ITIA

Tungsten

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Recycling of Tungsten

The technology – history, state of the art and peculiarities

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Zn-reclaimed cemented carbide powder. Courtesy of Tikomet Oy

Recycling technologies

Recycling is an important contribution to a sustainable economy. Tungsten recycling has a long history, with the first industrially used recovery technologies dating back to the 1940s. Since the early days of tungsten's industrial use, it was common practice to handle this relatively rare and expensive commodity with great care, trying to use it efficiently and not to spoil materials which could be re-processed.

The first materials to be recycled were the processing scraps (so-called new scrap), generated during production of tungsten-bearing goods. They were easy to collect and their value was obvious to those dealing with them in their factories. Technologies to recover tungsten from this new scrap were developed and quickly almost no tungsten was lost any longer from new scrap. Dealing with old scrap, tungsten-containing products at the end of their service life, is more demanding. Industries or individuals which may have used such products are, in some cases, not aware of the value of raw materials contained and, as the complexity of products increases, it even could be difficult to spot that such end-use products may contain tungsten at all. A whole series of additional aspects concerning collection logistics, sorting, dismantling, etc emerges and will have an impact on the economy of recycling.

The ITIA Newsletter May 2018 dealt with these aspects, elaborating on the current share of tungsten recycling; discussing the economic limitations; and looking forward to the future potential of this endeavour, to make the industrial use of tungsten an even more sustainable one. In the current Newsletter, the technologies to recycle tungsten will be presented. Each technology was developed with some specific materials or material combinations in mind. Some are rather old, others were developed more recently. Some cover a big share of tonnage recycled today, others are more exotic and limited to special fields of application; some may even be considered academic. There are technologies to deal with well-defined tungsten scrap and to recycle such scrap in the most direct and efficient way to something which can be used again, while other processes may consume more resources in the form of chemicals and energy, but would be able to deal with a wider variety of tungsten scrap materials. There are recycling processes, which recover tungsten from scrap in a way that the resulting products have virgin quality, opening the door for practically infinite recycling of tungsten without any compromise to end-product quality. No matter whether the process was invented a long time ago or more recently, it is common to all of them that they are further improved and optimised in industrial practice to minimise environmental impact and to maximise yield and efficiency, thereby improving their economy as a "side effect".

There still seems to be some confusion in the market when it comes to recycling technologies for tungsten and it is therefore worthwhile to summarise the state of the art in this field and to emphasise the potential and limitations for each technology. There is no such thing as "the best" recycling technology. It all depends on the type of scrap which has to be addressed, and the type of recycling product which is aimed for. This article aims to enable the reader to understand which recycling technology might be best suited for treatment of a certain scrap type and to achieve a well-defined quality of the recycled material.

A variety of tungsten recycling technologies were developed in the past, which today are globally used for industrial recycling. They can be divided into three main groups: ***direct recycling***, ***chemical recycling*** (also called indirect recycling, including the variety of semi-direct recycling) and ***melting metallurgy*** (**Figure 1**).

The origins of today's technologies date back to the 1940s, with the major processes being developed until the 1970s. They have proven to be reliable routes to fulfil today's requirements concerning economy and ecology. Over time, they were steadily modernised and adapted by the use of advanced technology and safety standards.

As ***direct recycling*** is understood, the as-supplied material is transformed to powder of the same composition by either chemical or physical treatment, or a combination of both. Prerequisites for direct recycling are [1]:

- The composition of the scrap must be the same as for the final product (within narrow limits)
- The scrap must be of high purity, not only concerning impurities but also correctly sorted in terms of composition (and size).
- The process must offer the possibility of converting the scrap to a powder of a metallurgical acceptable form.
- No contamination by foreign materials during processing.

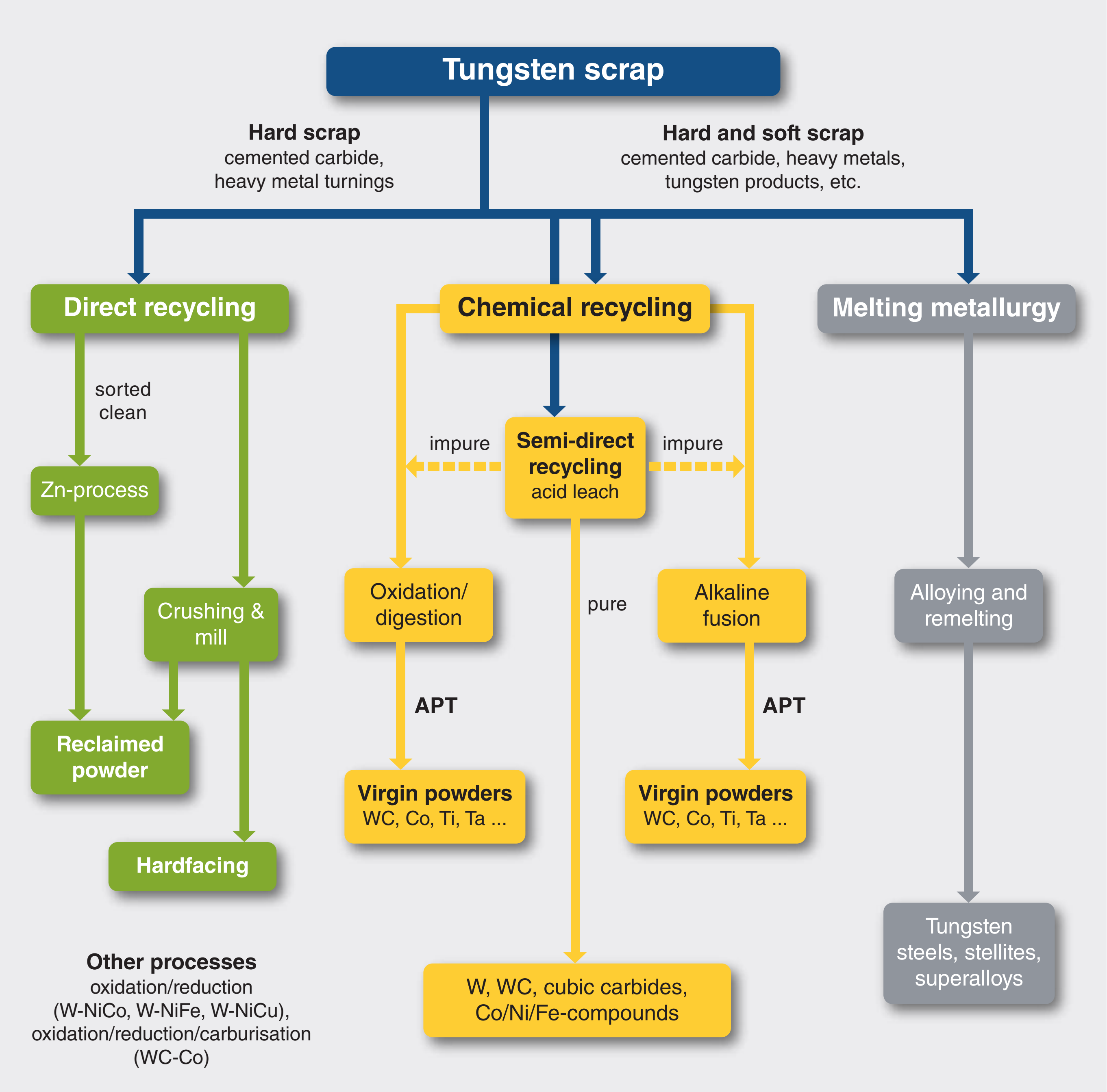


Figure 1: Overview of the most important recycling technologies for secondary tungsten (scrap). The processes can be classified into direct recycling, indirect or chemical recycling, semi-direct recycling and melting metallurgy.

Examples of the most important direct recycling processes are given below. Direct recycling is combined with a minimum of energy consumption, chemical waste generation, and lowest production cost.

Chemical recycling implies that the scrap is converted chemically into “virgin” APT (ammonium paratungstate), the major high-purity intermediate for most tungsten products, with the exception of melting metallurgy. It is done in a similar way to that used for the processing of tungsten concentrates. However, tungsten as W metal or WC must be first oxidised by air, chemicals or electric energy, in order to transform to the hexavalent state (W^{+6}), which is then soluble in an alkaline leach process. Sometimes only a part of the scrap is converted chemically (“semi-direct” recycling) leaving the respective tungsten material (W, WC) intact in powder form for subsequent re-use.

Currently, most “soft” scraps (cutting or grinding sludge, sweepings, powders, turnings, etc.) and the majority of non-sorted hard scraps are recycled via the chemical conversion route. In the interests of economy, preferably more impure scrap qualities, which are not easily converted by other methods, should pass this way. Compared to direct recycling, chemical recycling consumes more energy and chemicals. If present (eg in cemented carbides), cobalt, tantalum and niobium are recovered in separate processing lines to improve process economics.

Melting metallurgy is the process route for tungsten steels and superalloys. Tungsten-bearing scrap can substitute ferrotungsten in steels and high purity tungsten metal scrap can be directly used for addition to superalloys.

Direct recycling

The zinc-process

History

It is said that Edward Moore Trent of Powderloys Limited, Coventry, observed in 1944 that cemented carbide drawing dies, made of WC and Co, were strongly attacked by zinc metal at elevated temperatures during drawing of brass wire (a copper/zinc alloy). Based on this observation, he filed a patent with the idea to treat cemented carbide parts with liquid zinc (US Patent 2,407,752/1946 – *Process of Separating Hard Constituents from Sintered Hard Metals*) for the recovery of useable WC powder. As the cemented carbide parts bloated during the zinc-treatment, the reaction mass could be easily disintegrated. A subsequent acid leach dissolved the zinc/cobalt phases, leaving behind the valuable WC powder. Today, this process would be classified as a semi-direct recycling method, as only WC remained intact. No industrial use of this patent is reported.

