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INTEGRATED PROCEDURE FOR RECYCLING AND VALORIZATION OF USEFUL COMPONENTS FROM SECONDARY RAW MATERIALS BASED ON HARD METALS

Ž. Kamberović[1], Z. Anđić[2], M. Korać[1], N. Gajić[3], B. Tomović[3]*

[1]Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[2]Innovation Center of the Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia
[3]Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

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Abstract

Wide application of hard metals requires increased consumption of their constituents. Their high cost and scarcity impose the need for finding new, both ecologically and economically justified ways for their production. In presented research, on the basis of previous research, a review of an integrated technological procedure of recycling and valorization of useful components from hard metals secondary raw materials is given.

Integrated procedure for processing of hard metal's waste enables the preparation of a wide range of powders with required properties, a high efficiency and reducing the duration of individual stages of procedures for their processing. Therefore, besides conservation of natural resources there are also significant economic and energetic benefits. The developed technological procedure is in service of sustainable development.

Keywords: *hard metals; secondary raw materials; recycling; integrated procedure.*

Introduction

The hard metals are materials entirely obtained by procedures of powder metallurgy, which include pressing and sintering of powder mixtures composed of appropriate carbides of one or more of the elements such as tungsten, titanium,

[*] Corresponding author: Nataša Gajić, *ngajic@tmf.bg.ac.rs*

tantalum, niobium, and metallic binder. The most commonly used binding metal is cobalt. The quantity of cobalt depends on the type, required chemical composition and use of hard metals. The carbide and cobalt content in hard metal are ranging from 85 to 95% and from 5 to 15%, respectively [1, 2].

Excellent mechanical properties of hard metal, such as high hardness, strength, wear resistance and corrosion resistance, have led to wide use of these materials in various fields of industry: production of cutting tools, parts of tools for metal processing by deformation, tools for traction (for the production of throns), tools for mining (crown mining drills), tools for the pressing of powder materials, tools for sheet metal pressing, and punching tools, tools for deep drawing and the production of munitions [3, 4].

Increasing quantities of waste materials in recent years also include waste based on hard metals. Because of that the developed countries make recommendations for the so-called "Green construction" which are applied in practice. The one of the main preconditions for further economic and social development is introduction of new, simpler and cheaper technologies, which will ensure obtaining of new products with superior performance and thus providing a more efficiency and reducing dependence on imported strategic and scarce materials. Considering the strategic importance and high cost of the constituent elements of hard metal, there is the need for development of a recycling process and evaluation of useful components from secondary raw material based on these metal materials. The costs of tungsten carbide (WC) production from primary tungsten are 4 times higher than those of WC recycled from scrap, according to international estimates. It can be clearly concluded that the recycling process is not only economically justified, but very desirable, especially in those areas where powder metallurgy has primate [5, 7].

Technological procedure for regeneration of tungsten from secondary raw materials based on hard metals, as one of the most valuable tungsten raw materials, was described and published by the Schreiter among the first authors in the West. In his description, he gave pattern of industrial plants, according to which recycling of tungsten from secondary raw materials in Germany in 50s was conducted [8]. Developed technologies of processing of waste hard metals are mainly based on chemical techniques. However, due to environmental restriction, some of the developed technologies are not functionally in many Western countries [9-12].

Chemical, physico-chemical, electrochemical and mechanical methods are used for recycling and valorization of components from secondary raw material based on tungsten [2, 6, 12-15].

Pyrometallurgical methods include oxidation roasting of hard metal's scrap and then processing of products to obtain a powder mixture directly applicable for the repeated production of the hard metal. Chemical methods include obtaining of elemental powders of tungsten and cobalt, the alkaline melting of scrap with $NaNO_3$, dissolution of cemented metal in the aggressive media, the treatment of cemented metal carbides with vapor phase Cl, CO, S and the extraction process with the oxidative pretreatment. Also process of chlorination of hard metal's scrap, mechanical disintegration of hard metal's pieces in the presence of a mixture of H_2SO_4 and HNO_3, melting of hard metal with zinc, the leaching process of hard metal's scrap using H_2O_2 in the presence of an inorganic acid and carbidization in two steps are included [16-19].

Physico-chemical methods include electromagnetic separation and thermal treatment in the plasma. Electrochemical method involves process of anodic oxidation in presence of HNO_3 as a basic electrolyte and electrolysis of cemented tungsten oxides waste [13]. Mechanical methods relate to a process of grinding of hard metal waste. Wide range of powders could be obtained by process of recycling and valorization of useful components from secondary raw materials based on hard metals [20].

