## NEWSLETTER

#### INTERNATIONAL TUNGSTEN INDUSTRY ASSOCIATION

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The ITIA President, Bob Fillnow (right) and the Chairman of the HSE Committee, Carmen Venezia who are both with Osram Sylvania Products inc.

## 17th Annual General Meeting, Lisbon

The presentations were by experts in their respective fields and the conference room remained unusually full at all times, not least during the showing of an educational video on tungsten (sponsored by the Austrian Ministry of Education and Wolfram Bergbau). The new format in which the afternoons are left

free for private business meetings has been a success. Evenings offered light relief, with entertainment by belly dancers and wine tasting at a local adega.

# 10th International Tungsten Symposium

To be hosted by Zhuzhou Cemented Carbide Group Corp Ltd and China Minmetals Corp, the next symposium will take place in the Tongcheng Lake Resort, Changsha in Hunan Province. The event will begin on Monday 19 September and conclude with lunch on Wednesday 21 September. Optional works' visits to the ZCCG plant or the Shizhuyuan mine will be scheduled from Wednesday afternoon through Thursday 22 September.

The title of the symposium will be "Evolution of the Tungsten Industry and the Major Challenges Ahead" and plans for papers and speakers are well advanced, with a mix of market and technical topics.

Further details will be added to the ITIA's website next year and recipients of this Newsletter will automatically be sent registration forms. The last issue in June mainly comprised the first part of an article by the ITIA's Technical Service (Professors Wolf-Dieter Schubert and Erik Lassner of the Vienna University of Technology) on "Tungsten for a Cleaner Environment".

The second part follows in this issue and was written with the kind collaboration of Dr Peter Schade of Osram GmbH, Schwabmünchen.

## TUNGSTEN FOR A CLEANER ENVIRONMENT

Wolf-Dieter Schubert and Erik Lassner (Vienna University of Technology) and Peter Schade (Osram GmbH, Schwabmünchen)

### **PART II:**

TUNGSTEN AS SUBSTITUTE FOR A TOXIC METAL AND AS COMPONENT IN ENERGY SAVING DEVICES

### SUBSTITUTION OF LEAD BY TUNGSTEN

Lead in regard to its worldwide used tonnage ranks number five in metals after iron, aluminum, copper and zinc. Lead has several outstanding properties for various applications. A crucial disadvantage of lead in general is the toxicity of its compounds to humans and animals. Lead is a heavy metal poison. Nevertheless, it was used since ancient times and millions of people suffered from chronic lead poisoning, not knowing about the origin.

Lead is an accumulative poison and already active at low concentrations in the blood. It may enter the body by ingestion, inhalation or absorption through the skin. It is toxic to the central nervous system, kidneys, cardiovascular system and the development of the red blood cells. Especially dangerous is lead poisoning for fetuses and developing children: delayed development, diminishing intelligence and altered behavior can be the consequences. Severe poisoning may cause sterility, abortion, and neonatal mortality and morbidity.

The growing scientific evidence about the toxicity of lead compounds and especially the growing environmental awareness of the people worldwide provoked more stringent regulations and partly also the prohibition to use lead in special applications.

One example regarding this is that ducks and geese eat spent shot pellets they mistake for food, resulting in big numbers of deaths. Therefore, in the US and Canada as well as in Mexico and many European countries lead shot for water fowl hunting is banned.

Another example is the Green Bullet Program of the US army, which uses no lead-containing ammunition for training purposes. In this regard it is interesting to note that more than 65,000 tons per year of lead are used for ammunition in the US.

Possibilities for the substitution of lead especially in applications where it represents a danger for the environment are:

- lead shot and lead containing projectiles for hunting and clay pigeon shooting (Fig.9),
  - small caliber military training projectiles,
    - weightings for sport and commercial fishing.