In 1971 the idea of a Zn-treatment of cemented carbides was taken up by Paul Barnard (US Patent 3,595,484) who proposed to substitute the acid leach as described above by a vacuum distillation process of zinc (boiling point: 907°C; at atmospheric pressure). In this case, both WC and Co remained as a final powder product. This second part of the treatment rendered the breakthrough of the Zn-process for industrial implementation.

The process was commercialized in 1975 by Teledyne Inc’s facility in Huntsville, US. Basically, the treatment today still follows the guidelines of the Barnard patent, but significant developments in engineering were made for further improving the economy of the process.

Process

Carefully sorted and cleaned cemented carbide scrap is exposed to liquid Zn and Zn-vapour in graphite crucibles under argon or nitrogen at processing temperatures between 600°C and 900°C (furnace temperatures of 800°C to 1050°C) for several hours, depending on scrap composition, size of parts, WC grain size, etc (**Figure 2**). Coatings and solders must be thoroughly removed from the cemented carbide parts prior to processing, as otherwise they will be present as contaminations in the recycled material and finally the ready-to-press (RTP) powder. Liquid zinc reacts with the binder (Co-, Ni- or Fe-based) to form intermetallic phases which lead to a volume expansion of the binder and bloats the scrap parts. After vacuum distillation of zinc, the material is porous and friable and can be readily disintegrated (**Figure 3**). The condensed zinc can be re-used. The reclaimed carbide/metal sponge contains less than 50 ppm Zn (**Figure 4**).

Distillation of zinc starts at atmospheric pressure at temperatures above the boiling point of zinc (furnace temperatures of 1000°C to 1050°C), and the pressure is gradually reduced to a final pressure of 10^{-2} mbar, which takes another few hours. The cooled-down material is crushed, ball-milled, and screened to <200 mesh. The top screen is recycled in the next batch [2].

The chemical composition of the final product is almost identical to the original, with the following exceptions:

- Pick-up of approximately 0.1% Fe (during milling operations)
- Depletion in carbon by 0.12 – 0.15%

The energy consumption is approximately 4kWh/kg, which compares favourably to virgin WC produced via the chemical route (12 kWh/kg) [1]. Compared to the features of indirect conversion, the cost of zinc reclamation is reduced by 20 – 30% for WC-Co grades and by 30 – 35% for WC-TiC-Ta(Nb)C-Co grades [2].

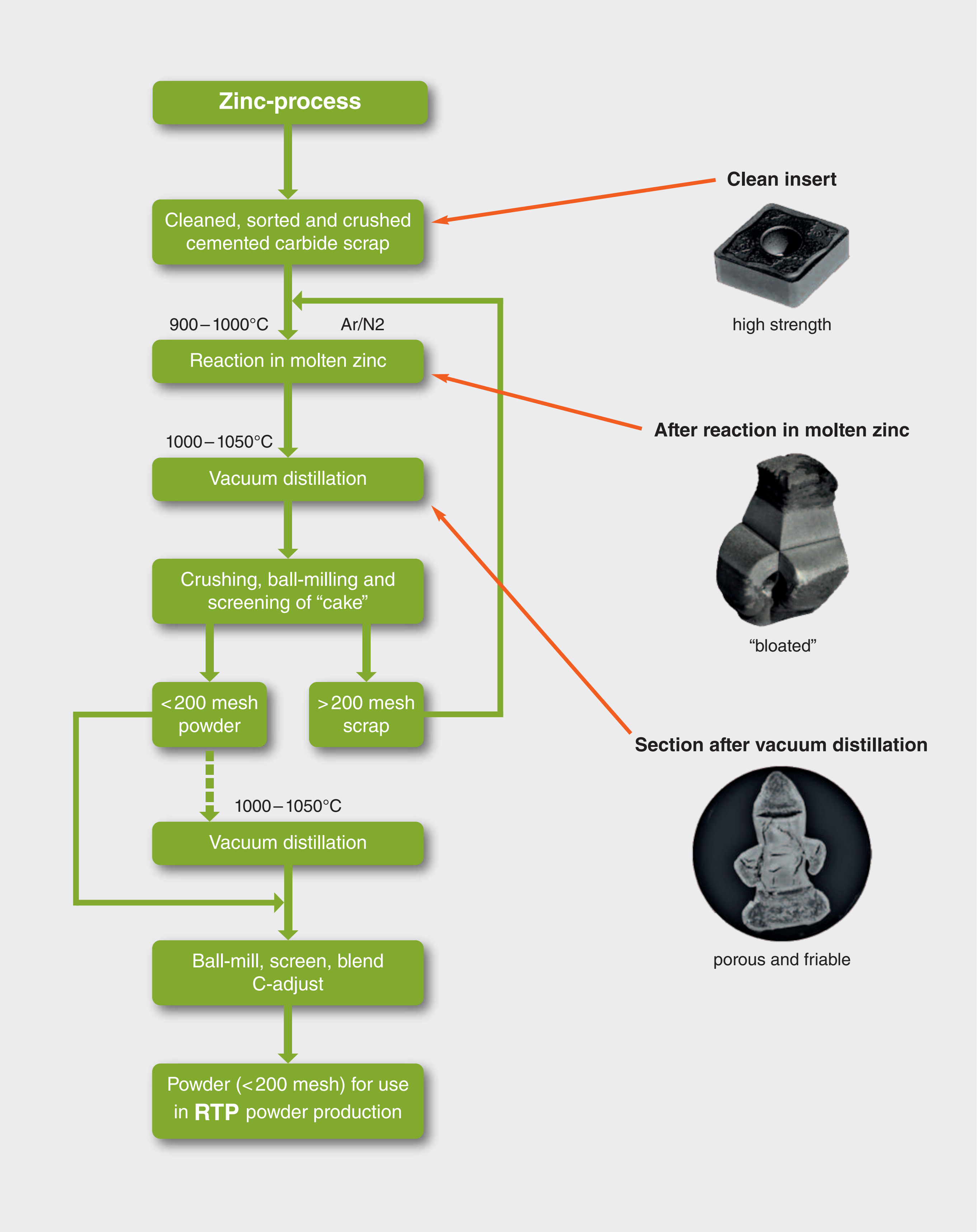


Figure 2: The zinc-process [2]. Sorted and cleaned cemented carbide scrap is converted into a friable powder with the same composition as the scrap (direct recycling). Coated scrap has to be de-coated and solders have to be removed prior to processing. RTP signifies ready-to-press

Figure 3: Changes in morphology during the Zn-process. Sorted cemented carbide round tool scrap as input material for Zn-recycling (**A**). Round tool scrap after reaction with molten zinc and vacuum distillation (**B**). Final Zn-reclaim powder after ball milling, screening and carbon adjustment, ready to use for RTP (ready-to-press) powder production (**C**). Courtesy of CERATIZIT S.A.

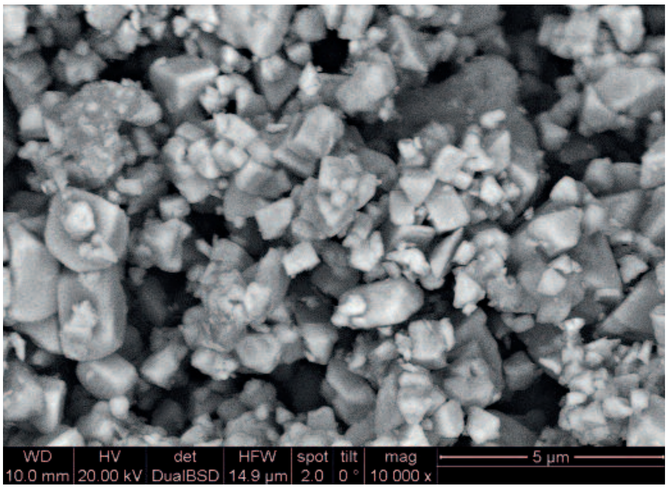


Figure 4: Scanning electron microscopical image of a tungsten carbide (light grey particles), cobalt (darker grey areas) zinc reclaimed grade powder. Courtesy of Prof. Schubert/TU Wien

Process Variations

Coarse-grained cemented carbides sometimes need an additional bloating process of the scrap to increase the WC grain size in the scrap to counterbalance any size reductions occurring later during crushing and ball milling (during RTP conditioning). The bloating is done by heating the scrap in graphite crucibles under hydrogen or argon up to 1900°C (**Figure 5**). The new generation of zinc processing equipment optimises the energy balance of the process by using the exothermic phase changes of Zn-condensation and re-sublimation for the heating of a subsequent scrap charge.

Figure 5: Bloated cemented carbide mining bits. Bloating is done by heating the scrap under hydrogen up to 1900°C. Courtesy of Wolfram Bergbau und Huetten AG

Sometimes a second distillation step is performed after coarse crushing to achieve a low amount of Zn in the residual powders. Further disintegration of the powder after sieving below 200 mesh can also contribute to the achievement of a higher quality (homogeneity) of the recycled powders. 10 to 50 wt% of these powders are commonly added to virgin powder batches for the manufacturing of cemented carbide parts. If well-sorted production scrap is used, the share can go up to 100%.

