itia NEWSLETTER

INTERNATIONAL TUNGSTEN INDUSTRY ASSOCIATION

Rue Père Eudore Devroye 245, 1150 Brussels, Belgium Tel: +32 2 770 E-mail: info@itia.info Web: www.itia.info

Tel: +32 2 770 8878 Fax: + 32 2 770 8898 Web: www.itia.info

21st Annual General Meeting, Xiamen,

22-26 September 2008

Xiamen Tungsten Company Ltd, which hosted this conference in the (highly recommended) Sheraton Hotel, was founded in 1997 following the reorganisation of the former Xiamen Tungsten Products Plant. Welcoming 280 delegates - a record since the first Tungsten Symposium in Stockholm in 1979 - and noting that Xiamen meant "a gate of China", Burghard Zeiler began his opening address by warmly expressing the thanks of all present to Mr Liu Tonggao and Mr Zhuang Zhigang, Chairman and President respectively of Xiamen Tungsten Company, for their generous hospitality in hosting the meeting and for inviting delegates to visit the Xinghuokeng Tungsten Mine; and

to Mr Chen Qifang, Chairmen of Chaozhou Xianglu Tungsten, for arranging a tour of the company's plant at Chaozhou.

Zeiler, who was presiding over his last meeting after serving three years during an exceptionally busy and progressive time in ITIA's development, reported that ITIA and IMOA were setting up separate Secretariats in 2009. He noted that the break with IMOA was long overdue as the work programmes of the two trade associations, whose joint membership totalled 132 companies and whose budgets had each multiplied fourteen-fold, could not be run with the same staff of two persons despite the use of external consultants. It had been an excellent relationship which would not end totally as IMOA would let office space to ITIA in the same building in London.

Reverting to ITIA's work programme, Zeiler believed that ITIA could be proud of the initiative it had taken to set up the Tungsten Consortium and the industry had been very fortunate that five companies had been prepared to join together to underwrite the Consortium, enabling it to get on with its work irrespective of subsequent membership. But, important as were

New President and Vice-President of ITIA

Elected at the AGM, Jesper Gullberg, Lead Buyer Raw Materials, Sandvik Tooling, succeeded Burghard Zeiler as President of the Association for the next two years and Stephen Leaby, Chairman and CEO of North American Tungsten Corp, became Vice-President.

Elections to the Executive Committee

- ▼ *Robert Bunting*, CEO, Beralt Tin and Wolfram (Portugal) SA,
- **▼** *Thomas Eizenhöfer*, General Manager of Business Unit, HC Starck GmbH,
- ▼ *Wang Lixin*, President, China Minmetals Non-Ferrous Metals Co Ltd

REACH and HSE, the education of this and future generations about tungsten must, in his view, be a crucial part of ITIA's endeavours.

Articles in the Newsletters which taught even those already in the industry about tungsten, let alone those with enquiring minds; the development of the website; and updating of the brochure "Tungsten" were key functions of this exercise, useful to all ages and experts and non-experts alike.

Zeiler concluded by thanking his colleagues on the Executive Committee for their devotion to ITIA's activities; to the HSE Committee for managing an onerous work programme so efficiently; to the Technical Consultancy for their stimulating contributions; and to all members for their support as evidenced by the presence of representatives from 51 out of 61 member companies.



XTC Chairman, Liu Tonggao (centre) and President, Zhuang Zhigang (right), with the ITIA Secretary-General

Our happy faces reflected the mood at that time before doom and gloom descended.

Below: Chen Qifeng, Chairman of Chaozbou Xianglu (right) with Thomas Eizenhöfer, General Manager (Business Unit) of HC Starck GmbH (left) and Shin Un-Jic, Industrial Products Director, TaeguTec Ltd (centre)



TUNGSTEN IN STEEL

Wolf-Dieter Schubert, Erik Lassner and Herbert Danninger Institute of Chemical Technologies and Analytics — Vienna University of Technology

1. INTRODUCTION

Tungsten first found its unique place in technical applications in the mid-19th century, mainly in steel production, and until the first quarter of the 20th century, its importance in this field steadily increased, with the steel industry then the largest tungsten consumer. Tungsten was among the very first alloying elements systematically studied and used to improve steel properties, for example hardness, cutting efficiency and cutting speeds of tool steels. Different tungsten containing steels were developed in Austria, Germany, France and England followed by high speed steels in the USA. Pioneers in the field of tungsten applications in steelmaking were Franz Köller, Franz Mayr, Robert Mushet, Sir Robert Hadfield, as well as Frederick Winslow Taylor and Mansel White. Further historical details can be found in our article in the December 2005 issue of the ITIA Newsletter.

The development of high speed steels (HSS) is illustrated by *Table 1*, indicating that tungsten played the leading part from the very beginning.