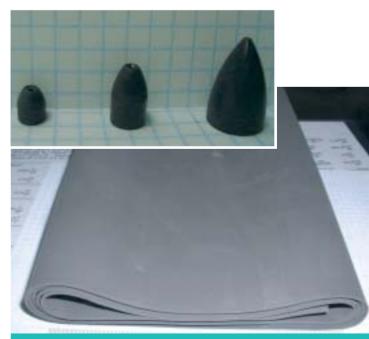


**Fig. 9:** Different kinds of "green" ammunition for water fowl and big game hunting.

By courtesy of Mr. R. Naumans, Hevi-Shot, USA.

In regard to the substitution of lead in applications where high density is of importance tungsten and tungsten alloys would be excellent materials, but much lower ductility, worse workability and the higher price are disadvantages. Therefore, a direct substitution is not possible in any application.

Thermoplastic tungsten — polymer composites or tungsten Heavy Metal-polymer composites with characteristics that preserve the performance attributes of lead, while avoiding its toxicity are the solution **(Fig.10)**. As thermoplastic polymers Nylon-based or Polyamine-based materials are in use. This composite material has a density equal to that of lead, offers greater yield strength than lead, can be injection molded, is non-toxic, and can be formulated to be very flexible or very stiff. It can be processed on conventional thermoplastic injection molding equipment into any three-dimensional shape. It can be handled and recycled without detriment to people or the environment.



**Fig. 10:** Tungsten Bullet Fishing Sinkers (left) and Rubber-Tungsten sheet (below); Density: 11 g/cc. By courtesy of Dov Chaiat; Tungsten Powder Technology; Israel.

Composite bullet cores are manufactured by compaction on mechanical presses from blended powders at room temperature. The cores are inserted into copper jackets and swaged to bullet shape. No sintering is necessary. The core density is 11.3 g/cm<sup>3</sup>.

Tungsten sources are coarser tungsten powder derived of pure scrap or from Heavy Metal scrap. Heavy Metal is a two phase composite of tungsten with nickel and iron. It is used either as W-10%Ni,Fe composite or the nickel-iron binder phase can be selectively dissolved and tungsten remains in the form of spheroids having particle sizes of 30  $-150~\mu m$ . Because of the globular shape this powder is ideal to mix with any polymer.

The higher price compared to that of lead is not in any case a disadvantage. The extremely high costs for remediation of lead contaminated indoor and outdoor firing ranges compensate for the higher price of the tungsten bearing ammunition.

#### ENERGY SAVINGS DURING LIGHTING AND AIR CONDITIONING

To save fossil energy through intelligent technologies is a further important contribution to a more conscious dealing with our environment; and tungsten products in modern light sources take their part. For illustration, a single DULUX®EL 20 W lamp (Registered trade-mark of OSRAM) will save around 1,200 kWh of elecricity throughout its life compared with an ordinary incandescent lamp, corresponding to around 300 kg of coal or 280 litres of oil to generate this amount of power

## **Tungsten in Modern Lighting Systems**

Tungsten is used in the form of wires, coils, and coiled coils in incandescent lamps, and as electrode in low- and high-pressure discharge lamps. **Table 1** gives a comparison of maximum lamp efficacies and burning life of the different lamp types.

#### **Incandescent Lamps**

In its, probably, most well known application, as tungsten filament in incandescent lamps, tungsten metal has boosted artificial lighting at the beginning of the 20th century. However, only up to 5% of the electric energy is used for lighting, the rest being dissipated as heat. Important improvements combined with notable energy savings have been reached during the first half of the last century. By application of coiled and double coiled tungsten filaments, inert gas filling, including noble gases (Ar, Xe), and higher filling pressures, the efficacy has been increased to 15 lm/W. Higher light outputs are determined by higher temperatures, so that the evaporation of tungsten and the high temperature creep strength limit the life time of the lamps.

#### **Tungsten Halogen Lamps**

By using the temperature dependent chemical properties of tungsten-halogen and tungsten-oxygen-halogen compounds, the detrimental wall blackening of the lamp envelope by the evaporation and condensation of tungsten can be avoided, so that higher filament temperatures (up to  $3000^{\circ}$ C) and higher filling pressures lead to higher efficacies of up to 27 lm/W and higher life times.

