State of the art on the recovery of refractory metals from urban mines

Authors : Mrs. Witold KURYLAK (IMN) T. Retegan (Chalmers), K. Bru, N. Mennade (BRGM), L. Cassayre (LGC), L. Sundqvist, G. Ye (Swerea), J. Yang (GTK), J. Koffeman, Y. Yang (TU Delft), K. Leszczynska-Sejda, G. Benke (IMN)

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Author(s)	Mrs. Witold KURYLAK T. Retegan (Chalmers), K. Bru, N. Mennade (BRGM), L. Cassayre (LGC), L. Sundqvist, G. Ye (Swerea), J. Yang (GTK), J. Koffeman, Y. Yang (TU Delft), K. Leszczynska-Sejda, G. Benke (IMN)
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Summary

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DELIVERABLE 4.2 STATE OF THE ART ON THE RECOVERY OF REFRACTORY METALS FROM URBAN MINES

RECOVERY OF TANTALUM

Contributors: K. Bru, N. Mennade (BRGM), L. Cassayre (LGC)

The major end use of Ta is represented by more than 60% in the production of electronic components (Ta capacitors). This section has thus been divided into two main categories: recycling of electronic waste and recycling of non-electronic waste.

ELECTRONIC WASTE

Tantalum capacitors are used in many electronic applications such as laptops, smart phones, video and digital cameras, and game consoles. For example, mobile phones with cameras may contain up to 23 separate Ta capacitors. The average content of Ta in capacitors is 15-33 wt% and its content in PCB is about 172 ppm.

Ta is currently only recycled from scraps generated during manufacture of Ta containing electronic components, with high recycling rates. No mature technology has been developed to recover Ta from EOL products. Indeed, its recycling from post-consumer electronic waste is facing several technical bottlenecks:

- In electronic devices, Ta is concentrated in components dispersed into PCBs and consequently is difficult to selectively recover and concentrate.
- Ta compounds are covered by several layers of minerals (manganese dioxide, MnO_2) and plastics (carbon). This intimate mixing between parts of different chemical composition impedes recycling process to efficiently separate Ta.
- In addition, during the widely-developed pyro-metallurgical copper route used by e-waste recyclers in Europe (such as Boliden and Umicore), Ta easily oxidizes and migrates into the slag phases.

The recovery of Ta from capacitor scraps using an oxidation process followed by mechanical and chemical treatment was investigated by several authors [1, 2]. In these studies, sintered Ta electrodes inside the capacitor scraps are collected mechanically after the oxidation of the scraps in air and by combination with chemical treatment; tantalum oxide powder (Ta_2O_5) with high purity was recovered by reducing the Ta_2O_5 obtained through magnesiothermic reduction (Figure 1).
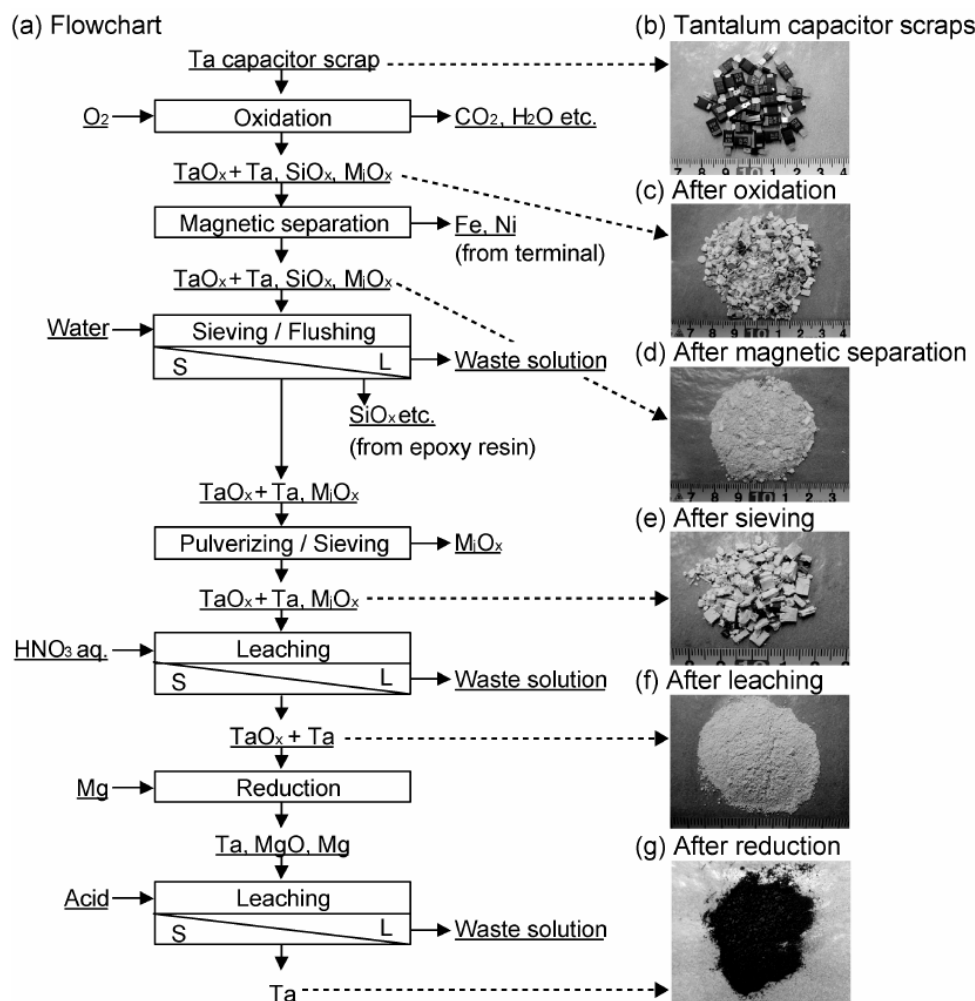
Figure 1: Flowsheet of Ta recovery from Ta capacitor scrap [1]

Several processes for reducing Ta oxide powder to Ta powder have been reported in the literature and are listed below:

- Hunter Process which includes a sodiothermic reduction process may produce Ta powder with capacitor grade [3];
- Reduction process of Ta oxide by calcium, this reductant being supplied to the oxide through molten CaCl2 [4];
- Reduction process of Ta oxide by alumina in a plasma reactor [5];
- Direct reduction processes such as calciothermic reduction and aluminothermic reduction [6].

Chlorination is another possibility to recover tantalum powder. Tantalum compounds are reacted with chloride wastes such as FeClx. It was found that tantalum was effectively separated and purified when tantalum powder is reacted with FeClx at 830°C under an argon atmosphere.

Finally, according to Katanoa et al. [7], the recovery of tantalum sintered compact can be performed by using steam gasification with sodium hydroxide at 530°C under nitrogen atmosphere to destroy mold resin and stabilize the halogenated compounds in sodium hydroxide to prevent exhausting halogenated gas. Mold resin can be decomposed by steam gasification with NaOH to recover the sintered compact of tantalum.

NON-ELECTRONIC WASTE

CEMENTED CARBIDES

Tantalum carbide is used mostly in the manufacture of cemented carbide insert and tools, which typically contain about 3% tantalum. The emphasis in recycling of cemented carbide scrap is to recover the contained tungsten, but the recovery of other metals such as tantalum is also considered. In 1998, 60% of cemented carbide scraps were reprocessed [8].

