itia NEWSLETTER

INTERNATIONAL TUNGSTEN INDUSTRY ASSOCIATION

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10th International Tungsten Symposium and 18th Annual General Meeting

The Chinese character for tungsten.

At the time of the Annual General Meeting in September 2004, the Metal Bulletin quotation for APT in Europe was US$90 per mtu; by September 2005, the quotation had risen by 266% to US$240. So given the strength of the tungsten market after so many years of weakness, it was not surprising that 230 delegates came to Changsha for the 10th International Tungsten Symposium organised by the ITIA. Or perhaps it was the allure of the hotel (the Dolton Resort Tongshenghu) which charmingly described itself as "the Hawaii in the East" and "the ideal paradise of fantasy for taking holiday and seeking amusements".

Our hosts were Zhuzhou Cemented Carbide Group Corp and China Minmetals Corp and their generous hospitality was greatly appreciated. Thanks are also due to the China Tungsten Industry Association as a co-organiser and to Hunan Non-Ferrous Metals (Holding) Group Corp for their supporting role.

Delegates were welcomed by Mr He Tong Xin, Vice-Governor of the People's Government of Hunan Province and the ambitious theme of the Symposium "Evolution of the Tungsten Industry and the Major Challenges Ahead" ensured a variety of technical and market papers, given by famous names within the Tungsten industry, over two and a half days.

A list of papers and speakers is given on the ITIA's website and a CD is available at US$500.

The President of the China Tungsten Industry Association (and former ITIA President), Zhou Juqiu, with the girls from China Swan responsible for the smooth and successful management of the whole event.

NEW OFFICERS ELECTED

At the 18th Annual General Meeting, Zhu Guang (Senior Vice-President, China Minmetals Corp) was elected President of ITIA for 2006-2007 in succession to Robert Fillnow (Marketing Director, Osram Sylvania Products Inc) and Burghard Zeiler (Managing Director, Wolfram Bergbau-und Hütten GmbH) was elected Vice-President.

WEBSITE

The ITIA website has been extensively revised and restructured. View it on the same address – **www.itia. info**

MEMBERSHIP

Welcome to:

▼ **King Island Scheelite Ltd**, which has acquired the mine retention leases for the King Island Scheelite Mine in Tasmania.

The ITIA's Technical Consultancy continues its series on the many aspects of tungsten with a look at the growth of the tungsten tree......

THE HISTORY OF TUNGSTEN

Erik Lassner and Wolf-Dieter Schubert
Vienna University of Technology

PART II:

THE GROWTH OF THE TUNGSTEN TREE –EVOLUTION IN CHEMISTRY AND TECHNOLOGY

In 1944 K.C. Li, President of Wah Chang Corporation in the US, published a picture in the Engineering & Mining Journal entitled: "*40 Years Growth of the Tungsten Tree (1904 – 1944)*" illustrating the quick development of the various tungsten applications in the field of metallurgy and chemistry ***(Fig.1).***

To compare the evolution of a technology with the growth of a tree, and the respective presentation, is a unique idea, and in the following we want to describe and discuss the historical generation of the diverse branches of the tree starting from 1850 up to now. This 150 years time span does reveal a fascinating picture of scientific and technological evolution.

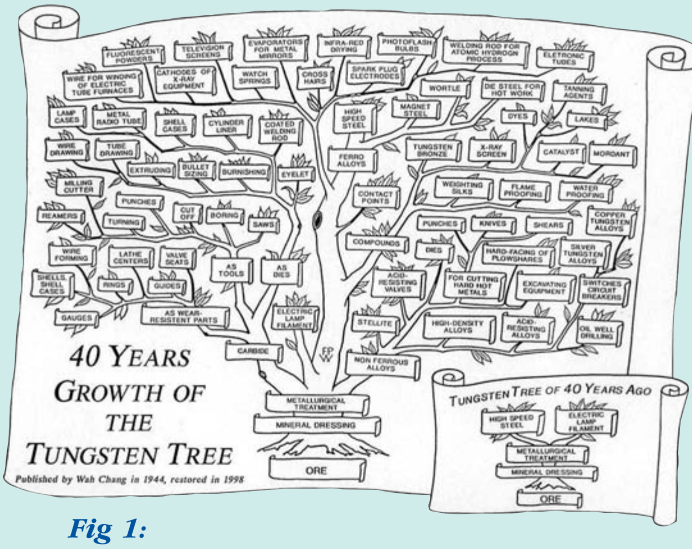


Fig 1:
This picture, published in 1944, illustrates the many applications of tungsten at that time. Four main branches were then developed; the steel branch being by far the thickest.

The branches are:

The steel branch - with a small side branch of super alloys (starting its development in 1855).

The filament branch - with mightier side branches of mill products (powder metallurgical produced tungsten and tungsten alloys) (starting its development in 1903).

The carbide branch - with a small side branch of Stellite alloys (starting its development around 1913).

The chemicals branch (starting with the patent of Robert Oxland in 1847).

THE STEEL BRANCH

- With a small Side Branch for Super Alloys

This branch was the first to grow on the tungsten tree in the middle of the 19th century. We call it today - together with its side branches – *Tungsten Applications in Melting Metallurgy.* The branch lost its supremacy gradually over time, especially with the growing market of hardmetals, but it has remained strong until today. About 20% of the total tungsten supply is used today in this field (but less than 10% in Europe, Japan, and the USA) and tungsten in steel is still the second biggest tungsten application.