Tungsten and its alloys are extremely used materials in the industry due to their good mechanical, electrical, electro-erosion, tribological and magnetic properties. Furthermore, tungsten has a high melting and boiling point, small evaporation rate at a high temperature and a small coefficient of thermal expansion [21].

Tungsten powders, obtained by procedures of recycling and the valorization of useful components from secondary raw material based on hard metals, successfully can be applied for the manufacture of nor for light bulbs, profiles for heating elements for high temperature furnace (wires, rods, sheets), electrodes for welding (plasma pistols, xenon lamp), the emission cathodes in electron tubes, the spiral for ultra high vacuum chemical vapor deposition, the rotating anodes in X-ray tubes, various contacts materials, and etc. Cobalt powder finds application in the production of permanent magnets, superalloys and wear resistant alloys [2, 4, 22-23]. In addition, materials based on cobalt have dental application and application in orthopedic surgery due to their biocompatible properties [24, 25].

Titanium and its alloys, as biocompatible materials, have considerable use in medical purpose due to their excellent properties, such as: the relatively high strength, low elastic modulus, high biocompatibility, and an extremely low level of toxicity, but compared to stainless steels and Co-Cr alloys they have worse tribological characteristics [26, 27].

Ceramic composites based on niobium, and composites based on tungsten, titanium and tantalum exhibits a significantly higher flexural strength, toughness, hardness and resistance to abrasive wear and erosion. They can be used for the production of brake discs, the cutting tools and Ti implants [28-29]. Also, the powders made by the process of recycling and the valorisation of useful components from waste of hard metal could be used for the preparation of a composite of a different architecture and different chemical compositions, such as [30]: W-Cu, WC-Cu, W-Ag, WC-Ag (highly conductive materials resistant to the contact welding), WC-Co-Cu (contact materials for vacuum circuit breakers), hard metals and etc.

The technological procedure

Technological procedures of integrated processing of hard metal's scarp can go in two directions. The first direction includes the processing of scrap to such a state that can immediately return to the process of production of hard metal, and the second relates to the technology of processing of scrap materials to metal powders, either as oxides, carbides, salts, or in the elemental form, which is further processed depending on their purposes.

Considering the above mentioned, integrated processing of hard metal's scrap enables the obtaining of products, such as:

silver,
cement copper,
powder mixture directly applicable for reproduction of a hard metal,
WO_3 powder,
powder of elemental tungsten,
WC powder,
$CoSO_4 \cdot H_2O$,
Co_3O_4,
powder of elemental cobalt,
TiO_2,
Ta_2O_5,
Nb_2O_5.

Pretreatment of scrap

Dissolution of solder residues from hard metal's scrap

The common phases of integrated procedures for both variations of processing hard metal's scrap are: dissolution of solder residues, oxidation annealing and milling of the oxidation products.

The dissolution procedure of solder residues is applicable to all types of hard metal with solder on them.

Dissolution is carried out at room temperature by slow addition of diluted nitric acid, concentration 33% HNO_3, in the container for leaching which is made of a hard wood (oak, beech or acacia), resistant to nitric acid and strikes of sharp pieces of hard metal scrap. The process of dissolution is extremely turbulent and takes place in accordance with the following reactions:

$$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_2 + H_2O \qquad 1$$

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \qquad 2$$

After dissolution process, which last until formation of NO_2 gas, pieces of hard metal are separated by decantation and washed out with water. Washing water is mixed with concentrated nitric acid (66% HNO_3) in a ratio of 1: 1, to give the acid for dissolution with concentration 33%. First, the silver is precipitated from the solution using copper chippings, then segregated, washed, dried and it casted in the form of anodes. The anodes are processed into fine silver by process of electrolysis. After cementation of silver, which is carried out in a glass container, and its separation, the copper cementation is carried out in a wooden container using iron scrap, after the washing and filtration, the cement copper is obtained. Cement copper can be used in copper smelters or for production of copper salts, especially in the copper (II) sulphate (bluestone).

The dissolution process of solder residues from the hard metal's scrap is shown in Figure 1 [2].