Today, tungsten is used as an alloying element in steels for the following steel grades [2,5,6]:

- High speed steels (HSS) in general terminology they are often simply called *tungsten steels* this steel consumes most of the tungsten used in steelmaking
- Hot work tool steels
- Cold work tool steels
- Plastic mould tool steels
- Heat and creep resistant steels
- Corrosion resistant stainless steels and valve steels

Table 1: Early history of high speed steels [1-4].

year	C	Cr	W	Мо	V	Si/Mn	Co	remarks
1868	1.5-2.4	0.5	5.0-8.0	-	1	~1.0/2.0	-	Mushet; first "self-hardening" steel
1886	2.0	12.0	×			×		Brustlein; J.Iron Steel Inst. 1886
1898	1.8	3.8	8.0	-	ı		-	Taylor-Wight ("overheated")
1905	0.25-2.0	1-7.0	4-30.0	2-15.0 alt. to W	0.1-1.0			Mathews US 779,171
1906	0.68	5.95	17.81	-	0.32			Taylor-Wight
1910	0.8	4.0	18.0	-	1.0		-	McKenna
1912	0.8	4.0	18.0	-	1.0		5.0	addition of Co
1923	0.8	4.0	18.0	-	1.0		12.0	dudition of Co
1939	1.4	4.0	18.0	-	2.0-5.0		-	high C, high V
1940	×	×	-	9.0	×		×	W ronlaced fully or partially by Mo
1740	×	×	6.0	5.0	2.0		-	W replaced fully or partially by Mo

The addition of tungsten to structural steels has decreased since 1940 because alloying with Mo and Cr as well as with V and Ni yielded better performance at lower cost. Important applications of those steel types have been outlet valves in combustion engines, crankshafts, rifle barrels etc.

From 1927, when cemented carbides (hardmetals) were developed, the proportion of total tungsten consumption used in steelmaking declined constantly to a current figure of about 20%, but nevertheless this means that steel is today still the second biggest consumer after hardmetals. This percentage is the average for entire global demand. Regarding regional markets the tungsten consumption of steel differs considerably, from 2 % in the USA to about 10 % in Europe and Japan and to about 30 % in Russia and China

2. WHAT IS THE EFFECT OF TUNGSTEN IN STEEL

When added to steel, tungsten forms tungsten carbides or complex carbides with other carbide forming elements, such as chromium, molybdenum and vanadium but also iron. It increases the amount of undissolved and excess carbide in the hardened steel, and the eutectoid point is shifted towards lower carbon concentrations. The consequence is the precipitation of fine or very fine grained carbides evenly distributed in the steel matrix. The chemistry of these carbides depends on the concentration of carbon and the alloying elements present as well as on the heat treatment applied. Complex carbides (M₆C, M₂₃C₆, MC) are responsible for retaining a fine-grained steel matrix by retarding the grain growth during heat treatment. The addition of tungsten will produce a larger carbide volume than other alloying elements — at the

same carbon level [1].

Good wear resistance is the most important property of tool steels, and tungsten, next to vanadium, is the most effective carbide forming element for increasing wear resistance. Furthermore, tungsten significantly improves the hot hardness and hot strength of steel and leads to increased yield strength and tensile strength without adversely affecting ductility and fracture toughness.

The effects of tungsten on steel properties in terms of carbide volume, shape and distribution, and fine-grained structure are [1]:

- more carbides and harder carbides increase hardness and wear resistance
- fine carbides and a fine-grained structure result in higher toughness for a given hardness level.

The high hot and red hardness (which is the retention of hot hardness over long-term exposure to high temperatures) and the high hot strength are the result of a microstructure containing numerous high-alloy carbides of a composition that enables precipitation hardening by age-resistant carbides and solid solution strengthening.

In some low carbon steels, as, for example, in case of creep resistant martensitic Cr Steels, precipitation strengthening by intermetallic phases occurs during creep exposure, such as Laves phases: $Fe_2(Mo,W)$.

3. HARDENING AND TEMPERING

Tungsten-containing steel requires a certain carbon level and furthermore a careful heat-treatment practice. Hardening is achieved by high-temperature austenitisation, in the case of HSS close to the onset of melting, to dissolve the alloying elements, followed by transformation during quenching and tempering to martensite with precipitated fine carbides (so-called *secondary hardening*). This produces a material which will retain most of its hardness up to about 550°C, and regain it again on cooling to room temperature. Higher hardening temperatures result in increased hardness after tempering. The temperature must be chosen in such a way that sufficient carbides dissolve, but overheating and grain coarsening must not occur. The grain size needs to be controlled to optimise toughness and to reduce distortion during subsequent tempering. The finer and the more uniformly distributed the solution resistant carbides remain the better is the resistance to grain

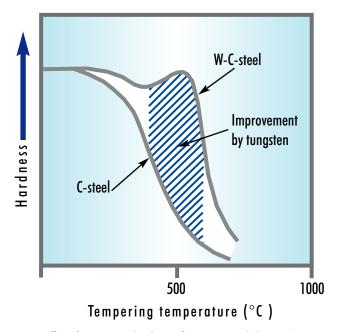


Fig.1: Effect of tungsten on hardness after tempering (schematic); [1] hardening is achieved by austenitization and subsequent quenching and multiple tempering at $\sim 550^{\circ}$ C to obtain a fine, mainly martensitic steel matrix with precipitated very fine alloy carbides (secondary bardening)

coarsening. At higher temperatures, the fine carbides coalesce and the effect is lost.

The effect of tungsten alloying on hardness during tempering is schematically shown in *Fig. 1*. During tempering at relatively high temperatures, nm-size carbides are precipitated that generate "secondary hardening" (see below).

In very hard tool steels, for example, cold work steels tempered at low temperature, the wear resistance is caused mainly by primary carbides which are not affected by hardening. These carbides are small and evenly distributed and very hard (*beavy-duty cold work tools*). Fine grained martensite adds to this effect.

