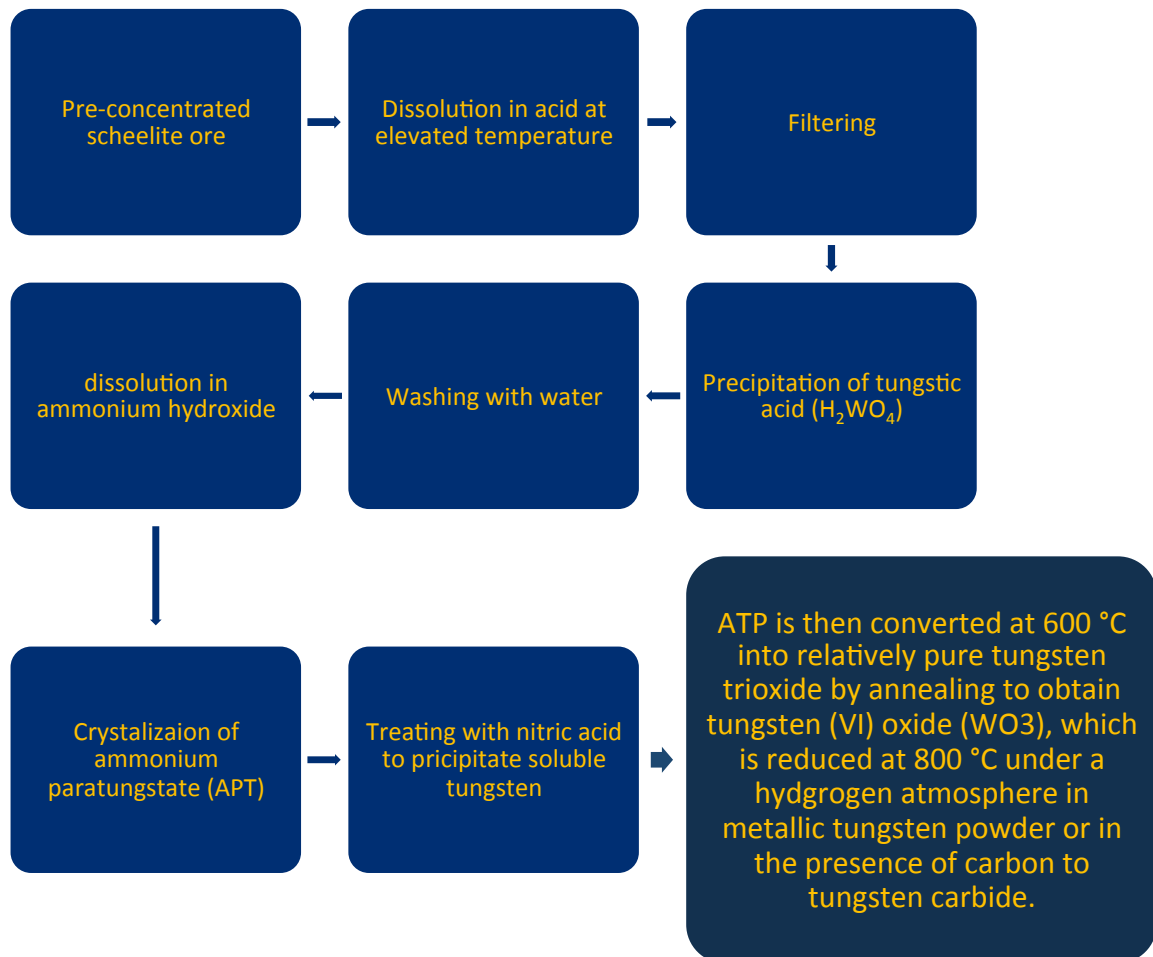
3.4 Caustic soda digestion

Caustic soda digestion of scheelite involves the reaction of calcium tungstate and sodium hydroxide to obtain soluble sodium tungstate and insoluble calcium hydroxide. This technique is applicable for either scheelite or wolframite ores.



In general, this technique is characterized by high caustic requirements and poor yield. For example, it was reported 4.4 grams of sodium hydroxide per gram of tungsten (18 moles in excess of the stoichiometric amount), and with 86.3 % yield, is required. Elevated temperature can be used to improve the tungsten yield, and then reducing sodium hydroxide consumption. Similar treatments as previous processes are required for produced sodium tungstate.

Flowchart 1: Many different processes for extraction of tungsten from its concentrates have already been proposed. Their key difference is on how to convert tungsten to the solution (in tungstate form); after then, APT is formed by introducing ammonium hydroxide solution. Following steps, repetition of acidic and basic treatment are employed for further purification of APT. This flowchart summarizes different steps in the acidic decomposition process.



4. Use of Tungsten in applications and substitution potential

4.1 Cemented Carbides

Cemented carbides, so-called hard metals, are the metallic composites of hard carbides powder, mainly WC, TiC and TaC. A tough metallic matrix (generally addressed as the binder) promises the integrity of carbides particles; Co, Ni and Fe, or a combination of these metals, are used for this purpose. Due to the tough matrix, the crack propagation is largely suppressed; the hard carbides particles transfer the applied force, though. Therefore, this family of materials offers high hardness and yield stress as well as superior toughness; the larger the volume fraction of carbide particles, the higher hardness is achievable. Similar chemistries, such as carbo-nitrides (TiCN), have also been developed.

The manufacturing processes for tools made of cemented carbides are based on sintering. A particular mixture of carbide powder and metallic powder are mixed together; a certain volume fraction is required to meet the expected mechanical properties for a given part. The mixture is then sintered via the liquid phase method. Cemented carbides play a very important role in engineering and tooling applications. This is because they can offer a very wide range of mechanical properties. Tungsten carbide is the most common hard phase sintered in a combination with cobalt powder as binder.



Figure 22: A common microstructure of hard metals (*WC_{Ag} switch contacts for medium and low voltage*); this important family of metallic composites in which hard carbides powders are sintered in a matrix of tough metals. Such microstructure results in high strength as well as sufficient toughness.

Table 4: The history of evolution in cemented carbides (Exner 1978); since their invention in 1922, many different chemistries and processes have been proposed for optimizing their mechanical properties for certain ranges of applications.

Year(s)	WC-base sintered alloys	Year(s)	TiC- (and TaC)-base sintered alloys	Year(s)	Related developments
1922–25	WC+Co (Widia*)	1929–31	TiC–Mo ₂ C+Ni, Cr, Mo (Titanit*)	1909	Stellites
1927	Graphite-free WC+Co	1930–31	TaC+Ni, Co (Ramet*)	1914	Molten sintered and hot-pressed WC
1928–29	WC with stellite binder	1931	TiC–TaC+Co	1917	Hot-pressed W–Cr–Ti–Fe–C alloys (Tizit*)
1931	WC–TiC+Co (Widia X*)	1931	TiC+Cr, Mo, W, Ni, Co (Böhlerit*)	1922	Infiltrated WC
1931	WC–TaC+Co (Carboloy*)	1938	TiC–VC+Ni, Fe	1930–31	Boride, and boride–nitride and boride–carbide hardmetals
1932	WC–TiC–(Ta, Nb)+Co (Firthite*)	1944	TiC–NbC+Ni, Co	1950–51	Infiltrated TiC-base alloys
1938	WC–Cr ₃ C ₂ +Co	1948–50	TiC–(Mo ₂ C, TaC)+Ni, Co(Cr)	1952–61	TiC+heat-treatable steel (Ferro-TiC*)
1951	Acid-resistant WC–Ni	1949	TiC–VC–NbC–Mo ₂ C+Ni	1953–55	Commercial boride hardmetals
1956	WC–TiC–Ta(Nb)C–Cr ₃ C ₂ +Co	1965–70	(TiC–Mo ₂ C)-mixtures+Ni, Mo	1955–60	Ceramic cutting materials (Al ₂ O ₃ and Cr ₂ O ₃ with TiC, TiB ₂ , WC, or Mo ₂ C)
1959	WC–TiC–HfC+Co	1968–70	Solid-solution and precipitation-hardened alloys (Ti, Mo)C+Ni, Mo	1955–73	Surface coatings on WC+Co (TiC, TiN, Al ₂ O ₃ , diamond)
1965	Hot isostatic compaction			1961–70	Ti(C, N)–Ni, TiN–Ni
1967–70	Submicrometre WC+Co			1970	Thermochemical surface treatment
1967–70	WC–Fe, Ni, Co			1970 to present	Cast hardmetals
1968	WC–TiC–TaC–NbC+Co				

4.2 WC/Co System

More than 70 % of cutting tools are made of cemented carbides, of which mainly are based of WC-Co (Bhaumik, Upadhyaya, and Vaidya 1992). WC-Co is now a well-established system, and was extensively investigated particularly in the 20th century. This system can offer superior mechanical and chemical properties; for a better understanding on these materials, a brief review on their metallurgical principles is essential. In the remaining part of this chapter, the most important aspects of these metallic composites are reviewed:

4.2.1 Wettability

Given the fact that the liquid phase sintering requires interfacial contact between the molten phase (Co) and the power particles (WC), the wetting response of the system is absolutely critical. The adequate solubility of tungsten carbide in the cobalt at high temperatures results in an excellent wettability between these particles and the cobalt matrix. Such behavior is very important because it accelerates the sintering process as well as the rearrangement of the carbide particles. Any modification in the composition of the binder leads to a change in the interfacial energy between the melt (molten cobalt) and the carbide particles, and then affecting the wettability.

It is known that all iron group metals (Fe, Co & Ni) show high wettability with WC which is explained in terms of their electronic structures and cohesive energies. The excellent wettability behavior of

WC-Co systems is due to their similar binding energies. Mo₂C shows very high cohesion energy making it a potential candidate for substituting WC.

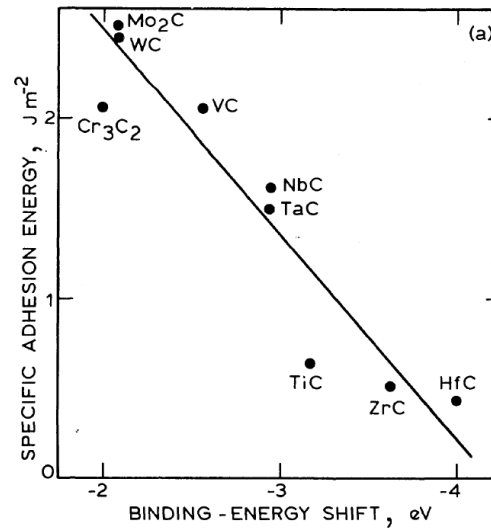


Figure 23: The respective cohesion energy of different carbides particles with liquid cobalt as expected (Exner 1978), carbides with lower binding energy shift (similar binding energy with cobalt matrix) shows higher cohesion energies.

TiC shows quite low adhesion energy (low wettability) in the cobalt matrix; it was experimentally confirmed as the addition of TiC powder in WC-Co system leads to an increase in the final average particle size and grain size distribution, and then drastically reduces the mechanical properties. However, a better microstructure was achieved in the presence of a binder with high nickel contents and/or with introducing molybdenum in the form of Mo₂C (Exner 1978), (Bhaumik, Upadhyaya, and Vaidya 1992).

All metals in the iron group show a very good wettability with cobalt liquid. Note that the atmosphere can strongly affect the wettability (quantified by measuring the wetting angle of the liquid droplet on solid surface). Experiments showed that the wetting angle can change from 18 ° to 42 ° (at 1400 °C) if changing the atmosphere from vacuum to the dry hydrogen (with an oxygen partial pressure of 10⁻⁹ Pa). Moreover, the insufficient wetting can be partially overcome by additions of electronic exchanging agents or by adjusting the carbon (or oxygen) potential of the ambient atmosphere. It was extensively reported that the WC-Co system can significantly be modified with regards to both carbide and binder phases. For instance, equivalent or even higher mechanical properties can be achieved by substituting the binder with nickel. Even superior properties can be obtained by using nickel in the presence of TiC (Exner 1978).

4.2.2 Residual Stress

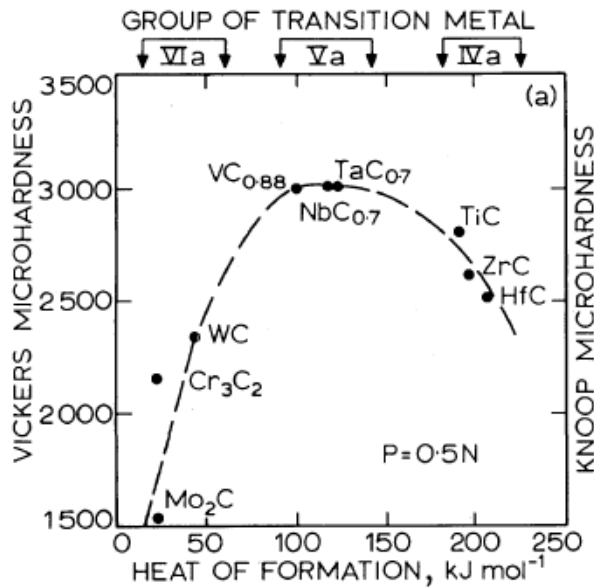


Figure 27: The hardness of different carbides (Exner 1978). Although WC/Co system shows an excellent wettability, other carbides are also interested due to their higher mechanical properties.

Due to the considerable difference between the thermal coefficient of carbides and metal binders, a significant residual stress generates during the cooling cycle from the sintering temperature. For example, the thermal contraction coefficient of cobalt is about three times larger than that of WC, leading to an induced tensile stress on the cobalt matrix (network) and induced compressive stress on carbide particles. It was observed that compressive stress on WC particles increases linearly with respect to the cobalt content. The theoretical simulations are also in agreement with the experimental measurements based on X-Ray diffraction technique; see Figure 27. The induced compressive stress on brittle carbide particles (e.g. WC) is actually beneficial due to suppressing the crack propagation, and then leading to better mechanical properties.

4.2.3 Particle Size

Changing the WC particles size can result in a very broad range of mechanical properties and applications. The cemented carbides can be as tough as high-strength steels with low hardness of about 800 HV10 in one extreme, and as hard as wear resistant ceramics with high hardness of about 2800 HV10 in the other extreme.

Their significant toughness is due to the tough metal binder which suppresses the crack propagation. Basically, the larger the volume fraction (or smaller the particle size) of carbide, the harder the composite. A typical particle size is about 5 μm with 6 to 30 percent binder; such materials are mainly used for manufacturing cutting tools which require a combination of high strength and toughness. On the other hand, hard metals with ultra-fined WC particle sizes ($\approx 0.2 \mu\text{m}$) are used to reach an extremely high hardness for applications in which only wear resistance is important.

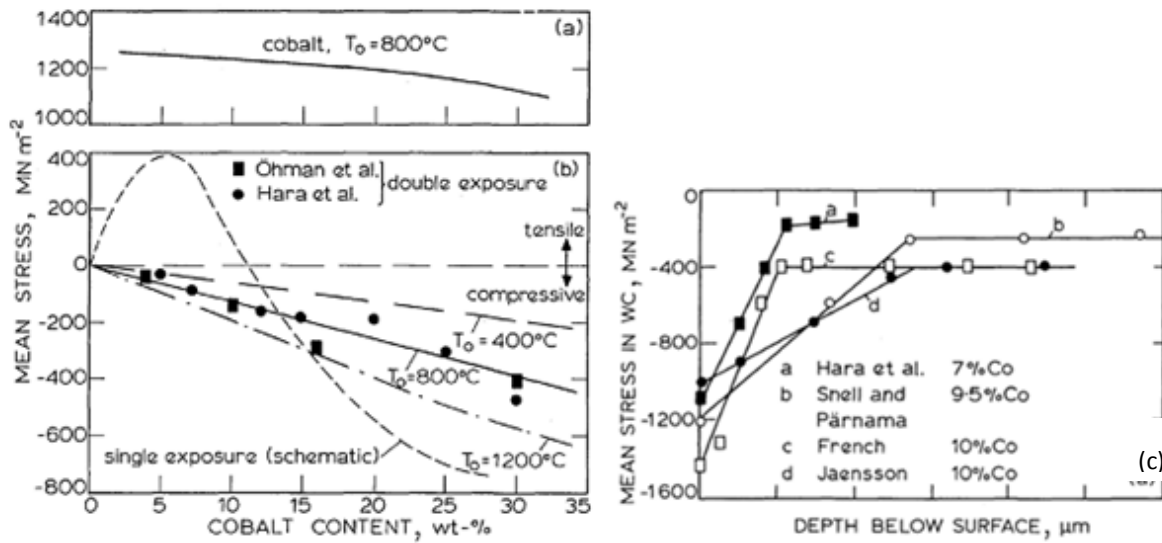


Figure 25: The induced residual stress in (a) binder (cobalt) as a function of cobalt content and (c) carbide particle as a function of depth below the particle-binder interface, in WC/Co system. (b) Tensile, compressive and total stress at a function of Co content and temperature (Exner 1978).