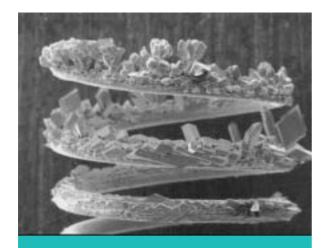
Tungsten halogen lamps use reversible chemical reactions described by the following equations:

$$W + X \Leftrightarrow WX (g)$$
  
 $W + X + O \Leftrightarrow WOX (g)$ 

in which X is a halogen (usually iodine or bromine). The reactions proceed to the right at low temperatures to react with evaporated tungsten, forming volatile compounds that do not condense on the wall of the bulb. In contact with the tungsten filament at elevated temperatures, the halides and oxyhalides decompose, redepositing tungsten on the filament (*Fig. 11*), and releasing halogen for the cycle again. Careful control of the cycle is needed to ensure that clean-up is sufficiently rapid to prevent wall-blackening, without being so rapid as to erode the tungsten filament legs at lower temperatures before normal burnout of the lamp occurs. Today, further distinct improvements have been reached by the application of modern multiple IR-reflecting SiO<sub>2</sub>/TiO<sub>2</sub> coatings of the outer lamp bulb; leading to energy savings of about 25 to 30%.

Table 1	<b>:</b> Comparison o	f Standard La	mp Types,	Lamp Efficacy,	and Burning Life
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Lamp Type	Max Efficacy (lm/W)	Burning Life (hours)		
Edison lamp /1878/carbon filament	1,4	40		
Incandescent lamps	15	1,000		
Halogen lamps	27	2,000		
Fluorescent lamps	104	16,000		
Compact Fluorescent lamps	65	12,000		
Gas Discharge lamps				
Mercury High-Pressure lamps	100	12,000		
Metal-Halide lamps	107	12,000		
Sodium High-Pressure lamps	150	20,000		
Sodium Low-Pressure lamps	200	10,000		



**Fig. 11:** Tungsten Redeposition and Crystal Growth during Life of a Halogen Lamp. By courtesy of P. Schade, OSRAM GmbH, Schwabmünchen.

#### Fluorescent Lamps

The fluorescent lamp is a discharge lamp in which UV radiation emitted by a low pressure discharge in a mixture of mercury vapour and a noble gas is converted to visible light by a fluorescent phosphor on the inside of the discharge tube wall. The necessary electron emission is produced by emitter-coated tungsten coils (Fig.12). The emitter material consists of a mixture of alkaline earth oxides. Lamp life is primarily determined by the continuous loss of emitter material from the tungsten cathodes induced by erosion processes during ignition. The new generation of fluorescent lamps is characterized by reduced tube diameters and shorter lengths. The luminous efficacy amounts to about 100 lm/W. Together with a higher life time, there are energy savings of about 20 % possible.

In the last 15 years important improvements with regard to the replacement of incandescent lamps for indoor and outdoor lighting by compact fluorescent lamps were achieved (so-called energy saving household lamps). These lamps give independence of the special design and

application field luminous efficiencies between 30 lm/W and 65 lm/W. For life times between 12,000 and 15,000 h, there are energy savings of about 75 to 80%, as compared to an ordinary incandescent lamp.

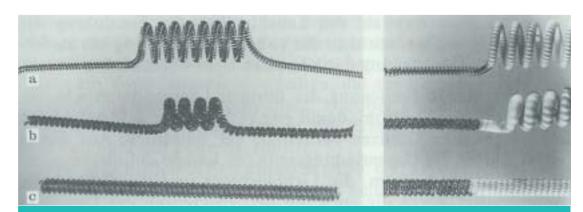
#### **High Intensity Discharge Lamps (HID)**

In HID lamps the power dissipation of an electric current passing through a gaseous medium at a pressure greater than or equal to 1 atm is converted into radiation. Much higher radiating temperatures can be achieved than in any incandescent lamp. Appropriate selection of the gaseous medium results in favorable spectral distribution of radiated power, with a much smaller fraction of IR rays. Therefore, these light sources are very bright, and are until 10 times as efficient as incandescent lamps.