4. FACTORS IN THE CHOICE OF TUNGSTEN AS ALLOYING ELEMENT

There are a series of factors which determine the choice of a specific element for steel production. Besides the necessity to fulfil the technical demands for a certain steel application to the maximum degree (red hardness, wear resistance, toughness), other factors co-determine the economics of steel manufacture, such as raw material costs and availability as well as manufacturing costs (for melting, casting, refining, forging, rolling, heat treatment, etc). Longer tool lives compensate for increased costs $\{2,6\}$.

In the past, availability of tungsten as a strategic material has had a strong impact on tungsten steels and their substitution, in particular during World War II, when high speed steels and tungsten carbide based hardmetals were needed for the armaments industry, and the lack in supply caused severe problems in manufacturing. Within short times, tungsten was substituted by molybdenum at least in part, with the advantage that only half the mass% is needed for secondary hardening compared to tungsten. Early problems with the easier decarburisation of such "new steels" * during heat treatment were solved soon by more sophisticated heat treatment facilities, such as the use of salt baths. Today, all tungsten tool steels have their equivalent molybdenum types [2], in some areas (like hot work die steels) W-alloyed steels have even lost their importance to molybdenum containing grades. Furthermore, tungsten as an alloying additive has completely vanished from the large area of structural steels. To a certain extent, tungsten is "back in the ring" in case of cold work and HSS steels produced by powder metallurgy, which proved an appropriate route for producing high quality tools with even higher alloy element contents.

Besides tool steels the increasing use of duplex steels for corrosion resistant applications in offshore oil- and gas production as well as that of creep-resistant 9-12% Cr steels for power generation is still an interesting and increasing market for tungsten, where the element has a strongly positive effect on the microstructure stability.

^{*} note that already in 1905 the "rules" of tungsten substitution by molybdenum were well known [4].



5. TUNGSTEN ADDITION TO THE STEEL MELT

Early tungsten alloyed steels were manufactured by the addition of more or less pure tungsten powder to the steel melt, or, alternatively, by addition of an iron-rich W prealloy, which was obtained from purified tungsten ore. This rather expensive procedure limited the application of tungsten steels because of the high price. In 1893 a new tungsten-rich prealloy (master alloy) was introduced by the Biermann´sche Metallindustrie in Germany, containing up to 80% tungsten, called *ferrotungsten*, production of which was possible directly from tungsten ore concentrates in an electric arc furnace, and which consequently was much cheaper. Other advantages of ferrotungsten are the lower melting temperatures, faster dissolution in the steel melt and a higher tungsten yield — all leading to a lower steel price.

Today, tungsten also can be added to the steel melt as selected tungsten scrap (Fig. 2) or scheelite ore concentrates.

The tungsten concentrations of theses sources are:

Tungsten metal scrap	90 – 98 %
Ferrotungsten	75 – 80 %
Scheelite ore concentrates	35 – 70 %

6. TECHNOLOGY OF TUNGSTEN STEEL MANUFACTURE

Conventional Steels and Cast Steels

Tungsten containing special steels are commonly produced via the EAF (electric arc furnace) -AOD (argon oxygen decarburisation)-ladle furnace-ingot casting-refining-hot forming-heat treatment-machining route *(Fig. 3)*. Depending on the steelmaker, different aggregates are used with the aim to produce a homogeneous steel matrix of desired composition and purity, with a uniform distribution of carbides.

Tungsten is added as scrap or ferrotungsten directly to the arc furnace (*Fig. 4*) to produce a base melt which is further refined in an AOD or VOD (vacuum oxygen decarburisation) converter or a ladle furnace, which is done to adjust the desired melt composition prior to ingot casting (*Secondary Metallurgy*). Addition of tungsten for final adjustments in this stage is made by ferrotungsten. Larger amounts of steel can also be fabricated by continuous casting.

Next stages of refining consist of either electroslag refining (ESR; *(Fig. 5)*) of the ingot or vacuum arc remelting (VAR) to improve cleanliness (in particular in terms of oxide inclusions and reduction in sulfur content), to induce a uniform as-cast microstructure and to minimize carbide segregation.

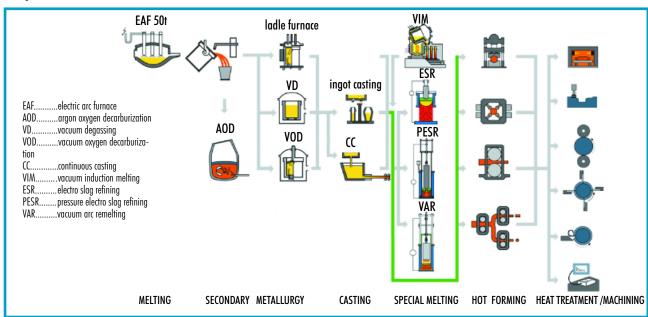




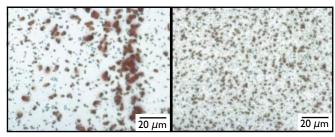
Fig. 4: Steel mill with two electric arc furnaces; each furnace consists of a refractory lined bearth, in which the feedstock is molten down using one or more graphite electrodes which enter the furnace through the refractory-lined roof; bttp://en.wikipedia.org/wiki/Electric_arc_furnace EAFs are the beart of a special steel production. To follow charge formation and meltdown is very spectacular but dangerous; melt capacity is commonly between 50 to 80 t, but can go up to 300 t. Tungsten is added to the furnace charge either as tungsten scrap or in the form of ferrotungsten

Nevertheless, the refined ingot still exhibits a coarse intergranular eutectic network of carbides formed on solidification that renders the as-cast ingot untolerably brittle and which has to be broken up during adequate hot working to improve microstructural uniformity. However, even after a high degree of deformation during metal working, carbide bands remain *(Fig. 6a)*, resulting in microstructural texture and anisotropic properties.