WAR DEMANDS FOR STEEL

In 1855, the British engineer Henry Bessemer took out a patent for his process of rendering cast iron malleable by the introduction of air into the liquid metal to remove carbon. This process, called the *Bessemer Converter Process*, formed the breakthrough for cheap mass production of steel in Europe, and within a short time this new technology spread all over the world. In both Europe and America there was a large demand for steel in those days, triggered by the rapidly growing railway industry but also by the large number of conflicts which took place between different nations or parties. Gun barrels and cannons were made of steel, and high strength tools were now increasingly in demand to render mass production of these strategic products. Large enterprises were formed based on this ordnance business, such as the *Armstrong-Whitworth Company* in Britain, the *Schneider Company* in France and, last but not least, the *Krupp Company* in Germany.

THE FIRST TUNGSTEN STEELS

The cradle of tungsten-containing high strength steel, however, was in Austria. A mighty siderite (iron carbonate) deposit, located in northern Styria, called "Erzberg" (Ore Mountain in literal translation) had supplied iron ore already for centuries, and was the reason why numerous smaller and bigger ironworks had settled in the surroundings. In two of them, the first tungsten steels were produced on an industrial scale.

The Austrian iron-wholesale trader, commodity speculator and mine owner Josef Jacob can be regarded as a pioneer in "believing" in *tungsten* as an attractive and promising commodity. After having received confirmation that a tungsten mineral supply would be possible in sufficient quantities, he started his costly and demanding experiments to alloy iron with tungsten in 1855 together with **Franz Köller** at the *Reichraming Steel Works* ***(Fig.2)***. Tests of this steel were carried out in 1856 at the *Polytechnic Institute* in Vienna which demonstrated a very fine silky grain, good weldability, and a significantly increased tensile strength at moderate toughness. Different application tests were performed in machine shops in Austria, Germany and France, demonstrating the potential of "wolfram steel" for the manufacture of files, boring and turning tools.

All these attempts finally led to the granting of a patent, dated March 10th, 1858 ***(Fig.3)***. Under the direction of Jacob and Köller, experiments were extended to the ironworks at *Mutterhausen* and at the wolfram mines of *Puy-les-Vignes* (Dept. Haute Vienne), France.

At about the same time also **Franz Mayr** of Kapfenberg, Styria is credited with producing tungsten cast steels with good success on a commercial scale. These activities will later be taken over by the *Böhler* works, which today, together with the Swedish *Uddeholm* group, are among the largest special steel producers worldwide.

TEETHING PROBLEMS

In 1862, Josef Jacob had to accept that his speculations to control the tungsten raw material market for the growing tungsten industry had failed, and he went bankrupt.

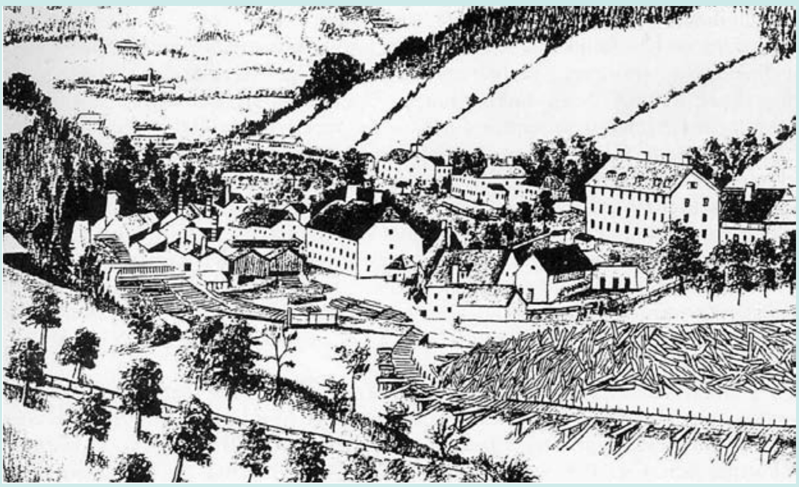
It is important to mention in this regard that the early experiences with tungsten steel were at first quite ambiguous, as the use of tungsten as an alloying element needed both an experienced steelmaker and a skilled metallurgist to overcome teething problems. Inexperience and the use of contaminated tungsten additives (still containing arsenic, phosphorous and sulfur stemming from the wolframite concentrate from which the additive was obtained) were frequently the reason for mistrust of the new steels which at first retarded their rapid overall distribution. Sometimes so-called *tungsten steels* did not contain any tungsten at all.

In addition, the price of tungsten metal still was very high and supply and demand of tungsten as a new commodity had not settled as there was no definite market.

ROBERT MUSHET SPECIAL STEEL

While early experimental research on tungsten steel was done in Austria, Germany and France, and these activities are more or less well documented in literature, the British steelmaker Robert Forester

Fig.2: *Drawing of Reichraming Ironworks as it appeared in the year 1880; the factory buildings are situated to the left. Tungsten steels were produced here for the first time in 1855; by courtesy of Dr. H.J. Köstler, Austria*