Experimental studies carried out on WC-10Co showed a phenomenological grain size-hardness relationship as below:

$$H_V = 550 + \frac{23550}{\sqrt{d_{WC}}}$$

where H_V is Vickers's hardness in unit of Kg/mm², and d_{WC} is WC particle size in nm. Note that a decrease in Co content influences the hardness in the same way as decreasing grain size (Saito, Iwabuchi, and Shimizu 2006), (Cha et al. 2001).

4.2.4 Pores

The presence of pores is a definite fact for all tools manufactured via sintering techniques. However, observations in metallographic cross-sections show that large pores and defects are not typical features in the cemented carbides structure. It was reported that size and number of pores are closely related to the volume fraction of the metallic binder; see Figure 29.

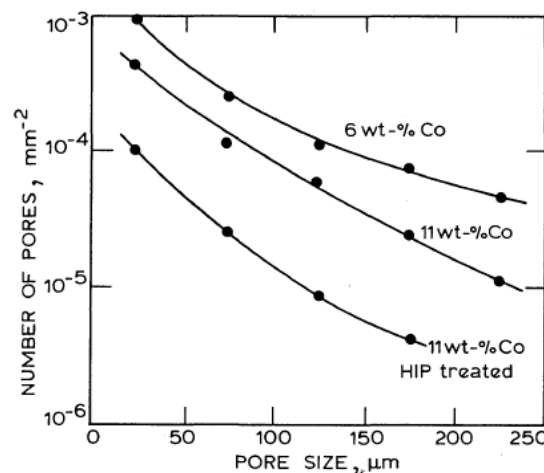


Figure 26: The influence of Co binder content on size and number of pores (Exner 1978).

4.3 Double-Cemented (DC) Tungsten Carbides

More recently, a new family of cemented tungsten carbide called double cemented (DC) has been introduced with the initial application in the oil industry in which there is always the risk of sudden failure; therefore, the need for tougher materials is essential. DC carbides are made of granules of WC/Co with sizes almost close to WC particles used in conventional cements. Such a microstructure results in a larger toughness due to the larger mean free path though the metal matrix between granules.

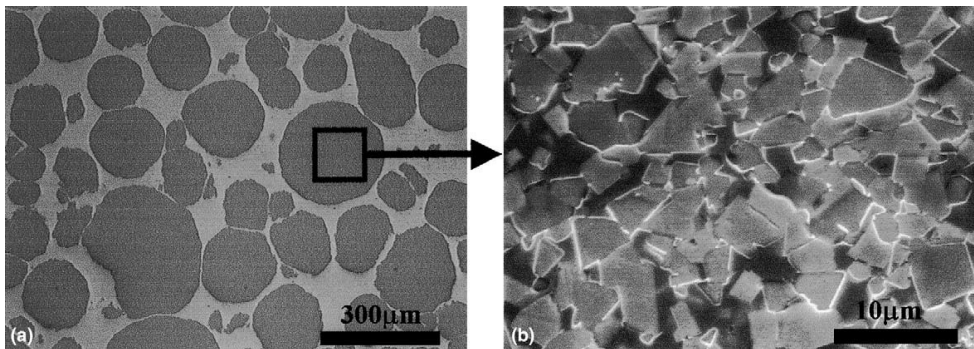


Figure 27: The microstructure of DC cemented carbides (Deng et al. 2011); the large mean free path between granules results in a better resistance against the crack propagation.

Moreover, DC cemented carbides exhibits an excellent wear-resistance and high hardness except at a very large binder content. Among other important properties, high elastic modulus (about three times higher than that of steel), high compressive strength (up to 8 GPa) and excellent conductivity make them an ideal candidate for the severe working conditions in the oil industry.

4.3.1 Manufacturing Process

As previously explained, the cemented carbides parts are manufactured via powder technology process: *ball milling, shaping, sintering, final machining*. The respective powders are first *ball milled*. Depending on size and shape of the desired part, shaping can be done via die pressing (for small simple tools), Powder Injection Moulding (PIM, for small parts or those with high aspect ratio) and Cold Isostatic Pressing (CIP, for large parts) following by machining to reach desired shape/dimensions. Sintering can be done via High-temperature Isostatic Pressing (HIP). The better the manufacturing process is the least amount of final finishing is required.

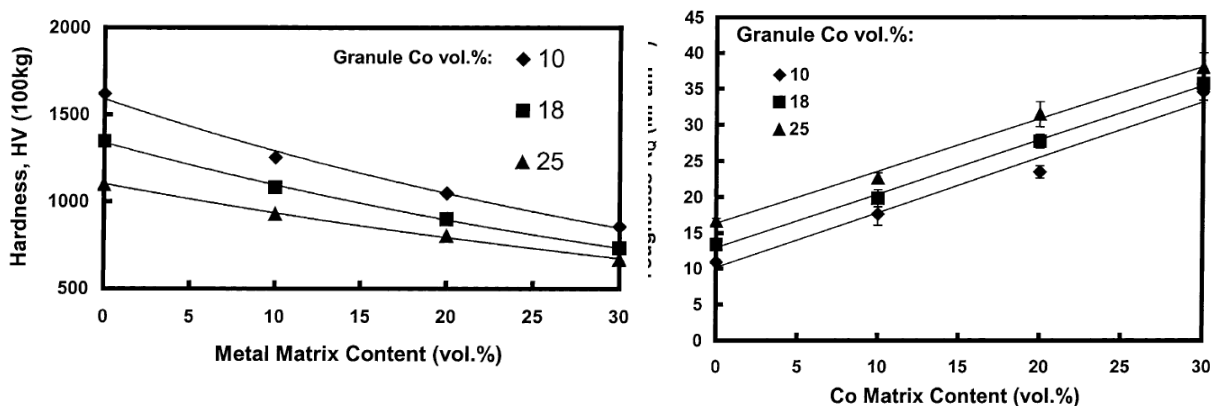


Figure 28: The effect of binder content on hardness and toughness of DC tungsten carbides (Deng et al. 2011); Note that volume fraction of metal binder in granules are as important as total binder content.

4.3.2 Applications

Basically, cemented carbides are used for two purposes. Firstly, it is used as the active layer/part which is in contact with other parts, where optimal mechanical properties as well as wear- and corrosion resistance and also high thermal conduction are required. Secondly, it is used to build the base parts and is protected by a layer of coating possessing all essential properties required for the contact condition. Hereunder, the most common applications of the cemented carbides are briefly explained.

WEAR PARTS

In these applications, cemented carbides are used as wear resistant coat such as for (Santhanam, Tierney, and Hunt 1990)

1. *Wire and section drawing*; interestingly, this application was the first goal for development of the cemented carbides. In 1930, a German light bulb manufacturer (Osram) looked for an alternative for their expensive diamond dies for drawing tungsten wire.
2. *Stamping and punch drawing*
3. *Compact dies & punches*; for manufacturing cans
4. *Cold and hot rolling*
5. *Food and medical industry*
6. *Relevant glass industry*

MACHINING

Cemented carbides introduce a combination of excellent physical and mechanical properties which make it an ideal candidate for these applications. Cemented carbides with WC particle size in the range of 0.5 μm to 5 μm and Co content in the range of 3 to 12 wt% are used. They are classified into two grades: *straight grades*, which is only composed of WC and Co and *steel cutting grades*, which contains other carbides and nitrides, (Ti, Ta, Nb)-(C, N) in their structure. The latter grades are used for the machining of cast irons, stainless steel, and Hardened steel. They can also be coated (Santhanam, Tierney, and Hunt 1990).

BASE OF COATED PARTS

In these applications cemented carbides play a different role than that for non-coated parts, because they are no longer the active component. They are coated by one (or several) protective layer(s) with exceptionally high hardness, low friction coefficient, high thermal conduction and stability, and oxidation resistance. The carbide part actually provides of high mechanical properties, e.g. rigidity, toughness and also creep resistance. Sufficient adhesion between these two parts is absolutely important.

By this method, thin layer(s) of very hard materials, such as diamond, could be coated on tough cemented carbide parts. Other hard carbides or nitrocarbids such as TiC, TiN, Ti(C, N) or even more complicated compositions can also be used. Coating layer can be deposited by different method such as CVD, PVD, PE-CVD. For instance, PE-PVD is used to produce diamond coat, or PVD to make very sharp edges (*Tungsten - An Indispensable Commodity* 2011).

MINING AND CONSTRUCTION

The main requirements for potential candidates for applications like road planning, soil stabilization and vertical- and horizontal drilling are considered to be high fracture toughness and abrasion resistance. Since high toughness is more important than abrasion resistance, very coarse WC particles, up to 20 μm , and high cobalt content between 6 to 10 wt% are used. In terms of tonnage, these applications are very important (*Tungsten - An Indispensable Commodity* 2011).

PARTNER IN COMPOUNDS

Capability of cemented carbides (sintered) parts to join other materials makes its processing quite feasible. In fact, cemented carbides are compatible with almost all important joining techniques such as brazing, laser and pressure welding, or projection welding. One of the most important applications is rock and oil drilling for which polycrystalline diamond or cubic boron nitride tip is sintered onto tough cemented carbide part at high temperature and pressure. This design combines high hardness and abrasion resistance of diamond with high mechanical properties of cemented carbide, leading to more durable and economic drilling (*Tungsten - An Indispensable Commodity* 2011)

FINE DRILLS

In these special applications, ultra-fine cemented carbides are used for production of drills used for drilling very fine holes in printed circuits down to several tens of micrometers.

4.4. High Speed Steels

4.4.1 Introduction

Tungsten is one of the first alloying elements systematically used to improve tool steels performance in the mid-20th century. Since then, the use of tungsten in steel industry has significantly increased, and this industry became the biggest tungsten consumer. Improvement of tool steels toughness and strength as well as hardness were the key reasons for introducing tungsten into the composition. Owing to the enhanced mechanical properties, and therefore longer life-time, the production cost decreased. Moreover, much faster cutting operations could be obtained, leading to higher productivity.

The tungsten consumption in steel industry decreased for several reasons. The introduction of cemented carbides in 1927 and its application as coating layer increased the durability and productivity of tools. Moreover, the shortage of tungsten supply during the Second World War made the western steel makers to change their steel composition by replacing tungsten with molybdenum (Mo); the modified composition resulted in comparable mechanical properties with that of tungsten, but to a lower price. Note that the atomic mass of Mo is about half of that for W; to introduce the equivalent volume fraction of carbide through the matrix, less mass fraction of Mo is required (1 wt % Mo is equivalent with 2 wt % W). Moreover, tool steels with a combination of Mo, Cr, V and Ni ended up to have better performances at lower prices. Nevertheless, the steel making industries are still the second largest tungsten consumers. However, the rate of tungsten consumption in steel industry varies in different markets, from 2 % (of total tungsten consumption) in the USA and 10 % in Europe and Japan, to about 30 % in Russia and China.

4.4.2 Tool Steels

“Tool steels” is a general name for a broad family of steels used for hot and cold forming, and also cutting materials, especially other metals, wood and polymers. For instance, they are the core materials for producing dies, rollers and punches in metal forming industries. Basically, tool steels composed of more than 7 wt. % alloying elements, W, Mo & V, and more than 0.6 wt. % carbon (C) are so-called *High Speed Steels (HSS)*; this name is due to their ability to cut metals at high speeds.

The presence of the alloying elements is crucial to result in the required properties for applications in which abrasion resistance at high temperatures is important. For example, typical materials for use in high-speed production need to retain the hardness and toughness at relatively high temperatures. The most important metallurgical principles will be briefly explained later in the chapter. HSSs are also suitable for applications in which durable sharp edges are required at relatively low temperatures, such as files, chisels, hand plane blades, and high quality kitchen and pocket knives.

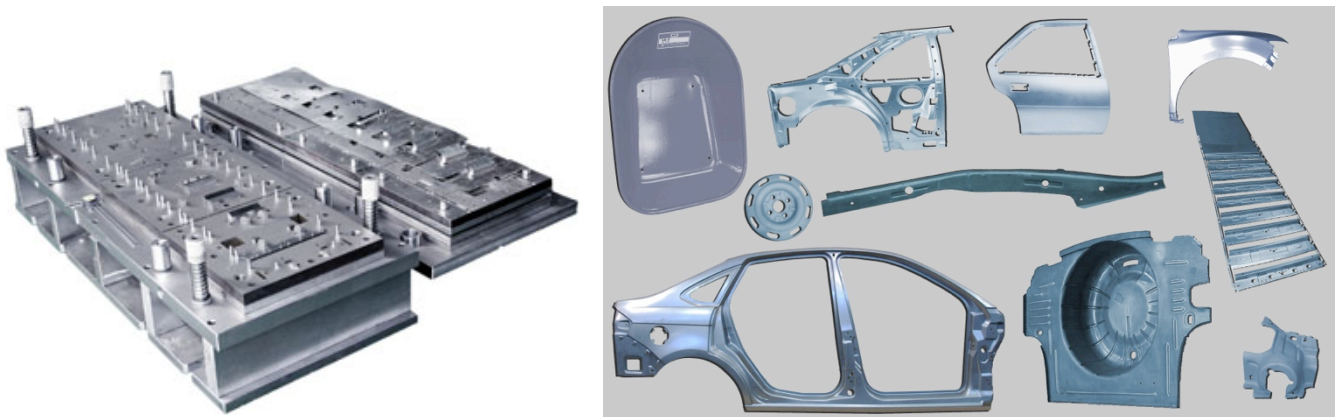


Figure 29: HSSs are very popular materials for stamping dies; this is due their very high hardness respecting the dimensional precision in a long term as well as their relatively good toughness. They are massively used in car industries (*Tool & Die Design and Making*) (*Metal Stamping Dies: Part 1* 2011).