As illustrated in Figure 2, there are two main routes for recycling cemented carbides: chemical processes (which concerned, in 1998, about 35% of the scraps) and physical processes (about 25%). The physical processes are less expensive than the chemical processes, generate no waste products, and produce a powder essentially ready for use. Chemical processes are thus employed where direct recycling methods are not feasible, mostly because of contaminations. Indeed, much of the tungsten carbide scrap is generated in a contaminated form, due to grinding dusts, floor sweepings, powder from dust control systems, as well as improper storage of the scrap.
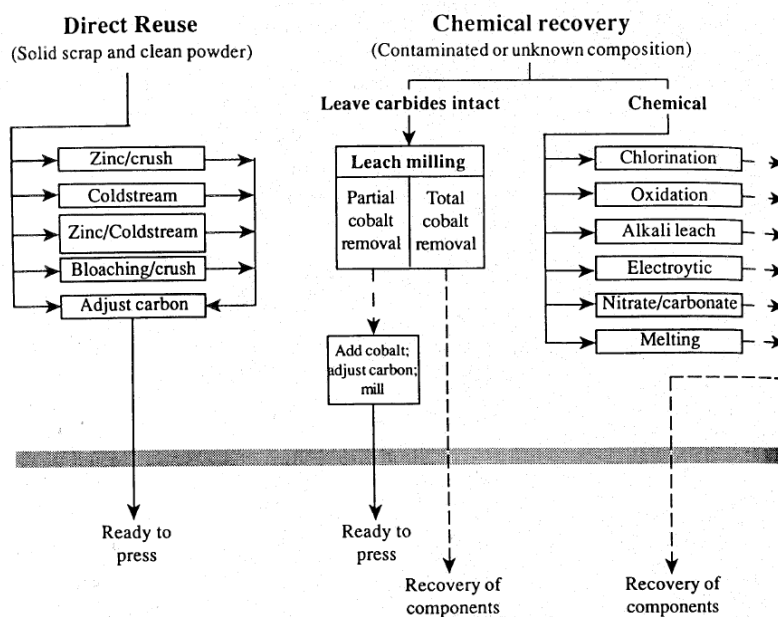

Figure 2 : Recycling processes for cemented carbide scraps [9]

PHYSICAL PROCESSES

These processes are not purification processes, thus careful sorting (using visual inspection, flotation in mercury, or x-ray methods) and pre-treatment (using treatment with acid) to remove soil, brazing material, iron, solder, refractory coatings (etc.) is essential.

The physical processes use the tools as the source material. The two major processes are the Zinc Process and the Coldstream Process. However, the Coldstream Process has been largely replaced by the Zinc Process [10]. The Zinc Process is operated at about 950°C, where zinc metal is added to the scrap source. The resultant reaction of zinc with the binder leads to the formation of a lamellar structure, with a significant increase in volume, which causes the scrap to swell. Zinc dissolves the binder phase of the cemented carbide without changing the composition of the material. Vacuum distillation is then carried out in the same vessel, leading to zinc separation. The treated carbides can then be reused in a new batch of cemented carbides that requires the same or similar composition, with a minor carbon adjustment. Yields are as high as 95% and the overall energy requirement is about 4 kWh/kg [10].

CHEMICAL PROCESSES

In the chemical processes, carbide scraps with different content of various metals, including tantalum, are treated chemically to extract tungsten and cobalt values first. The chemical process involves the recovery of tungsten oxide or ammonium paratungstate through an oxidation process combined with a purification process. The oxidation process can be one of many types, including thermal oxidation, chemical oxidation, mechanochemical oxidation, and electrochemical processes [11]. These processes convert tungsten carbide to tungstate ion, from which ammonium paratungstate is synthesized.

Depending on the process, the contained tantalum is collected under various forms, like, for instance, an oxide sludge, which is suitable as source material for the tantalum extraction plant. The advantage of this process is that almost any type of cemented carbide scrap can be reused and that the resultant product is equivalent to virgin material.

METALLURGICAL PRODUCTS & SUPERALLOYS

Ta can be used either in Ta-based alloys (pure or with a low content of alloying element) or in superalloys, where Ta is a minor element, with a content of 1 to 12 wt.% [12]. No information was found about available recycling method for the first category.

There are two options for the recycling of Ta-containing superalloys: either a full separation of the alloy components in order to recover pure Ta, or a direct recycling by remelting without separation of the elements [13]. Even if it seems that no extraction process has reached industrial scale [13], the two options are discussed in the next sections.

TA RECOVERY BY REMELTING

In 1996, on the world scale, about 70% of the recycled superalloys scrap were remelted to regain the same alloy, while 20% was processed into low-grade materials (down-cycling) and the rest was delivered to nickel refineries [8, 13].Ta is thus significantly recovered from the superalloy scrap that contain it, where the Ta content can be reutilized to prepare fresh material.

A large amount of superalloys are used for high temperature applications such as jet-engine turbine blades. As mentioned for instance in the work of Woulds [14], the parts of the superalloys which have seen engine service cannot be recycled directly by vacuum induction melting, because of the presence of contaminants as S, O, Pb, Na and Cl from combustion products and protective coatings often present. Contaminated scraps can be treated according to the following procedure [14]:

- Arc refining at 1600°C, with oxygen blowing in a slag, in order to purge any low melting element ; this also results in the oxidation of Al, Ti, Zr and Hf from the superalloy. As illustrated in Figure 3, the arc refining step has no impact on the Ta content of the alloy.
- Chemical analysis of the remaining alloy in order to determine the corrective additions;
- Reconstitution of the superalloy by vacuum induction melting and solidification in a skillet.
- Thermal treatment, forging, cutting and rolling of the ingots

Figure 3: Major elements changes in arc refined superalloy B1900 [14]

TA RECOVERY BY EXTRACTION

The extraction of Ta from alloys is challenging, as hundreds of superalloys contain more than 20 alloying elements. A few methods, only developed at laboratory scale, aim at recovering Ta [13]:

- A pyrometallurgical method including an alkaline fusion followed by a leaching step and magnetic separation,
- An electrochemical method, involving an inorganic acid as electrolyte, and producing filterable Ta oxide [15].

OTHER TANTALUM WASTE

There are no established methods known for the extraction of Ta from catalysts or other end products using Ta containing chemicals.

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RECOVERY OF MOLYBDENUM

Contributors: L. Sundqvist, G. Ye (Swerea), J. Yang (GTK)

By far the largest use of molybdenum is in steels as an alloying element. It is therefore mostly recycled in the form of steel scrap. It is reported that 1/3 to 1/4 of the molybdenum used each year is recycled materials from the scrap [1].

Pre-treatments including grinding, sieving, shredding, cutting and sorting are used in recycling of molybdenum in the forms of steel scrap and others[2-3]. Such as in recycling of molybdenum in catalysts a spent catalyst was ground, sieved to a grain size not exceeding 0.20 mm, and agitated to provide homogenization, and then its elemental composition was determined and the characteristic particle size distribution obtained for the samples were measured with a laser particle microanalyzer [3].

The methods for extracting and recovery of Mo from the wastes include pyro-metallurgy, hydro-metallurgy and bio-metallurgy [4, 5]. Here the pyro-metallurgy method for extracting Mo from the wastes are outlined as the following.

STEEL SCRAP

Commonly the steel scrap is recycled by re-melting the steel scrap, for example, in the Electric Arc Furnace (EAF). Before this re-melting is implemented, the scrap normally needs to be pre-treated to: (i) ensure that the scrap has suitable size which makes it possible to be charged into the furnace; (ii) ensure a homogenous composition of the scrap; (iii) remove the impurities from the scrap. The extent to which a pre-treatment procedure is needed for the scrap depends on the source of the scrap where it is generated:

- Revert scrap is generated in the steelmaking process. This scrap is relatively pure with known chemical composition; it normally can be directly charged into the EAF without further treatment, or at most just by cutting the scrap into suitable size.
- New scrap is generated in the manufacturing of products by steel mill customers and recycled by scrap collectors and processors. This scrap normally is also quite pure, the pre-treatment for this sample normally entails sorting/classification (magnetic and/or manual), cutting (if regarded as necessary) and removing the impurities.
- Old scrap or obsolete scrap is generated when the steel product's service life is ended. The old scrap comes from various products and the chemical composition of the scrap is dependent on the origin of the scrap and how the scrap is pre-treated. The pre-treatment of the old scrap normally includes the following procedures: (i) demounting/sorting (magnetic and/or manual); (ii) shredding/sizing in connection to the further sorting; (iii) removing of impurities (such as Cu, Zn, Sn, etc.).

Recovery of Mo from the steel scrap is normally carried out in the EAF, where the scrap is smelted and thereby Mo is largely recovered in the alloyed steel product.