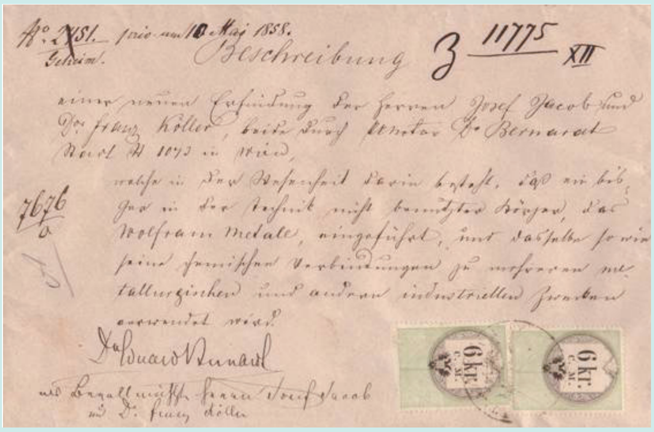


Fig.3:
Josef Jacob and Franz Köller patented the production of tungsten steel in 1858 (Tom.VII/fol. 76, No. 7676; grant of the patent: May 10th). According to this patent, tungsten was added to the steel melt either as tungsten powder (obtained from tungstic acid) or as wolfram metal which was produced by heating roasted or unroasted wolframite with charcoal in a closed crucible. The resulting loose mass consisted of metallic tungsten, charcoal, iron and manganese. Also the British engineer Robert Oxland took out a patent in 1858 (though this was partly a communication from Jacob and Köller).

Mushet (1811-1891; ***Fig.4***) was working in complete secrecy. According to Robert Hadfield (1858-1940), the famous British metallurgist and steelmaker, Robert Mushet also patented a number of methods of producing tungsten steels, but no patent numbers are quoted in his work [J.Iron & Steel Inst. 64 (1903) 14-118]. It is thus not clear whether or not these patents were granted at all, or whether he lost his patents because of lack of funding.

In 1868 Mushet had discovered that on addition of small amounts of tungsten to the steel melt a new steel quality for turning tools with remarkable properties was formed. Tools made from this steel required no water-quenching. The steel was self hardening in air. Harder metals could be cut at faster speed and the lifetime of the tools was prolonged by a factor of 5 to 6.

Soon it became known as *Robert Mushet`s Special Steel* (R.M.S.). The product was the first real tool steel and the forerunner of modern high speed steels. Its commercial production began in Sheffield after 1870.

The tungsten percentage in such steel was usually between 5 and 8%, the carbon percentage between 1.5 to 2%. In addition, it contained silicon (1.0-1.6%) and manganese (1.7-2.6%), which contributed to the self-hardening effect.

According to Hadfield one may say:
"*There is no doubt that Mushet did more than any others to perfect the production of tungsten steel for tools.*"

HIGH SPEED STEEL

A further milestone in the development of tungsten-containing steel took place in the USA. In the 1890s **Frederick Winslow Taylor** (1856-1915; ***Fig.5***) and **Maunsel White**, of Bethlehem Steel Works, Pennsylvania, experimented with Mushet-type tool steels. Qualities containing higher portions of chromium and tungsten as usual (up to 18%) were heat treated to cut through metal at even higher rates. Their subsequent development led to the introduction of High Speed Steel. This tool steel was first exhibited in 1900 at the World Exhibition in Paris, and astonishing results in speeds of cutting soft steel were practically demonstrated to the public. *High speed steels* revolutionized the engineering practice in the early 20th century and the "secrets" of heat treatment were rapidly uncovered by other steelmakers.

Taylor-and White-type steels are still used today in practically every machine shop of the world.

STEELMAKING AND ALLOYING PRACTICE

Tungsten steel like other special steels in the beginning was exclusively produced in crucibles. However, after 1900 the crucible was increasingly superseded by Siemens Martin or electric furnaces. For many years the addition of tungsten used in the production of self-hardening steel was by the oxide or by means of a metallic powder. This was a rather expensive process. As a direct consequence, therefore, tungsten steel had been quite costly. For example, Mushet's Special Steel was sold rather by the pound than by the ton.

Already the early pioneers, like Oxland, Köller and Mushet had experimented in preparing alloys of tungsten and iron but had failed obviously because of introducing detrimental impurities. This lasted until 1893 when *Ferrotungsten* was introduced to the market by the *Biermann Works* in Hannover (Germany) as a considerably cheaper commodity. This could be produced directly from the ore concentrate in electric furnaces and was therefore much cheaper than tungsten powder. Due to the lower melting point, its dissolution in the steel melt was much faster.

Finally, in 1940 a second tungsten master alloy, called Melting Base, was offered on the market. It was produced from tungsten scrap material.

Fig. 4:
Robert Forester Mushet (1811-1891); the father of modern tool steel. He not only invented self-hardening steel but significantly contributed to the success of the Bessemer Converter Process.
He has been an outstanding steelmaker and a pioneering metallurgist.

Copyright: Sheffield Industrial Museums Trust.

TUNGSTEN AS A WAR METAL

Although the use of tungsten for high strength steels was well known at the beginning of the 20th century, and considerable contributions were made by both British and US steelmakers, most of the tungsten used for steel was processed in Germany and Austria. There, tungsten metal was considered early as a strategic material, and large amounts of tungsten were used for the ordnance industry. It was used for tool steels, armour plates, cannons, shells and - in large amounts - for gun barrels. For example, the whole Austrian-Hungarian army was equipped with tungsten-bearing *Böhler* steel to the end of World War I, and about a third of the German army by the respective *Krupp* steels.

In this regard it is worth mentioning the commentary given by K.C. Li in the Foreword of his book on TUNGSTEN, published in 1947:

"*Before 1914 it was the belief of some Allied military experts that in six months Germany would be exhausted of ammunition. The Allies soon discovered that Germany was increasing her manufacture of munitions and for a time had exceeded the output of the Allies. The change was in part due to her use of tungsten high-speed steel and tungsten cutting tools. To the bitter amazement of the British, the tungsten so used, it was later discovered, came largely from their Cornish Mines in Cornwall*".