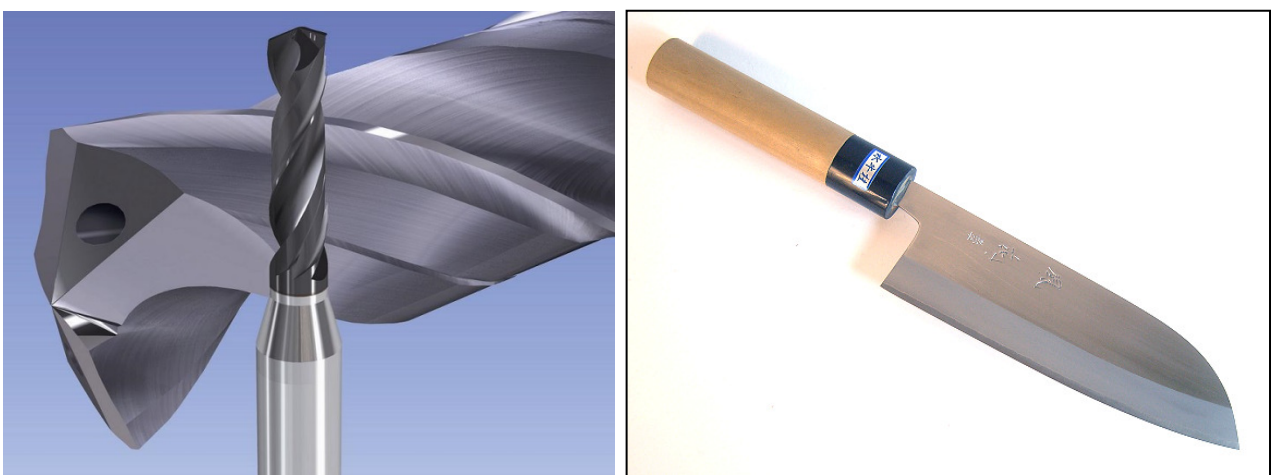


Figure 30: Cemented carbides are very common materials for drills; possessing excellent toughness together with a hard coating layer make them an ideal class of materials for this purpose. Before coating, the required geometry is applied by cutting tools made of HSSs. These steels possess a very high hardness which is essential for high precision operation (*Tungsten Carbide Drill Facts*). Japanese chefs know what to use! High hardness of HSSs retains the sharp edge of knife for a long time (Schmid).

METALLURGICAL PRINCIPLES

Carbon is the primary element in all grades of steels controlling the final obtainable mechanical properties. Carbon plays three major roles in steels:

- It determines the hardenability. The higher the carbon content is a better hardenability is expected; it implies that the same volume fraction of martensite can form at lower cooling rate. Therefore, increasing the carbon content is the less expensive way to increase the hardenability of steels.
- It strengthens the steel via solution hardening; small carbon atoms interstitially dissolve within the steel matrix.
- In the presence of alloying elements (W, Mo, V & Cr), increasing the carbon content results in formation of metallic carbides. Addition of a sufficient amount of carbon strengthens the alloy via both mechanisms (solution & precipitation hardening); the carbon content in HSSs is more than 0.6 wt. %. Table 5 presents the hardness range of carbides formed by alloying elements. As seen, WC and MoC possess similar hardness which makes Mo an interesting element to replace W in HSSs. Note that V forms the hardest carbide!

Table 5: Hardness Rockwell C of different alloying elements (Klingensmith 2009); Mo and W form carbides with almost the same hardness.

XC	CrC	MoC	WC	VC
HRC	66/68	72/77	72/77	82/84

4.4.3 Important Mechanical Properties

HARDNESS

By definition, hardness is a measure for resistance of materials to deformation; basically, hardness represents the yield strength of a material. It is measured for steels in Rockwell C. Hardened (cool worked) tool steels have hardnesses in range of 58 to 64 HRC.

Note that hardness and abrasion resistance are two different properties, even though they are closely related to each other. Local deformations on tool surfaces are related to hardness, no matter which type was used to produce the part; different grades of tool steels with similar hardnesses can exhibit different wear resistance. For example, cemented carbides show better wear resistance than HSSs, but with lower hardness; an optimal toughness and hardness is required for the best wear resistance.

TOUGHNESS

Toughness is defined as the resistance of material to failure, or the amount energy requires for failure to occur. Impact tests are the most common among the various methods which can be used to measure toughness, of which there are different types. Toughness is an important parameter for materials selection; low toughness increases the risk of sudden (catastrophic) failures. Tool steels do not require having very high toughness because they are expected to be employed in applications with frequent impacts.

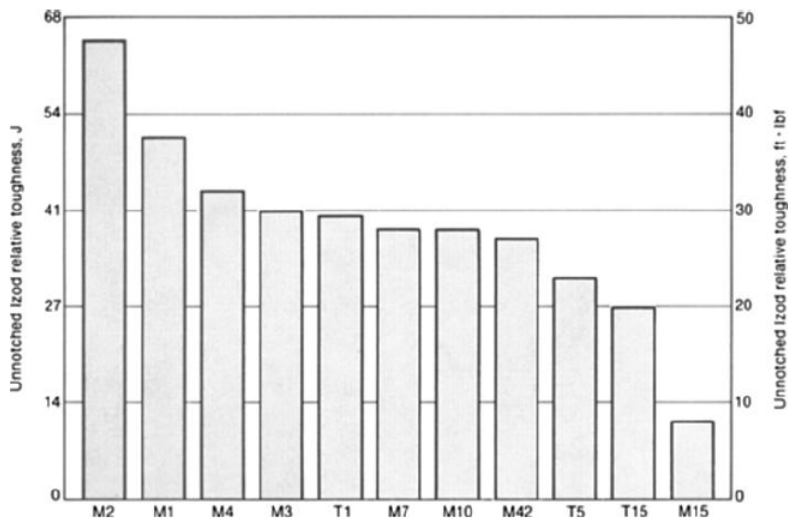


Figure 31: Toughness of several common tool steels (Bayer, Becherer, and Vasco 1990). Shock-resistance steel grades, S and H grades have much higher toughness compared to tool steels, T and M grades, as they are not

WEAR RESISTANCE

Wear resistance is the ability of material to resist against being abraded or eroded by contact with work material. A combination of good toughness and high hardness results in an optimal wear resistance behavior.

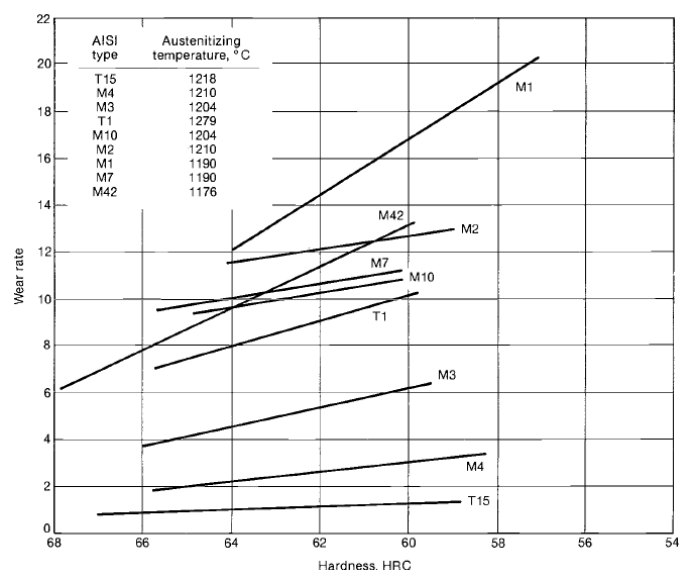


Figure 32: Wear resistance of the several HSSs as a function of increased hardness (by modified heat treatment) (Bayer, Becherer, and Vasco 1990).

4.4.4 Tool Steels Compositions

The upper limit of alloying elements content in the HSSs has always been a point of focus. The idea is whether or not the hardness and wear resistance of the HSS can be improved by continuously increasing the alloying elements content? The answer can be found in steel making process and its limitations. The HSSs ingots are produced after solidification of the melt whose chemistry is adjusted. The ingots are then processed by different fabrication techniques, e.g. metal forming, machining, etc., to make the desired tool.

As already explained, the presence of about 0.5 wt. % carbon in steels increases the hardness up to 60 HRC. Harder steels require higher amount of carbon to reach with the alloying elements to form hard carbide precipitates. Note that these carbides initially are formed during solidification of melt and therefore are poorly distributed in the ingots due to the segregation of alloying elements. Although subsequent heat treatment reduces the inhomogeneity, such non-homogeneity of hard carbides significantly decreases the toughness and wear resistance: this is due to the brittle network formed by carbides along which cracks can easily propagate. Furthermore, the elongation of carbides during the metal forming process leads to non-uniform texture. Vanadium levels over 3 wt. % are enough to cause such problems; therefore, Vanadium content is generally limited to about 2-2.5 wt. % in conventional HSS.

4.4.5 Powder Metallurgy (PM) HSSs

To overcome the limitations of the conventional steel making processes (solidification + metal forming), powder technology processes can be utilized. The powder technology allows producing HSSs with high V contents. Steel powder is produced by atomizing the molten metal (spraying), so that homogeneous particles are produced during fast solidification. Therefore, very fine and uniformly distributed carbides precipitates can form during the subsequent sintering process and heat treatments. Figure 33 illustrates carbide particle distribution in PM steels compared to conventional tool steels.

The Important advantage is that a higher toughness can be obtained as well as a better wear resistance, due to the continuous network of tough matrix. In spite of carbides network in conventional tool steels, carbide precipitates are uniformly distributed within the steels.

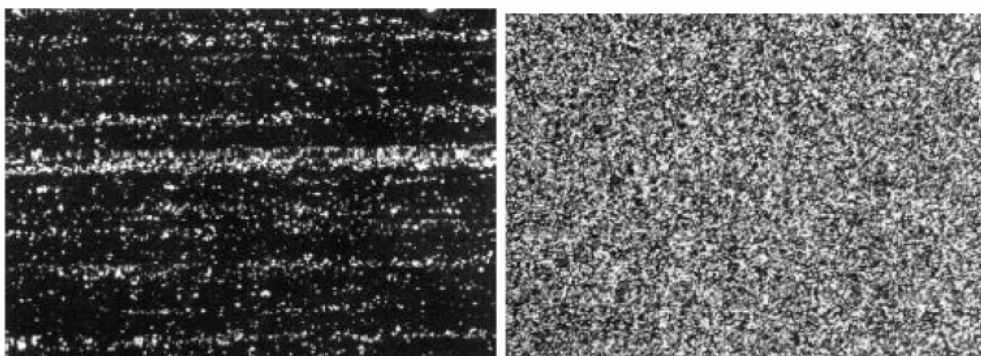


Figure 33: Different morphology of carbide precipitates in conventional processes (left) and PM routes (Rosso, ZUgues, and Actis Grande 2006).

4.4.6 HSSs grades

HSS belong to Fe-C-X multi-component systems in which X represents Mo, W, V and Co. Generally, component X and carbon are present more than 7 and 0.6 wt. %, respectively. Although the very first generations of HSSs were made by introducing W in steels composition, W has been replaced to a large extent by Mo for economic reasons.

HSS steels are classified into two major classes: *T-grade* HSSs with High W content and *M-grade* HSSs with high Mo content, according to the Unified Numbering System (UNS).

Table 6: The nominal composition of different HSSs (Bayer, Becherer, and Vasco 1990).

AISI type	UNS designation	C	Si	Cr	V	W	Mo	Co
Molybdenum high-speed tool steels								
M1	T11301	0.83	0.35	3.75	1.18	1.75	8.70	...
M2								
Regular C	T11302	0.83	0.33	4.13	1.98	6.13	5.00	...
High C	...	1.00	0.33	4.13	1.98	6.13	5.00	...
M3								
Class 1	T11313	1.05	0.33	4.13	2.50	5.88	5.63	...
Class 2	T11323	1.20	0.33	4.13	3.00	5.88	5.63	...
M4	T11304	1.33	0.33	4.25	4.13	5.88	4.88	...
M6	T11306	0.80	0.33	4.13	1.50	4.25	5.00	12.00
M7	T11307	1.01	0.38	3.75	2.00	1.75	8.70	...
M10								
Regular C	T11310	0.89	0.33	4.13	2.00	...	8.13	...
High C	...	1.00	0.33	4.13	2.00	...	8.13	...
M15	T11315	1.50	0.33	4.00	5.00	6.50	3.50	5.00
M30	T11330	0.80	0.33	4.00	1.25	2.00	8.00	5.00
M33	T11333	0.89	0.33	3.75	1.18	1.70	9.50	8.25
M34	T11334	0.89	0.33	3.75	2.10	1.75	8.48	8.25
M35	T11335	0.80	0.33	4.00	2.00	6.00	5.00	5.00
M36	T11336	0.85	0.33	4.13	2.00	6.00	5.00	8.25
M41	T11341	1.10	0.33	4.13	2.00	6.63	3.75	8.25
M42	T11342	1.10	0.40	3.88	1.15	1.50	9.50	8.25
M46	T11346	1.26	0.53	3.95	3.15	2.05	8.25	8.30
M48	T11348	1.50	0.33	3.88	3.00	10.00	5.13	9.00
M50(a)	T11350	0.80	0.40	4.13	1.00	...	4.25	...
M52(a)	T11352	0.90	0.40	4.00	1.93	1.25	4.45	...
M62	T11362	1.30	0.28	3.88	2.00	6.25	10.50	...
Tungsten high-speed tool steels								
T1	T12001	0.73	0.30	4.13	1.10	18.00
T4	T12004	0.75	0.30	4.13	1.00	18.25	0.70	5.00
T5	T12005	0.80	0.30	4.38	2.10	18.25	0.88	8.25
T6	T12006	0.80	0.30	4.38	1.80	19.75	0.70	12.00
T8	T12008	0.80	0.30	4.13	2.10	14.00	0.70	5.00
T15	T12015	1.55	0.28	4.38	4.88	12.38	1.00	5.00
(a) Intermediate high-speed tool steel								

There are also 7 T-grade HSSs and 17 M-grade HSSs.

The main role(s) of different alloying elements is: Cr for ease of the heat treatment (this is why Cr content has not changed in new grades), vanadium for grain refining and also to decrease Mo and W content (VC possesses very high hardness), and cobalt for resistance to high temperature softening. For example, M42 shows superior high temperature hardness, two times higher than M2; their only difference is the presence of high cobalt content in M42.

4.5 Tungsten Heavy Alloy (THA)

4.5.1 Introduction

Tungsten is a unique element with plenty of interesting physical and mechanical properties among which one can mention the high melting temperature and the exceptionally high density; this latter property is the basis for development of Tungsten Heavy Alloys (THAs). Thus, tungsten has conventionally been importance for shielding and collimating X- and γ -radiations.

The very high melting temperature of tungsten (3422 °C) makes it an ideal material for lots of applications. However, this can also be a drawback for tungsten as it is making a lot of standard manufacturing techniques impractical. For this reason powder metallurgy (PM) processes are frequently utilized to fabricate products made of pure tungsten; more specifically, the Liquid Phase Sintering (LPS) technique is employed for this purpose. Very fine tungsten powder are mixed with relatively low melting temperature elemental powder such as Ni, Fe, Cu, Co, etc.; the final product then has a multi-phase microstructure with fine tungsten particles surrounded by a continuous matrix of binder materials.

Various systems have historically been used for THAs of which W/Ni/Fe and W/Ni/Cu are the most popular. Tungsten heavy alloys (WHAs) with a W content of 90-95% possess a good combination of tensile strength as large as 1000 MPa and an elongation as large as 30 %, as well as high density of about 17-18 g/Cm³. Due to such a high density, these alloys have found a wide range of applications such as center of gravity (CG) adjuster, radiation shields and kinetic energy penetrators (KEP). In general, the mechanical properties of THAs depend on their microstructural features which can be modified by controlling the volume fraction and size of W particles and binders, as well as improving the adhesion of the W/binder interface. It is reported that relatively better tensile strength, toughness and elongation values (883 MPa, 29 mJ and 10 %) can be observed for 95W-5(Ni/Fe) alloy when the bonding strength between binder phase and tungsten is improved; It can prevent the cleavage of tungsten particles (Caldwell).