SPENT HYDRO-REFINING CATALYSTS

The ways in which the spent hydro-refining catalyst is pre-treated depend on the processes of recovering metals (Mo in this case) from the catalyst. Normally, it includes the following:

- Roasting to eliminate the C and S contents (de-oiling and de-coking) and/or to facilitate the transformation of the refractory metal oxide into other forms;
- Crushing/grinding to get fine materials;
- Leaching to get the soluble refractory metal-bearing compounds.

Molybdenum as well as other metals from the spent hydro-refining catalyst can be recovered by direct smelting reduction of the metal oxides in the catalyst in the presence of iron [6]. The final product from this process is a mixed ferroalloy containing cobalt, nickel, molybdenum, etc., the alloy contents of which can be further used for special steel production; the generated slag in this process can be safely dumped or used for building materials production. Swerea MEFOS has developed a process using a DC furnace where Mo, Co and Ni are recovered into a metal alloy, which can be used for special steel production, while the generated vanadium enriched slag can be used for FeV production. It should be noted that it is quite often the case that hydro-metallurgical and bio-metallurgical method are combined to extract the metal from the spent catalyst [5, 7]. One example of this combined process is shown in Figure 4, which is developed by Gulf Chemical & Metallurgical Corporation, the world's largest recycler of spent petroleum catalysts [8]. In this process, the spent catalyst is roasted with sodium salt in the hearth furnace under oxygen atmosphere; the resulting materials after cooling are subjected to grinding and water leaching. By filtration the obtained solid is charged into the DC arc furnace to produce metal alloy and fused calcium aluminate; the obtained liquor is further treated and used to extract molybdenum and vanadium oxides.
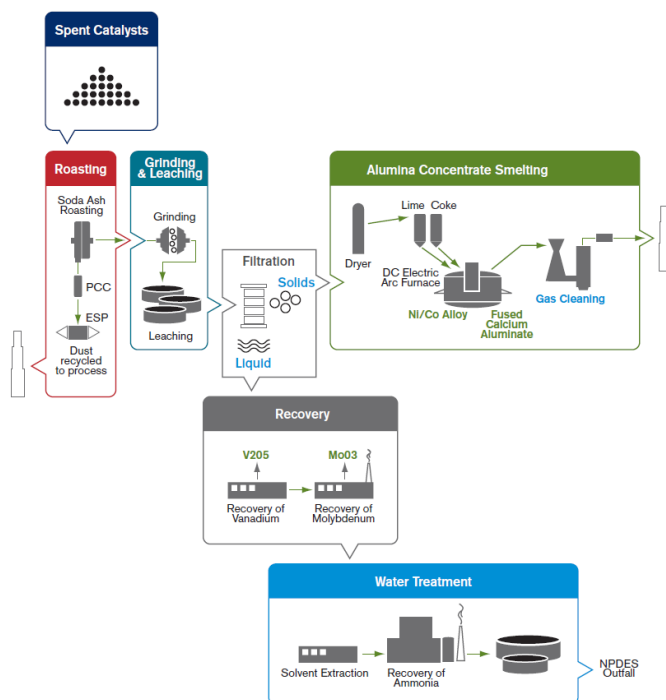

Figure 4. Recycling metals from the spent catalyst: an overview of entire process by Gulf Chemical & Metallurgical Corporation [8].

MOLYBDENUM FROM OTHER WASTE

Sorting and collecting are quite important pretreatment procedures for the recycling of molybdenum from other wastes (such as end-of-life screens), as the molybdenum needs to be enriched before it can be extracted

efficiently from these wastes. The pyro-metallurgical method for extracting Mo from other wastes is not explicit in the literature. However, the similar methods as for extracting Mo from the steel scrap and the catalyst can be expected.

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RECOVERY OF TUNGSTEN

Contributors: L. Sundqvist, G. Ye (Swerea), J. Koffeman, Y. Yang (TU Delft), J. Yang (GTK)

According to report [1] approximately 50% in the world (In Western Europe even 62%) of tungsten is used in the production of cemented carbides (WC); some 17% of tungsten is used to produce specialist steel alloys, such as high speed steel, heat resistant steel and tool steels, all largely utilised in metal cutting applications and specialist engineering applications. In the region of 15% of tungsten would be used to make "mill products"; the mill products would comprise tungsten rod, sheet and wire, electrical contacts, etc. Pure tungsten mill products are used as light bulb filaments, vacuum tubes and heat-ing elements [2]; the balancing 18% of tungsten is used by the chemical industry and in other specialist applications.

The recycling methods should be:

- economic (savings in raw material costs can be achieved by recycling)
- environmental (recycling reduces the environmental impact)
- strategic (tungsten is a valuable and limited resource mined in only a few countries)

The methods for extracting W from the wastes include direct recycling, semi-direct recycling, pyro-metallurgy and hydro-metallurgy [3, 4].

a) Direct recycling. The wastes are transformed into powder with the same chemical composition of the wastes by chemical and/or physical treatment; thereafter the powder is used to produce new products.

b) Semi-direct recycling. Heavy metal pieces (such as cemented carbide scrap pieces) are selectively dissolved by chemical method, leaving undissolved tungsten carbide to be recycled.

c) Pyro-metallurgy. Scrap is smelted in the furnace and the tungsten in the scrap is used as alloying element and thereby recycled.

d) Hydro-metallurgy. Chemical methods are applied to recycle tungsten in the form of compounds, which can be used as a substitute of tungsten ore.

The techniques that are needed for pre-treating of W-bearing scrap depend on the types of wastes and the way in which they are to be recycled. These techniques include the following:

- Physical dismounting/sorting and/or sorting by chemical analysis into different grades. The sorting will lead to a purpose-oriented recycling of various W-bearing waste;
- Crushing, screening, milling and grinding. This will produce a waste being adapted to a specific recycling process;
- Acid cleaning to remove the impurities;
- Roasting, chlorination, alkali fusion, oxidation and electrolytic dissolution, etc. The tungsten is transformed into other compounds (such as APT, ammonium paratungstate) that can be recycled in an easy way.

The techniques that are needed for pre-treating of spent Ni-W catalyst are similar to that for pre-treating of Ni-Mo catalyst.

CEMENTED CARBIDE SCRAP

There are two main types of recycling processes applied: chemical processes in which scrap goes through the same hydrometallurgical process as concentrates from tungsten mining and zinc process in which scrap is processed directly into tungsten carbide-cobalt alloy powder in a furnace process [5]. For example, in the USA about 65% of tungsten carbide was recycled in which 35 % was by using chemical processes, 25 % by using the zinc process and 5 % by using other processes.

The cemented carbide scrap can be recycled by the following processes:

a) Zinc process (direct recycling) [6]. This direct recycling process is considered to be the most important one for recycling cemented carbide scrap. The scrap is first carefully sorted by grade, cleaned to remove any brazing or impurities, crushed, and then immersed in molten zinc in the presence of argon gas. The molten zinc reacts with the cobalt binder phase in the scrap at temperatures ~ 900° C or higher; this will result in a porous cake due to volume expansion of the scrap. After the reaction is complete the zinc in the cake is distilled off under a vacuum condition, leaving a spongy type material, which can be easily crushed and milled into powder. The obtained powder, if high purity is needed, can be further purified by employing an electrochemical treatment. The final powder, which is essentially the same as that of its original with respect to the grain size and chemical composition, can be directly used to produce new cemented carbide products. A diagram which illustrated the zinc process is shown in Figure 5.
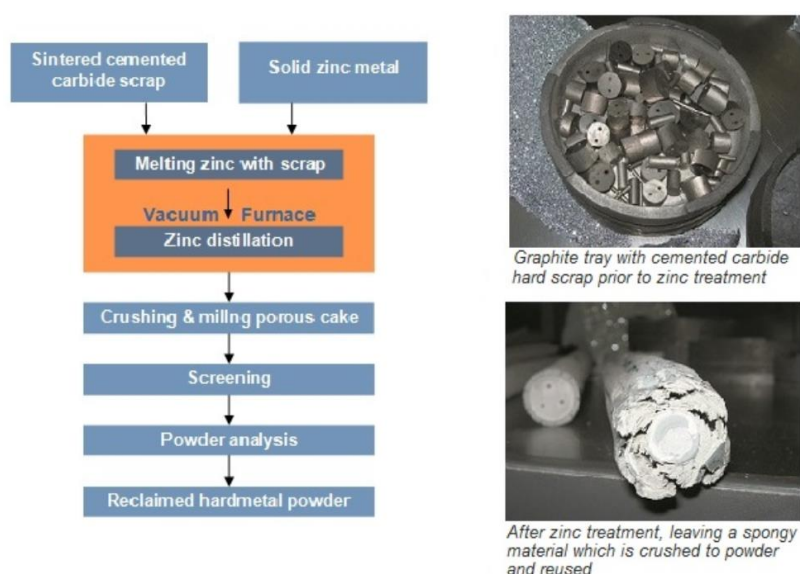

Figure 5. Illustration of the zinc process for direct recycling of tungsten from cemented carbide scrap [6].