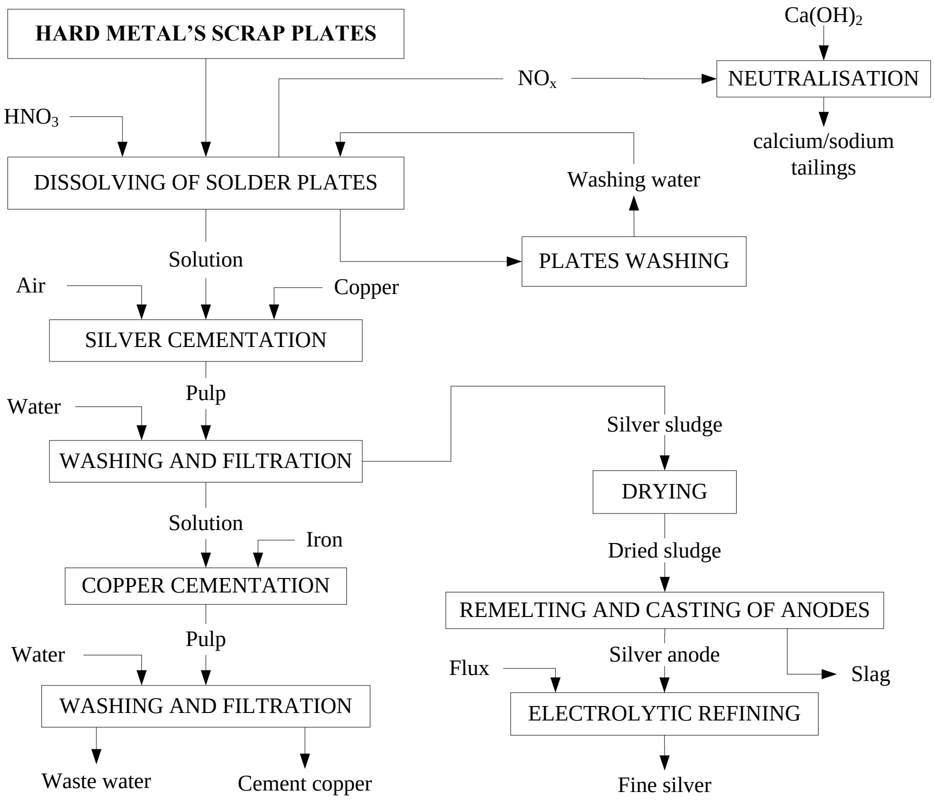

Fig. 1. The technological procedure of dissolution of solder residues to obtain fine silver and cement copper

<u>Oxidative annealing</u>

As mentioned, one of the common phases of the integrated procedure for processing of hard metal's scrap, for both variants, is oxidation annealing of scrap after its separating from the solder. In the process of oxidation of the hard metal's scrap, some of their components oxidized to the higher oxidation state: W to WO_3, Co to Co_3O_4, Ta to Ta_2O_5, Nb to Nb_2O_5, Ti to TiO_2 and C to CO_2. Then the complete decomposition of physical structure is performed and the volume of material is increased 8 - 12 times. Previous, very compact pieces of hard metal, after oxidation, become very porous, brittle, crumbly heaps of materials. Massive pieces of non-oxidized scrap plates are separated from the rest of the mixture and again are subjected to the process of oxidation annealing. Oxidation of scrap is carried out in an electric box furnace at a temperature of 1273 K for 8 h, in the presence of air.

<u>Milling of the product of oxidation annealing</u>

The last common phase for both variants of the integrated procedures for preparation of scrap is the milling of products of oxidation annealing. After the oxidative annealing is done, the material is milled in a ball mill made of hard metal and then is sieved in order to remove any possibly remaining non-oxidized small pieces. The milling process is performed in mill, with balls size of 8 mm in diameter made of hard metal at 58 rpm, for a period of 12 h and using ethanol as liquid medium. The mill is in the form of a pot with hermetic closure, made of wear-resistant steel. Milled fine-grained oxides are generally used in the processing of the powder mixture which directly applicable for reproduction of hard metal, while the milled coarse oxides use in the process for obtaining the components mixture in the form of oxides, carbides, salts, or in the elemental state.

The procedure for obtaining a mixture of powders by processing of the milled fine-grained oxides

After preparation of scrap, which included dissolving of solder plates, oxidative annealing and milling products of the oxidative annealing, the technological procedure of integrated processing of hard metal's scrap can go in two directions. The first direction implies the processing of scrap and the preparation of the powder mixture which is directly applicable for the repeated production of the hard metal, and includes: reduction of fine-grained oxides in a hydrogen atmosphere, homogenizing, carbonization and milling the products of carbidization.

In Figure 2 the technological procedure of processing the hard metal's scrap to obtain powder mixture directly applicable for reprocessing is shown [2, 5, 6].