The following lamp types are in use:

- Mercury high pressure lamps
- Sodium high pressure lamps
- Metal-halide lamps
- Xenon- and Xenon-Mercury short arc lamps.

Each system comprises an inner discharge tube (arc tube) containing the high pressure gas or vapor enclosed in a hermetically sealed outer envelope. The outer jacket is required for thermal insulation, protection of the arc tube seals from oxidation, and absorption of any short wavelength UV rays that may be emitted from the arc tube. Arc tubes for mercury and metal halide lamps are quartz; arc tubes for high pressure sodium lamps are fabricated from translucent polycrystalline alumina (PCA) to withstand corrosion by hot molten and gaseous sodium. The energy coupling takes place via tungsten electrodes. A schematic drawing illustrating the principal components of a Sodium High Pressure Lamp is shown in  ${\bf Fig.~13.}$ 



**Fig. 12:** Tungsten Electrodes for Fluorescent Lamps; left: (a) coiled coil; (b) triple coil; (c) rod coil; right: emitter coated tungsten electrodes. By courtesy of Mr. D. Hofmann, OSRAM GmbH, Augsburg.

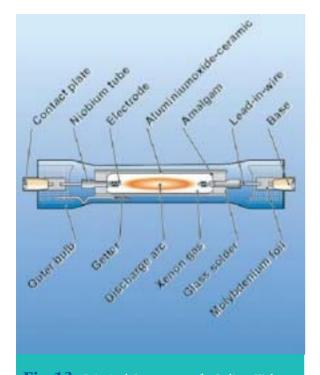


Fig. 13: Principal Components of a Sodium High Pressure Lamp. By courtesy of P. Stadahl, OSRAM GmbH, Berlin.

Due to the lowering of the work function of tungsten by thoria additions (0.7 to 2.0 wt.%) from 4.5 eV for pure tungsten to about 2.7 eV, thoriated tungsten electrodes are used, especially for d.c. lamps. The substitution of the radioactive thoria is an important challenge for the future. A replacement of thoriated tungsten electrodes by doped and/or pure tungsten electrodes is in progress, especially for a.c.-lamps and for new developments.

HID lamps are for high output, high luminous efficiency and long operating times. Their main applications are lighting of roads, outdoor areas, halls, shopping areas, floodlighting, plant irradiation, photography, medical technology and automobiles. Two important examples are discussed below:

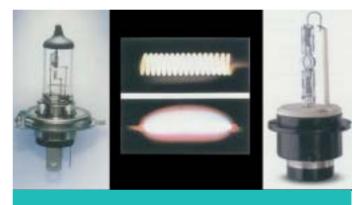
#### Tungsten electrodes at extreme material limits

In modern short arc lamps with mercury discharge and very high pressures of about 200 bar as well as electrode gaps down to <1mm,

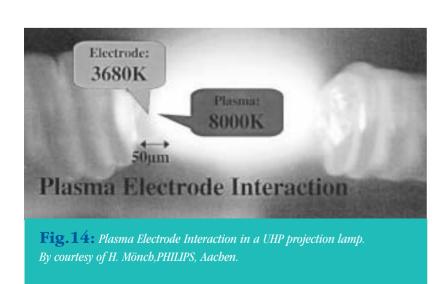
high purity tungsten electrodes are loaded near the tungsten melting temperature (Fig.14). By addition of traces of bromine and oxygen, a transport cycle is realized, which, due to the back transport of evaporated tungsten, holds the electrode gap constant and the wall of the envelope clean. The result is a miniaturized lamp with very high luminance (of up to  $2 \text{ Gcd/m}^2$ ) and more than 15,000 to 20,000 h lifetime. These properties make the lamps ideal for the projection market.

#### Car beadlights

In automotive lighting halogen lamps can be successfully replaced by gas discharge lamps. **Fig. 15** shows a comparison between a halogen lamp (H4) and a modern discharge lamp (D2), together with the geometrical shape of the light output. For example, XENARC® lamps (Registered trade-mark of OSRAM) produce twice as much light (3,200 lm) from their 35 W power consumption as conventional halogen headlight lamps. The increased average lamp life amounts to 2,000 h. Due to their high luminance and high luminous flux, headlights can be reduced in size to give more design possibilities.