The advantages of the zinc process can be summarized as follows: attractive economics compared with chemical recycling; environmentally friendly technology (zinc recovered and reused, no emissions as the process is a furnace process, lower energy consumption and lower carbon dioxide emissions compared with the processing of virgin raw materials such as concentrates from mining operations)[5].

b) Cold stream process (direct recycling) [7, 8]. In this process (as shown in Figure 6) air blast is employed to accelerate the particles against the target with sufficient energy to cause fracture of the scrap materials. The resulting shattered material is air classified to recover fine particles, which can be directly used to produce new cemented carbide products.
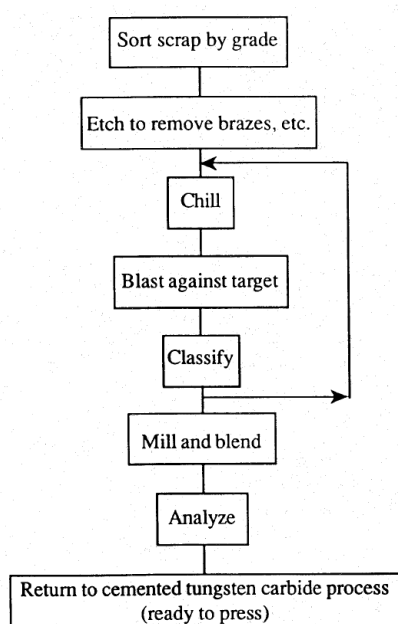
Figure 6. Flow sheet of the coldstream process for direct recycling of tungsten from cemented carbide scrap [8].

c) Chemical treatment process. One example of the chemical treatment process is the oxidation-leaching process [9]. In this process, the scrap is prepared by oxidation at high temperature and alkali treatment, which will facilitate the conversion of the tungsten carbides into tungstic oxide or sodium tungstate; followed by leaching and purification, pure tungstic oxide can be obtained and used as raw materials to produce other products. Normally the tungsten in unsorted cemented carbide is recycled by this process.

Other available chemical methods:

- Chlorination and fusion at high temperature with sodium nitrite or sodium nitrate as an oxidizing agent and sodium carbonate as a diluents.
- Acid leaching, bloating followed by leaching, electrolysis, or leach-milling. It could be recycled by melting to produce tungsten melting base, menstruum tungsten carbide, or specialty alloys, such as satellites.

d) Selective dissolution process (semi-direct recycling) [10]. In the semi direct recycling process, a specific component is dissolved chemically, which will leave the other components unchanged. Semi direct recycling can be used for binary- and/or ternary-phase alloys. Table 1 shows different examples of semi direct recycling methods [11].

Table 1: Semidirect recycling, Tungsten - Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds [11]

Scrap	Principle	Method
Hardmetal pieces	Selective dissolution of the Co binder	Attack by acid (H_3PO_4) Leach milling (mixed chemical and mechanical attack) Electrolysis (acidic solution)
	WC or WC + mixed carbides can be recycled to hardmetal grade powder preparation.	
Heavy metal pieces	Selective dissolution of the $Ni-Fe$ binder	Attack by acqueous $FeCl_3$ solution
	Powder consists of approximately 40-μm tungsten spheres and can be used in plasma spraying.	

One example of the selective dissolution process for recycling of cemented carbide is shown in Figure 7. In this process the cemented carbide is electrolyzed to dissolve its cobalt binder. Thereby the WC is recycled and can be used for new product manufacture.
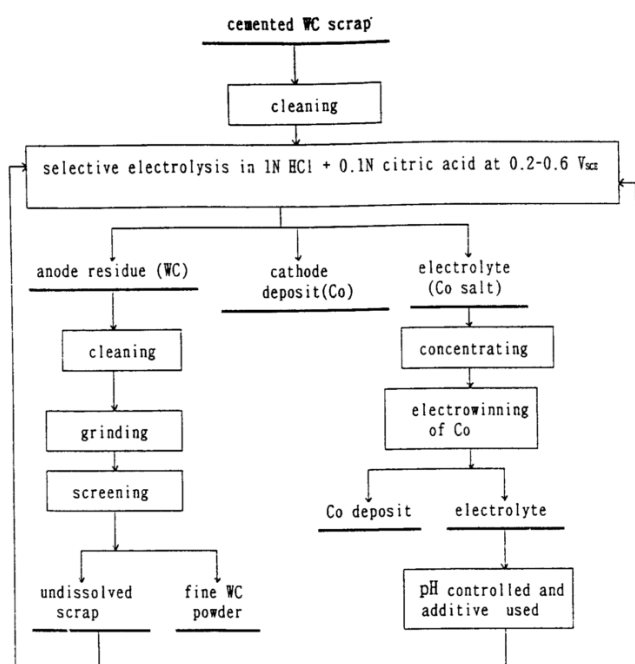

Figure 7. Flow sheet of the selective dissolution process for semi-direct recycling of tungsten from cemented carbide scrap [10].

HEAVY METAL ALLOY SCRAP

Heavy metal scrap is preferably recycled as metal power, which is implemented by oxidizing the scrap, milling and screening, following by hydrogen reduction. The obtained powder can be mixed with other metal alloy powder to make a ready-to-press powder for the manufacture of new products [9]. Tungsten in the heavy metal scrap can also be recycled as WC by the melt bath process, as shown in Figure 8 [12]. In this process the heavy metal scrap is charged into the Fe-C melt; the tungsten in the scrap will be converted into WC, and thereafter WC can be recycled by, for example, the zinc process.
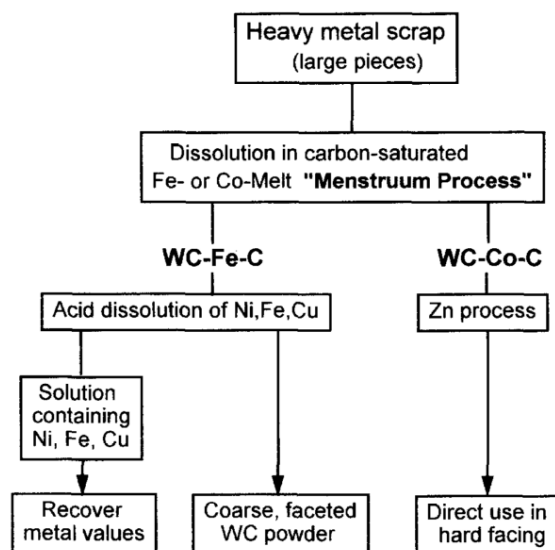
Figure 8. Flow sheet of melt bath process for recycling of tungsten from heavy metal scrap [12].

Other methods:

- Coldstream process for turnings and solids with binder contents of less than 3 percent; this process is based on impact phenomenon caused by impingement of high velocity particles against a cemented carbide plate [13].
- Menstruum process, which produced macrocrystalline tungsten carbide by dissolving sintered scrap in a carbon-saturated iron melt and then leaching the nickel, iron, and/or copper with acid;
- Melting, in which the scrap was used as a source of tungsten in the production of ferrotungsten, tool steels, or tungsten melting base; and chemical processing.
- Electrolysis, which uses the scrap as an anode in an electrolytic solution, could be used to dissolve the tungsten from hard heavy metal alloy scrap prior to chemical processing.
- Leach-milling and leaching with an iron chloride solution to dissolve copper, nickel, and iron selectively were other possible methods for recycling heavy metal alloy scrap.