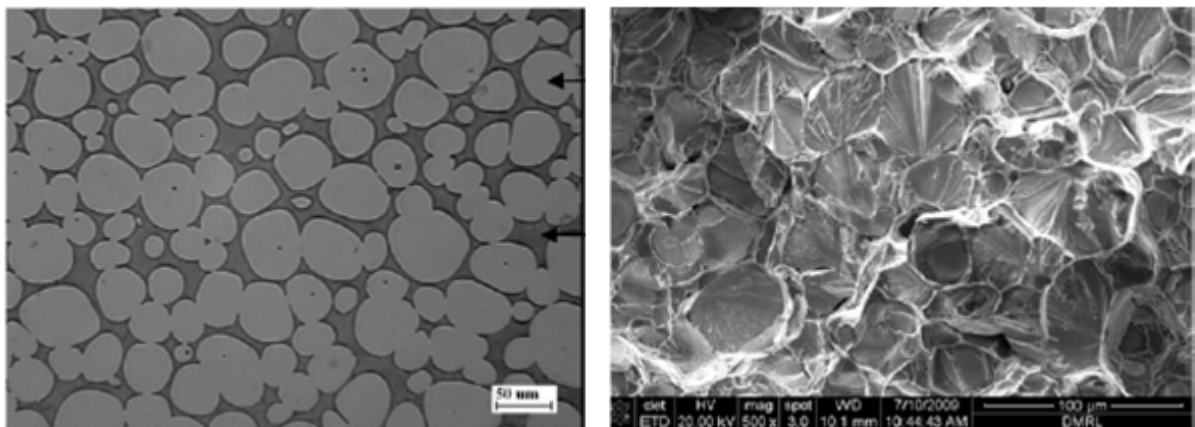


Figure 34: (Left) the optical image of a THA with the nominal composition of 95W-3.5Ni-1.5Fe; tungsten particles are embedded in a continuous matrix of binder can be observed. (Right) the fractograph of the same alloy after failure; the poor adhesion on W particles/binder interface led to cleavage along the binder matrix (Das, Appa Rao, and Pabi 2010).

4.5.2 Manufacturing Process

WHAs parts are manufactured from very fine, high purity tungsten powder blended with a few percent of other metal powders, typically Ni and Fe. The blended metal powder is compacted under high pressure (up to 30 ksi) to form a near net geometry of the desired part. Pressed parts are then subjected to high temperatures to sinter under hydrogen atmosphere. As the parts are slowly heated, hydrogen reduces metal oxides existing on the surface of metal particles, and provides clean, active surfaces. Upon subsequent increase of temperature, the diffusion takes place between particles. This process (sintering) results in about 20 % linear shrinkage and 50 % volume shrinkage. The driving force of this phenomenon is the surface energy which tends to reduce the total area of free surfaces by eliminating the pores.

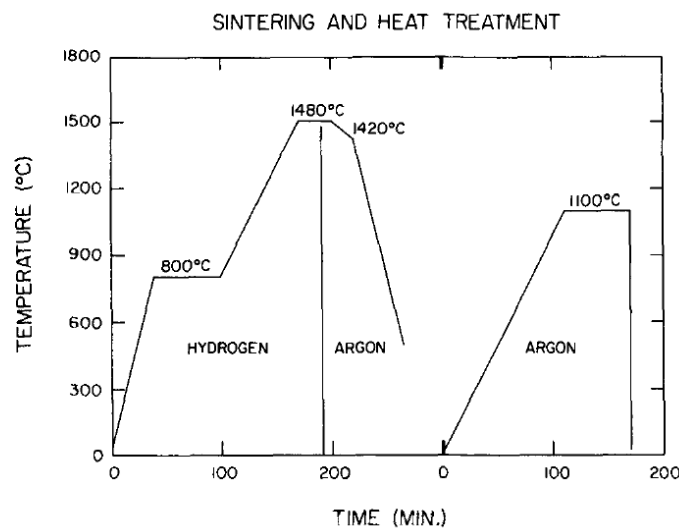


Figure 35: The sintering heating cycle of common W-Ni-Fe alloy (Bose 1988) new sintering technology based on microwave heating leads to comparable microstructure but in much shorter time (Mondal, Upadhyaya,

Moreover, the low melting point metal powder activates the LPS at sufficiently high temperatures at which the LPS is the main sintering mechanism. The average W grain size increases via Oswald-Ripening mechanism. Finally, a two-phase structure forms in which W particles are surrounded by the ductile matrix phase. Figure 3 shows the elemental map of two WHAs: 91W/7Ni/1.5Fe/0.5Co and 95W/3.5Ni/1.5Cu.

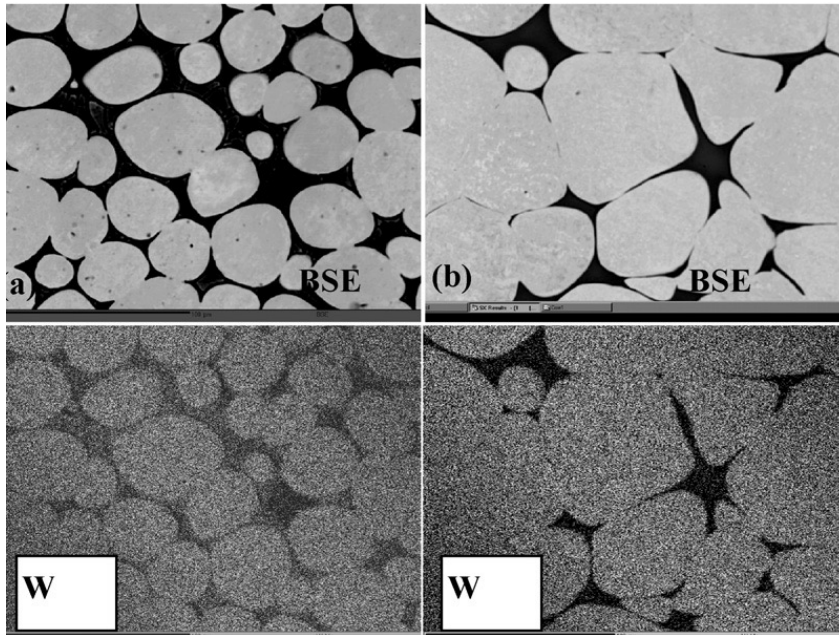


Figure 36: W distribution map for two common THAs: 91W/7Ni/1.5Fe/0.5Co (left) and 95W/3.5Ni/1.5Cu (right) (Das, Appa Rao, and Pabi 2010).

4.5.3 Comparative Properties

RADIATION SHIELDING

WHAs provide a unique combination of density, mechanical strength, machinability, corrosion resistance, and economy. This family of materials provides distinct advantages compared to its alternatives (with high density).

THAs, however, cannot be used for applications with temperatures above 500 °C; their mechanical properties rapidly fall off due to the softening of the low melting temperature matrix at relatively higher temperatures. Moreover, for applications in which the service temperature succeeds 300 °C, slightly occurrence of surface oxidation is envisaged. Platinum group metals can also be used for applications with reactive atmospheres together with elevated temperatures, but at extremely high cost (Caldwell).

Table 7: Comparative properties of WHAs and two alternatives for shielding applications (Caldwell); all these three classes of materials have conventionally been used for shielding and collimating high energy radiations because of their high *absorption coefficient* and *density*. As seen, THAs offer superior properties almost in all cases.

Material	Density (g/cc)	Tensile Strength	Stiffness	Machinability	Toxicity	Radioactivity	Cost
WHA	17.0-19.0	moderate	high	excellent	low	none	moderate
Lead	11.4 max.	very low	very low	very low	high	none	low
Uranium	18.7-18.9	moderate	medium	special	high	present	high

DENSITY

In some applications, the only important requirement for material selection is the density, e.g. counter-balance weights at aircrafts. WHAs can approach the density of pure tungsten (19.3 g/cm³) as well as offering adequate mechanical properties; lead creeps under its own weight at room temperature.!

The density of THAs is mainly dependent of the manufacturing process and whether or not pores are present in the microstructure of the alloy. The density also varies on composition; the lower the binder content, the higher density is expected.

Table 8: The density of several common THAs grades (Caldwell).

TP Alloy	Composition (Wt. %)	MIL-T-21014D Classification	Typical Density	
			(g/cc)	(lbs/in ²)
SD170	90W-(3Ni/Fe)	Class 1	17.14	0.619
Dens21	90W-(7Ni/Fe)	Class 1	17.20	0.622
SD175	92.5W-(3Ni/Fe)	Class 2	17.62	0.637
Dens23	92.5W-(7Ni/Fe)	Class 2	17.66	0.638
SD180	95W-(3Ni/Fe)	Class 3	18.13	0.655
Dens25	95W-(7Ni/Fe)	Class 3	18.16	0.656
SD185	97W-(3Ni/Fe)	Class 4	18.57	0.671

4.5.4 Applications

RADIATION SHIELDING

Modern industrial radiography and oncology systems currently utilize beam energies that can exceed 2 MeV from isotopic sources and well over 20 MeV from small accelerators. THAs are an excellent material for such applications.

AIRCRAFT COUNTERBALANCE

Various weights are used in order to avoid wing twisting and also adjust the center of gravity. They are generally coated in order to avoid oxidation or reactions with chemical cleaning materials.



Figure 37: THAs shields for medical and industrial applications (*Tungsten-filled Radiation Shielding: RPT*) (*DENSIMET tungsten alloy for efficient radiation protection*): Note that cylindrical shields are always designed to have an offset in order to avoid radiation leak.



Figure 38: Counter-weights for well logging are to sink into the muds and balance the upward pressures (*Tungsten Alloy Well Logging Counterweight 2012*); a combination of high density and sufficiently high mechanical properties makes THAs suitable for this



Figure 39: Crankshaft equipped with balance-weights of THAs (*Contemporary Crankshaft Design*).

WELL LOGGING

Because oil logging requires entering the earth as deep as possible to get the characterization of wells, high-performance logging facilities must be heavy enough to easily sink through materials such as muds and strong enough to withstand the hydrostatic pressure of this harsh environment. Due to the high density (18.5 g/cm^3 , max.) and hardness (36 HRC max.), high wear-resistance, high impact resistance and excellent durability, tungsten heavy alloys (WHAs) are very suitable materials for oil logging counterweight down-hole logging of underground water, oil and gas, etc.

BORING BARS (VIBRATION DAMPERS)

The high density of THAs, together with their relatively high elastic (Young's) modulus and composite microstructure, make them ideal materials for low chatter boring bars and long extension tool-holders of various types; WHAs are very stiff and resistant to deflection. Their high density coupled with the two phase microstructure provides effective vibration attenuation.

KINETIC ENERGY (KE) PENETRATORS

Traditionally, depleted uranium (DU) alloys (U-0.75Ti), were used as penetrator materials in all KE projectiles. The high density of these materials permits the long rod penetrator (installed in the projectiles) to deliver a large quantity of KE to a small area of the target; it leads to a deep intrusion of the penetrator in the target. Due to the environmental and health hazards of these alloys, there was this aim to replace DU alloys with an alternate material. Figure 43 plots the penetration characteristics of several candidate materials for KE penetrators in respect to their densities and limit velocities.

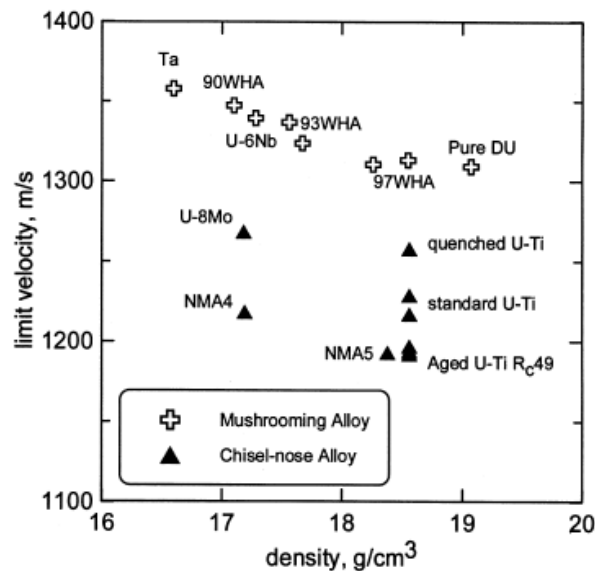


Figure 40: Comparative plot of penetration characteristics of different candidate materials in respect to their limit velocity and density (Upadhyaya 2001).

Table 9: Requirements for an ideal KE penetrator (Upadhyaya 2001).

Attribute	Function
High density	Imparts high impact energy
No intermetallic phase	Avoids poor interfacial bonding
High strength	For greater heat generation for a given strain
Low heat capacity	Heat generated results in rapid temperature rise
Low work-hardening rates	Easier flow softening
Low strain-rate hardening rates	Shear localization occurs at lower strains
High thermal-softening rate	Shear banding initiated at lower temperature

Note that high density is not the only factor governing the penetration of a projectile; Table 9 summarizes the main requirements of an ideal material for use as KE penetrator.

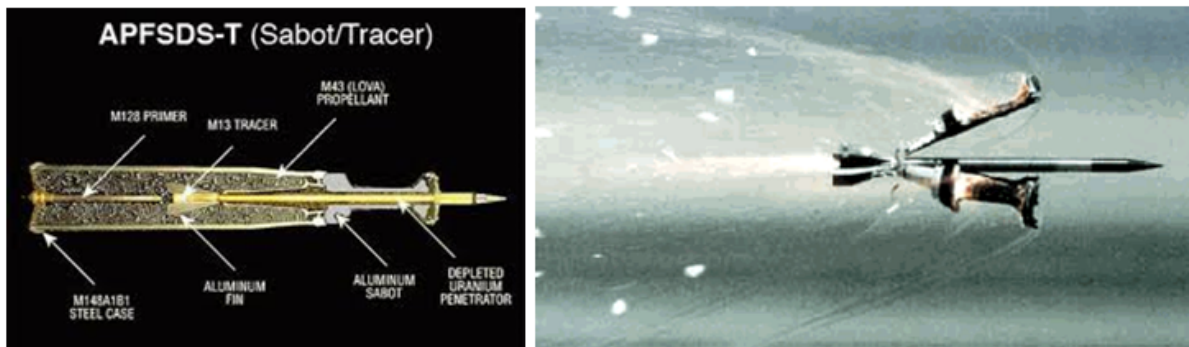


Figure 41: KE penetrator design (*Railgun Round Punches Through Steel Plates at Mach 5* 2011), (*Tanque Araentino (TAM)* 2013).

4.6 Tungsten in Chemicals

4.6.1 Pigments

INTRODUCTION

The commercially available tungsten compounds are generally used as the feedstock manufacturing chemical products. The main common character of all tungsten compounds is the fact that they possess interesting colors. Moreover, their color can be strongly modified by changing their chemical nature (oxidation number); as is shown in Figure 46, slightly different oxygen content in tungsten oxide leads to a range of attractive colors!



Figure 42: Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), ammonium paratungstate ($(\text{NH}_4)_{10}(\text{W}_{12}\text{O}_{41}) \cdot 5\text{H}_2\text{O}$), tungsten oxide (WO_3) and tungstic acid (H_2WO_4) are the main available tungsten compounds (*Sodium Tungstate* 2014), (*Ammonium Paratungstate* 2014), (*Tungsten Oxide*), (Stanovsky); they generally have colored nature making them interesting for being used as pigments.

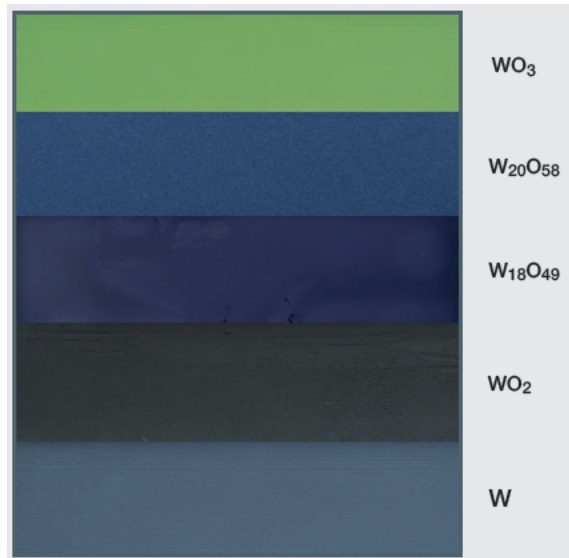


Figure 43: The influence of non-stoichiometric chemical composition on tungsten oxide color (*17th Annual General Meeting 2004*); WO_3 is actually the standard oxide which is produced in tungsten producing sites. By controlling the reduction reaction, a variety of sub-stoichiometric compounds can be formed.