**Fig. 15:** Modern Automotive Lighting: Comparison of H4and D2-Lamp (XENARC®). By courtesy of OSRAM GmbH, München.



#### **Smart Windows**

Smart windows are another example for saving fossil energy in a very elegant way. Smart windows are based on electrochromism. Light striking an electrochromic window causes a color change that reduces the transmitted light. Not only visible light radiation is reduced, but also infrared wavelengths, which are responsible for heating the space behind the window. Therefore, smart windows save on air conditioning cost and by that reduce energy consumption.

Electrochromism is the property of a material or a system to change its optical properties (colour) reversibly if an external potential is applied. It is associated with an ion insertion/extraction process. Electrochromism is in principle a device property. Such a device consists of several layers as for example: substrate (mostly glass), covered with a transparent, conducting film in contact with a film of the electrochromic substance followed by an electrolyte film, an ion storage film and another transparent conductor, as shown in **Fig. 16** below.

Tungsten trioxide was the first discovered compound with electrochromism and today it remains the most viable option for respective devices. The basic reaction for the electrochromic process is presented by the following equation:

 $WO_3 + xI^+ + xe^- \rightarrow I_xWO_3$ Colourless Blue

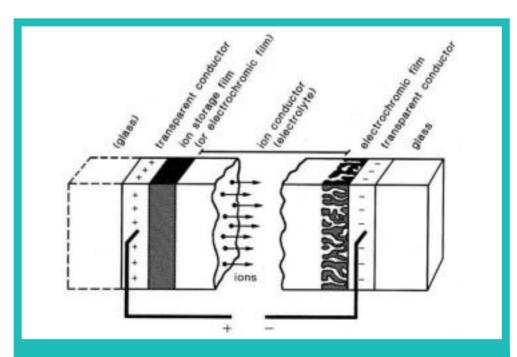
I stands for  $\mathrm{H^+}$  or an alkali metal ion,  $\mathrm{e^-}$  for electron, and x is about 0.3

Tungsten trioxide thin films exhibit a high amount of structural disorder and transform easily from an optically transparent to an absorbing state under ion insertion. The electron insertion/extraction is responsible for the actual electrochromism. The optical effects are associated with the amount of  $W^{6+}$  transformed to  $W^{5+}$ .

Thin films can be produced by evaporation, sputtering, CVD, anodization or the sol/gel technique.

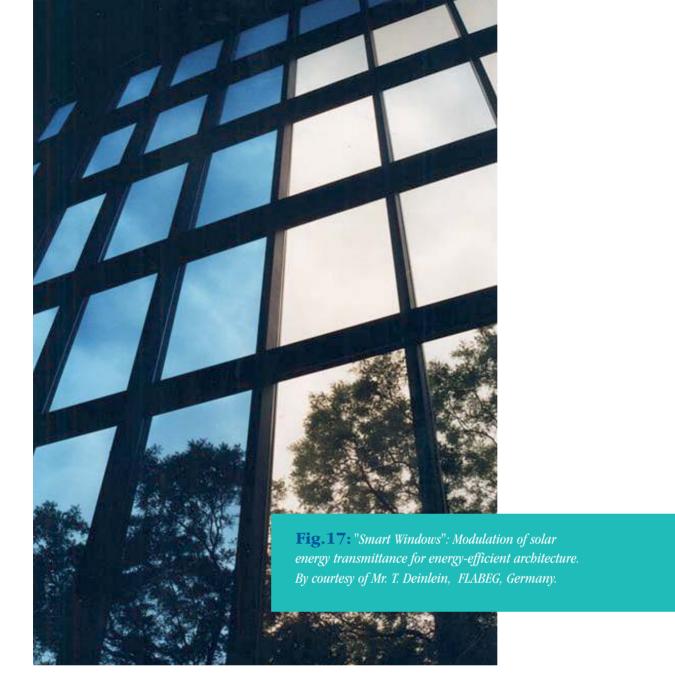
The disadvantage of the first generation of smart windows was that their response could not be moderated for winter months. The today's solution is a sandwiched combination device of a photoelectric and an electrochromic system called a photo-electrochromic cell (PEC). The dynamics of the reaction are similar to the basic electrochromic effect. The darkening of the panel is proportional to the incident light. But in the PEC system the darkening of the panel actually takes place in a separate system that is electrically driven by the light falling on the front photoelectrode. The novel aspect of the panel is the ability to switch the photocurrent on and off.