Lower-alloyed tungsten steels can be also produced via the blast furnaceoxygen converter-ladle furnace route. This is a standard route for producing large chromium steel castings used e.g. in steam power plants.

PM steels

Today, about 10% of high speed steels are produced by powder metallurgy (PM). This proportion is steadily increasing in particular in the field of cutting tools. The first PM tool steels appeared on the market in the $1970s_{[2]}$ and PM since then has led to a series of attractive alternatives to conventionally ingot-cast tool steels.

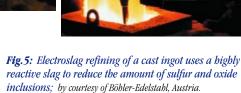


Conventionally cast material (a)

Powder-metallurgy material (b)

Fig. 6: Carbide distribution and size of a conventionally cast HSS in comparison to a PM grade; by courtesy of Ch. Sobar.

In case of cast materials oriented carbide bands form on hot working whereas in PM steel the carbides are evenly dispersed in a segregation-free steel matrix; PM HSS exhibits virtually isotropic properties and combines high hardness and wear resistance (high carbide volume) with excellent toughness.



This treatment improves both cleanliness and homogeneity of the steel, and thus significantly improves the steel properties; ESR or pressure-assisted PESR is common practice in Europe, and an alternative to vacuum arc remelting (VAR) which is prevalent in the US.

The production of PM steels (*Fig. 7*) starts with a melt of the desired composition, produced in an arc or induction furnace, which is then atomized by an inert gas, usually nitrogen, to form spherical particles. Such powder particles (diameter less than 1 mm, in part even $<100~\mu m$) are then transferred into a steel container, which is evacuated, sealed and subsequently hot isostatically pressed (HIP) in argon at about 1150°C / 1000 bar. The resulting fully dense billet is then hot worked to bar steel or forged pieces, or can be directly used as finished product.

PM steels exhibit a very uniform, isotropic and fine-grained steel matrix due to the uniform distribution of alloy carbides *(Fig. 6b)*. They reflect the very fine microstructure formed during melt atomisation which is practically free of segregations. PM also renders possible the production of higher alloyed steel grades than are accessible by ingot metallurgy or of non-conventional, e.g. V-rich, variants. Furthermore it has been shown that PM HSS offer significantly higher fatigue endurance strength in the high cycle regime [7].

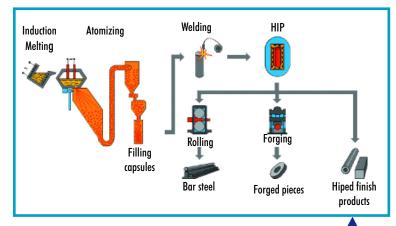


Fig. 7: Flow chart for Powder Metallurgy (PM) production of high performance steels; by courtesy of Böbler-Edelstabl, Austria.

Tool Steels

Tool steels are used for hot and cold forming and for cutting of materials, particularly other metals, wood or polymers. This presumes that their strength and hardness must exceed that of the materials being cut or shaped [2,6].

Tool steels are usually classified into four groups:

- High Speed Steels with W content of 1.5 to 20%
- Hot Work Steels with 1.5 -18% W
- Cold Work Steels with 0.5 3 wt% W
- Plastic Mould Steels, with W content of $\sim 1\%$.

HIGH SPEED STEELS

Where tool steels contain a combination of more than 7 % tungsten, molybdenum and vanadium and more than 0.6 % carbon, they are referred to as high speed steels (HSS). This term describes the ability to cut metals at high speed.

Tungsten is still the most prominent alloying element in HSS on a world-wide basis, although its originally large contribution has decreased in Western countries. About 95% of HSS are used for machining tools (drills, taps, milling cutters, gear cutters, saw blades, knifes, etc.), the rest for chipless forming (punching tools, dies, rolls). Typical applications are shown in *Figs. 8 to 14*. Compositions of selected high speed steels are presented in *Table 2*.

All groups behave similar but they differ slightly with regard to decarburisation sensitivity, carbide formation, and heat treatment. They are austenitized closely below the onset of melting prior to air cooling or gas — in some cases also oil - quenching for hardening. All show appreciable secondary hardening after tempering (550-600°C) and can be hardened up to HRC 63-68. This is their most important feature, responsible for the retention of hardness at the high cutting edge temperatures occurring during machining.