Fig. 5:
Frederick Winslow Taylor (1856-1915).
The founder of High Speed Steel together with Maunsel White;
he is also known as the originator of scientific management in business.

http://en.wikipedia.org/wiki/Frederick_Winslow_Taylor.

SUPER ALLOYS – A SMALL SIDE BRANCH

Super alloys are complex materials, initially on the basis of Iron, but later on Nickel and Cobalt, and may contain up to an additional 20 elements. Their development started in 1940, but the introduction of tungsten begun somewhere in the 1950ies. The tungsten content ranges between 1% and 25%.

The main driving force for super alloy development was and still is today jet propulsion (turbine blades) with the intention to increase the working temperature for improving the fuel efficiency. Tungsten accounts for solid solution strengthening, strengthening by intermetallic compound formation, and formation of carbides.

THE FILAMENT BRANCH

With mighty Side Branches of Mill Products (powder metallurgical produced tungsten and tungsten alloys)

This branch was the second one sprouting from the tungsten tree in 1903. It was the first application of tungsten as an element (metal) making use of its extremely high melting point and its electrical conductivity. Tungsten filaments since then illuminate the world and have revolutionized artificial lighting in general. The branch lost its importance later in the century by partial substitution of light bulbs by more efficient light sources. Nevertheless, still today incandescent lamps are produced by the billions. Every year, about 20 billion meters of lamp wire are drawn, a length which corresponds to about 50 times the earth-moon distance. Lighting consumes today between 4% and 5% of the total tungsten production.

In addition, this branch formed the origin of a much bigger side branch in regard to tungsten consumption – the ductile tungsten metallurgy.

THE AGE OF ELECTRIC LIGHTING

By the second half of the 19th century the carbon filament lamp boosted electric lighting. This type of lamp was not quite satisfactory, because lifetime was short and the efficacy low. Therefore, at the beginning of the 20th century the search started for a more satisfactory filament material than carbon. A strong but fruitful competition arose between the US and several European companies, offering diverse lamps with metal filaments like osmium, tantalum, and, finally, tungsten.

THE FIRST TUNGSTEN LIGHT BULBS

In 1902/1903 Alexander Just and Franz Hanaman, laboratory assistants to the Professor of Chemistry at the Technical High School of Vienna, developed a commercial process in which a very fine-grained tungsten powder was mixed with a solution of sugar and gum. The past was then extruded through diamond dies, wound into wire loops or coils, cut into "hairpins" and then heated to a red heat in a suitable atmosphere to remove the binder. Each "hairpin" was then mounted in clips, and raised to bright incandescence by the passage of an electric current in a hydrogen atmosphere. At the highest temperature the fine tungsten particles sintered together and formed a solid metallic filament. These filaments, although elastic, were quite brittle; but could be formed to shape at a red heat [*Smithells*/1945].

A patent was granted in 1904 (British Patent 23,899) and the rights were bought by the German *Auer-Gesellschaft* (later: *OSRAM Werke GmbH*).

From about 1906 the majority of tungsten filaments used in light bulbs was based on this "squirting" process ***(Fig.6; Fig.7)***, although a large number of alternatives were established within the research labs of the lighting companies. Well-known names are related to this early, pioneering time of tungsten light bulbs, such as **Emil Rathenau**, **Werner von Siemens**, **Auer von Welsbach**, **Hans Kuzel, Fritz Blau**, **Hermann Remané**, **Werner Bolton**, and, of course, last but not least, **William David Coolidge**. At this time also patent licence agreements were made between the German *Auer Gesellschaft* and the *General Electric Company* in the US.

Brand names were applied for, such as *OSRAM* (made up of Osmium and Wolfram), *WOTAN* (composed of Wolfram and Tantalum), *TUNGSRAM* (composed of Tungsten and Wolfram) and *MAZDA* (after the Persian god of light).

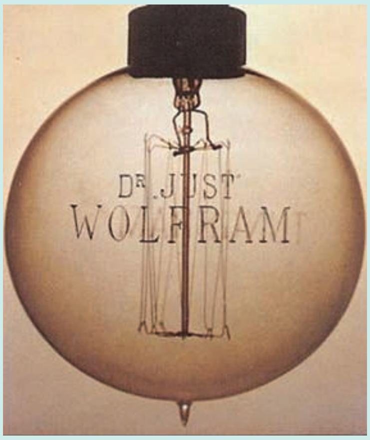


Fig.6:
Dr. Just "WOLFRAM" lamp; Alexander Just and Franz Hanaman patented their manufacturing of "squirted" tungsten filaments in 1904 (BP: No. 23,899). Up to 1911, most light bulbs in Europe and the USA were equipped with such filaments. The lamps produced significantly more light than the carbon filament lamps, with about a third of the energy required;

(photo by courtesy of Dr. Peter Schade; Osram Schwabmünchen)

Fig. 7:
Early advertisement poster promoting tungsten light bulbs, equipped with "squirted" tungsten filaments produced by Alexander Just

(by courtesy of OSRAM Munich)

DRAWN TUNGSTEN WIRE

Up to now, any attempts to draw tungsten into ductile wires had failed because of the brittleness of tungsten metal at moderate temperatures. The big breakthrough took place in 1909, when **William Coolidge** (1873-1975; ***Fig.8***) and his team of the *General Electric Company* in the US were successful in producing ductile tungsten filaments by suitable heat treatment and mechanical working (British Patent: 23,499/1909). The method since then is called the *Coolidge Process* for making tungsten ductile, and the main features of the process are still valid for today's technology.