The Zn-process can be applied for all currently available cemented carbides grades, such as Co-, Ni-, or Fe-based cemented carbides. In principle, it also works for cermet materials (Ti(C,N)-based cemented carbides), as well as tungsten heavy metal or tungsten copper parts [3], but is not yet applied on an industrial scale.

Limits

The use of Zn-reclaim for recycling of cemented carbides is currently limited for a series of reasons. First of all, as the quality of the scrap is the most important prerequisite for a successful processing of the scrap, it is also a limiting factor in practice. Any insufficient sorting will directly affect the quality of the RTP powder and the subsequently sintered cemented carbide part. This implies that optimised collection and sorting technologies are becoming crucially important for increasing the amount of upcoming shares in direct recycling; although Zn-reclaim renders the most economic recycling technique for cemented carbides (**Figure 6**). This challenge has to be seen from today's strategies of extended use of alternative binder grades (CoNiCr-grades, FeNiCo-grades) or composite materials (parts made from two or even more different grades) in application, which pose a new problem in scrap identification. The use of a standardised bar code identifiability of individual grades (brought up during part manufacturing) might contribute in the future to a more efficient and reliable automatic sorting.

Zn-reclaim is also limited by the size of the parts, although unreacted parts can be recycled to a new charge. Therefore, large parts have to be disintegrated into smaller parts, prior to processing (if at all possible). Further, high-binder grades (up to 30% binder) are not optimal candidates for this kind of processing, as significant sintering of the binder can occur during the Zn-treatment.

Figure 6: X-ray fluorescence assisted sorting. Sophisticated technology is required to guarantee premium quality reclaim powders. Courtesy of Tikomet Oy

Last, but not least, repeated recycling through Zn-processing will enrich certain impurities, such as iron (picked up during ball milling) or other elements which are introduced by inaccurate sorting or insufficient separations of coatings. Thus, it is easy to understand that only a certain percentage of cemented carbide recycling will be possible by the Zn-process, and the contribution of chemically recycled scrap or the use of primary raw materials are necessary to keep trace elements below the required threshold limit for production of high quality cemented carbides.

Today, about a third of cemented carbide hard scrap is recycled by the Zn-process in Europe and the US [4], and about two thirds through chemical recycling. The total tonnage of available hard scrap for Zn-treatment will certainly increase in future due to market increases and improved material collection strategies.

Mechanical pulverizing of cemented carbide scrap

Salvaging cemented carbide tool bits by crushing them and re-sintering of the broken pieces under pressure was originally proposed in 1933 (US Patent 1,895,367). The mechanical disintegration could be facilitated by heating the scrap in hydrogen to about 1800°C followed by rapid quenching and the introduction of thermally induced stresses and pores ("Bloating"; US Patent 2,138,672).

There are different possibilities to crush and mill cemented carbide scrap but, due to their high intrinsic hardness and wear resistance, a significant pick-up of iron and other contaminants always occurs. Therefore, it was proposed in 1954 (US Patent 3,184,169, **Figure 7**, [5]) to pneumatically pulverise scrap cemented carbides by entraining the material in a high pressure, high velocity stream of air to accelerate parts against a target with sufficient energy to cause fracture (velocities up to twice the speed of sound). The air is cooled by expansion from a venturi-shaped nozzle, protecting the scrap from oxidation. After screening or air classification, oversize material is treated again. Contamination is prevented as there are no moving parts and the

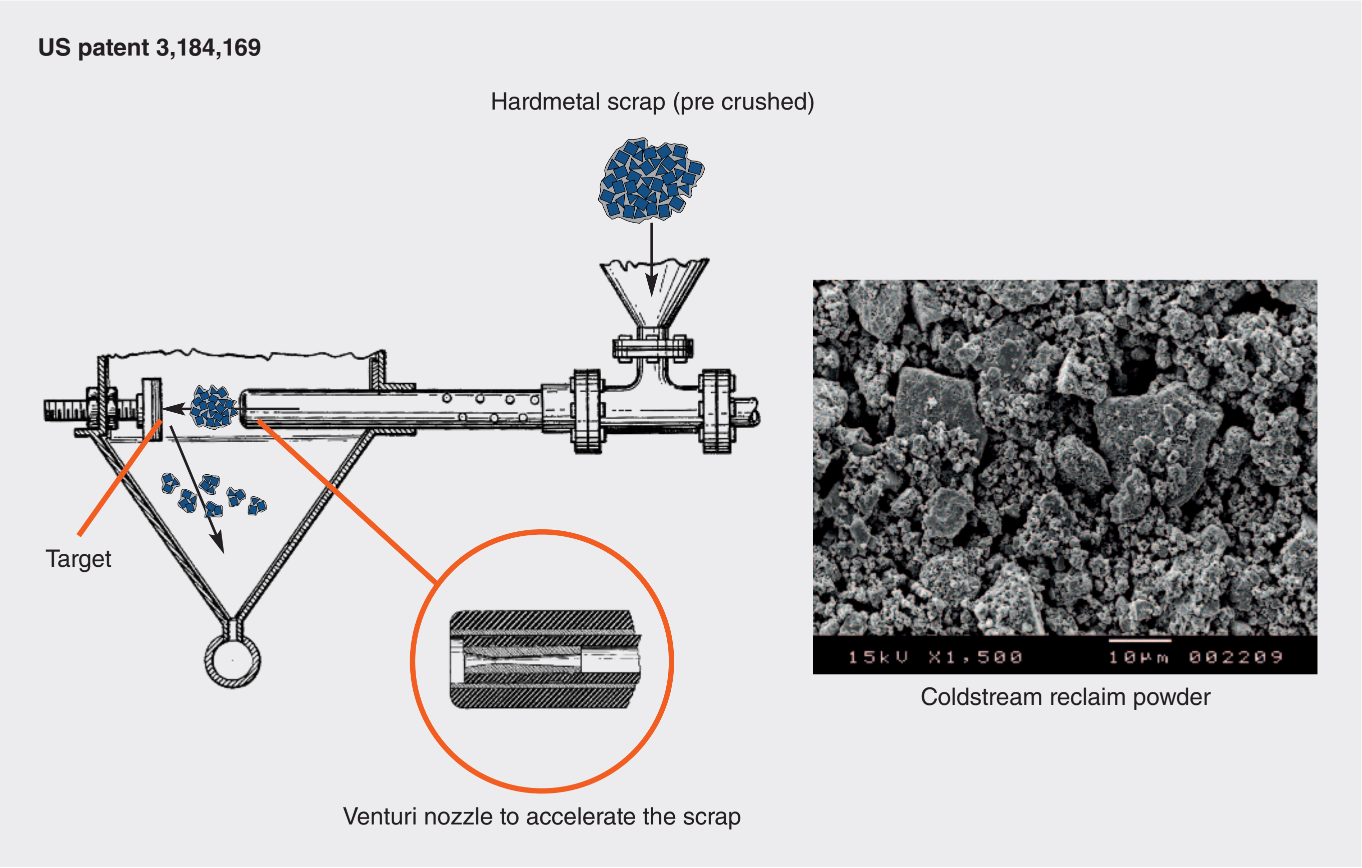


Figure 7: The Coldstream Process based on US Patent 3,184,169 [5]. Sorted, cleaned and pre-crushed cemented carbide scrap is entrained in a high pressure, high velocity stream of air and accelerated against a target with sufficient energy to cause fraction and pulverisation (left). Scanning electron microscopic image of the pulverised powder (right).

target, the main wear part, can be of the same composition as the feed material. Later, this process became well known as *The Coldstream Process* [6]. Mechanically pulverising methods have only limited share in the modern cemented carbide recycling industry due to the high iron pick-up (up to 1 wt%). However, they might be used in less quality conscious markets and applications, or as a feed for hardfacing applications. In hardfacing, tungsten-containing cermets (Ti(C,N)-based hardmetals) might be used as well, which would otherwise not be recycled.

Oxidation-reduction of heavy metal turnings

Heavy metal turnings (composed of W-NiFe, W-NiCu and W-NiCo) can be oxidized by air at about 800°C (**Figure 8**).

Figure 8: Flow-sheet demonstrating the direct recycling of clean heavy metal turnings by oxidation in air and subsequent hydrogen reduction. Original turnings and the respective oxidised materials are shown in the images to the right hand side. On oxidation different tungstates are formed besides WO_3 which give their colours to the reaction product $[(Fe,Ni)WO_4]$. Contaminated material is pressure digested and tungsten is converted into high purity APT by chemical recycling. Courtesy of Prof. Schubert/TU Wien

Overheating during the exothermic reaction has to be avoided to prevent local melt formation. The oxidised product is subsequently milled, screened and finally reduced in hydrogen atmosphere at 900°C to 1000°C in the same type of pusher furnaces used for W-powder production. The resulting powder can be directly used for production of new heavy metal parts [2].

Oxidation, reduction and carburisation of cemented carbide scrap

Clean WC-Co cemented carbide scrap can be reclaimed by, subjecting the carbide to oxidation, to produce a mixture of tungsten oxide and cobalt tungstate. Subsequently the oxide / tungstate mix is reduced by hydrogen and finally after mixing with carbon black, carburised to form a WC-Co powder mix, which can be consolidated to cemented carbide again [13].