MILL PRODUCTS FROM METAL POWDER SCRAP

- Pre-treated by crushing, sorting, and then cleaning with acid before production of air- or vacuum-melted alloys.
- The preferred use for pure tungsten scrap powder was as a source of tungsten in the production of cast or menstruum tungsten carbide.
- In addition, pure tungsten metal scrap could be recycled by using the following methods: chemical processing; melting, in which the scrap was used as a source of tungsten in the production of ferrotungsten, stellites, tool steels, or tungsten melting base; oxidation-reduction; and the coldstream process. Electrolysis, which uses the scrap as an anode in an electrolytic solution, could be used to dissolve the tungsten prior to chemical processing.

STEEL SCRAP

The steel alloy products can be recycled to produce new steel products as long as the tungsten content is considered; otherwise the tungsten in the steel is just "down-cycled" without using its material properties.

SPENT NI-W CATALYSTS

As described for Ni-Mo spent catalyst, similar pyro- and hydro-metallurgical methods can be applied to recycled tungsten and other metals from the spent Ni-W catalysts.

TUNGSTEN ELECTRODES

Tungsten electrodes can be recycled by either hydro- or pyro-metallurgical process as long as the radioactive thorium in the electrode is considered.

NEW TECHNOLOGIES

SEMI DIRECT RECYCLING OF CEMENTED CARBIDES

The Christian Doppler Laboratory for Extractive Metallurgy of Technological Metals, located in Austria has an ongoing research on semi direct recycling of cemented carbides. This organisation states that at this moment, most of the applied techniques for cemented carbides recycling are based on direct recycling. Depending on the scrap quality the latter is not appropriate, because of the remaining coating material in the recyclate which reduces its utilizability.

First a leaching step detaches the coating of the cemented carbide scrap as well as the binder metal. For the remaining hard phase contingent upon its characteristic a suitable treatment for reuse is sought. Secondly adequate hydrometallurgical techniques allow a recuperation of the dissolved cobalt [14].

RECYCLING OF SCRAP TUNGSTEN CARBIDE ROLL COLLARS

Y.T. Liao, T.Wu and T.Chou have reported a research on recycling scrap tungsten where crushed crystallites of scrap tungsten carbide roll collars are mixed with swarf, dropped into a centrifuge and then processed by electroslag remelting. After heat treatment refinement, recycled tungsten alloy roll collars containing only 20% tungsten are made. This experiment demonstrates that tungsten carbide roll collars made by powder metallurgy can be reused after being scrapped to make recycled tungsten alloy roll collars by melting. The trial production data for the recycled tungsten alloy roll collars provide strong evidence that their wear performance and cost savings are better than ordinary alloy collars and that they effectively reduce consumption of tungsten [15].

RECYCLING USING MOLTEN SALT

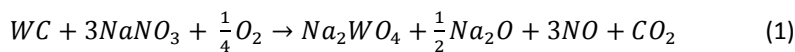This technique of recycling tungsten is reported by T. Ishida and T. Itakura [16]. This method uses molten salt solution to obtain an aqueous solution of Na_2WO_4 from cemented carbide. After this treatment, the aqueous solution of Na_2WO_4 is converted into an aqueous solution of $(NH_4)_2WO_4$ by an ion exchange treatment. The molten salt solution- and ion exchange treatments is explained below.

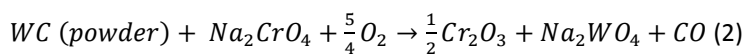Because of the strict environmental regulations, the following points are necessary for this research:

- High efficiency recovery
- Reduction in chemicals used and conservation energy
- Low environmental loads
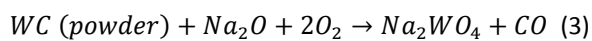
MOLTEN SALT SOLUTION TREATMENT

The molten salt solution process causes a reaction of WC-Co cemented carbide alloy with $NaNO_3$ and dissolves the generated Na_2WO_4 molten salt in water. Figure 9 shows two pictures of the process. The tungsten carbide reacts with NaNO3 as described in function 1.

$$WC + 3NaNO_3 + \frac{1}{4}O_2 \rightarrow Na_2WO_4 + \frac{1}{2}Na_2O + 3NO + CO_2 \qquad (1)$$

Chromium and vanadium from the cemented carbide change into water-soluble Na_2CrO_4 and $NaVO_3$, which then get mixed in with the aqueous solution of Na_2WO_4. Then, powder scrap is used to cause the reaction of function 2, which reduces the Na_2CrO_4 and creates Na_2WO_4.

$$WC\ (powder) +\ Na_2CrO_4 + \frac{5}{4}O_2 \rightarrow \frac{1}{2}Cr_2O_3 + Na_2WO_4 + CO \text{ (2)}$$

Na_2O from the reaction described by function 1 then reacts with WC powder and oxygen, which creates Na_2WO_4, as described in function 3

$$WC\ (powder) + Na_2O + 2O_2 \rightarrow Na_2WO_4 + CO \text{ (3)}$$

The Na_2WO_4, which is obtained by the reactions described by functions 1, 2 and 3 is then sent to the ion exchange process as an aqueous solution.
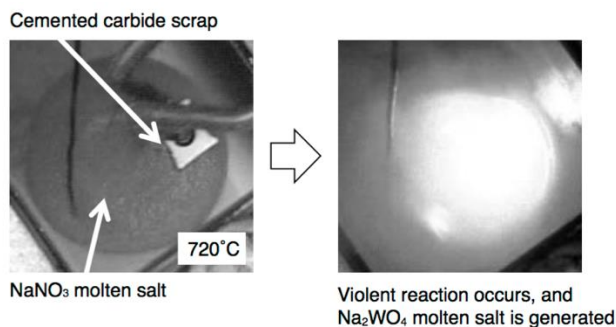

Figure 9: Molten salt to NaWO4, Development of Technologies for Recycling Cemented Carbide Scrap and Reducing Tungsten Use in Cemented Carbide Tools

ION EXCHANGE TREATMENT

This treatment starts with passing the aqueous solution from the molten salt treatment through a resin tower filled with ion exchange resin. This is depicted in Figure 10.
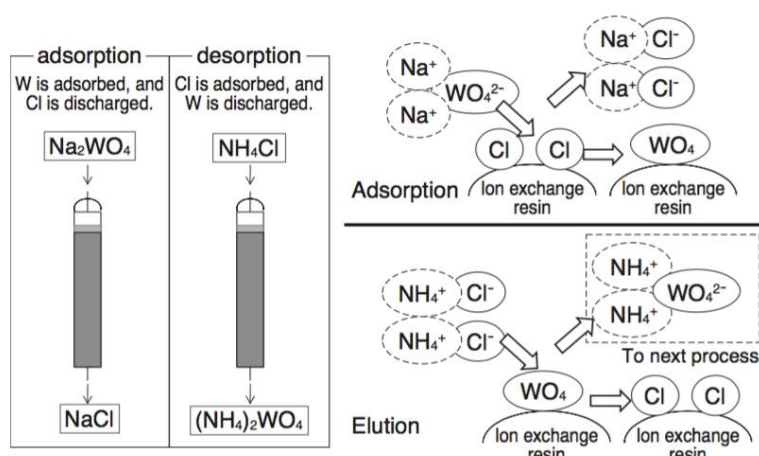
Figure 10: Diagram of ion exchange, Development of Technologies for Recycling Cemented Carbide Scrap and Reducing Tungsten Use in Cemented Carbide Tools

The purpose of the ion exchange treatment in the tungsten recycling process is to obtain an aqueous solution of $(NH_4)_2WO_4$ by so arranging that $WO_4{}^{2-}$ ions contained in aqueous solution of Na_2WO_4 are adsorbed on the anion exchange resin and are eluted by ammonium salt such as NH_4Cl.