COLOR SPACE

It is model to describe colors. *Isaac Newton* first made a study of color and developed the useful Newton color circle; each color has a range of coordination which can be calculated. Taking into account the light intensity, a third axis representing the brightness can be added, which cover the full range from the bright to the dark colors.

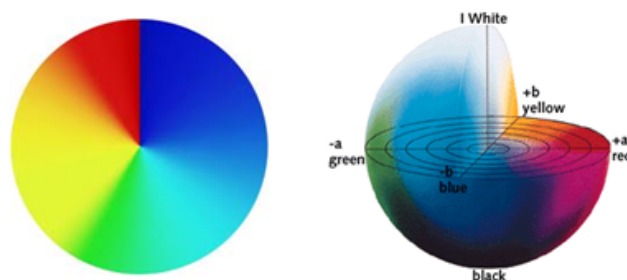


Figure 44: The color space which was first introduced by Isaac Newton (*Color Space Color Model*); every color identified by three parameters: a & b (determining the color) and l (brightness), and its contrast of a approximated by the following formula: $\Delta E = \sqrt{a^2 + b^2 + l^2}$.

Pigments function is to selectively absorb light so that the desired color (in terms of both color/wavelength and intensity) can be generated. Generally speaking, unlike fluorescent or phosphorescent materials, pigments only subtract certain wavelengths from the light spectrum. Pigments structure, impurity (type & concentration) and morphological specifications such as particle size influence the resulted optical properties.

There are three classes of applications for pigments: *Automotive*, *industrial paints*, and *decorative paints*. Depending on the working conditions, different requirements are expected of employed paints (and therefore pigments). Nevertheless, the fashion issues have the top importance in case of decorative and automotive applications.

APPLICATION OF TUNGSTEN-BASED PIGMENTS

- *Tungsten trioxide* and *tungstic acid* (not-modified pigments) are used for bright yellow glazes.
- *Tungsten Bronzes* are materials with perovskite structure (like BaTiO_3) and general XWO_3 chemical formula. They result in a variety of colors from red to violet depending on the impurity content and type.
- *Metal tungstates* are compounds with XWO_4 formula; X can be elements such as Ba resulting white color or multi-elements (e.g. Zn/Ni) resulting yellow color. This family of material has also been so interesting due to their ferro-electric properties (*Chemicals*).
- Colored organic dyes and pigments which are precipitated by *Phosphotungstic acid* and *phosphotungsto-molybdic acid*. This family of organic dyes shows higher strengths and stability to heat, light and water compared to earlier versions. Such dyes are frequently used as paints (printing inks) for plastics and rubbers.

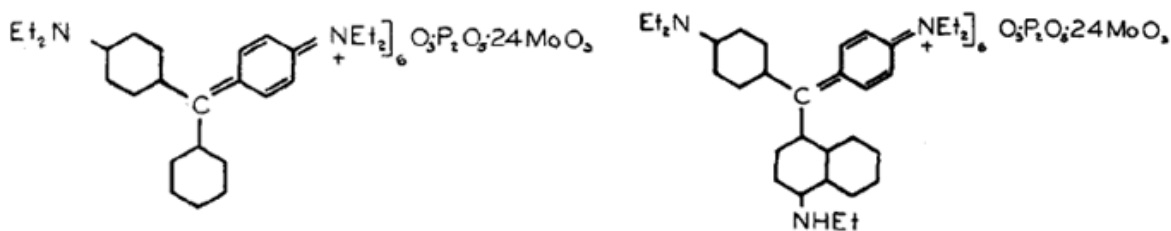


Figure 45: Colored organic dyes precipitated by phosphomolybdic acid, resulting in (left) brilliant green; (right) Victoria pure blue (Williams and Conley 1955); substitution of Mo with W results in a range of colors. These pigments were already discovered in 1935.

4.6.2 Dry Lubricants

INTRODUCTION

Dry lubricants are used to reduce the friction between two sliding surfaces without the presence of a liquid phase. Such solid lubricants are able to be used at significantly higher temperature. *Graphite*, *Molybdenum* and *tungsten disulphide* are the most common classes of dry lubricants.

The origin of this lubricating property refers to their crystalline structures and its layered nature. It is well known the binding energy between hexagonal basal planes of graphite is considerably lower than that of in-plane. Such anisotropic crystal nature leads to slide of the basal planes over each other under applied force. Meanwhile, such structure still has a perfect thermal stability due to the covalent nature of bonds on basal planes. Based on the same idea, molybdenum and tungsten disulphide were then developed.

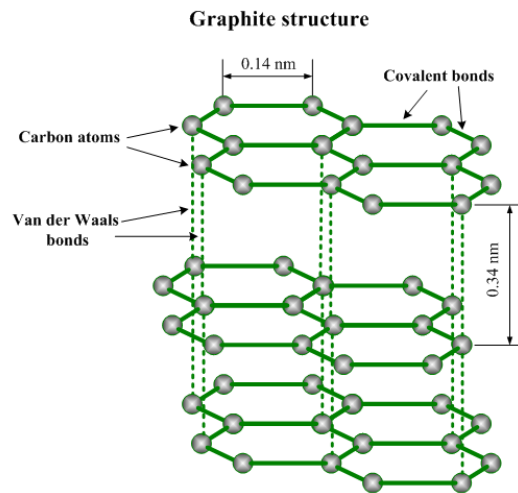


Figure 46: Crystal structure of graphite (Kopeliovich). Strong in-plane covalent bonds and weak inter-planar Van der Waals bands are schematically illustrated. Dry lubricants made of MoS₂ and WS₂ were introduced based on the same idea.

There are three methods to introduce dry lubricants on a desired surface:

- The lubricant is applied as a very pure thin film (about 1 μm) via one of these methods: immersion, spray, brush, dipping techniques and sputtering.
- The lubricant is introduced by a cohesive layer which can be either organic (e.g. epoxy, phenolic and amide systems) or ceramic. Note that such lubrication system is two times thicker than the first version.
- Complicated techniques such as plasma spray or making composite structure can be used to apply lubricant powder for advanced applications.

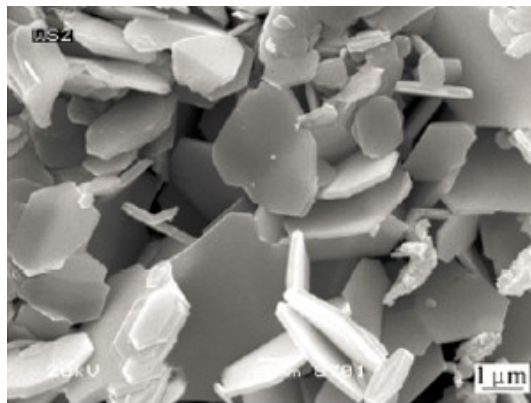


Figure 47: Tungsten di-sulphide particles (*Technology*).

TUNGSTEN IN LUBRICANT

OIL

Based on the same idea for use of layered structures (WS₂) for lubricating contact surfaces, nano-spheres uniformly dispersed within conventional lubricant oils have also been employed. Due to their geometrical uniformity and small dimension, an improved lubrication can be resulted using these nano-spheres (*Technology*).

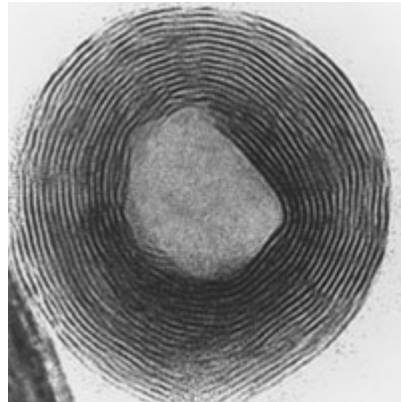


Figure 48: Tungsten di-sulphide nano-spheres (*Nano-Armor: Protecting the soldiers of tomorrow*).

4.6.3 MoS₂ vs. WS₂

WS₂ has found to exhibit superior lubrication properties compared to MoS₂ and graphite. Graphite is generally the first choice as lubricant for common applications, and can be replaced by MoS₂ in case of working at oxidizing conditions. Due to a considerable higher price of WS₂, it is extensively used for special high-tech applications at which even MoS₂ cannot withstand the severe conditions (combination of high temperature and load). For example, WS₂ is the only choice for aerospace application; in fact, it was first was designed to meet the requirements of aerospace applications at NASA.

Table 10: Comparison of lubricity properties of MoS₂ and WS₂ (*Comparison between Molybdenum Disulfide (MoS₂) & Tungsten Disulfide (WS₂)*).

Properties	WS ₂	MoS ₂
Melting point (°C)	1250, decomposed at 1260	Decomposed at 1185
Coefficient of Friction (COF)	0.03 Dynamic; 0.07 Static	COF < 0.1
Thermal stability in air	COF < 0.1 till 594 °C	COF < 0.1 till 316 °C
Thermal stability in argon	COF < 0.1 till 815 °C	COF > 0.1 till 482 °C , increasing rapidly at this temperature
Load bearing ability	400 psi	250 psi

4.6.4 Catalysis

DENOX CATALYSTS

The high temperature combustion of fossil fuels and coal in the presence of oxygen leads to the production of unwanted nitrogen oxides (NO_x). These oxides cause acid rain and degrade the ozone layer. Lots of attempts have been made to remove these dangerous oxides from the stack gases. The selective catalytic reduction (SCR) was found to be an effective solution. The idea is to reduce these oxides by ammonia (or other reducing agent such as unburnt hydrocarbons present in the waste gas effluent) in the presence of oxygen and a catalyst to form water and nitrogen. Effective SCR De NO_x catalysts include a variety of metal oxides; however, *vanadium* and *tungsten oxide* supported on *titanium* have found to be the most promising design for NO_x reduction.

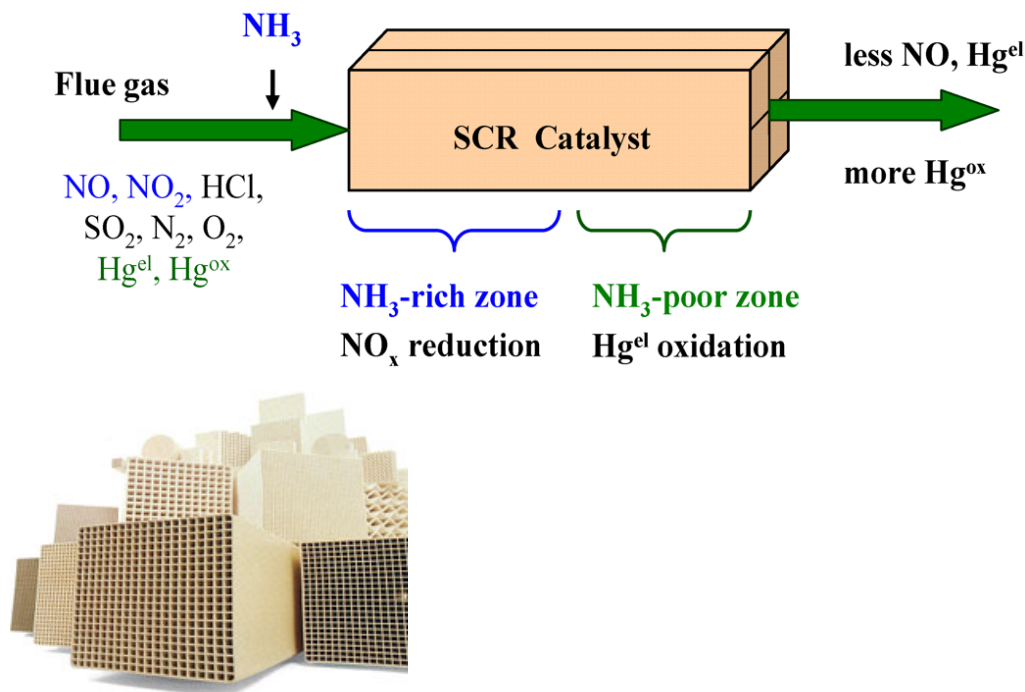


Figure 49: Schematics of the performance of SCR catalysts (Dranga, Lazar, and Koeser 2012). They are usually manufactured in honeycomb structure to have the maximum contact surface with the streaming gas (SCR/SNCR De NO_x). V_2O_5 is the most common active surface for low temperature application, but tungsten oxides are used for relatively higher temperatures.

$\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts have long been used to reduce the NO_x gases emitting from stationary power plants (Chen, Li, and Ge 2010). The trace of V_2O_5 that is too low to form a monolayer catalyzes the NO_x to N_2 reaction, while WO_3 sub-layer stabilizes the TiO_2 matrix (to avoid its transformation to rutile) as well as facilitating the catalytic reaction on V_2O_5 top layer (Economidis, Pena, and Smirniotis 1999); 78% TiO_2 / 9% WO_3 - 0-5% V_2O_5 (with other minors such as SiO_2) is a common composition for SCR catalysts (17th Annual General Meeting 2004). V_2O_5 is the active component for reduction of NO_x ; however, it also catalyzes the SO_2 to SO_3 reaction. This is the reason that its concentration is kept low while increasing its catalytic efficiency for NO_x reduction using WO_3 and some minors such as SiO_2 (Forzatti, Nova, and Beretta 2000). The main drawback of the SCR catalysts

is their low working temperature range which is between 300- to 400 °C; higher tungsten content is believed to broaden this temperature window to lower temperatures (Forzatti, Nova, and Beretta 2000). Moreover, NH₃-SCR catalysts have been commercialized in Europe for diesel engines after EURO IV regulations; it is believed that ammonia assisted catalytic reaction enhances the conversion from NO_x to NO in V₂O₅-WO₃/TiO₂ catalysts (Nova, Ciardelli, and Tronconi 2006) (*17th Annual General Meeting 2004*).

Tungsten trioxide, basically, plays as both chemical and structural promoter. Given the fact that Molybdenum is in the same group of the periodic table as tungsten, a similar chemical behavior is expected. SCR catalysts based on V₂O₅-MoO₃/TiO₂ chemistry have also been commercialized, but found to have loss efficiency compared to equivalent (in molar basis) tungsten based catalysts (Lietti, Nova, and Ramis 199). This substitution has very high importance especially due to sharp rise in tungsten price over the last decade.

SCR have found increasing interests to reduce emissions in mobile applications such as large diesel engines like those found in *ships, diesel locomotives, and automobiles*. The stationary applications (e.g. large *utility and industrial boilers* and also on *municipal solid waste boilers*) of DeNO_x catalysts, however, are more commercialized because ammonia is used to remove nitrogen oxides with efficiency in the range of 70- to 95 %.

PETROCHEMICAL CATALYSTS

There are different petrochemical processes for each of which suitable catalyst(s) are required to obtain economic productivity: *dehydrogenation, isomeration, aromatization, hydrocracking*. For example, large organic molecules can be broken into smaller molecules by a hydrocracking process resulting in production of larger quantities of gasoline and other valuable fuels.

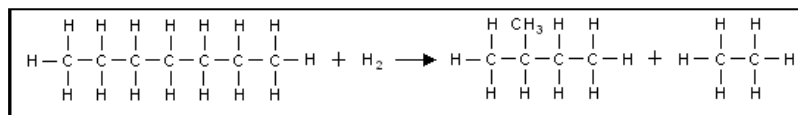


Figure 50: A hydrocracking reaction in which heptane (big molecule) breaks into two small molecules.

Conventionally, crude oil is purified for sulfur removal because these compounds are found to be corrosive for pipelines and are also the reason for acidic rain. For avoiding this, W (Mo)-Ni (Co)-S based catalysts are being used so that sulfur is extracted as hydrogen sulphide (H₂S). This well-established process is called *Hydrodesulphurization (HDS)* (*17th Annual General Meeting 2004*). Similar processes are introduced to remove nitrogen (HDN) and aromatic compounds (HDA). WS₂-Ni, MoS₂-Ni and MoS₂Co catalysts on alumina (AL₂O₃) or silica (SiO₂) supports are used as for these processes. Nowadays, Mo-Co and Mo-Ni are the work horses for HDS and HDN as they were found to have a better efficiency.