Chemical Recycling

The majority of tungsten scraps are still chemically recycled to obtain high purity starting materials for the modern PM industry. Chemical recycling (also called indirect recycling) is flexible in treating almost all kind of tungsten scraps, and relies on well-approved hydrometallurgical processes, developed at first for the primary raw materials route (concentrates). This allows the build-up of major production lines, where both primary and secondary raw materials are well integrated, and synergies between the two material flows can be established. It also renders a throughput of large amounts of scrap volume. Producers in both Europe and the US will have today about a 50/50 share between primary and secondary raw materials for the production of intermediates.

Chemical Recycling can be applied to all sorts of PM tungsten, such as cemented carbide, tungsten heavy metal, contact materials (W-Cu, W-Ag), tungsten metal, tungsten carbide, and tungsten oxide. It can be used for the recovery of tungsten chemicals (if economically feasible) and is able to treat both “soft” and hard scrap. It enables the industrial manufacturing of high purity materials (APT, AMT, WO_3, W, WC) and also renders the economic recovery of valuable by-products (Co, Ni, Cu, Ag,Ta, Nb), stemming from the scrap.

History

It is hard to trace back to when and where the first chemical processing of tungsten scrap took place. However, the early chemical fusion in bath processes, which were developed for tungsten concentrate processing, already used the addition of oxidising alkali salts, such as chlorate and nitrite, to the sodium carbonate or sodium hydroxide melt (eg British Patent 122,051/1919). Such additions are necessary to oxidise tungsten scrap, when added directly to the process.

First experiments using sodium nitrate showed that this is a difficult-to-control process due to very high reaction rates at a temperature of 700°C to 1000°C. Different patents were then filed to control the explosive character of the fusion process (for example: US Patent 1986 4,603,043/1986 – *Controllable Nitrate Fusion*).

Later the alkaline fusion technique (pyro metallurgy) to treat concentrates was gradually replaced by alkaline autoclave leaching (hydro metallurgy), which is easier to control. In this process, scrap cannot be used directly, as it has no intrinsic oxidation step which is needed to make the scrap soluble in aqueous solutions. A new recycling route had to be established and was first patented in 1975 (US Patent 3,887,680/ 1975 – *Process for Recovering Tungsten from Tungsten Carbides containing an Iron Group of Metals*), based on an even older patent published in 1955 (US Patent 2,704,240 – *Process of Preparing Tungsten Oxide from Sintered Masses containing Tungsten Carbide*). Oxidation of the tungsten bearing scrap (W, WC) was now performed in air to form tungstates. Larger parts needed to be crushed prior to oxidation in air (which is less “aggressive” as compared to the fusion techniques). Subsequently, the tungstates ($CoWO_4$, $NiWO_4$, etc) were pressure leached, similar to wolframite concentrate (which is an iron manganese tungstate). It is now called the oxidation/digestion route (see Figure 1).

Besides alkaline leaching of tungsten, alternatively the respective binder metals can be leached selectively, with WC powder or W powder remaining as valuable residue. These processes are called semi-direct recycling and can be applied to all sorts of soft and hard scraps. Depending on the quality of the residue material, these powders can be used as an alternative to virgin materials, or in the case of low-quality, they may be further treated via alkaline fusion or the oxidation/digestion route.

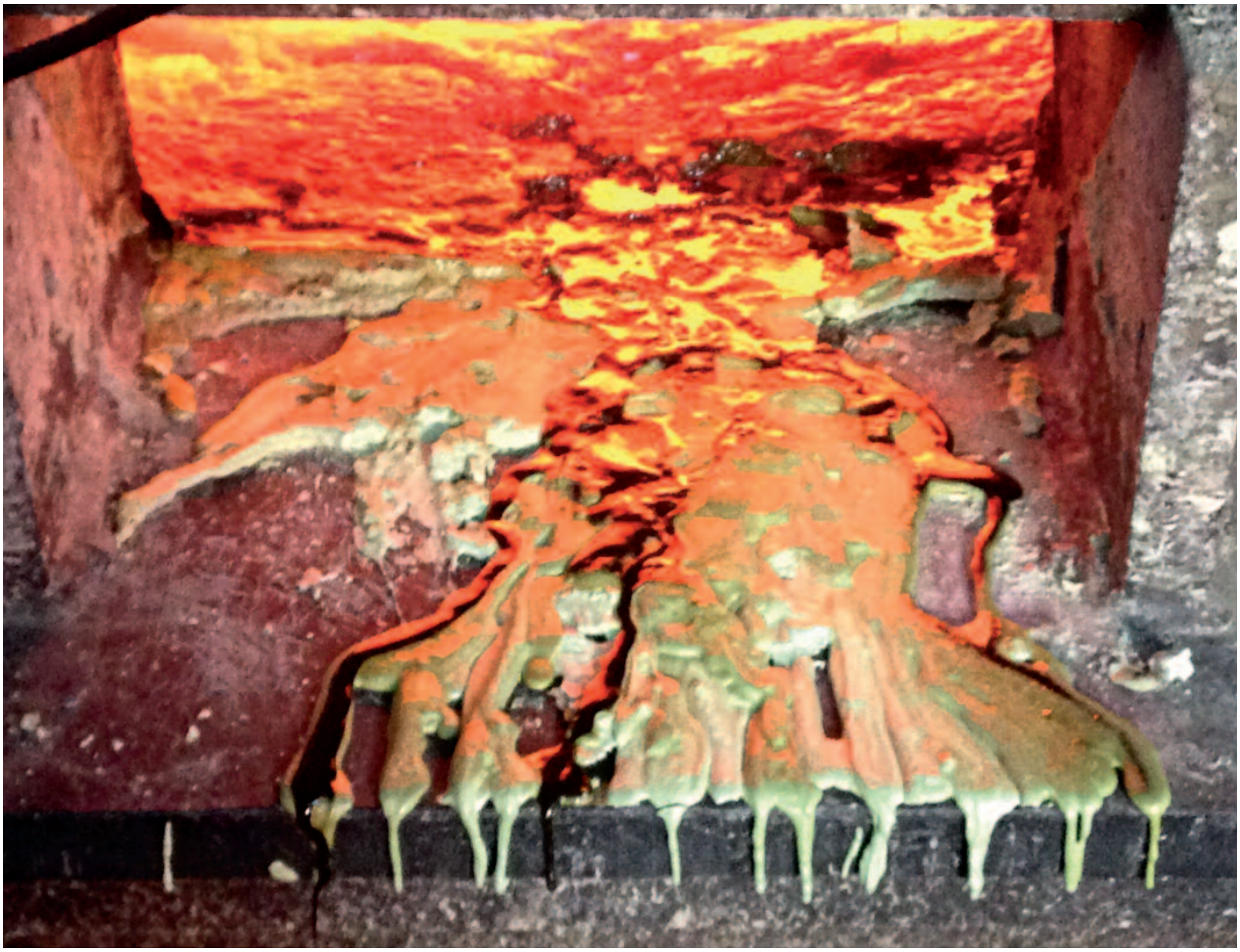


Figure 9: View into a smelting furnace. Tungsten scrap is reacted with sodium nitrate, hydroxide and carbonate to form water soluble sodium tungstate, which is leached in hot water and the solution is filtered. Courtesy of H. Schulze, Mexico D.F.

Alkaline fusion

Alkaline fusion combines the two steps of oxidation and digestion in one step. It is carried out at high temperature (commonly between 550°C – 800°C) in smelting or rotary furnaces with sodium nitrite or sodium nitrate as oxidizing agent and sodium carbonate and/or sodium hydroxide as flux and diluent. Sodium tungstate is the desired reaction product, which is leached in hot water and the solution is filtered. This removes scrap attendants such as Fe, Mn, Co, Ni, Cu, Ta or Ag, which form water insoluble compounds (**Figure 9**).

Due to the strongly exothermic reaction and the massive formation of gases, the process must be carefully controlled to avoid overheating and explosion-like behaviour. In addition, the process is a far from environment friendly operation, as nitrous fumes are formed (which have to be converted, eg to harmless N_2 or nitrous oxide), and non-reacted sodium nitrite and sodium nitrate pose problems during subsequent purification of the sodium tungstate solution, in particular when using solvent extraction [7].

More recently, new methods have been developed to avoid or master the reactivity of the violent reaction, either by changing to a new melt system with less exothermic occurring reactions, such as working in a $NaOH/Na_2SO_4$ fusion bath [7], using air as oxidising agent, or to move to smaller, better controllable units, where the scrap is directly added to a $NaNO_3$ melt in a well controllable form, and the presence of free $NaNO_3$ in the resulting sodium tungstate is avoided by the operation mode (**Figure 10**, [8]). Subsequent purification of the tungsten solution is done by ion exchange equipment, and the nitrogen oxides in the off-gas are transformed to nitrogen gas by modern DeNOx-catalysts [9].

The big advantage of the alkaline fusion process is its versatility in terms of scrap input and scrap throughput. Difficult to oxidise materials, such as tungsten heavy metal hard scrap or tungsten copper hard scrap can be processed by this method.