With this method, it is shown that it is possible to adsorb approximately three times as much tungsten as the conventional amount. There seems to be a problem with some side reactions, which resulted in the resin tower becoming clogged, but these could be solved by keeping the aqueous solution basic [16].

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RECOVERY OF RHENIUM

Contributors: K. Leszczynska-Sejda, G. Benke (IMN), T. Retegan (Chalmers)

Processing of rhenium-laden manufacturing scrap and end-of-life materials, such as catalysts and superalloys, is relatively new to the rhenium industry. Since this is such a new faction of the rhenium industry, the research possibilities are almost endless, but should definitely include the utilization of primary processing techniques, as well as the implementation of end-of-life recycling programs.

Diversity of rhenium applications cause its various form and physical and chemical properties. Consequently recycling processes are individually matched for a specific materials [1].

SUPERALLOYS AND ALLOY SCRAPS

Due to the high temperature properties of tungsten and rhenium, it is not uncommon to find these metals in alloys together. Thus, W-Re scrap may be recycled via an oxidative pyrometallurgical roasting technique. Initially, the scrap is roasted at 1,000° C, under an oxidizing atmosphere to produce rhenium heptoxide, which is subsequently condensed in the cooler part of the tube furnace. This material is then sent for digestion in water. The aqueous rhenium is subsequently precipitated as potassium perrhenate upon the addition of potassium chloride. The potassium perrhenate is filtered and further purified via continued dissolution and recrystallization. After purification, the salt is dried and sent for reduction under a hydrogen atmosphere at approximately 350°C. Experimental results show that 93.1% of the rhenium was recovered to produce a 99.98% pure Re product [1,2].

H.C. Starck has patented a process for the elevated temperature digestion and recycling of rhenium-containing superalloys. Initially, the superalloys are digested in a molten salt melt containing NaOH, Na_2CO_3, and Na_2SO_4 at temperatures of 850-1100° C in a directly fired rotary kiln. In addition to this, oxidizing agents such as nitrates and peroxides of the alkali metals are added. The melt from this process is then cooled and sent to a comminution process for size reduction. The material is then leached using water as the lixiviant to dissolve the 6 and 7th group elements present in the superalloy. This slurry is then filtered to separate the insoluble Co, Ni, Fe, Mn and Cr from the leach liquor. Magnetic separation is then applied to the insoluble components for further separation and concentration. The pregnant leach solution is sent to an ion exchange step.
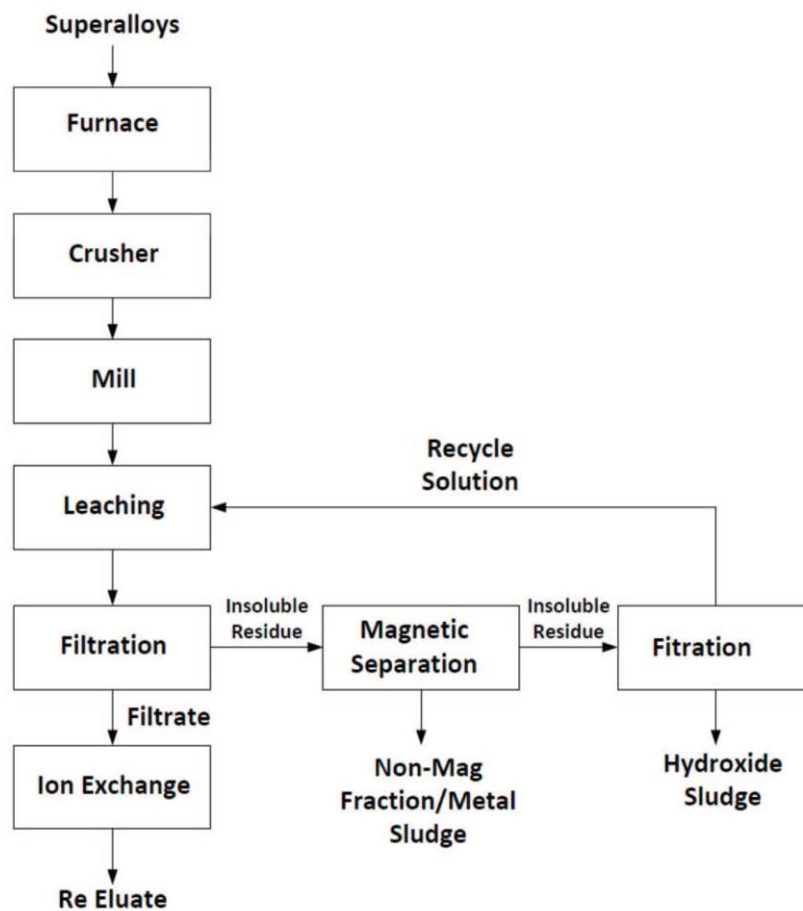
Figure 11. Rhenium recovery from superalloys

Through the use of electrolytic decomposition of rhenium superalloys, Stoller et al. have patented a process that involves the use of titanium baskets as electrodes.

The baskets containing the superalloy scrap are fed to a polypropylene electrolysis cell containing a 18% HCl solution. The electrolytic dissolution is carried out for 25 hours at a frequency of 0.5 Hz, current of 50 amps, voltage of 3-4 V and a temperature of 70° C. The remaining scrap is then filtered from the pregnant solution and sent for further dissolution in sodium hydroxide/peroxide solution. After completion, this filtrate is sent to ion exchange for the recovery of rhenium and molybdenum. Rhenium is recovered using the ion exchange processes.

Shredded solid materials can be effectively processed by Toma Group, where it is oxidatively calcined and volatile Re_2O_7 is absorbed in ammonia solution. This allows to process wastes: from rhenium powder production, spent catalysts, scraps from mechanical processing of superalloys.

The Innovator company (in Poland) launched a plant where rhenium from plasma surface processing is leached by a mixture of mineral acids while superalloys scraps are electro-dissolved in hydrochloric acid. Solutions are gathered together and sent to ion exchange unit.

Volatile compound of rhenium (Re_2O_7) in flame-based processes of copper and nickel ores processing is collecting in ashes and washing solutions produced in dust collecting apparatus. Re_2O_7 in ashes is washed out

by water. The methods of as-obtained solution and washing solutions processing may differ and depend on rhenium concentration and local opportunities. Here we can differentiate the following:

- precipitative, when pourly soluble rhenium compounds are produced, such as: sulfides, monovalent metal rhenates(VII) for example $KReO_4$, ammonia divalent metal rhenates(VII) for example $Zn(NH_3)_4(ReO_4)_2$;
- extractive, when ReO4- ion is transferred to organic phase containing amines or organic derivatives of phosphoric(V) acid;
- reductive, precipitation of elemental rhenium by for example cementation with zinc dust;
- membrane, using nanofiltration and electrodialysis;
- sorption, rhenium adsorption on for example active carbon or sorption on appropriately chosen ion-exchange resin.

Solutions with low rhenium concentrations can be treated by sorption. Method for rhenium recovery from acidic solutions with ~50mgdm3 Re content with 95% yield was developed in Poland. In this method rhenium adsorbed on an ion exchanger is eluting by ammonia solution and the product after concentration is crystallized as ammonium rhenate(VII). This method was used for washing acids processing in sulfuric acid plants located in copper smelters. It allows to produce 8 Mg of rhenium per annum.

SPENT PT-RE CATALYSTS

Petroleum-reforming catalysts containing rhenium and platinum for the improvement of the octane level of fuels. After being deactivated, an effective method for the recovery or rhenium and other PGM metals is necessary. There are two basic methods by which this is achieved

1. Complete dissolution of the alumina substrate.
2. Selective dissolution and recovery of rhenium and platinum.

COMPLETE DISSOLUTION OF ALUMINA SUBSTRATE

During complete dissolution of the alumina substrate, sulfuric acid may be used for dissolution of alumina, rhenium and, to some extent, platinum. The rhenium-rich solution is separated from the platinum-containing residue and aqueous aluminum using ion exchange. Rhenium is eluted from the organic amine resin by way of hydrochloric acid addition. After elution, the rhenium-rich eluate is neutralized using ammonium hydroxide. This solution is then evaporated to form a super-saturated solution, and cooled to allow for crystallization of ammonium perrhenate. After continued redissolution and recrystallization, a high-purity ammonium perrhenate precipitate is produced. As an alternative to sulfuric acid, sodium bicarbonate may also be used as a lixiviant. The proposed advantage of this process is the complete removal of the ion exchange circuit. Experiments were performed on crushed and uncrushed catalysts in both packed columns and agitated leach vessels. Experimental results showed that that rhenium is preferentially leached in the sodium bicarbonate solution. Rhenium recovery reached 97% for crushed catalysts, and 87% for uncrushed catalyst samples. After dissolution, the aqueous rhenium is crystallized via evaporative crystallization as an ammonium perrhenate intermediate product [1,2].