Table 2: Composition of Selected **High Speed Steels** (mass %)

Grade (AISI)	С	rD	Мо	W	V	Со	Grade (DIN)
T-1	0.75	4.1	1	18.0	1.1	1	HS 18-0-1
M-2	0.95	4.2	5.0	6.0	2.0	ı	HS 6-5-2
M-1	0.83	3.8	8.7	1.8	1.2	1	HS 2-9-1
M-7	1.02	3.8	8.7	1.8	2.0	1	HS 2-9-2
M-4	1.3	4.0	4.5	5.5	4.0	0	-
M-42	1.10	3.9	9.2	1.4	1.2	7.8	HS 2-10-1-8

The molybdenum-free grade **T1** (*Table 2*), which contains 18 % W, has not changed in composition since 1910, and was the main type used up to 1940, when substitution by molybdenum took place. Today only about 5 % of this type is used in Europe and only 2 % in the USA. In Russia and the Peoples Republic of China, both countries self-sufficient in tungsten, only limited substitution of tungsten by molybdenum and vanadium has taken place.

Grades M-2, M-7, and M42 constitute the most popular groups of HSS used today in the Western countries and Japan. The combination of tungsten and molybdenum (about 10 % in total) maximizes hardness and toughness and maintain these properties at working temperatures. Their composition varies in different parts of the world. On the Japanese and US market one finds mainly low tungsten - high molybdenum grades (M1, M7 types), whereas the European market prefers the M2 and M42 types.

Improvements in performance of HSS have been achieved not only by the methodical approach in alloying technique but even more significant progress has been made in developing an optimum heat treatment practice $_{[8]}$. For example, maximum hardness after tempering can only be obtained if the hardening temperature is sufficiently high and the holding time sufficiently long to ensure uniform heating of the whole part. However, the heat treatment must be chosen in such a way that a sufficient amount of carbides dissolve but no overheating and grain coarsening may occur, i.e. temperature and time control, especially at the peak temperature, are crucial. Frequently slight overtempering is aimed at, to slightly lower hardness than maximum for the benefit of toughness. Multiple tempering (usually 3x) isgenerally done to eliminate any retained austenite that would lower the hardness.

Hot hardness and wear resistance are improved by higher V additions (e.g. in **M4** type HSS) and such alloys are used for the machining of hard alloys and high strength steels, stainless steels and aluminium. Cobalt additions improve the high temperature properties by favourably influencing the carbide matrix on secondary hardening and restrict the growth rate of the carbides at high temperatures; furthermore, solution strengthening by Co is the most thermally stable strengthening

mechanism, e.g. at very high cutting speeds $_{[2]}$. Manganese and silicon contents are generally low, typically <0.4%. Some of the HSS may contain minor additions of sulfur (<0.25%) as they improve machinability.

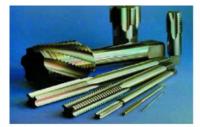








Fig.8: HSS is used for bobs, taps, chasing tools, milling cutters, twist drills but also for cold forming tools (shaping punches, coining and deep drawing dies); by courtesy of Böbler-Edelstabl, Austria.



Fig.9: HSS knifes are used in large numbers for slitting or transverse cutting of steel tapes, such as tin plate or galvanized sheet; by courtesy of M. Gstettner, Böbler Miller Messer und Sägen GmbH, Austria.

Fig. 10: Rotary blade cutters with tungsten steel blades are used for cutting of contoured pieces from multilayer glass and fiber fabrics; pre-fabricated part (rowing boat) made of fiber-reinforced-plastic composite materials; by courtesy of Robuso Solingen and Bootswerft Empacher GmbH; Germany.



Fig. 11: Heavy-duty machining tools are not only used for the machining of steel but also of non-ferrous metals such as nickel-base and titanium alloys; the teeth of the saw blades are made of HSS (M42 bimetal blade); by courtesy of K. Rotbkebl, Wikus, Germany.



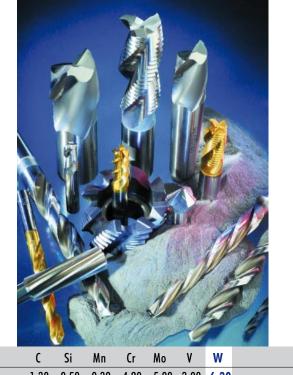
of wood is still a stronghold of the classical T-1 HSS grade; courtesy of M. Gstettner, Böbler Miller Messer und Sägen

GmbH, Austria.

C	Si	Mn	Cr	W	Mo	V	Со	
0,89	0,25	0,30	4,10	1,20	4,50	1,90	-	
0,90	0,30	0,30	4,10	6,40	5,00	1,80	-	



Fig. 14: Injector needle of a fuel injection system made of HSS; by courtesy of Böbler-Edelstabl, Austria.



1,30 0,50 0,30 4,20 5,00 3,00 6,30

Fig. 15: Heavy-duty machining tools produced from powder metallurgy HSS;

by courtesy of Böbler-Edelstabl, Austria.

Segregation-free and bomogeneous metal powders of highest purity are processed to bomogeneous and segregation-free high speed steels of virtually isotropic properties;

Table 3:
Composition of Selected PM High Speed Steels (mass %)

Grade	С	Cr	Мо	V	W	Со	others
S290 MICROCLEAN	2.0	3.8	2.5	5.1	14.3	11.0	-
S390 MICROCLEAN	1.64	4.8	2.0	4.8	10.4	8.0	
S790 MICROCLEAN	1.29	4.2	5.0	3.0	6.3	-	-
CPM®VIM CRU® 20®	1.35	3.75	10.5	2.0	6.25	-	S opt.
CPM®Rex® 76® (HS)	1.50	3.75	5.25	3.10	9.75	8.50	S opt.
CPM® Rex M4 HC (HS)	1.42	4.0	5.25	4.0	5.50	-	S, Mn

Global HSS production for 2007 is estimated to have been about $260,000t_{[9]}$. The percentage of PM steel (*Fig. 15*) is steadily increasing, in particular in the field of complex-shaped cutting tools (gear cutter, end mills, taps and broaches). More carbide forming elements can be added compared to conventional HSS, and a finer particle size and more uniform, isotropic distribution of the carbides is achieved. PM steels show better workability and grindability, less distortion on heat treatment, excellent surface finishing and higher productivity.