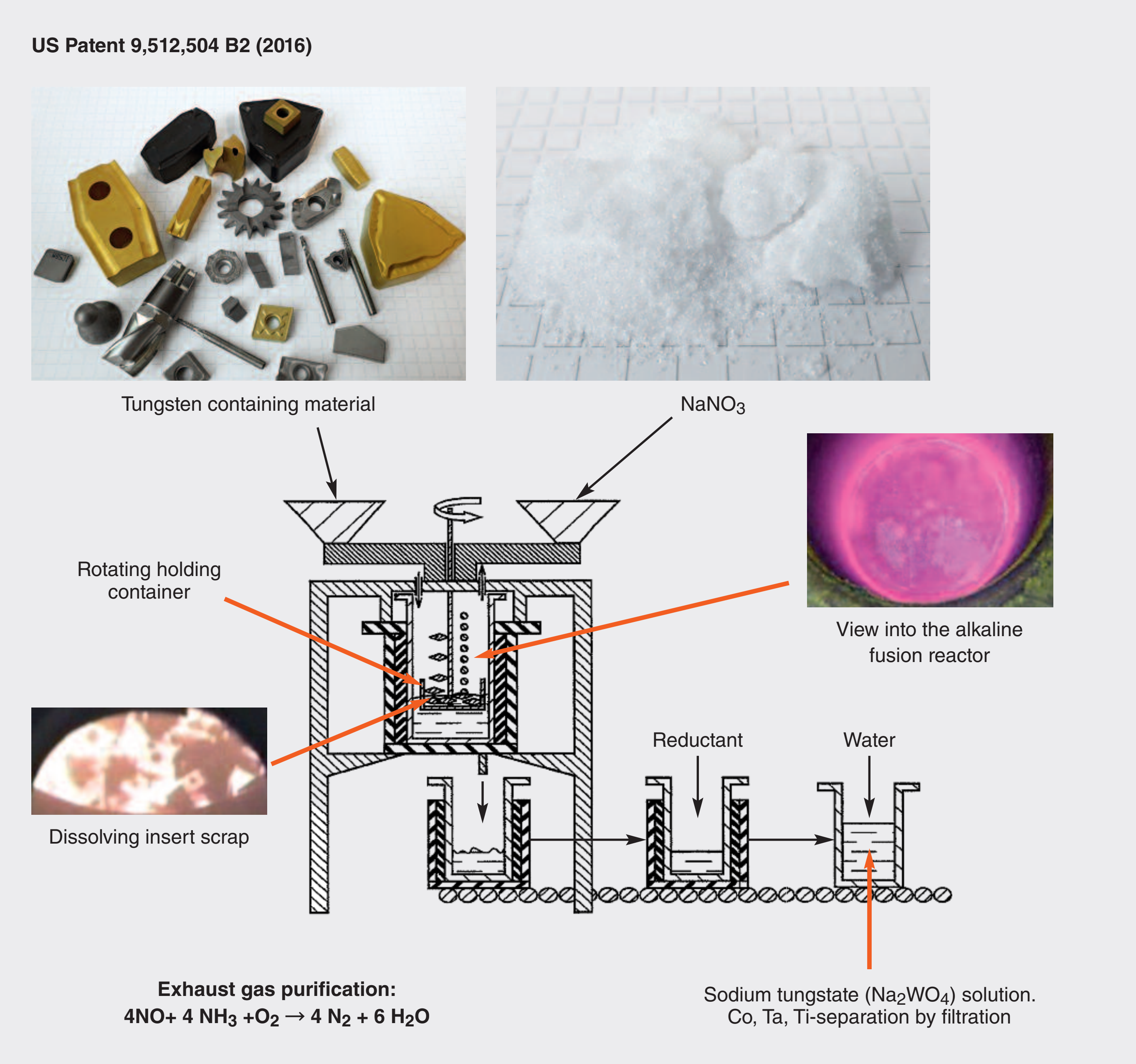


Figure 10: Schematic presentation of a novel alkaline fusion process. The tungsten-containing hard scrap is added to a rotating holding container and reacts with molten $NaNO_3$ at operating temperatures of 700°C to 850°C. Excess $NaNO_3$ is subsequently reacted with tungsten soft scrap ("reductant") to form Na_2WO_4. The melt is dissolved in water to form an aqueous solution of sodium tungstate, and separated from non-soluble Co-, Ti- and Ta-oxides. NO gas formed by the treatment is detoxified by modern DENOx-catalysts. Courtesy of A. Ikegaya, ALMT Corp

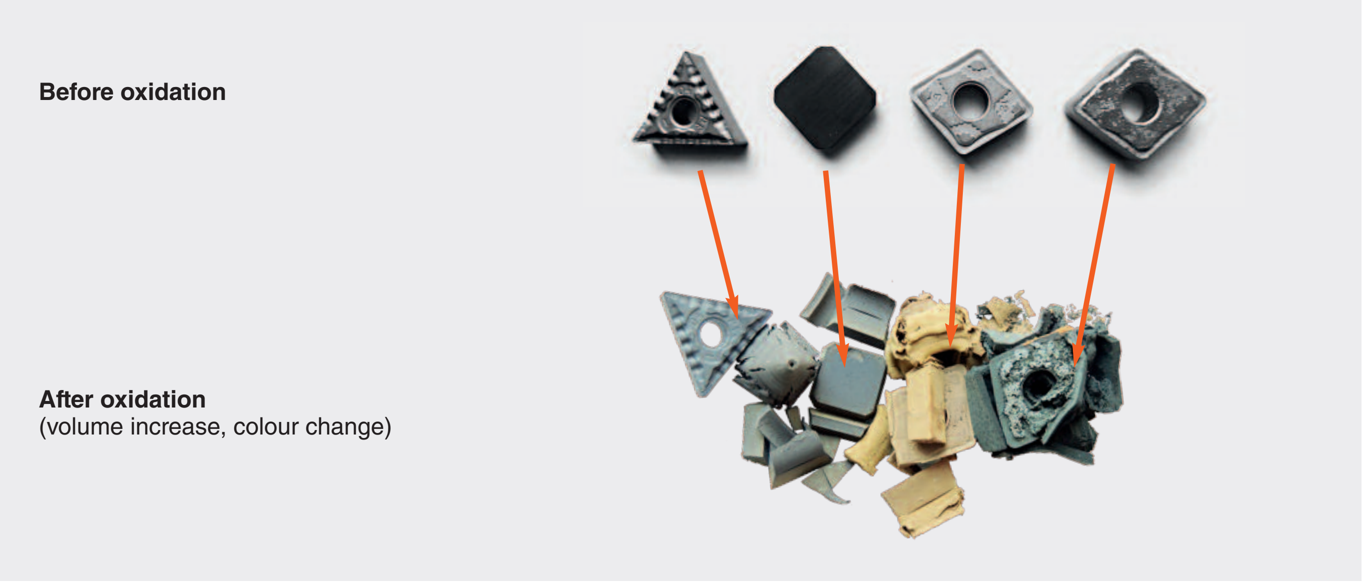


Figure 11: Oxidation of tungsten scrap in air at 900°C. Four different cutting inserts, from left to right: Ti(C,N)-based cermet, WC-Co-Ni grade, WC-Ni-Cr grade and WC-Co grade, before and after oxidation. The cermet (to the left) is not affected and only the surface is slightly oxidised. All other inserts are fully oxidised. The colour of the oxidised insert is a function of the composition (ie third from left: yellow colour of Ni tungstate).

Oxidation and alkaline digestion

This method consists of two steps. First, soft or hard scrap is oxidized in air to form a mixture of tungsten oxide and tungstates, depending on scrap composition (WO_3, $CoWO_4$, $NiWO_4$, Cr_2WO_6, $CuWO_4$, etc; **Figure 11**). Large scrap parts must be mechanically disintegrated to smaller sizes to improve their oxidation behaviour and enhance the throughput (Step 1). Secondly, the friable oxidation product is then treated to recover the tungsten content by digesting the oxidation product in an aqueous solution of sodium hydroxide under controlled conditions of temperature and pressure (Step 2).

Oxidation is carried out in air or oxygen-enriched air at a temperature preferably between 800°C and 900°C in multiple hearth furnaces (**Figure 12**), pusher-type kilns or rotary furnaces. Pressure digestion is performed under conditions similar to those used for wolframite digestion

Figure 12: Multiple hearth furnace for oxidation of tungsten scrap. Courtesy of Wolfram Bergbau und Huetten AG

(20% NaOH, 150°C – 200°C, 5 – 12 bar), and can be carried out in the same aggregates as used for tungsten concentrate, ie primary raw materials (**Figure 13**) [1].

The tungsten-bearing solution is filtered in filter presses. The filter residue contains valuable concentrates of scrap attendants such as Co, Ni, Cu and Ta, which are either converted into high-purity materials on site or, alternatively, by another specialised company. Preselection of certain valuable grades can increase the profitability of processing. The further purification is done in the same way and in the same aggregates as used for processing of primary raw materials (concentrates).

Oxidation and digestion currently represents the workhorse of chemical recycling in large production plants globally (**Figure 14**). It can be well integrated into plants originally built to convert primary raw materials into high purity tungsten products. The resulting W and WC powders have the same properties as those originating from concentrates (*Reclaimed Tungsten Powders with "Virgin" Properties*).

Semi-direct-recycling

Binary- or ternary-phase tungsten alloys can also be recycled by removing one component (in most cases the binder) by selective dissolution in acids or alkaline media, leaving the other phase(s) intact. By dissolution of one component, the integrity of the structure is lowered and easy disintegration becomes possible.