The most unexpected result was that on working (swaging) sintered tungsten bars down to smaller and smaller sizes they became increasingly ductile. At low diameters the wire could even be diamond wire-drawn at moderate temperature.
In Coolidge's lab note book entry for July 16, 1909 one may find [*Briant*/1995]:

"*swaged tungsten (3/8" square) down to 128 mils; then to 78 mils; then to 53.5 mils – then bent it cold*"

When on a visit to Berlin in 1909 William Coolidge demonstrated his ductile tungsten wire in the form of a small spool to **Fritz Blau**, technical director of *AEG* (one of the largest tungsten lamp producers in Germany at that time), who had also been investigating the problem of brittleness. He at first was confronted with disbelief which was followed by enthusiasm [*Gurland/1996*]:

"*I (Coolidge) remember this circumstance very well because of the excitement and surprise and incredulity which he (Blau) manifested at the time. He asked me over and over again what it was. I told him that it was pure tungsten wire, only to have his question repeated again and again.*"

Commercializing the ductile wire process started in 1911 ***(Fig.9)*** and rapid further development work was carried out in close cooperation between the *General Electric Company* and the German Lighting Industry. Within a short time tungsten light bulbs spread all over the world equipped with ductile tungsten wires. Today, the ability to handle tungsten wires and coil filaments without breakages is the backbone of the incandescent lamp industry [*Briant/1995*].

It is fascinating in this regard to read that already in such pioneering times more than 100,000 light bulbs were manufactured per day in Berlin/Germany.

Also in Japan tungsten light bulbs were produced already in 1911 by Tokyo Electric (later Toshiba) with the brand name MAZUDA ***(Fig.10).***

Fig.9:
This ad from the 1917 Popular Science magazine explains the Mazda "mission":
NOT THE NAME OF A THING, BUT THE MARK OF A SERVICE
The brand name Mazda refers to the newly introduced tungsten filament lamp and was used in the USA by both General Electric and Westinghouse. Mazda lamps produced before May 1911 utilized sintered tungsten filaments; whereas later drawn tungsten filaments were used.

By courtesy of Mr. Istvan Meszaros, General Electric Company, Hungary.

Fig.10:
Tungsten light bulbs were produced by Tokyo Electric in 1911 with the brand name MAZUDA – a result of a close collaboration with General Electric;

by courtesy of Mr. Satoshi Yamaguchi, Toshiba.

DUCTILE TUNGSTEN
- Today an even bigger Side Branch

The Coolidge process was not only an important invention for ductile tungsten filaments, but can be regarded as the birth of tungsten powder metallurgy in general, and for the production of ductile tungsten products, such as rods, wire, sheet, etc., in particular. The development of this side branch started shortly after Coolidge's invention around 1915. In regard to tungsten consumption, this branch is today much bigger than the mother branch, i.e. the filament branch. The direct sintering process, today used only in filament production, was replaced later by indirect sintering, at first in ceramic-lined muffle furnaces but since the 1960ies these have been substituted by ceramic-free furnaces which render working temperatures beyond 2000°C.

Fig. 8:
William David Coolidge (1873-1975)
The originator of ductile tungsten and modern powder metallurgy.
Coolidge's ductile tungsten formed the basics for many more discoveries; for example: the Coolidge X-ray tube.

By courtesy of Mr. Istvan Meszaros, General Electric Company, Hungary.

TUNGSTEN ALLOYS
- Produced by Powder Metallurgy

This is a side branch of the above branch which started its sprouting about 1935 with the production of the first *Heavy Metal Alloys.* Initially, these alloys, based on tungsten with additions of iron, nickel, cobalt or copper were developed to provide high-density materials with excellent machining properties. Later, however, the requirements were significantly increased due to new, demanding applications, in particular in the field of the ordnance industry (high kinetic energy penetrators).

W-ThO₂ followed in 1953, W-Re in 1956; only to name the most prominent alloys. In all cases a more or less intensive research took place in order to improve qualities, to vary properties or to adjust them to special applications. In some fields respective efforts are still going on today.

THE CARBIDE BRANCH

- With a small Side Branch of Stellite

The hardmetal industry originated with the discovery of high speed steels and *Stellite* (see below) for the machining market, on the one side, but has been closely related as well to the growing electric lamp industry from its very beginning. It was the search for a replacement of expensive diamond dies used in the wire drawing of tungsten filaments which finally rendered the breakthrough. Initiated by a shortage of industrial diamonds at the beginning of World War I, in Germany researchers had to look for alternatives. Earlier work on tungsten carbide by the Frenchman **Henri Moissan** (a Nobel Prize winner in chemistry in 1906) was recalled, who had described the hardness of tungsten carbide close to that of diamond.

CAST AND SINTERED WC/W_2C

In 1914 cast tungsten carbide parts were made by **Voigtländer** and **Lohmann** of *Metall-Fabrikations GmbH*, in Essen, Germany (German Patent No. 286,184). The material was called Lohmanite and contained about 4% C. It was of eutectic microstructure (consisting of WC and W_2C), very hard but brittle. However, it was used to some extent for drawing dies. Later in 1914 a further patent was granted to Voigtländer and Lohmann on sintered carbides (German Patent No. 289,066), but again the material was too brittle. Several other but similar materials followed on the market, such as *Thoran, Miramant, Wallramit, Volumit, Tizit* or *Elmarid*. Some were employed in drawing dies or other tools [*C. Agte/1963*].