Figure 51: (Left) catalysts for hydrocracking process (*Hydrocracking catalysts*), and (Right) catalysts for HDS/HDN/HAD processes (*17th Annual General Meeting 2004*) the total formula for a HDS reaction is: $C_xH_yS + 2H_2 \rightarrow C_xH_{(y+2)} + H_2S$

REFORMING; WATER-GAS SHIFT (WGS)

The WGS reaction is used for production of *water gas* ($CO + H_2$), in which a stream of hydrocarbon (e.g. methane) is passed through a bed of coal. *Mond gas* is the industrial water gas which consists of a combination of CO_2 , CO and H_2 . Since non-saturated CO causes difficulties in next stages, it is converted to CO_2 by passing the stream over the finely divided nickel catalyst. Pure hydrogen can finally be collected by CO_2 removal upon alkaline wash. Pure hydrogen has two main applications: *ammonia production* and *fuel-cells*.

FUEL CELLS

Proton Exchange Membrane (PEM) Fuel Cell, so-called Polymer Electrolyte Membrane Fuel Cell, technology was invented by General Electric (GE) in the early 1960s, and became announced in mid-1960s when the company developed a small fuel cell. High efficiency, high energy density and low or zero emission are the main advantages of PEM fuel cells. Since their invention, a huge variety of applications such as for transportation, stationary and portable power and micro-power have been proposed.

The main concept of PEM fuel cells can be divided into three main stages:

- *Hydrogen reduction reaction (HRR) on cathode*
- *Transport of proton through the polymer membrane*
- *Oxygen oxidation reaction (OOR) on anode*

These reactions take place within respective catalyst layers.

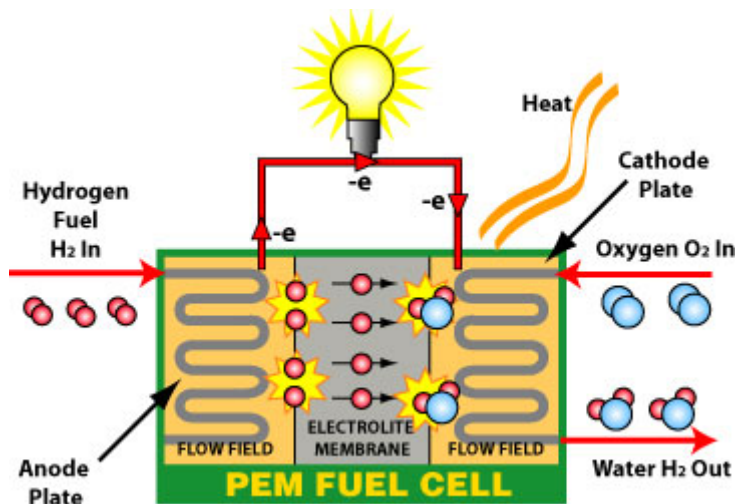


Figure 52: Schematic of a PEM catalysts functioning (*Fuel Cell R&D*); the idea of selective membrane is for allowing proton to pass but extracting electron to produce electricity.

Platinum based catalysts supported by carbon are the first generation of catalysts used in fuel cells. Due to the similar electronic structure and catalytic properties of tungsten compounds (e.g. *tungsten carbide*, *tungsten bronze*, *isopolytungstates* and *tungsten oxides*) with platinum-group elements, they have been the point of interest as alternative materials for replacement of this precious element. There are still some technical difficulties for their manufacturing as they are usually non-stoichiometric compounds. For example, high quality WC particles without any surface contaminations should be produced for resulting in an acceptable efficiency. Note that WCs is commercially produced by reduction of W or WO₃ upon placing through a stream of hydrocarbons (e.g. methane & acetylene). Consequently, they are generally contaminated by graphitic carbon.

Besides catalysts for anodic and cathodic reactions in PEM full cells, there are some tungsten compounds which can be used in PEM fuel cells as the proton conducting membrane. Particularly, *heteropoly acids* (HPAs) (e.g. *12-phosphotungstic acid*, PWA) have the ability to form different protonic species and hydrogen bonds with different strength; hence, such materials serve a great protonic conductivity. Due to such valuable ionic properties and low cost in respect with polymeric membranes, HPAs became very attractive for fuel cells applications.

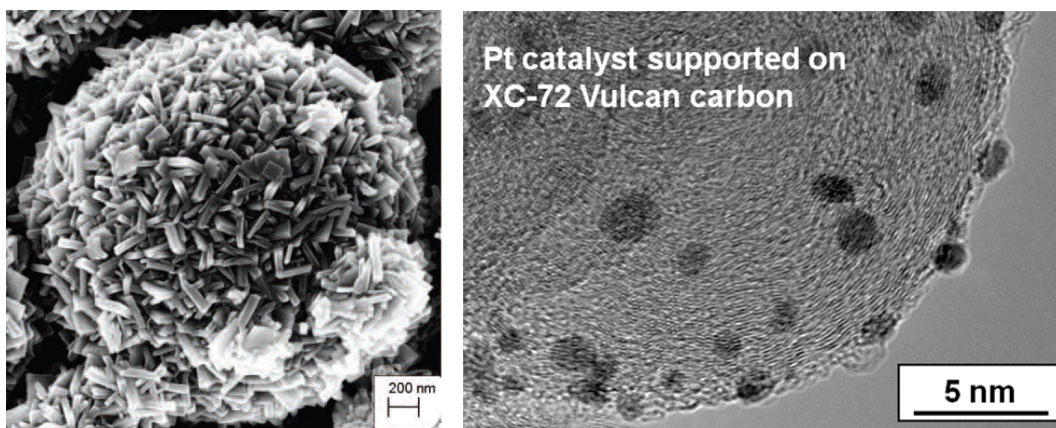


Figure 53: (Left) tungsten oxide high surface mesoporous catalyst surface and (Right) Pt catalyst particles distributed on carbon surface (Christian et al. 2011), (*Fuel Cell R&D*).

4.6.5 Other Applications

MEDICAL

- Dental Filling Materials
- X-ray Shielding

MINING & MINERAL SEPARATION

Based on the same principle as the DMS method (refer to Chap. 2), several tungsten compounds such as *sodium polytungstate* (SPT) and *lithium metatungstate* (LMT) are used as safe and effective dense medias ($\rho=3.7 \text{ g/Cm}^3$) for the separation of minerals (Christian et al. 2011).

4.7 Electrical and Electronic Applications

4.7.1 Gas Tungsten Arc Welding

INTRODUCTION

Gas Tungsten Arc Welding, also known as *Tungsten Inert Gas (TIG)*, is a well-established arc welding method using non-consumable tungsten electrode. The welding pool is protected by flow of an inert gas (e.g. argon, helium or a mixture of them) or other gases such as carbon dioxide. Each shielding gas introduces special properties to the arc; for example, the arc starts easily in argon atmosphere but provides higher temperature in helium atmosphere. Filler metal is usually used, which could be similar to the welding parts; for example, nickel based fillers can be used for repairing or building-up purposes of the cast iron. Power supply is the next equipment which usually provides a constant current in this process. For obtaining a perfect welding, many parameters must be controlled.

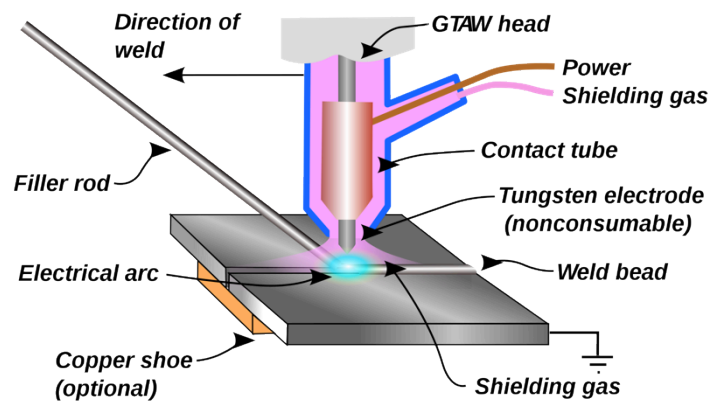


Figure 54: Different elements in a standard TIG welding (*Gas Tungsten Arc Welding 2014*)

TIG is one the most precise welding technique, and results in the best properties at final welded parts among arc welding methods. However, it is relatively (relatively complicated and also slow. Choosing this technique must have a specific reason because it is one the most expensive techniques.

DESIGN FACTORS OF ELECTRODES

There are several different factors determining the total performance of tungsten electrodes; in the following they are briefly explained:

Work Function

Work function is the main characteristic of a suitable material for this application. The lower the work function of an electrode, the lower the voltage necessary to strike the arc, and thus it is easier for an arc to start. An electrode with low work function has the advantage of a stable arc and low temperature at electrode tip during welding; the latter effect influences the grain growth rate.

Even though tungsten has a low work function compared to other common metals (4.5 eV) it is still too high for this application. Therefore, tungsten is usually doped up to 2 wt. % with rare earth metals such as Lanthanum, Cerium and Thorium.

Table 11: Work function of four low metals for TIG application [2]; Work function is usually reported in eV. Tungsten work function is further reduced after being doped by elements such La.

Material	Oxide eV	Metal eV
Lanthanum	2.5	3.3
Thorium	2.6	3.35
Cerium	3.2	2.84
Pure Tungsten	No oxide present	4.5

Migration and Evaporation Rate

The migration and evaporation rate determine the life-time of the electron. Due to its very low vapor pressure, tungsten can withstand applications at relatively high temperatures. However, after being doped with rare-earth metal oxides, the durability of the tungsten electrode is controlled by the consumption rate of these alloying elements. For evaporation, however, the alloying elements need to migrate to the surface of the electrode tip. If the evaporation rate is higher than the migration rate, lack of elements occurs on the surface and electrodes behave as pure tungsten materials. Therefore, the ideal situation would be with the equal (and obviously slow) rate of migration and evaporation, and furthermore as slow as possible.

Electrode Size and Geometry

Electrode size and geometry are important factors for consideration and depend on the welding parameters such as current type, AC or DC and current level; these operating conditions are related to factors such as piecework geometry and type.

GRADES

There are five grades of tungsten electrodes classified based on their composition. They are also classified to sub-grades depending on concentration of dopant(s). They are usually labelled by specific colors to easily be identified in working environments.

Table 12: Different grades of tungsten electrodes for use in TIG technique (Sprinkle 2010).

Iso Class	WP	WC20	WL10	WL15	WL20	WT10	WT20	WT30	WT40	WY20	WY3	WZ8
Iso Color	Green	Gray	Black	Gold	Sky-blue	Yellow	Red	Violet	Orange	Blue	Brown	White
Comp. wt%	Pure, 99.5%	2% CeO ₂	1% La ₂ O ₃	1.5% La ₂ O ₃	2% La ₂ O ₃	1% ThO ₂	2% ThO ₂	3% ThO ₂	3% ThO ₂	2% Y ₂ O ₃	0.3% ZrO ₂	0.8% ZrO ₂

APPLICATIONS

The main advantage of TIG is to produce focused plasma, and thus high intensity, resulting in a very fine welding area. This property makes TIG an interesting technique for welding thin pieces. TIG makes very narrow heat affected zones (HAZ), and therefore does not change the primary properties of the welding pieces. Owing to the great shielding atmosphere provided by very pure inert gas, the composition at the welding pool can be highly controlled. The combination of these properties makes TIG a popular method for high-tech applications such as aerospace industries in which parts made of highly alloyed steels are utilized. Such alloys are composed of light metals such as aluminum and magnesium; therefore, they are very sensitive to the heat treatment (HAZs).

TIG is not only used for joining purposes. Many manufacturing defects, e.g. porosity made during casting, can be repaired by this technique. Basically, surface defects can be very dangerous (and leading to catastrophic failures). For example, the casting defects from the investments casting technique employed for manufacturing different gas turbine components (made of superalloys) are carefully repaired using the TIG method. Very concentrated welding and clean pool are the main reasons that led to TIG to be the only technique used for this purpose. For the same reason, it is the preferred method for repairing damaged parts; for example, TIG is used for building up the cast irons using nickel fillers.

4.7.2 Electrical Contacts

INTRODUCTION

There are two classes of electrical contacts: switch contacts and connector contacts. The requirements for both classes are almost the same, but the working conditions are different because contact connectors are rarely engaged and disengaged. High voltage switches have to break high current/voltage during the service. Therefore, a combination of thermo-mechanical and electrical properties are required for such applications.

Figure 58 (left) shows an arcing connector attached in SF₆ circuit breaker for ultra high, high and medium voltage application. Such switches require withstanding extreme mechanical and thermal loads. For Example, temperature can rise up to 20'000 Kelvin while starting the arc. It should be mentioned that SF₆ circuit breakers are commonly used in electrical power systems in the voltage range between 33 KV to about 800 KV. The type of materials used for producing the switch depends on the severity of the applied loads, determined by voltage/current range.



Figure 55: Tungsten based switch (left) used at SF₆ circuit breaker (right) (Böning).

REQUIREMENTS OF SWITCHES ALLOYS

The main characteristic feature of working conditions for switches is the possibility for exposing to mechanical load at high temperature resulted from high a current/arc. For decreasing the contact resistance (and then contact temperature), high contact force must be applied between contact surfaces. It can then cause significant mechanical erosion during engaging or disengaging of switch. Therefore, the expected requirement of a potential candidate material for this application would be:

- High electrical conductivity
- Chemical inertness
- High corrosion and wear resistance
- High thermal conductivity
- Low thermal expansion
- Arc erosion resistance

Tungsten-copper composites can be an interesting material for this application; large volume fractions of tungsten particles with the low thermal expansion coefficient in the matrix results in relatively low thermal expansion of final alloy. Surface evaporation of copper binder decreases the surface temperature. Electrical contacts are usually made of metal materials; however, polymeric switches can also be utilized especially when working with high voltage/current.

DESIGN & PROCESSING OF SWITCHES ALLOYS

Basically, tungsten and copper are not mutually soluble, but the so-called W-Cu alloys are metallic composites in which copper forms a continuous matrix for the tungsten particles. This structure combines the advantages of both metals, resulting in a material with high heat and wear resistance (due to presence of tungsten particles) and excellent thermal and electrical conductivity (as well as proper machinability). For use as electrical contacts, an optimal combination of properties is obtained with 10 to 20 wt. % copper. Copper content in the range up to 50 to 90 wt. % are also possible, but for use in other applications. The last point to be mentioned is that W-Cu alloys properties vary according to ratio of copper to tungsten content. The larger the tungsten volume fraction, the electric arc and wear resistance increase while the thermal and electrical conductivity reduce.

In order to decrease the porosity level, sometimes a third element (mainly Ni or Fe) is added, thus the final material would be a ternary two-phase alloy. Such alloys have been point of interest in 90s in projectile industries.

One fabrication approach for W-Cu composites is based on forming a tungsten skeleton, followed by liquid copper infiltration and then liquid phase sintering of the mixture of tungsten powder and copper. This technique results in a final shape with no distortion during sintering even with liquid phase with volume fraction as large as 80 vol.%. The main weakness of these two processes is the difficulty to reach a complete dense structure due to the mutual insolubility of tungsten and copper. This is why a third element is usually added. Figure 59 shows the W-Cu and W-Ni binary phase diagrams. Obviously, copper and nickel make fully soluble system. The other option, as could be concluded from the phase diagram, is increasing the temperature (>1400 degree) which results in higher solubility, but also leads to problem of copper evaporation.