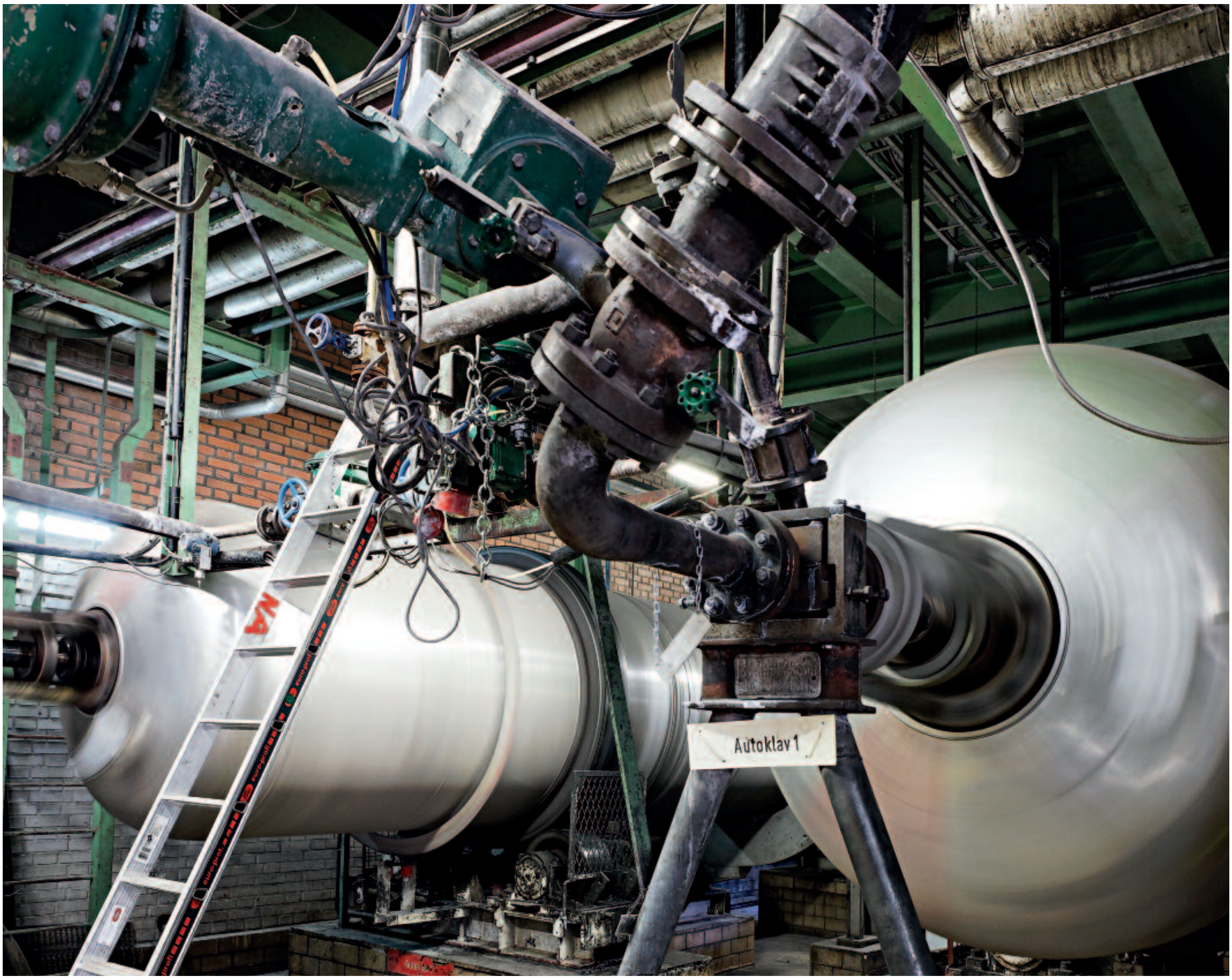
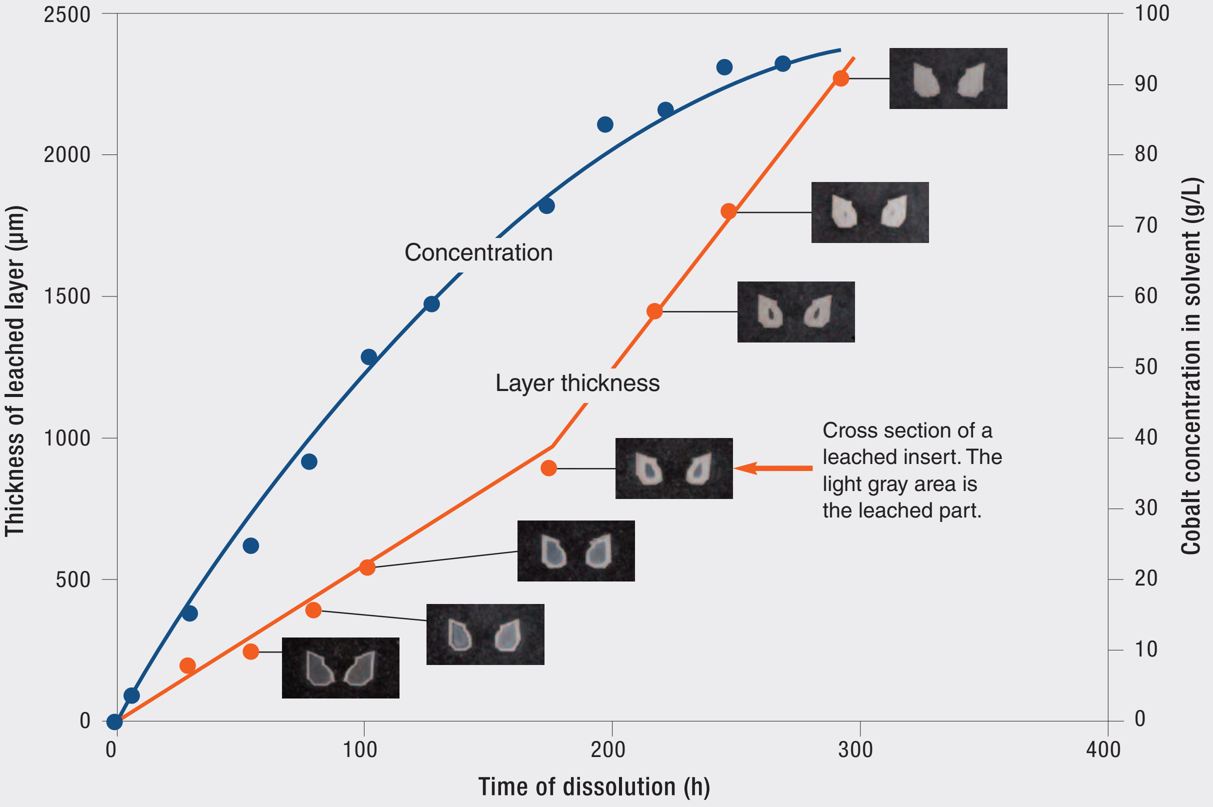


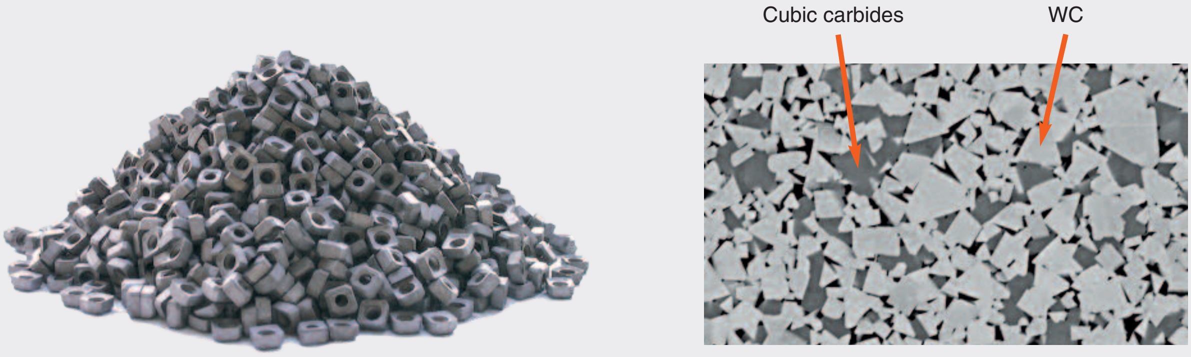
Figure 13: Pressure digestion autoclaves. Courtesy of Wolfram Bergbau und Huetten AG

Figure 14: Oxidation of tungsten scrap in air or oxygen-enriched air at 700 to 900°C and subsequent digestion in NaOH depicts today's most frequently used chemical recycling route. Purification of the aqueous sodium tungstate solution can be carried out in the same aggregates as used for primary raw materials. Finally, high purity virgin W and WC powders are obtained.

Most binder alloys in tungsten- or tungsten carbide-based composite materials are readily soluble in acidic aqueous media (whereas W and WC form passive layers), so they can be separated from the tungsten valuables by an acid leach. Several mineral acids are used industrially, in most cases hydrochloric acid, but sometimes also nitric acid, sulphuric acid or phosphoric acid. In the case of other noble metals, such as Cu or Ag, a higher oxidation potential is necessary for metal oxidation in aqueous solution, and oxidising agents must be added, except when using nitric acid (which has a stronger oxidation potential, per se). If adding oxidising species, organic acids can also be used for binder separation (**Figure 15**) [10].



Progress of acetic acid leaching of a hardmetal insert over time [10]



Hardmetal inserts after leaching of the binder

SEM image of the porous hardmetal insert microstructure after leaching of the binder

Figure 15: Acetic acid leaching of WC-Co cutting inserts containing cubic carbides. As the tungsten containing part keeps both the chemical state and the morphology, but the binder metals are dissolved in a liquid phase, this process is called semi-direct recycling. The WC-powder mixed with the cubic carbides can be reused for alloy manufacturing. The solution is processed for recovery of the respective binder metals (Co).