In 1919, the three major German lamp producers, *DGA* (Deutsche Gasglühlicht Aktienfesellschaft), *Siemens and Halske* and AEG (Allgemeine Elektrizitäts Gesellschaft) consolidated into the *OSRAM Werke GmbH*. As a result their research departments were amalgamated into the *OSRAM study group*, with **Franz Skaupy** acting as head in Berlin. Each of the three companies and their research departments already had experiences in the respective fields of tungsten chemistry and metallurgy; thus together they represented a mighty team to solve the task to manufacture improved and cheap drawing dies for tungsten filament production

A NEW MATERIAL IS BORN

At first further melting experiments were performed, which failed as did sintering experiments with fine-grained WC powder. Also carburization of sintered tungsten compacts did not end up in useful materials. Finally, the first breakthrough was achieved by Heinrich Baumhauer through infiltrating a porous WC body with molten iron. Interestingly, this development was not performed at the laboratories of the study group, but at the production works of the former Siemens lamp works in Berlin-Charlottenburg [*Kolaska*/1992]. Baumhauer applied for a patent on March 18, 1922 (German Patent No. 443,911).

The research of Baumhauer stimulated further efforts in the study group. Karl Schröter, chief engineer at the *OSRAM study group* improved the tungsten carburization. In a further step WC powder was mixed with iron, nickel or cobalt powder, then compacted and sintered. Based on these experiments a patent was submitted on March 30, 1923 which was granted on Oct. 30, 1925 ***(Fig.11)***; German Patent No. 420,689). Karl Schröter is stated as the only

DEUTSCHES REICH

AUSGEGEBEN AM 30. OKTOBER 1925

REICHSPATENTAMT

PATENTSCHRIFT

— № 420689 —

KLASSE 40b GRUPPE 1

(P 46003 VI/40b)

Patent-Treuhand-Gesellschaft für elektrische Glühlampen m. b. H. in Berlin*).

Gesinterte harte Metallegierung und Verfahren zu ihrer Herstellung.

Patentiert im Deutschen Reiche vom 30. März 1923 ab.

Die Erfindung betrifft eine gesinterte harte Metallegierung aus Wolframcarbid, die sich zur Herstellung von Werkzeugen und Arbeitsgeräten aller Art, insbesondere Ziehsteinen, eignet und die sich von bekannten Legierungen vornehmlich dadurch unterscheidet, daß sie aus einem Wolframcarbid mit etwa 3 bis 7 Prozent Kohlenstoffgehalt und einem zusätzlichen Hilfsmetall von wesentlich niedrigerem Schmelzpunkt, wie etwa Eisen, Kobalt oder Nickel, in Mengen bis höchstens 10 Prozent besteht. Das Wolframmetall bildet somit den überwiegenden Bestandteil, mindestens 80 Prozent der Gesamtmenge der Legierung. Die neue Legierung hat eine durchaus genügende Härte, zeichnet sich jedoch außerdem zufolge guter, gleichmäßiger Verteilung der einzelnen Bestandteile durch außerordentliche Festigkeit aus.

Zur Herstellung der neuen Legierung wird zweckmäßig pulverförmiges, 3 bis 10 Prozent Kohlenstoffgehalt aufweisendes Wolframcarbid gemeinsam mit dem fein verteilten, in den angegebenen Grenzen gehaltenen Hilfsmetall zu Körpern gepreßt und bis zur Sinterung erhitzt. Durch den Zusatz des erwähnten Hilfsmetalls wird der Sinterungspunkt des pulverförmigen Wolframcarbides derart erniedrigt, daß die Sinterung zu festen, sehr widerstandsfähigen Körpern bei Temperaturen eintritt, die etwa 1000° unterhalb des Schmelzpunktes des reinen Carbides liegen. Die Durchführung des Herstellungsverfahrens gestaltet sich dadurch wesentlich einfacher, leichter und auch billiger als die meist übliche Herstellung, bei der die etwa 2500° betragende hohe Schmelztemperatur des Wolframcarbides erreicht werden muß. Auch gibt die an sich bekannte Herstellung durch Pressen und Sintern die Möglichkeit, dem hergestellten Körper jegliche beliebige, beim Schmelzen oft nur schwierig zu erreichende Formen zu geben.

Als Ausgangsmaterial zur Herstellung der neuen Legierung kann Wolframcarbidpulver dienen, das entweder in bekannter Weise durch Karburierung von Wolframpulver aus der Gasphase oder durch Mischen und Hocherhitzen von Wolframpulver mit Kohlenstoff, z. B. Ruß, Zuckerkohle, Graphit o. dgl., erzeugt ist. Als besonders günstig hat sich ein Kohlenstoffgehalt von etwa 7 Prozent erwiesen, jedoch kann der Kohlenstoffgehalt auch kleiner sein und zwischen 3 und 7 Prozent schwanken.

Der Kohlenstoffgehalt kann aber auch selbst etwas größer sein, also etwa bis 10 Prozent betragen, denn ein geringer Überschuß des Kohlenstoffgehaltes bei der Herstellung der Legierung ist praktisch ohne Belang, da dieser Überschuß beim Sinterungsprozeß größtenteils fortgeht und die Legierung sich beim

*) *Von dem Patentsucher ist als der Erfinder angegeben worden:*

Karl Schröter in Berlin-Lichtenberg.

Fig.11:

First patent on sintered hardmetal. Karl Schröter is stated as the only inventor. However, the credit belongs to the whole OSRAM study group.