ALTERNATIVES FOR SWITCHES ALLOYS

W-Ag alloys

W-Ag alloys result in improved electrical and thermal properties compared to common W-Cu alloys, but are more expensive. Moreover, they suffer from lower wear resistance.

WC-Ni alloys

WC-Ni alloys offer higher hardnesses and arc wear resistance, but lower electrical conductivity than previous grades. They are suitable for air switching operations that experience strong arcs, for which mechanically resistant materials are required. They are used in DC switchgear and miniature circuit breakers used for low voltage circuit breaker; see Figure 60.

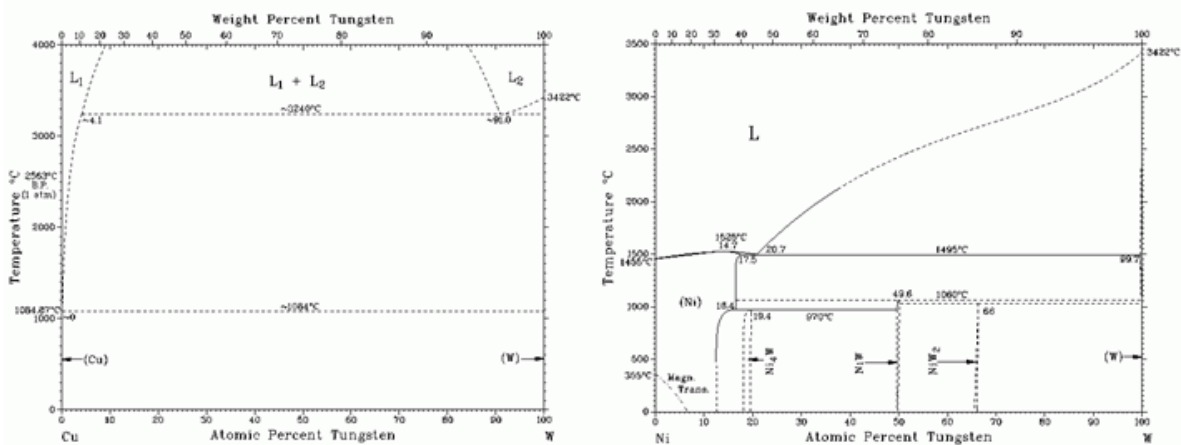


Figure 56: Phase diagrams of W-Ni and W-Cu systems (*Phase diagram Cu-W*) (*Phase diagram Ni-W*).





Figure 57: (Left) DC switchgear equipment, and (Right) typical miniature circuit breaker (TEO – traction automation system), (ABB: another market leader available from Burnand XH 2011)

4.7.3 Connector contacts

Obviously, in connector contacts mechanical properties are not as important factors as in case of switches. Therefore, the grades with superior electrical and thermal properties are preferable. The fabrication process is extrusion followed by drawing of sintered alloys.

As previously explained, switches material is burnt-off either via evaporation or erosion. Figure 61 shows the dependence of material consumption in respect to tungsten content; as seen, the alloy with 80 wt. % tungsten results in the most stable material. In reality, however, it can vary between 60 and 90 % depending on voltage/current and other working conditions, as well as economic reasons.

Ni is usually added to reduce the porosity level which results in a longer durability; however, it leads to a reduced conductivity. It is also reported that alloys with fine grain structure exhibit a better arc resistance at high voltages.

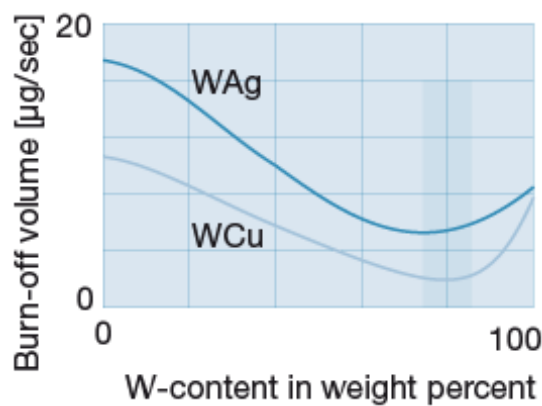


Figure 58: Burning rate of contact material as function of W content (Böning).

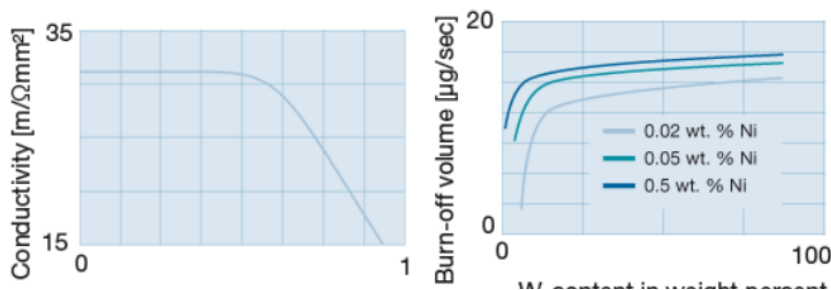


Figure 59: The effect of Ni addition on performance of contact material (Böning)

4.7.4 Electric Discharge Machining (EDM)

INTRODUCTION

The Electric Discharge Machining (EDM) (also known as spark machining or spark erosion) is very precise manufacturing process with which, in principle, a desired shape (semi-finished) is obtained by a series of electric discharges. The electric discharge between the electrode and the piecework is generated by applying relatively high electric voltage. During the spark erosion, however, both materials (electrode and piecework) are removed; there are several technical solutions to minimize the electrode consumption. Based on the idea of using an electric discharge to remove material different applications have been developed for this technology:

DIE-SINK EDM

Sinker EDM, also known as *cavity type EDM* and *volume EDM*, was first invented in Russia and then developed in the US. This technique is used to develop a pattern in a piece of material; for that, the electrode (together with piecework) is submerged in an insulating liquid (usually oil). Thousand sparks per second hit at random locations leading to form (pattern is applied by removing material layer by layer; “deepening” emphasizes this mechanism) a desired pattern.

WIRE-CUT EDM

In this variant, discharge occurs between a wire electrode and the piecework with the main purpose of fabricating tools; for that, sparks generated from a very fine wire (and automated by computer) result (verb refers to “sparks”) in a precision as high as 4 μm . Cutting plates as thick as 30 cm for manufacturing punches, tools and dies from hard metals (which are difficult to be machined) are the main uses of this technique. Its main advantage is that no mechanical damages are introduced to the piecework; moreover, due to highly focused input heat in this process, very narrow heat affected zones (HAZs) form.

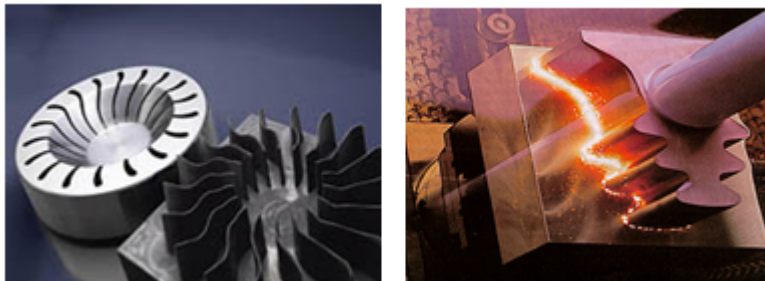


Figure 60: Sinker EDM complicated geometries with very high precision can be fabricated by this method (Mercatech, Inc.) (AG60L Sinker EMD).

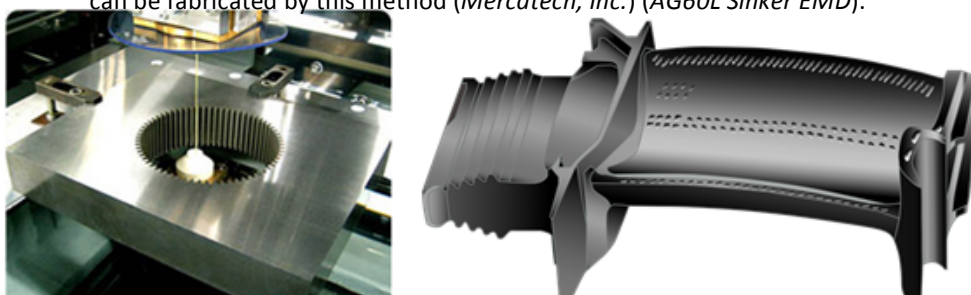


Figure 61: Wire-Cut EDM (*Wire EMD*), (*Electric Discharge Machining* 2014); very narrow wire is the source of spark. Therefore, material is removed with very high precision from the piecework surface.

EDM is an expensive fabrication technique because of its high energy consumption rate. It is not a common technique for mass production, but is actually a very interesting technique for *prototype production*. Wire-cut EDM can also be used to form very precise and small holes; this is very important especially for the finishing stage of other manufacturing processes such as casting. For example, the front blades and sometimes vanes in gas turbines are designed to be air cooled during working. However, casting does not have such a high precision; see Figure 64.

MATERIAL SELECTION

As expected, an ideal material for use in electrode must possess an optimal combination of mechanical and electrical properties. *Brass, copper, silver* and *tungsten* are potential candidates for this application; however, each of them suffers from a few disadvantages; for example, copper and silver possess excellent electrical properties but with very bad mechanical properties. They are, therefore, suitable for applications in which relatively low mechanical performance is required.

Tungsten copper, tungsten silver or *tungsten-carbide silver* alloys would be ideal materials for sinker EDM electrodes which are expected to withstand severe mechanical conditions. For example, WC-Ag electrodes are frequently used for manufacturing dies made of tungsten carbide. Indeed, the economic aspects have to be taken into consideration when choosing electrodes.

Finally, graphite based electrodes are of point of interest for many applications; the main disadvantage of graphite is its low mechanical properties.

4.7.5 Resistance/ Spot welding (RSW)

In Resistance/ Spot welding (RSW), two plates are joined to each other by forming a local welding pool made by a relatively high current from two electrodes; a combination of materials resistivity and contact resistance (the air gap) determines the rate of heat generation. For obtaining a good joint, an optimal combination of the weld penetration and the contact force (the force applied by the two contact electrodes) are required. The use of the RSW technique is limited to relatively thin sheets and rods; it is not a flexible fabrication technique for a wide range of geometries and sizes. For example, it can be used to join parts as small as lamp filament to parts as large as automobile seats. Heating/cooling radiators, wire connection and joining different parts at switch gears are among other applications of this technique.

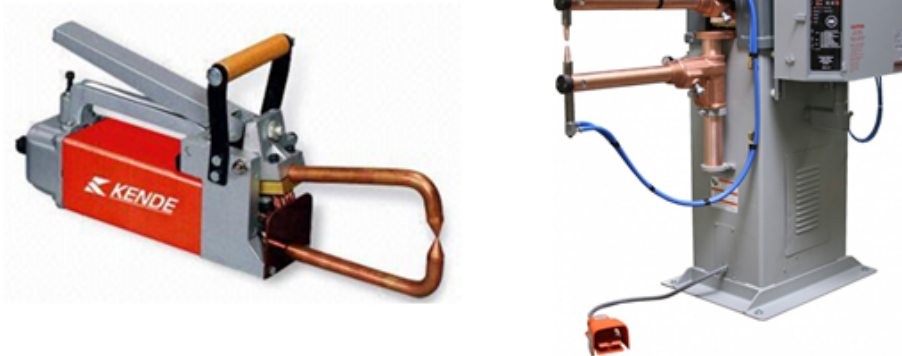


Figure 62: RSW machines (Left) portable and (Right) automated (*Resistance Welding Process*).

Given the fact that the contact electrodes in the RSW technique are repeatedly under mechanical load, possessing superior mechanical properties are very important for a candidate material for this application. Such material is expected to possess low resistivity in order to reduce joule heating (to avoid increasing temperature of electrode that degrades it) and relatively high thermal conductivity to dissipate heat from the electrode tip. Therefore, the metallic composites based on tungsten carbides (such as W-Cu, W-Ag and WC-Ag (Cu)) are exceptionally unique materials for this application.

4.7.6 Heat sink

The heat produced in the integrated systems must be adequately dissipated to avoid temperature raise; for heat dissipation, a material with very high dimensional stability and good thermal conductivity is required. Therefore, the main requirements are:

- *High thermal conduction*
- *Low thermal expansion coefficient*

Metallic composites based on *tungsten particles* offers a promising combination of excellent dimensional stability and thermal conductivity.

Table 13: List of important physical properties of W-Cu alloys (*Tungsten Copper*); as seen, an optimal combination of thermal conductivity and dimensional stability can easily be obtained by modifying the composition of composite.

Composition (wt%)	Density (g/cm ³)	Coefficient of Thermal Expansion ($\times 10^{-6}/K$)	Thermal Conductivity (W/m.K)
W-10Cu	17.1	191	6.3
W-15Cu	16.4	198	7.1
W-20Cu	15.5	221	7.6
W-25Cu	14.8	235	8.5
W-30Cu	14.2	247	9.0

Thermal mounting plates, chip carriers, flanges, and substrate for high-power electronic (semiconductor) devices are several common applications for these alloys; CuW75% is a popular composition for use in heat sinks.

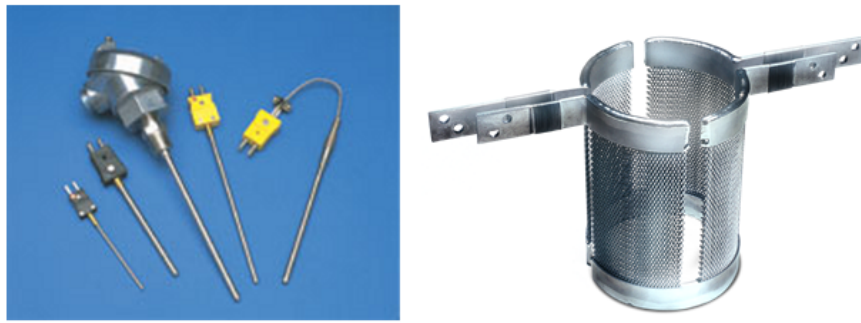


Figure 63: Heat spreader used in integrated circuits are made of tungsten-copper metallic composites (*Heat Sink* 2014)

4.8 Other Applications

4.8.1 Accessories for High Temperature Operations

Candidate materials for previous applications were expected to offer a range of mechanical and physical properties. Owing to very high melting temperature (3422 °C) with the capability to keep its superior mechanical and physical properties (such as very low vapor pressure) at elevated temperatures (as high as 2800 °C), tungsten is an idea material for use in different parts of high temperature furnaces such as heating coils, radiation shields and charge carrier. Other high temperature applications are:

- Crucible for single crystal growth
- Pure/alloyed tungsten or tungsten carbide nozzle for ceramic wool production
- Tungsten-rhenium thermocouples for elevated temperatures (as large as 2760 °C)

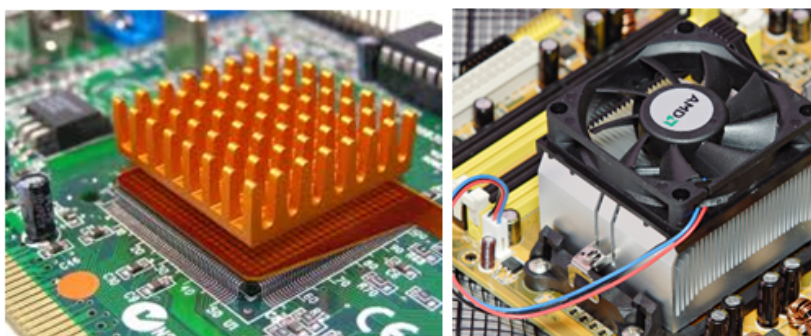


Figure 64: (Left) tungsten-rhenium thermocouples used for high temperature measurements (*Contact - electrical thermometers*), and (Right) tungsten heater owing to very high melting temperature, low vapor pressure and excellent thermal stability, tungsten is an ideal material for many high temperature applications (*Doped tungsten doubles the lifetime*).