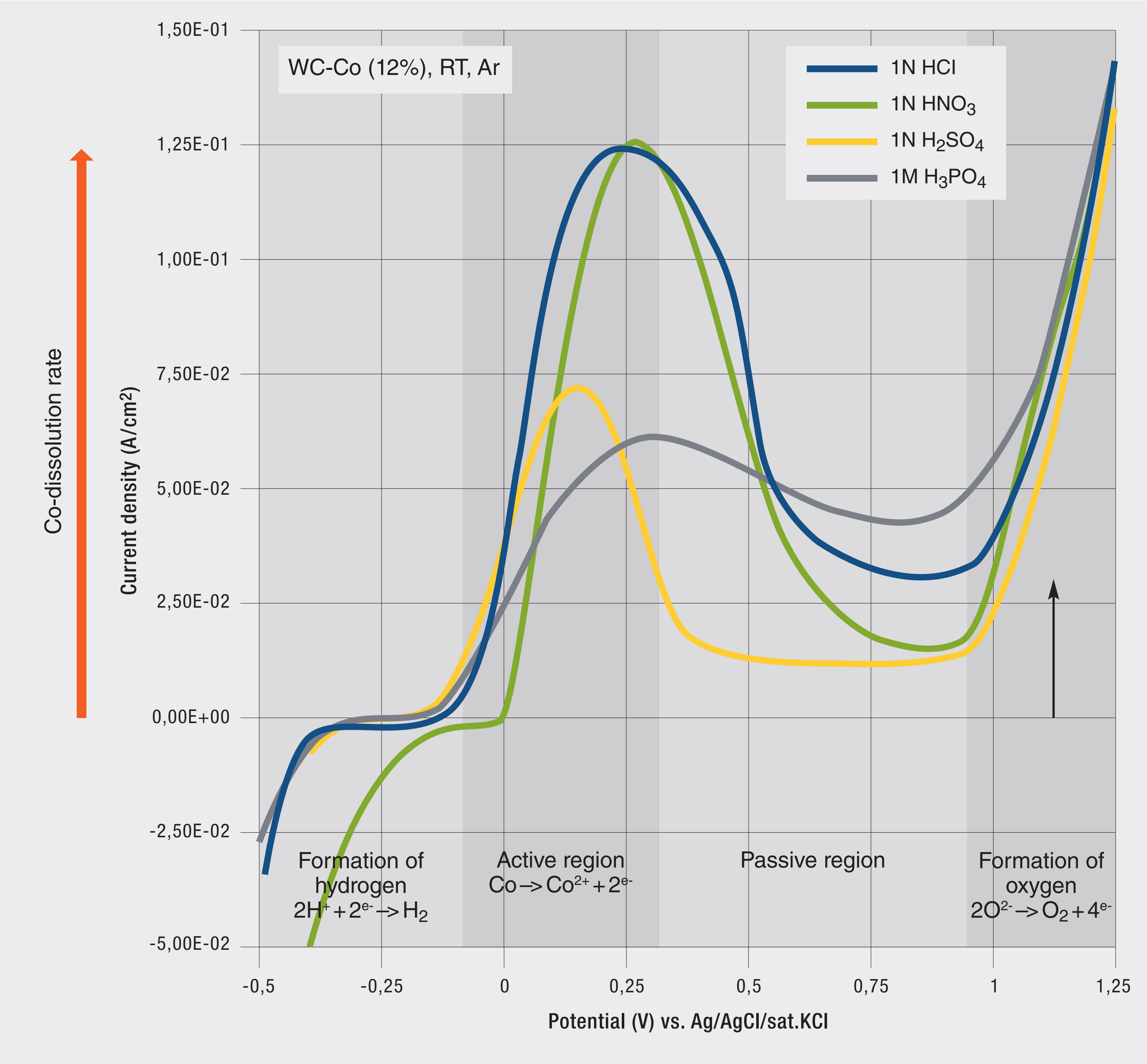


Figure 16: The leaching rate in acids can be enhanced by anodic dissolution of the tungsten scrap in an electrochemical device. The diagram plots current density as a function of the applied potential. An increase in current density, equal to the dissolution rate of the binder, is obtained by increased potential between -0,10V to 0.25V (increased oxidising "power"). At higher potential (>0.25 V) the scrap passivates and the dissolution rate decreases sharply. For the investigated WC-12% Co cemented carbide scrap, the highest dissolution rate is observed with hydrochloric acid and nitric acid, followed by sulfuric acid and phosphoric acid. Such diagrams can be used to optimise leaching processes.

Acid leaching can be done for both hard and soft scraps. The dissolution of the binder metals can be enhanced by mechanical activation (stirring, tumbling, etc.) in the form of a leach/milling process [11], but also by using an electrochemical device, to establish a higher oxidation potential for the binder oxidation and thus higher dissolution rate (**Figure 16**). In this case, the scrap is operated as an anode where the binder dissolves in the acid. To counteract contact resistances formed between the reacting scrap particles, rotating devices are preferred (for example: US Patent 4,234,333/1980 – *Process for Recovering Metal Carbide from Cemented Carbide*). Although the dissolution rate can be increased, the whole process becomes more complex, which has to be considered in the calculation of the economics.

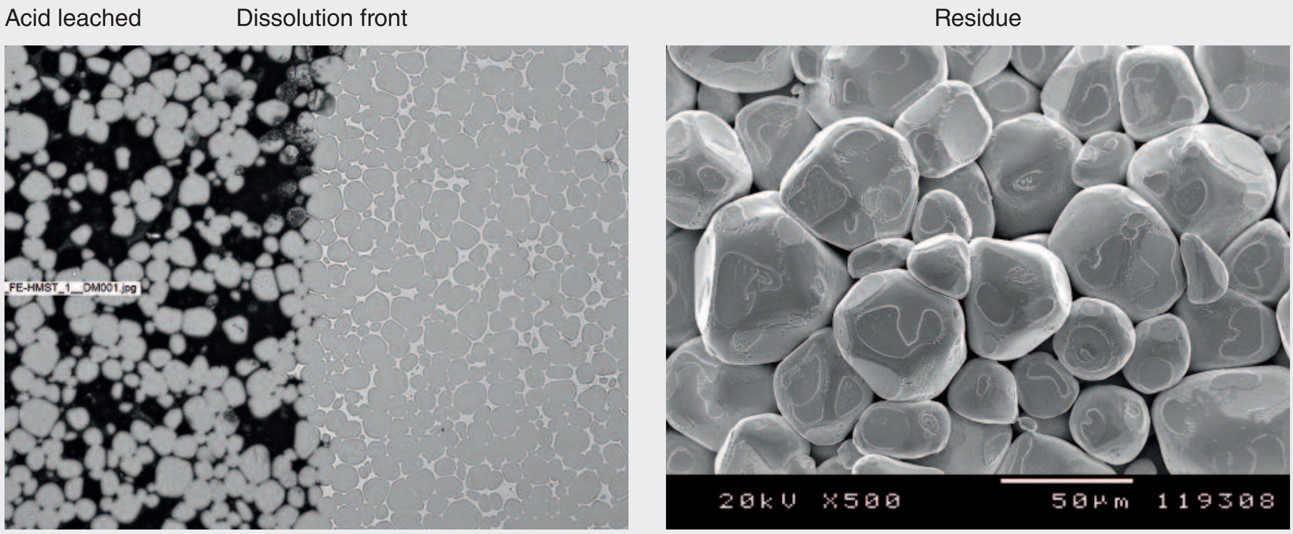


Figure 17: Section of a heavymetal part (W-NiCu) partly dissolved in a mix of sulfuric and phosphoric acid (left). The NiWCu-binder is dissolved in the acid, whereas the rounded W particles remain as residue containing Ni in solid solution (right). Courtesy of T. Zimmerl/ Master thesis (2007, TU Wien)

In the case of tungsten heavy metal scrap, it is more difficult to leach the binder due to its higher corrosion resistance. A combination of acids (eg phosphoric acid/ sulphuric acid) to avoid precipitation of colloidal tungstic acid (**Figure 17**) or additives like iron(III)-chloride have to be used [1].

Alkaline media can also be applied for dissolution of tungsten-bearing scrap, such as aqueous solutions of ammonia (for example: British Patent 857,969/1959 – *Improvements in or relating to the Production of Tungsten Powder*; US Patent 3,635,674/1972 – *Process for Recovery of Refractory Carbide Particles from Pieces of Cemented Carbides*), caustic soda (for example: *British Patent 848,462/1958 – Improvements in or relating to the Production of Tungsten Powder*) or sodium carbonate [12]. However, no large-scale operation is known to the authors.

Chemical recycling has been the focus of a large number of patents or scientific investigations in the past, but most of the reports are lacking any clear statements about their economic feasibility as compared to standard processes, where the high throughput rate increases their economic viability. Such processes might, however, be interesting for small scale operations for specific scrap materials such as thoriated tungsten, tungsten-based hardfacing materials, cast or infiltrated wear-parts, tungsten-containing catalysts (DeNOx or crude oil treatment….), etc.

Melting Metallurgy

Superalloys, stellites, Menstruum WC, and cast eutectic carbides require very pure scrap (for example, sintered tungsten metal production scrap) while for steel melting metallurgy impure scrap can be used, such as heavy metal parts and turnings, cemented carbide scrap (all depending on composition), etc.