Typical compositions and grade designations are presented in *Table3*.

Table 4: Some of the more important **Tungsten Hot Work Steels** (mass %)

Grade (AISI)/(DIN)	С	Cr	Мо	V	W	others
H 21	0.35	3.5	-	0.35	9.0	Si, Mn
H 24	0.45	3.0	-	0.5	15.0	Si, Mn
H12	0.35	5.0	1.5	0.4	1.5	Si, Mn
X30 WCrV53	0.32	2.4	-	0.6	4.3	Si, Mn

HOT WORK TOOL STEELS

This steel type is mainly used for producing casting and pressing tools in light and heavy machinery. Historically, it was important in the development of metal extruding and die casting. Tungsten hot work die steels contain W, Cr and V as their main alloying elements, *Table 4*.

Tungsten containing hot work steels lost their importance during the past years due to their pronounced chill crack sensitivity. They are less tough than molybdenum hot work steels and are more prone to distort on hardening. However, for applications where very high temperatures and severe wear exist, tungsten hot work steels are still potential candidates [2].

COLD WORK TOOL STEELS

Historically these were the first tungsten-alloyed steels. Cold work tool steels are tool steels which are limited in use up to surface temperatures of not more than 200°C. They combine high hardness (up to HRC 63), compressive strength and wear resistance with good toughness, acceptable impact strength and high dimensional stability.

Cold work tool steels are either oil or air hardening steels, or high chromium, high C steels *(Table 5)*. The function of tungsten is to increase the carbide hardness and proportion, to result in a fine structure and improved toughness. Here, too, a carefully controlled heat treatment is necessary. Moreover, tungsten accounts for the secondary hardening effect on tempering. Tungsten decreases toughness but increases wear resistance and strength.

Oil and air hardenable cold work tool steels are used for taps, reamers, broaches, gauges, hobs, punches, slitting saws, drills, coining and

Table 5: Some of the more important Tungsten Cold Work Tool Steels (mass %)

Grade (AISI)/(DIN)	С	Cr	Мо	V	W	Mn	others
01 / 100 MnCrW4	0.95	0.5	-	0.12	0.55	1.10	~0.3 Si
105 WCr6	1.05	1.0	-	0.5	1.10	0.95	~0.3 Si
X 165 CrMoV 12	1.60	11.5	0.6	0.2	0.5	0.30	0.35 Si
D6 / X 210 CrW12	2.10	11.5	-	-	0.7	0.35	0.35 Si

blanking dies, and drawing dies [2,6]. Medium carbon, high chromium steels have a high compressive strength and wear resistance and are used for cutting tools, blanking and punching tools, woodworking tools, thread rolling dies, drawing, etc.

PM cold work tool steels with higher alloy additions (higher carbide volume) were developed for the blanking and punching industry as well as for cold forming applications (Fig. 16). They exhibit a uniform, isotropic carbide distribution and small carbide size and feature extremely high wear resistance and high compressive strength at good toughness due to improved homogeneity and the absence of segregations.

The lower distortion during heat treatment is particularly beneficial for production of complex-shaped precision tools, e.g. for powder pressing.

PLASTIC MOULD STEEL

Such steels have to withstand operating temperatures and pressures as well as corrosive effects of polymers and abrasive effects of fillers as occurring in the plastics processing industry. Long tool life and therefore low cost per plastic part is decisive. Good corrosion resistance and good surface finishing are critical. In particular in the latter regard, tungstencontaining PM steels have entered this market successfully (Fig. 17). Plastic mould steels contain up to 1.2 % W.

SURFACE MODIFICATIONS OF TOOL STEELS

Tool steels, in particular HSS, can be surface treated by nitriding, laser or plasma overlays of hard coatings (e.g. stellites Fig. 18) as well as by chemical or physical vapour deposition of hard carbides and nitrides (Fig. 19). Coatings such as TiN, TiAlN or CrAlN significantly increase tool lives but increase tool costs. Nevertheless, most tools in highly demanding applications are coated today since the higher cost are well balanced by the higher productivity during machining.

Chemical composition (average %)								
	C	Si	Cr	Mo	V	W	Со	
	2,45	0,55	4,15	3,75	9,00	1,00	2,00	



Fig.16: Tungsten-containing cold work tool steels are used for the blanking and punching industry, for cold forming applications, knifes and tools for the plastics industry;

by courtesy of Böhler-Edelstahl..



Fig. 17: Tool steel for the plastics industry; screw tip and feed screw for injection molding; the demands on the parts have risen due to the increased use of glass fillers; tools are increasingly made by powder metallurgy technology; CPM®;

by courtesy of Crucible Materials Corp.