4.8.2 X-Ray tube

For the generation of X-ray, basically, high energy electrons are accelerated in a large electric field are designed to hit a target; a continuous X-ray spectrum together with characteristic radiation of the

target material can then be collected. An ideal source of electrons is considered to have relatively low work function; therefore, electrons can easily be collected by applying a small positive bias, but after heating.

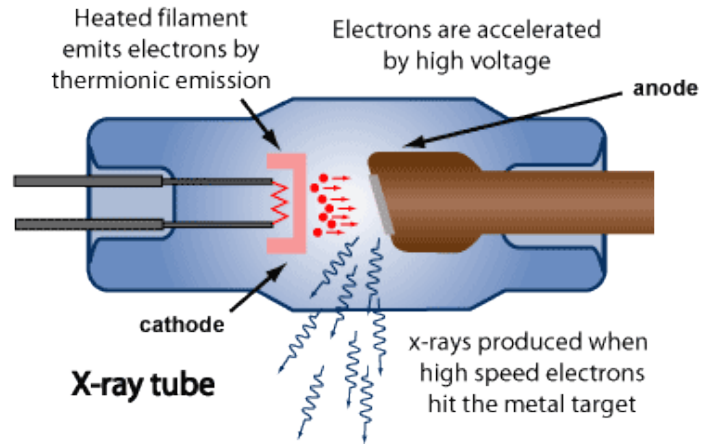


Figure 65: The schematic illustration of a typical X-ray tube (*X-Rays*): a potential material for filament possess very low work function and vapor pressure.

Owing to tungsten's *low work function* and very low *vapor pressure*, it is adequate material for fabricating filament for X-tubes. Given the fact that tungsten offers excellent thermal stability, the geometry and structure of the filament are precisely controlled during service.

The anodes are generally made of tungsten, molybdenum and copper. The higher the atomic number of the anode, the higher X-ray energy can be generated; high energy X-ray shows more penetration in other materials. In medical applications, tungsten X-ray tube with rhodium (Rh) and Silver filters leads to optimal results.

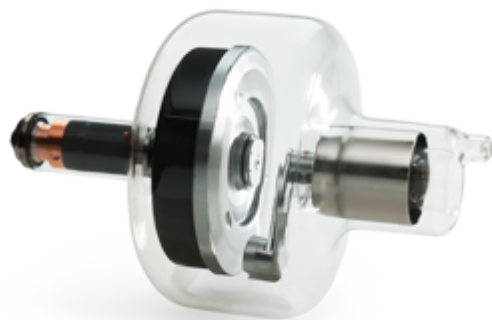


Figure 66: Tungsten Anode for Rotating X-Tube (*Rotating X-ray anodes and accessories*); such X-rays are used for medical purposes.

4.8.3 Electron Source for Scientific Research

There are several classes of electron guns each of which produces the electron beam with a particular mechanism; different guns result in electron beams with different characteristics. Such beams are used in different research facilities such as *transmission electron microscope (TEM)* and *scanning electron microscope (SEM)*. Tungsten filaments, LaB6 guns and more recently *field emission (FE)* guns produce electron beams with a very narrow energy spectrum.

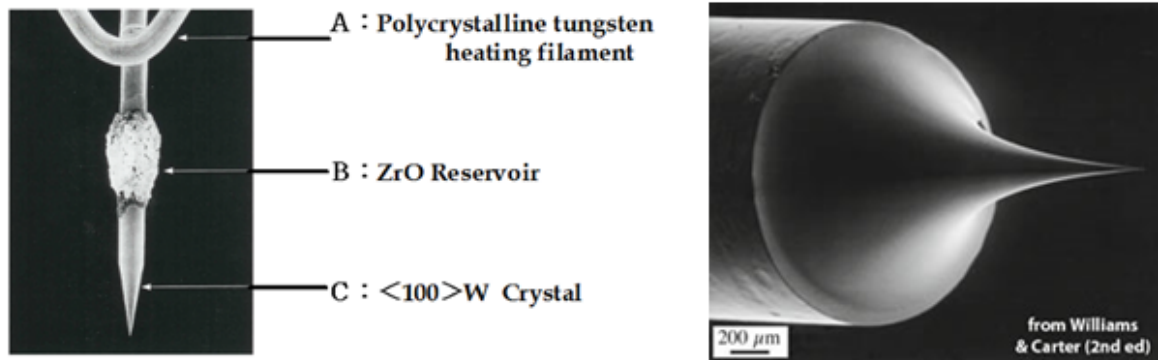


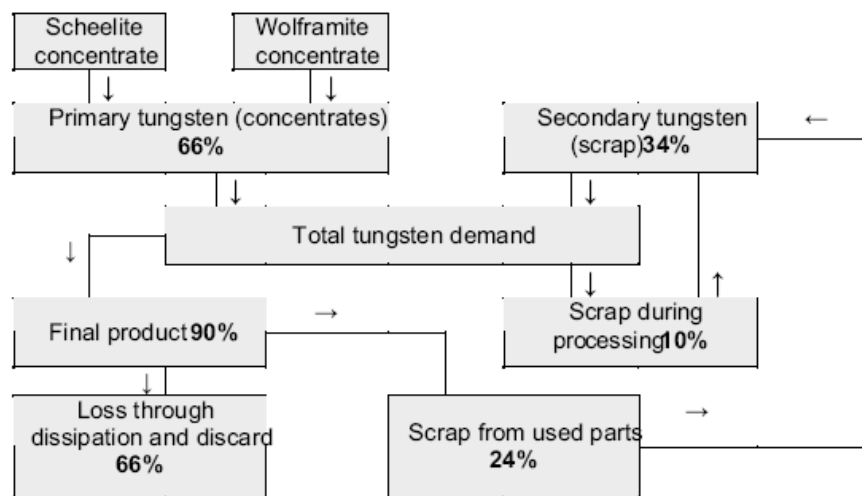
Figure 67: Different designs for novel FE tungsten guns (Yu, Makiuchi, and Chen 2010), tungsten possesses a very low work function, vapor pressure and thermal expansion which turn it to an exceptional material as a source for electrons.

5. Recycling

The secondary tungsten reserves (W-containing scraps) have found considerable importance, especially since the first shock of the tungsten market in the early years of 21st century, in such a way that all the key players in the tungsten supply chain have massively started to collect tungsten-containing scraps, either from their domestic production or by importation. For example, china has increased the use of the secondary tungsten reserves since 2010 in order to increase its annual production about 20% (see section 2.1). Note that China is the largest tungsten production and supplier possessing the largest tungsten deposits in the world; however, this is not a reason to ignore the importance of W-containing scraps as rich reserves for tungsten.

According to Roskill’s 2012 report, tungsten carbides and tungsten alloys consume about 80% annual tungsten production. Among various tungsten products, its recovery from cemented carbides (hard metals, WCs) and tungsten alloys is the most economic taking into account their availability and ease of processing. 25% of world tungsten production was sources by these secondary tungsten resources (Merriman 2013)

Flowchart 1: The following chart presents the tungsten supply chain in 2010 (*Strategically Important Metals* 2010). A significant portion of world tungsten production was sourced by tungsten-containing scraps; the global interest in secondary resources raised due to the price rise especially since 2009. Note that a certain extent of deviation can be found in different reports (25% in 2012 reported in (Merriman 2013) and 34 % in 2010 reported in (*Strategically Important Metals* 2010)); the use of secondary reserves continuously increased over the last year.



Given the fact that tungsten is required in the form of WC for re-use in new cemented carbides parts (55% of tungsten consumption), the cemented carbides scraps usually only requires to be partially recycled by break the WC/Co bulk composites into the separate WC powder. Therefore, the term “recycling” in tungsten supply chain does not always imply the complete extraction of tungsten from its compounds into the pure elemental form. Basically, scraped cemented carbide parts are the most important tungsten secondary reserves. Several of the most common processes for tungsten recovery from its products are explained in this section.

5.2 Zinc Melt Method (ZMM)

In the zinc-recovery process, the cemented carbide scraps are immersed through a molten zinc bath in an electrical furnace and under an atmosphere protected with an inert gas at 650 °C to 800 °C. The binder metal (normally Co or Mo) dissolves in Zn; the binary Zn-Co phase diagram shows that the solubility of cobalt in liquid zinc is about 10 mol. % at the range of working temperature, which is sufficient for the complete dissolution of the binder. Zinc will finally be distilled at 700-950 °C. The optimal conditions for this process depend on Co content (Altuncu et al. 2013).

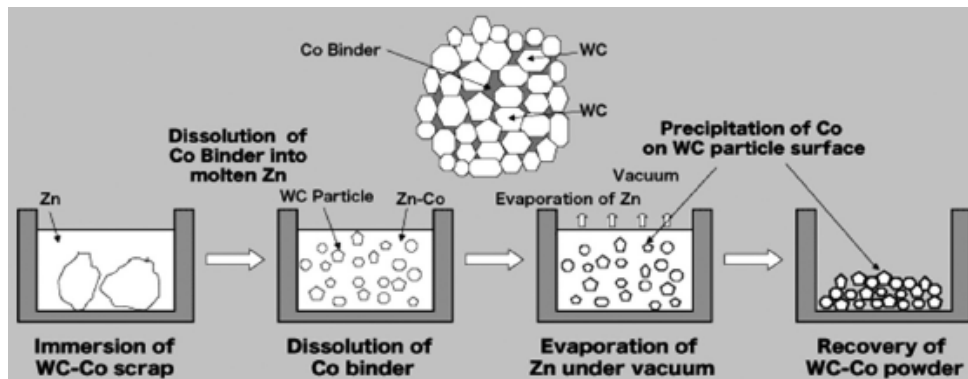


Figure 68: The ZMM process for tungsten recovery from the cemented tungsten carbide; Zinc bath dissolves the binder metal (usually Co) but does not affect the primary tungsten carbide powder (Altuncu et al. 2013).

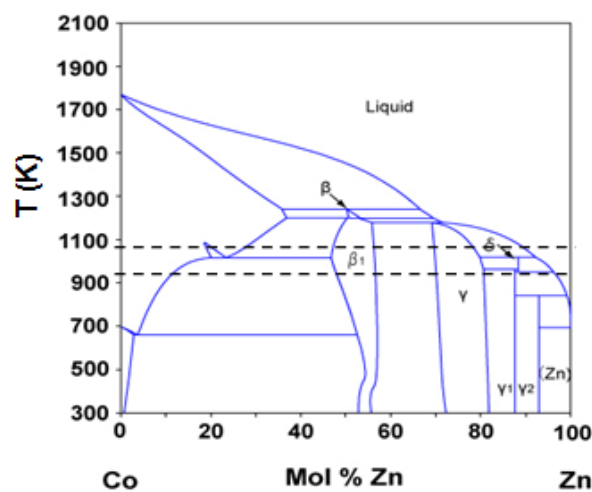


Figure 69: Zinc-Cobalt phase diagram (Reference to be added); the solubility of Co in Zn is between 5- to 10 mol. % (approximately) in the range of working temperature, which is sufficiently high for dissolving the metal binder.

Due to very low vapor pressure of zinc, it can be separated from the liquid (via evaporation) leading to Co precipitation on tungsten primary particles. This powder will be agglomerated via spray drying to be ready for subsequent sintering (Altuncu et al. 2013). Figure 68 shows the size/shape of cemented carbide powder from cutting tools scraps, and final granulated WC/Co powder. This method was developed by an American company, *Bureau of Mines*, which is now estimated to be the operating process in about 80 % of tungsten recovery plants worldwide (Jana et al. 1996).



Figure 70: Tungsten recovery from cemented carbide via ZMM (Altuncu et al. 2013).

ACIDIC DISSOLUTION

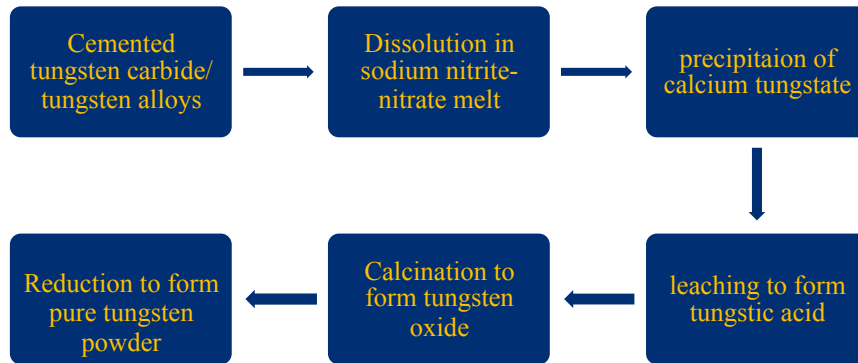
In the process, the Co matrix is dissolved in nitric acid, phosphoric acid and hydrochloric acid media. As a result, the WC particles may be separately obtained (Fruchter and Moscovici 1996).

5.3 Full Recovery of tungsten (to its pure/element form)

There is sometimes an interest to recycle tungsten in its pure form. The ZMM, however, cannot produce pure tungsten, but resulting in dissembled WC particles covered by a thin layer of Co. The general scheme of the processes developed for complete recovery of tungsten (into its pure form) is the same as that for tungsten ore concentrates; therefore, tungsten producing sites can replace their feedstocks with these secondary tungsten reserves (tungsten-bearing scraps). Note that scraps made of both cemented carbides and tungsten alloys can be recovered in such process. In all processes proposed for the complete recovery of tungsten, the main steps are quite similar; below they are briefly explained:

1. Disintegration of tungsten-containing scrap in a melt of sodium nitride, sodium nitrate or a mixture of them. The melt composition is adjusted based on tungsten content in the scrap.
2. Precipitation of crystalline calcium tungstate in lower temperatures (60- to 90 °C)
3. Formation of tungstic acid upon the reaction of hydrochloric acid and calcium tungstate
4. Calcination of tungstic acid into tungstic oxide
5. Reduction by hydrogen to produce pure tungsten powder

Flowchart 2: Tungsten recovery from tungsten containing scraps (Fruchter and Moscovici 1996); such processes can be used for the recovery of tungsten from both cemented tungsten carbide and tungsten containing alloys.



6. Summary

According to British Geological Survey (BGS) 2012 report, tungsten (together with rare earths) was ranked at the top of the list of commodities with the risk of supply (with the index of 9.5 out of 10). The reader is requested to distinguish the differences between the rare earths (such as Nb, La & etc.) and tungsten; the scale of world tungsten consumption is as large as 70'000 tons (of W) of which 70 to 80 wt. % are consumed in cemented carbides, high-speed steels (HSSs) and hard alloys. In fact, high tech technologies (such as for catalysts) which require tungsten with high (to ultra-high) purity are minors in the tungsten supply chain; they do not have strong weights in the market which are usually evaluated by APT and WO_3 prices. As a conclusion, the criticality of tungsten does not highly influence these high tech technologies, but the heavy industries are the main targets of the tungsten shortage.

Increasing demand on tungsten in industrialized countries together with the limited supply capacity of the current producers (due to the geopolitical reasons) led to instability in the world tungsten market in recent years. The only solution to control the market is increasing the total supply capacity to meet the growing demand. Basically, there are two approaches to realize this objective:

Increasing production: it can be realized either by *operating new mines* with the current production processes or by developing *new technologies* to make the use low grades ores economic. Since 2010, new mines have started in different countries such as Vietnam, Spain and Australia, which strongly influenced the tungsten market by partly filling the gap between supply and demand.

Recycling: since 2008, recovery of cemented carbides has found an important place in many tungsten production sites. The recovery of tungsten from cemented carbides is very straightforward so that any production sites can use them as their second feedstock instead of using primary concentrates (coming from ores). Given the fact that tungsten is feasible to be recovered from cemented carbides, HSSs and hard alloys (covering about 80% of the market), it seems that the current rate of recovery can be significantly increased: improving the recycling rate will at last partially meet the tungsten shortage in the market.

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