The advantage of the latter is that all oxidic substances (such as grinding media, etc.) end up in the slag, and traces of foreign elements, which are soluble in the metallic melt, are distributed homogeneously. Any tungsten going in this direction cannot be recycled again by other methods, with the exception of re-melting.

High speed steel blanks or turnings are collected according to their specific composition and can be added directly to a new steel charge (**Figure 18**). If added to a metal collection container for ordinary steel recycling, tungsten is lost for the tungsten recycling loop.

Figure 18: Tungsten recycling in melting metallurgy. Scrap is added to the electric arc furnace (EAF, below) to adjust the desired steel composition (ie for HSS applications). The melt is then transferred to an argon oxygen decarburisation converter (AOD, above) for further refining. Courtesy of GT Engineering, Italy and voestalpine BÖHLER Edelstahl GmbH & Co KG

Summary

A wide variety of recycling technologies for tungsten exists today. Processes are tailored to deal with different scrap types and to produce well-defined recycling products. For every combination of given input and expected output there is the optimal process (or a combination of such processes). Future developments in recycling technology will focus on (1) improved process economy and minimisation of environmental impact, (2) increased flexibility concerning input scrap quality and variety and (3) improved process stability and ability to deliver the desired quality of the recycled material. It is fair to assume that a combination of different recycling approaches will be necessary to push global tungsten recycling rates to an even higher level. Cost (and resource) efficient direct recycling technologies will increasingly be used where sufficient well-sorted and defined scrap can be collected. Certain end-use applications may perform perfectly well even with a broader property spectrum in the recycled material, leading to either an extended use of tungsten products (ie new applications) or a more cost effective one, via the potential of direct recycling. The higher the global recycling rate becomes, the more important will be the role of the chemical recycling technologies, which are capable of removing impurities effectively and producing recycling products with virgin properties. This is a kind of "reset button" guaranteeing a low impurity level in the top-quality tungsten end products. With this combination of direct and chemical recycling, the tungsten industry is in a position to push recycling activities to the economic limits and to sustain highest quality at the same time. A certain amount of primary tungsten will always be needed to cover global market growth and to replace dissipation and dilution losses.

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ITIA News

31st Annual General Meeting, 26–27 September 2018, Chengdu

Opening the meeting Gao Bo, the ITIA President, extended a warm welcome to Chengdu to all 270 delegates from 120 companies and 28 countries and thanked Zhuzhou Cemented Carbide Group and Zigong Cemented Carbide Corp Ltd for hosting the event and for inviting delegates to visit their plants in Zhuzhou and Chengdu respectively after the AGM. He also thanked Mr Tang Jie, Member of the Standing Committee of Zigong Municipal Committee and Director of the Publicity Department of Zigong City, for agreeing to deliver a welcome speech at the event.

Gao said there was a Chinese proverb: Do not go to Sichuan when you are young, and do not leave there when you are old. It implied the comfortable and slow life rhythm in Sichuan might weaken the career ambition of the young but definitely suited the life of elderly people. He added that Sichuan was home to the Hot Pot, to Mahjong, to the Giant Panda and its sanctuaries, to the Teahouse and to the most humourous and good-natured people in China. He hoped that delegates would find time to escape the demands of the tungsten business and sample these delights in Chengdu.

Returning to business, Gao noted that the most ambitious project launched by the Association in 30 years – a Tungsten End-Use Analysis – had resulted in the circulation to ITIA members of the first reports prepared by SMR GmbH (Steel & Metals Market Research) covering segments “Mining and Construction” and “Transport” presented to members last year. He reminded members that Markus Moll of SMR would make a summary presentation focussing on “Consumer Durables”, “Defence” and “Energy” segments exclusively for ITIA members at the AGM.

Gao added that, as always, the programme of presentations aimed to keep delegates up-to-date with developments over the past year, especially in terms of demand for tungsten. Given the increasing spotlight on recycled material, there would be a panel of experts to debate market growth and

“Fairy Lotus Dance” performed by staff of Zigong Cemented Carbide

An amazing “Face-Changing”entertained guests at the hosted dinner

Mr Xie Kangde (right), President of Zhuzhou Cemented Carbide Group and his colleague, Mr Hu Qiming (centre), a long time ITIA Executive Committee member, lead delegates to visit their plants in Zhuzhou

technology in this area, led by an expert – Dr Zeiler himself – who in May had co-authored an article in the Newsletter on the subject which had received more compliments than in all ITIA's 31 years of publishing its Newsletters combined. It was not just technical stuff but very much market-oriented and thus of great interest to all in the tungsten industry.

Gao said that his first year as ITIA President had been an honour which he had managed to enjoy thanks to the extensive support received from the former President, Ulrika Wedberg; from the Vice-President, Dominic Heaton; from fellow members of the Executive Committee; from members of the HSE Committee; and from all ITIA members as a whole. No one would be surprised when he drew particular attention to the work of the ITIA staff. He had mentioned Burghard Zeiler whose second thoughts

Visit to Zigong Cemented Carbide's plant in Chengdu

Group photo at Zhuzhou Cemented Carbide Headquarters after awaking from his first operation on his leg after his biking accident were for ITIA (the first were for his two grandchildren!). Great credit was also due to Rose Maby who ran the ITIA office and to Ranulfo Lemus and Carmen Venezia who managed the HSE work programme.

Closing the meeting, Gao thanked the speakers and panellists for their hard work necessary in preparing presentations, and ITIA members and delegates for their contributions. He looked forward to seeing all delegates at the next AGM in Italy.

Obituary

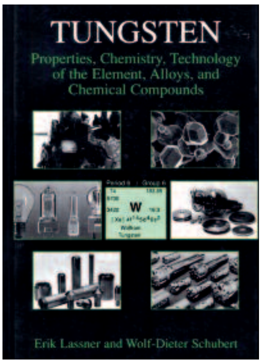
Erik Lassner (1930–2019)

Erik died aged 89 after a fall at his home in March. Born in Graz in 1930, he studied chemistry at the Technical University in Graz, Austria and then worked for Metallwerk Plansee as Laboratory and R&D Manager between 1956 and 1975, before joining Wolfram Bergbau und Hütten GmbH as Plant Manager and becoming a Director. He retired in 1993.

Erik was the author of many technical and scientific publications, not least the seminal book on tungsten entitled *TUNGSTEN – Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds*, which he wrote with his friend, Wolf-Dieter Schubert, and which was published in 1999. He was a consultant to ITIA from 2003 to 2009, ending his invaluable service with the publication of the brochure *Tungsten* of which he was co-author once again with Wolf-Dieter Schubert.

Apart from his technical expertise, Erik was renowned amongst his friends for his mouth-watering culinary skills and his knowledge of wine, whilst his hobbies of cross-country skiing and cycling ensured a healthy appetite.

His wife, Gudrun, died in 2005; he is survived by his partner, Helma.



TUNGSTEN

Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds

Erik Lassner and Wolf-Dieter Schubert

ITIA Membership

Welcome to:

- **Elbrus Mining Co** – a Russian Company which holds the licence to develop Tyrnyauz Tungsten Deposit
- **Greystone Alloys Inc** – a US Company which trades, processes and recycles tungsten carbide, tungsten hard metals and refractory metals
- **Höganäs Germany GmbH** – a Company producing high quality tungsten carbide powders and metals for surface coatings and ceramics
- **Jiangxi Yaosheng Tungsten Co Ltd** – a Chinese Company which activities including mining, ore dressing, smelting, powder process and hard alloys
- **Lianyou Metals Co Ltd** – a Taiwanese Company active in refining secondary tungsten materials to sodium tungstate
- **Speciality Metals International Ltd** – an Australian Company which acquired the Mt Carbine Quarry and Mining Leases and is entering a joint venture for the development of the mine in North Queensland.
- **Xiamen Golden Egret Special Alloy Co Ltd** – a Chinese Company which is one of the largest producers of tungsten powder, tungsten carbide powder and sintered cemented carbide

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

Election to the Executive Committee

Members at the AGM unanimously approved the election of Mrs Stacy Garrity (Vice-President of Global Tungsten & Powders Corp), Mr Eduardo Martin (Senior Vice-President, Head of Global Sales of Sandvik Coromant) and Dr Hady Seyeda (CEO of HC Starck Tungsten GmbH) to the Executive Committee.

Recently elected members of the Executive Committee, William Thalman of Kennametal (2017) and Stacy Garrity of Global Tungsten & Powders

ITIA's 32nd Annual General Meeting, 15–18 October 2019

At ITIA's Annual General Meetings, members of the world Tungsten industry have the opportunity to meet, exchange information, contacts, knowledge and participate in debates on Tungsten.

OMCD Group will host the ITIA's 32nd Annual General Meeting in Stresa, Italy. On Friday 18 October, there will be a panel discussion on the Future of Hardmetal (Tungsten's Main Application) – "How to Deal with Uncertain Demand, Raw Material Criticality, Sustainability, Health, Safety & Environmental Classifications and Ethical Aspects?"

Details of the AGM, paperwork and updates can be found via https://www.itia.info/next-agm.html.

The outline AGM Programme is as follows:

Date	Meeting / Function
Tuesday 15 Oct	• ITIA HSE Committee • Tungsten Consortium Technical Committee
Wednesday 16 Oct	• Tungsten Consortium Steering Committee • ITIA Executive Committee • Reception and Dinner
Thursday 17 Oct	• AGM • Dinner hosted by OMCD SpA
Friday 18 Oct	• AGM • Visit to OMCD's plants

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