Fig. 18: Gang saw for producing wood boards out of a tree trunk; the saws are made of tool steel which is "stellited" (i.e.: the teeth exhibit an overlay of corrosion resistant tungsten-containing steelite);

by courtesy of A. Gaertner, BÖHLER MILLER Messer & Sägen GmbH, Austria



Fig.19: Highly-demanding HSS tools are often PVD or CVD coated to improve productivity in manufacturing;

by courtesy of W. Kalss, Oerlikon, Liechtenstein.



HEAT RESISTING STEELS AND CAST STEEL

In certain cases, tungsten is added when steels are used in higher temperature ranges. Heat resisting steels are either chromium nickel steels with up to 6% tungsten, or heat treatable 9-12% Cr-steels, where tungsten is added in the range of 1-2% to improve the creep resistance and long-term stability of the steels.

The main use for austenitic Cr/Ni steels is as valve steels for combustion engines, which contain around 2% W. Similar steels are used for components of steam and gas turbines, such as blades, discs, bolts and pins. Heat treatable creep resistant chromium steels can be used up to about 620°C for continuous operation in power plants (*Fig. 20*). They are currently considered to possess the maximum creep strength of all heat-resistant steels for boiler components and piping systems (*Fig. 21*) [10]. Such steels are also used in a slightly modified form for large cast chromium steel components in steam power plants, such as inner and outer casings or valve housings in the high pressure and medium pressure part of the turbine (*Fig. 22*).

STAINLESS STEELS AND VALVE STEELS

Tungsten is added to ferritic-austenitic stainless steels (so-called "stainless super duplex steels"). Such steels exhibit excellent corrosion resistance and strength properties. Due to their pronounced resistance against stress corrosion cracking, fatigue, pitting, crevice and erosion corrosion they are ideal materials for components in offshore *(Fig. 23)*, waste water, sea water desalination and chemical plants with aggressive chloride-containing media.





 C
 Si
 Mn
 Cr
 Mo
 Ni
 V
 W
 Nb
 N

 0,12
 ≤0,12
 0,45
 10,50
 1,10
 0,75
 0,20
 1,00
 0,05
 0,05

Fig.20: Compressor rotor disk of a gas turbine ready for installation; made of creep resistant steel T505 (upper image); and turbine rotor (below):

© Siemens AG, Bilder: Martin Adam



Fig.21: Thick walled seamless pipes of T/P92 materials (X10CrWMoVNb9-2 [max.2% of W]) are produced in a piercing mill according to the Mannesmann process.

This material can be used in new modern power plants (T: up to 625°C, pressure: 285 bar) for pressure piping's, headers and other pressure parts; by courtesy of B. Strob, V & M Deutschland GmbH, Germany..



Fig. 22: Intermediate pressure inner casing (half), as part of a steam turbine. Weight of the casing is 60 tons. It is made of a martensitic CrMoV-alloyed steel grade containing approx. 1% tungsten (G-X12CrMoWVNbN10-1-1); by courtesy of R. Hanus, voestalpine Giesserei Linz GmbH.

8. TUNGSTEN IN STEEL —A "FINE" BUT NICHE MARKET

Most of the tungsten used in steelmaking today is used for tool steels, in particular high speed steels, where tungsten has remained the major alloying element in most grades. However, this segment of steel only refers to less than 0.03% of the global steel market (2007: about 1.3 billion tons), and thus tungsten-containing steels constitute a very narrow niche in the World of Steel. Based on data for tungsten consumption in 2007 (64,600 t), and considering the respective share of tungsten for steelmaking worldwide (\sim 20%), it can be estimated that roughly 13,000 metric tons of tungsten are used for steels, globally.

Since the early days of tool steel, tungsten addition has remained a synonym for improving the high temperature properties of steel, in particular hot hardness, resistance to plastic deformation and wear at high temperatures, and tools made of tungsten steel can be found in all areas of the modern manufacturing industries (whether metals, wood, plastics, or composites). New PM tungsten steels (with higher W contents as compared to conventional steels) have contributed to find new markets and to compete against tool alternatives, such as hardmetals. In addition, tungstencontaining high temperature steels are used increasingly in the new generation of power plants, and thus help to reduce CO_2 emissions, and large amounts of low-tungsten alloyed stainless steels can be found in the oil- gas- and waste-water industry.

Fig.23: Large swivel (left) and multiplyer part (right) made of tungsten-containing stainless super duplex steel, highly resistant to seawater corrosion;

by courtesy of G. Eichelberger, Böhler-Edelstahl

C	Si	Mn	Cr	Мо	Ni	٧	W	Nb	N
0,12	≤0,12	0,45	10,50	1,10	0,75	0,20	1,00	0,05	0,05

Literature:

- M. Kroneis, Tungsten in Steel, in: Proc. 1st International Tungsten Symposium, Stockholm, pp. 96-107, Mining Journals Books Ltd., London (1979).
- [2] H.W. Rayson, Tool Steels, in: Materials Science and technology, Vol.7, pp. 583-640, VCH (Weinheim), ISBN: 3-527-26820-0 (1992).
- [3] H.A. Brustlein, J. Iron Steel Inst. London, Part II, 770 (1886).
- [4] J.A. Mathews, US 779,171 (1905).
- [5] E. Lassner, W.D. Schubert, TUNGSTEN, Kluwer Academics / Plenum Publisher, New York (1999).
- [6] G. Roberts, G. Krauss, R. Kennedy: Tool Steels. ASM, Materials Park OH (1998).
- [7] C. Sohar et al.: Metal Powder Report 2009, currently in press.
- [8] H.F. Fischmeister, S. Karagöz: "Cutting performance and microstructure of high speed steels: Contributions of matrix strengthening and undissolved carbides",. Met. Trans. 29A ,205 (1998).
- [9] B. Hribernik, private communication.
- [10] B. Hahn, W. Bendick, VGB Power Tech 6/2006.