SELECTIVE LEACHING OF RHENIUM AND PLATINUM

The methods used to selectively recover platinum and rhenium from spent catalysts without completely dissolving the alumina substrate vary from calcination of the catalysts to selective leaching in alkaline or acid conditions at ambient and elevated temperatures.

By calcination of the catalyst at temperatures up to 1,150° C, the γ-Al2O3 undergoes a phase transition to the chemically stable α-Al2O3 phase, lowering the dissolution of the alumina catalyst. The platinum and rhenium can then be selectively leached in concentrated (5 mol/L) sulfuric acid solutions containing sodium chloride and a potassium persulfate oxidant Kpumaneva reports that rhenium and platinum recoveries are as high as 95.5% and 97%, respectivel. Additionally, a U.S. patent has been granted involving the selective leaching of platinum and rhenium at elevated temperatures (50-300° C) and pressures (207-9,000 kPa). In this process, a dilute solution of sulfuric acid (0.001-1.0 mol/L) is used in the presence of ammonium [1,4].

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RECOVERY OF NIOBIUM

Contributors: Y. Yang (TU Delft), G. Ye (Swerea)

Niobium (previously known as Columbium), a sister of tantalum, is mainly applied in form of ferronobium for production of high strength steels. Being a component of superalloys it leads to high thermal strength in turbines and aircraft engines. In oxide form it is in particular applied in optic glass and lenses because it increases the refraction index. Electronic components made of nioboxide gain more and more in importance. This includes e. g. frequency filters made of the one crystal quality of Nb_2O_5. Anti-reflex layers in form of sputter targets are made of nioboxid using PVD. Companies, such as H.C. Starck, provide the possibility to reprocess niobium containing materials into the alloying addition nickel niobium.

Through H.C. Starck's integrated recycling process production scraps from niobium and nioboxide can be refined into pure metal/oxide qualities and supplied to customers [1].

Niobium is consumed mostly in the form of ferroniobium by the steel industry and as niobium alloys and metal by the aerospace industry.

According to USGS [2], Niobium was recycled when niobium-bearing steels and superalloys were recycled; scrap recovery specifically for niobium content was negligible. The amount of niobium recycled is not available, but it may be as much as 20% of apparent consumption. The recycled Nb is likely only from the manufacturing scrap.

According to UNEP report [3], there is significant less activity for the recycling of niobium and tantalum. Today, the recycling metallurgy of these metals, their reclamation from tin slag and process residues is well-established (Figure 12). EoL recycling rate of niobium is less than 1%. The main contribution of Nb recycling seems to be from the manufacturing scrap recycling only.
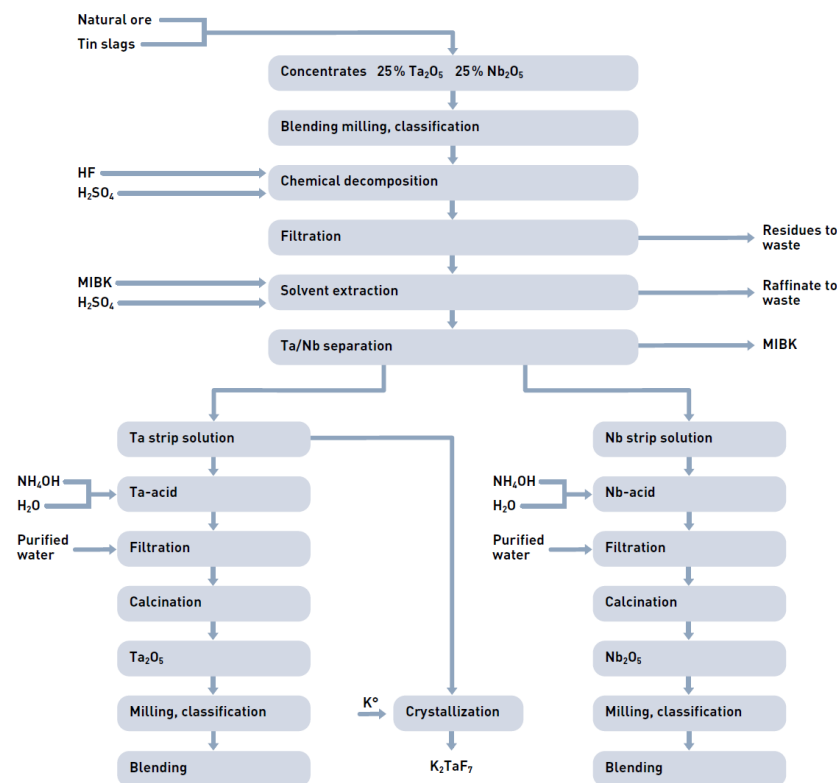
Figure 12. Flowsheets for the reclamation of niobium and tantalum from different sources [4]

USGS report [2] describes the flow of niobium in the United States in 1998 with emphasis on the extent to which niobium was recycled/reused. Niobium was mostly recycled from products of niobium-bearing steels and superalloys; little was recovered from products specifically for their niobium content. In 1998, about 1,800 metric tons of niobium was recycled/reused; about 55 percent of that was derived from old scrap. The niobium recycling rate was calculated to be 22 percent, and niobium scrap recycling efficiency, 50 percent.
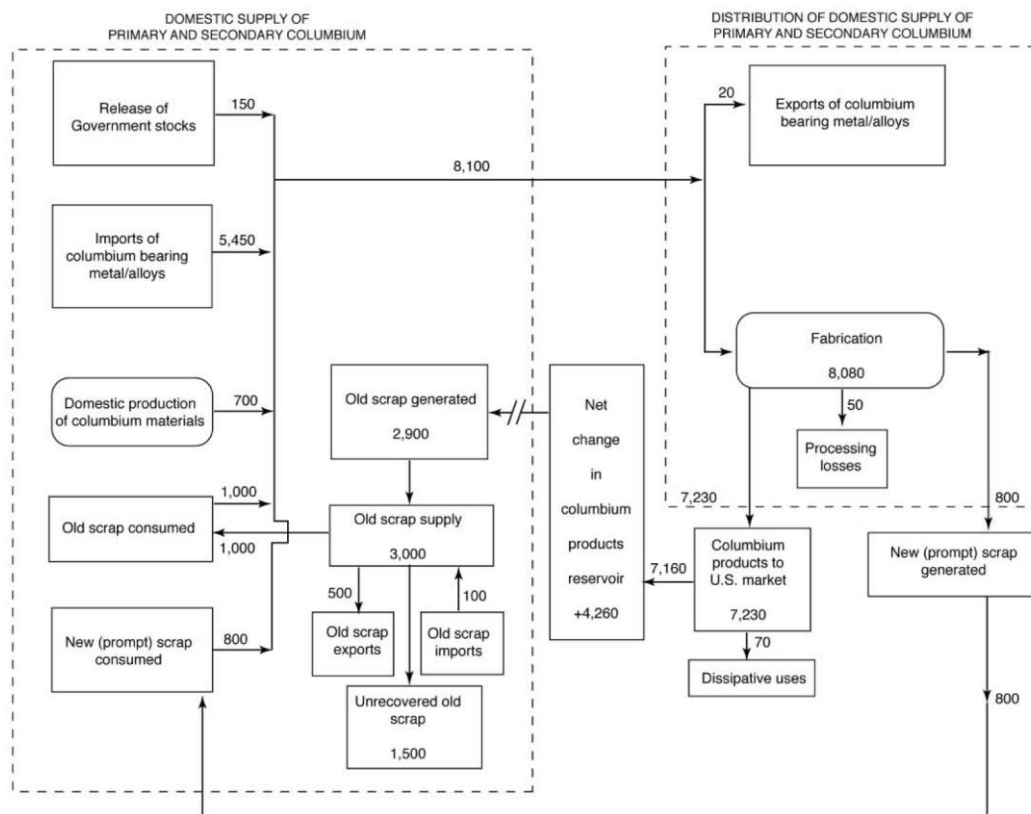
SOURCES OF NIOBIUM SCRAP