Energy savings in air conditioning using such windows were calculated to about 20% of the overall energy consumption. Currently, the windows are used in "pilot-scale" projects, and the near future will demonstrate their large scale technical feasibility. An example for the use of electrchromic windows is presented in **Fig. 17**.



**Fig. 16:** Basic design of an electrochromic device, indicating transport of positive ions under action of an electric field.

By courtesy of C.G. Granquist, University of Uppsala.



#### **OUTLOOK**

The examples discussed in the present article show how tungsten and tungsten compounds contribute to a cleaner environment and in saving fossil energy. Further progress will be possible by technical innovations, such as "alternative" fuels, including biofuels, improved combustion technologies, improved catalysts, etc., but the impact of these activities on health and environment will depend mainly on international and national legislation. The acceptance of more stringent regulations by the people will play an important role, and we have to understand and to accept that improvements will always be combined with higher costs.

In regard to  $SO_2$  and lead emissions originating from fuels the situation has changed significantly during the past years. The purification of fuels from sulfur via catalytic processes to very low sulfur levels and new lead-free fuel formulations was a big success worldwide, and further improvements can be expected.

In contrast,  $NO_x$  and particulate emissions are still a big problem, especially in densely populated areas. Big emitters, such as power or waste incineration plants, are more or less clean, because they are equipped with modern catalysts and exhaust cleaning units. But the enormous amount of trucks and diesel engine driven passenger cars still

originate  $NO_x$  and particulate concentrations far above the tolerable limits. In regard to  $NO_x$  it is not the fuel quality, which is responsible, but the high combustion temperature of the diesel engine resulting in a partial oxidation of nitrogen from the air. So both improvements in fuel quality and post-treating of exhaust gases to reduce emissions will be necessary in future, and tungsten bearing catalysts will play their role.

The most "simple" contribution of protecting our environment would be to save fossil energy by a more careful dealing with energy itself. However, there is little support still by both industries and individuals. Less transport of materials by trucks, in particular by old, contaminating vehicles, extension of rail systems and of public transport in urban areas, improvements in transport logistics, increasing use of advanced light sources, etc. might all contribute in a more careful dealing with energy and a cleaner environment. However, as long as there are no clear governmental regulations, and strong lobbies exist on counteracting such activities, and, most important, fossil energy still is too cheap, there is little prospect of success of such considerations. However, the latter aspect might rapidly change in future and will then have an impact on a more conscientious use of fossil energy.

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#### **Metalworking Products**

An Allegheny Technologies Company 1 Teledyne Place, Labergne, TN 37086, USA Tel: +1 615 641 4245; Fax: +1 615 641 4268 Email: joakes@atimwp.com

#### Mi-Tech Metals Inc

4701 Massachusetts Avenue Indianapolis, IN 46218, USA Tel: +1 317 549 4290; Fax: +1 317 549 4293 Email: sales@mi-techmetals.com

#### Minxia Non-Ferrous Metals Inc

120 Schor Avenue, Leonia, NJ 07605, USA Tel: +1 201 592 2219; Fax: +1 201 461 1370 Email: joylin99@yahoo.com

#### Osram Sylvania Products Inc

Hawes Street, Towanda, PA 18848, USA Tel: +1 570 268 5000; Fax: +1 570 268 5113 Email: susan.dunn@sylvania.com http://www.sylvania.com

#### HC Starck (New Jersey) Inc

160 E Union Avenue, East Rutherford New Jersey 07073, USA Tel: +1 201 438 9000; Fax: +1 201 438 0891 Email: info.kulite@hcstarck.com

#### **Tungco Inc**

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#### **Umicore USA Inc**

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