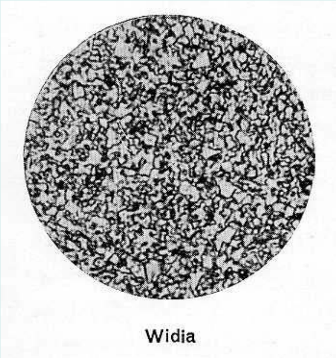


Fig. 12:
WIDIA (i.e. hardmetal) has revolutionized the machining industry. This microstructure refers to an early Widia-N grade (WC-6Co). Magnification: 500 times (source: Widia-Handbuch 1936).

inventor, but he has never let anyone doubt that the success was a result of the combined efforts of the whole *OSRAM study group* ("*No Child of Chance*"/*Gurland/1995*).

Field tests were made in 1923 in the shops of *OSRAM* and diamond dies were quickly replaced down to 0.3 mm.

THE AGE OF HARDMETALS

Several similar patents followed by the study group which were applied for only in Germany, Great Britain, and the US. The patent rights were bought at the end of 1925 by the *Friedrich Krupp Aktiengesellschaft* in Essen/Germany, which had recognized the high potential of this new class of materials for the machining (and later also for the ordnance) industry. However, patents were acquired also by *General Electric* in the US (then forming a subsidiary: *Carboloy*) and sublicenses were given to F*irth Stirling, Allegheny, Fansteel* and others.

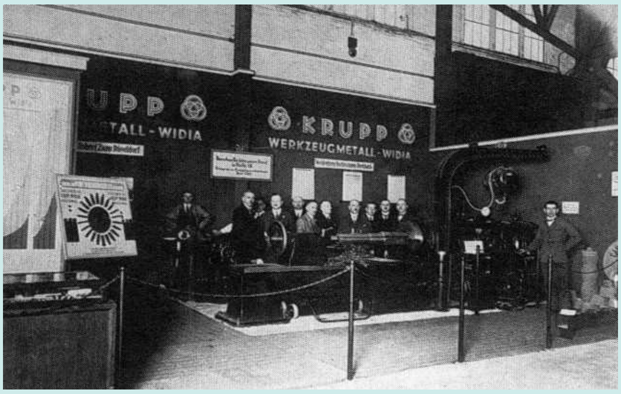


Fig. 13:
Presentation of WIDIA at the 1927 Leipzig Fair. By courtesy of Krupp archives.

On June 10, 1926 the name WIDIA was entered into the register of trademarks (referring to the German words *Wie Diamant* – i.e: *Like Diamond*) and an arduous work started to transform lab scale experiments into industrial production [*Kolaska/1992*]. The first product (Widia N – WC-6Co – ***Fig. 12***) was presented at the Leipzig Spring Fair in 1927, where a marvelling group of international engineers followed the machining of high-strength manganese steel ***(Fig. 13).***

AGAIN A WAR METAL

At first only small amounts of WIDIA were produced at the Krupp works ***(Fig. 14)***, and even less in the rest of the world. Still the price of the material was extremely high. However, the increasing demand for steel and tools in Germany at the beginning of the thirties rapidly increased the sales from about 12 t per year to 500 t at the end of World War II [*Aronsson/2005*] ***(Fig. 15)***.

These data clearly demonstrate the importance of the new material for the German industry prior to and during war time. In this regard it is again interesting to read K.C. Li's commentary in his book on TUNGSTEN:

During World War II, the Germans were the first to use tungsten carbide core in high velocity armour piercing projectiles. It was these tungsten projectiles, more than Rommel, that almost made German's North African campaign a success. The famous British tanks virtually "melted" when hit by these tungsten carbide projectiles.

Nevertheless, in particular after World War II, hardmetals became an international commodity and rapid advancements occurred in both science and technology. Today the product hardmetal has reached a very high technical standard and is produced by almost all industrial countries in more than 200 production units worldwide [Kolaska/1992]. Their application is extremely widespread and includes metal cutting, machining of wood, plastics, composites, and soft ceramics, chipless forming (hot and cold), mining, construction, rock drilling, structural parts, wear parts and military components.

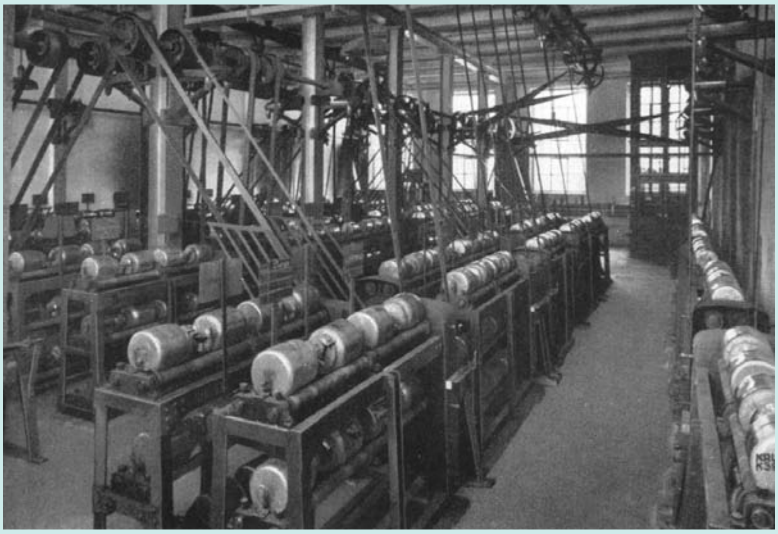


Fig. 14:

Production facility at Widia/Essen in the early thirties. Note the small ball mills used in early manufacturing. Hardmetals were produced in the range of 50 kg per day.