Further Reading:

H.W. Rayson; G. Roberts et al.; H.F. Fischmeister et al. (references see above).

Acknowledgements:

The authors appreciate the help of the following colleagues: B. Hribernik, BÖHLER-UDDEHOLM AG;

H.Lenger, D. Caliskanoglu, G. Zeiler, H. Wukitschewicz,

G. Eichelberger, all at BÖHLER Edelstahl GmbH & Co KG;

M. Gstettner, A. Gärtner, BÖHLER MILLER Messer & Sägen

GmbH; R. Hanus, Voestalpine Giesserei Linz GmbH;

W. J. Prodinger, BÖHLER UDDEHOLM Precision Strip GmbH

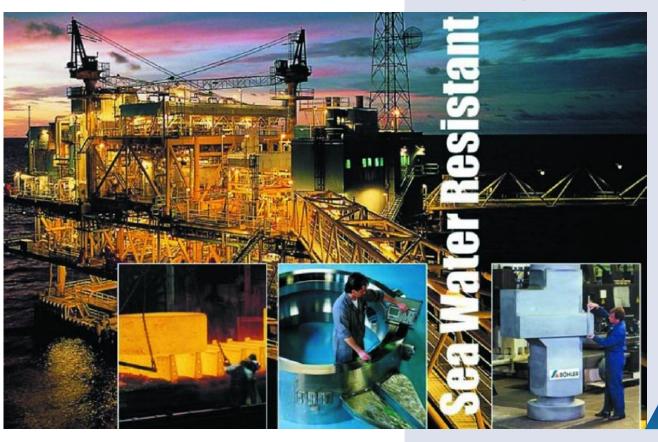
& Co KG; W. Kalss, Oerlikon Liechtenstein, B. Stroh, M. Jarrar,

 ${\tt V}\ \&\ {\tt M}\ {\tt Deutschland}\ {\tt GmbH},$ Germany, K. Rothkehl, Wikus,

Germany, G. Riedel, Cronimet, Germany,

 ${\rm H.}$ Empacher, Bootswerft Empacher, Germany and

J. Beckman, Crucible Speciality Metals, USA.



Tungsten Consortium Compliance with REACH - a service from the ITIA.



With the membership of CCCMC on behalf of the Chinese tungsten industry successfully negotiated, the Consortium is proceeding apace with the laboratory test programme in order to fill data gaps to allow the conduct of risk assessments and, ultimately, to enable companies to register their products and continue their business in the EU. A website — www.tungstenconsortium.com - has been set up for Consortium members, charting progress with the tests and providing an extensive reference source to the massive

amount of documentation in circulation about REACH. By the end of November, all companies had been obliged to pre-register their substances and the Tungsten Consortium planned to review the lists of companies within each SIEF (Substance Information Exchange Forum) in order to make contact about agreeing Lead Registrants and exchanging information about available studies in order to avoid unnecessary testing.

Reportedly there were some 2.5 million pre-registrations submitted and, as most of these were no doubt made at the last moment, it is not surprising that the REACH IT system of the European Chemical Agency (ECHA) in Helsinki cracked under the strain; the exercise was delayed until the New Year.

Membership

Welcome to:

- Advanced Material Japan Corp,
 - a Japanese trading company focusing on tungsten
- ✓ Atlas Copco Secoroc AB,
 - a Swedish producer of percussive and rotary rock drill tools.
- Malaga Inc.
 - a Canadian company producing tungsten concentrate at the Pasto Bueno property in Peru.
- Matsushita Electric Industrial Co Ltd.
 - a Japanese company whose tungsten business is in Panasonic lamps.
- Ormonde Mining Plc,
 - an Irish company, developing the Barruecopardo Tungsten Deposit in Salamanca Province, Spain.
- ▼ Playfair Mining Inc,
 - a Canadian company, involved in tungsten exploration at several sites.
- Vietnam Youngsun Tungsten Industry

the first ferro-tungsten producer in Vietnam.

Wolfram Company JSC,

a Russian company involved in mining, smelting, downstream processing and trading.

ITIA 22nd AGM,

September 2009, Vancouver

North American Tungsten Corp has generously offered to host ITIA's 22nd AGM in Vancouver and the provisional outline programme is given below:

Monday 14 September 2009

Consortium Technical Committee Joint meeting of the HSE and Executive Committees

Tuesday 15 September 2009

Consortium Steering Committee Executive Committee Dinner

Wednesday 16 September 2009

AGM (morning)
Consortium Committee (afternoon)
Dinner

Thursday 17 September 2009

AGM (morning)
Mine/Plant Visit — to be arranged

Further details will be posted to our website in late May, including a registration form.

Apologies to readers who missed the June 2008 issue. The principal article was suddenly withdrawn as the Newsletter was going to print and cancellation was the only option.

For a full list of members, contact details, and products or scope of business, please refer to the ITIA website — www.itia.info.