Figure 13. U.S. niobium materials flow in 1998. Values are in metric tons of contained niobium

Although most niobium-containing steels comprise less than 0.1 percent niobium, some stainless steels can comprise as much as 1.25 percent niobium. A major market for niobium among stainless steels is in type 347, which contains about 0.8 percent niobium. Stainless steel scrap is almost always used to produce more stainless steel. The scrap is mainly recycled as either home or purchased scrap; demand is usually a function of demand for the stainless steel itself. Niobium mostly in the form of high-purity (vacuum-grade) ferro-niobium and nickel niobium is added to cobalt- and nickel-base superalloys in such applications as jet engine components. The most important niobium-containing superalloy, nickel-base alloy Inconel 718, comprises about 5 percent niobium. Of the total superalloy scrap processed worldwide in 1996, about 70 percent was recycled into the same alloy; about 20 percent, downgraded; and the remaining 10 percent, sold to nickel refineries [5].

Although niobium is not recovered from the scrap steel and superalloys that contain it, recycling of these scrap materials is significant, and niobium content, where applicable, can be reused. Much of the niobium recycled in steel is diluted to tolerable levels; it effectively becomes a substitute for iron or other alloy metals rather than being used for its unique properties or is oxidized and removed in processing. New niobium-bearing scrap is generated mostly from manufacturing plants that produce steel products and fabricators of parts made from superalloys. This type of scrap is usually quickly returned to steel plants and superalloy meltors for remelting. Some major sources for old niobium-bearing scrap are junked automobiles (estimated 10-year lifetime) and scrap from discarded or obsolete parts made from superalloys (estimated 20-year lifetime), such as jet engine components. In 1998, niobium scrap sources consisted of steel scrap (estimated to be about 70 percent of the total) and superalloy scrap (estimated to be about 30 percent of the total). A major end use for niobium has been in niobium-bearing high-strength low-alloy steels for oil and gas pipelines (estimated 60-year lifetime).

These steels were introduced during the 1970s and will be a potential significant future source of niobium-bearing steel scrap.

DISPOSITION OF NIOBIUM SCRAP

In 1998, the quantity of niobium recycled/reused from old scrap represented about 12 percent of domestic niobium supply. With no U.S. niobium mining industry, niobium-bearing old scrap is important to the niobium supply chain. Of the estimated 3,000 t of niobium contained in old scrap that was available for recycling in 1998, about 33 percent was used for domestic niobium supply, and about 50 percent was unrecovered. Most of the unrecovered material was in the form of steel scrap that was abandoned in place, lost to the environment, or shipped to landfills. Scrap that was abandoned or in landfills could possibly be recycled in the future.

RECYCLING EFFICIENCY

Most niobium is recycled/reused in the form of niobium-bearing steel and superalloy scrap. In 1998, a niobium recycling efficiency was estimated to have been about 50 percent compared with 52 percent for steel.

PROCESSING OF NIOBIUM-BEARING SCRAP

IRON AND STEEL SCRAP

Scrap is collected by scrap dealers and processed into a physical form and chemical composition that can be consumed by steel mills in their furnaces. The shredder, which is the largest and most expensive piece of equipment used in recycling, fragments vehicles and other discarded steel into fist-sized pieces. Baling presses are used to compact the scrap into manageable bundles. Scrap dealers sort scrap materials, and steelmakers carefully purchase scrap that does not contain undesirable elements that exceed acceptable levels. The scrap is mainly melted in basic oxygen and electric arc furnaces (BOF and EAF). In recycling of high-strength low-alloy steel one has to be aware that about 0.05% of Nb will most likely be oxidised to the slag phase and lost during recycling to EAF or BOF. In the fabrication of new steel products, new steel scrap with known chemical composition is produced. Preparation of the new scrap for recycling is usually limited to cutting, cleaning, and baling prior to shipment back to the steelmaker.

Stainless steel is recycled in a similar manner as iron and steel scrap, but the volume of material is less, and the value is greater. Increased demand raises the value of scrap, which enables more scrap to be recycled. Scrap dealers compete for stainless steel on national and international bases, and the scrap may be handled at several locations before it is sold for use [5]. Scrap separated by alloy type usually brings the highest price. Balers are used to compress the scrap; shredders are rarely used. In recycling of Nb bearing stainless steel scraps, due to it's high affinity to the oxygen, it is also expected that Nb will also oxidised to the slag phase and be lost. Adding this type of scrap to AOD for cooling is a much better option to recycle/reuse Nb, as in the end of the decarburization stage there is a reduction step that will probably reduce Nb back to the metal.

SUPERALLOYS

Superalloys are alloys developed for high-temperature conditions where stresses (shock, tensile, thermal, or vibratory) are high and where resistance to oxidation is required. The processing of superalloy scrap can be difficult and complicated. Hundreds of superalloys contain more than 20 alloying elements, and each element must be considered when designing and evaluating processes for separating and recovering the valuable metals. Each piece of superalloy scrap must be identified and its composition certified before it is sold. Turnings are degreased, fragmented, and compressed for remelting. Balers are used to compress superalloy scrap; shredders are rarely used. Superalloys are usually air melted or vacuum melted. Recycled scrap is acceptable for most air-melted alloys. Product specifications, however, usually prohibit the use of recycled scrap in vacuum-melted alloys to reduce the chance that detrimental impurities may be included in the final product, such as in critical components for jet engines. Owing to the high cost and/or periodic scarcity of superalloys, scrap recycling is used extensively [6].

Scrap is a preferred furnace charge for superalloy melters and can provide about 50 percent of a superalloy furnace charge. Scrap is prerefined, prealloyed, and easy to handle. New or home scrap turnings are the largest form of superalloy scrap. Vacuum-quality turnings are collected to produce a furnace-ready charge that can be easily melted. The first step is a qualitative verification of chemical purity to isolate severely contaminated material from chemically clean material. Turnings are crushed into chips, which are then cleaned of residual cutting fluids and dirt. Lot homogenization and certification follows; processed scrap is required to meet the same chemical requirements as the finished heat. In the case of alloy Inconel 718, which has a lower melting point than its constituents, using processed scrap in the melt saves on electrical costs and melting time [7]. This scrap is then either remelted in the plant where it was originally produced (home scrap) or sold for remelting at another plant (new scrap).

OUTLOOK

The principal use for niobium is expected to continue as an additive in steelmaking, mostly in the manufacture of microalloyed steels used for automobiles, bridges, pipelines, and so forth. The production of high-strength low-alloy steel is the leading use for niobium, and the trend of niobium demand, domestically and globally, will continue to follow closely that of steel production. With about 80 percent of niobium being consumed in steelmaking, niobium recycling trends will be determined most by trends in the recycling of steel. U.S. scrap supply was reported to be a function of market price, which affects the collection of obsolete scrap; levels of activity in the metalworking industry, which influences the generation of prompt industrial scrap; and melting activity, which impacts the availability of home scrap [8].

The outlook for niobium also will be dependent on the performance of the aerospace industry and its use of niobium-bearing alloys. Niobium consumption in the production of superalloys, which is the second largest end use for niobium, will be most dependent on the market for aircraft engines. Because nickel-base superalloys (such as alloy Inconel 718) can account for about 40 to 50 percent of engine weight, they are expected to be the materials of choice for the future owing to their high temperature operating capability [9]. Thus, the rate at which niobium is recycled will also depend upon the rate at which products that contain niobium-bearing superalloys are recycled

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ANNEXES