Source: Widia-Handbuch 1936.

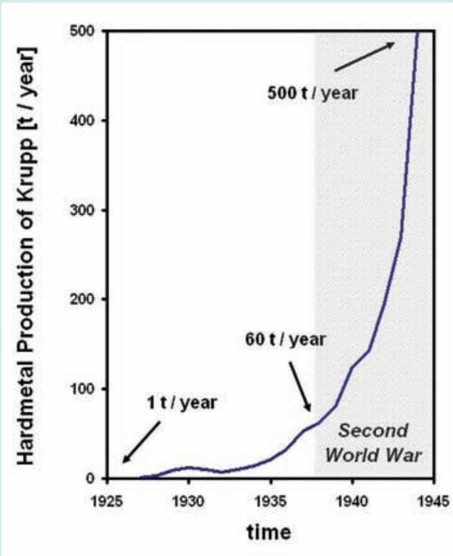


Fig. 15:

Production of WIDIA in Germany during the years 1926 and 1944.

By courtesy of: Prof. Aronsson, Sweden [The Origin and Growth of Cemented Carbide].

STELLITE

- A small Side Branch

The name *Stellite* is closely related to its inventor, a man of outstanding gifts: Elwood Haynes. Born in 1857 he developed his interest in metallurgy already at college, where his senior thesis was devoted to "*The effect of tungsten upon Iron and Steel*".
During this period he had already prepared a series of high strength tungsten steels, independently of the work of Taylor and White, which was patented significantly later.

In 1894 Haynes invented one of the first gasoline-powered automobiles in the US ***(Fig.16)*** and created a corporation to build cars until 1902.However, his main interest still was in metallurgy. In 1905 he started experiments with nickel, chromium and cobalt, hoping to find an alloy suitable for "*electric contacts in the make-and-break spark mechanism*" of his automobile [*Gray/1979*]. He obtained patents on alloys based on cobalt-chromium and cobalt-nickel, which he called *Stellite*, because of their bright and nontarnishing surfaces. In 1912 he extended his experiments to additions of tungsten. On testing these alloys in lathes at the *Haynes Automobile Company* the results were striking. Operators were able to turn out a normal day's work by midafternoon, approximately a 50 percent increase in efficiency [*Gray/1979*]. A patent was granted in 1913 (US Patent No. 1,057,423/1913), and at that time all steel tools in the automobile plant were already replaced with *Stellite*.

Stellite can be regarded to a certain extent as cast "forerunner" material to today's sintered hardmetals. It was the first time that cobalt came into play for a tool material instead of iron and this might have animated the related research.

Modern *Stellite* contains besides cobalt, chromium, tungsten and carbon also other elements like Mo, Ni, and Fe. The tungsten content varies between 4% and 19%. *Stellite* has completely lost its importance as a cutting material due to modern hardmetals and is used today for hard facing, wear parts, and corrosion resistant parts.

THE CHEMICALS BRANCH

Since the dawn of tungsten chemistry to the end of the 18th century and the beginning of the 19th century colored tungsten compounds have attracted people. The first to mention the beauty of the yellow tungsten oxide, **Rudolf Erich Raspe** (1737-1794) had already proposed to use it as artists´ colour. Later, **Friedrich Wöhler** (1800-1882) examined the group of colourful tungsten bronzes. By the end of the 19th century tungsten salts were used to make coloured cotton fast or washable and to make clothes used for theatrical and other purposes noninflammable. The tungstate of calcium and other metals were applied in preparing screens for X-ray work and tungsten sulfides found a limited use in the lubricant industry.

In the 1930's, new applications arose for tungsten compounds in the oil industry for the hydrotreating of crude oils, in particular for desulfurizing, and in the sixties new catalysts were born containing tungsten compounds to treat exhaust gases.

However, during all these years, the amount of tungsten used for manifold chemical applications was always small in comparison to steel, mill products or hardmetals. Beyond that, in many applications tungsten compounds were substituted by other materials and only small amounts are still used today in the form of tungsten oxides, tungstates, tungstic acid, silicotungstic acid, phosphotungstic acid or tungsten sulfides for the paint, enamel, rubber, wax, plastic, textile, paper and oil industry.

FINAL CONSIDERATIONS

PEOPLE WRITE HISTORY

The history of a chemical element – like tungsten – is linked to a series of people, their fascinating personalities, talents and pioneering insights at the time of their advancements. It is a story of scientists (Agricola, Lehmann, Scheele, Bergmann, de Elhuyar, Köller) and technologists (Raspe, Oxland, Jacob, Mushet, Taylor, White, Just, Coolidge), and a story of the respective times. It is also the story of tedious and competitive work within research groups to finally render the breakthrough of materials which were thought about at first in the heads of individuals in their offices or labs.

However, to write an article on the history never can cover the whole "truth", because some might have contributed significantly but were not given due credit.

THE PLANT: *TUNGSTEN*

More than 150 years have gone since the tungsten tree was planted. Since then, it has further grown and has now reached a peculiar form, which is dominated by an increasingly thick bole (hardmetals) with two main branches (steel and mill products). The chemicals branch seems somehow atrophied but still has a large number of small leaves. Due to the unique properties of tungsten we can assume that also in future a steady further growth will occur, given the appropriate market opportunities.

Fig. 16:
Elwood Haynes, the father of Stellite, in his first car in 1894.
Credit: The Elwood Haynes Museum Archives, Indiana.

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ACKNOWLEDGEMENTS:

The authors appreciate the help of the following colleagues and institutions:
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