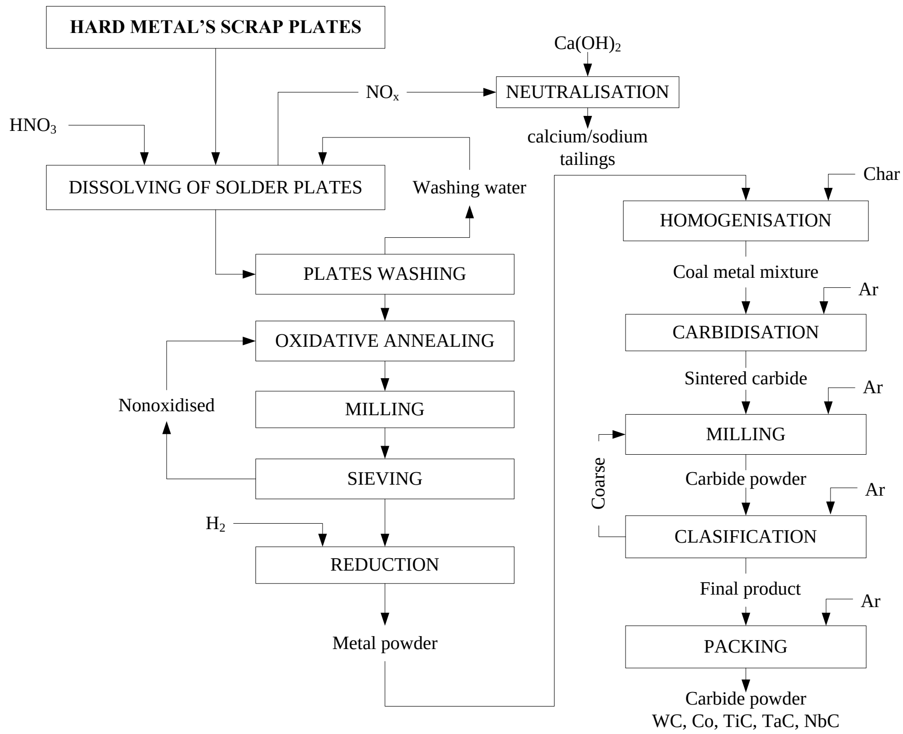

Fig. 2. The technological procedure of processing of secondary raw materials based on hard metals to obtain powder mixture directly applicable for reprocessing

As mentioned, after the preparation of scarp, the first variant of processing requires reduction of oxide mixture by introducing hydrogen, when the tungsten and cobalt oxides are reduced to the metal form, and oxides of Ta, Ti and N are reduced to lower oxides, because of their greater affinity to oxygen. The reduction process is carried out in electric resistance tube furnace into a stream of hydrogen, at a temperature of 973 – 1273 K for 5 - 6 h.

Also, the reduction of oxide mixture can be successfully carried out in a vertical tube reactor (Figure 3) [3, 34]. By development of vertical tube reactor for direct reduction of oxide with hydrogen, due to excellent contact between the particles of oxide and gas reducing, reduction process lasts for only couple of seconds, different to the reduction process in the horizontal tube, which lasted for couple of hours.

After this phase, follows carbidization of tungsten with simultaneous reduction and carbidization of Ta, Ti and Nb, when a mixture of carbide and cobalt are obtained and can be directly used for reproduction of hard metal. Cobalt does not carbidizate under those conditions, and serves as a binder during the sintering process of obtained powders mixture. As an agent for carbidization powdered carbon is used. The mixture of metal powder and powdered carbon must be as more homogeneous. Then homogenization is performed in the "double cone" mixer made of steel sheet before process of carbidization. The process of carbidization is carried out in an electric resistance furnace in atmosphere of argon at a temperature of 1373 – 1573 K for about 3 - 4 h. The products of carbidization are disintegrated to the desired granularity in the ball mill. The mill is covered with plates of alloyed steel, and the balls are made of hard metals. Depending on the required size distribution, a milling process lasts for a few hours under an atmosphere of argon.

Processing of the milled coarse oxides

Processing of the milled coarse oxides allows obtaining of all mixture components, depending on their purposes, in the form of oxides, carbides, salts, or in the elemental state. A method of processing the milled coarse oxides is divided into three stages:

1. The extraction of tungsten from a mixture of oxide, when the following products are obtained:
   - coarse dust WO_3,
   - elemental coarse tungsten powder,
   - tungsten carbide powder,
   - fine granulation WO_3 powder,
   - elemental fine granulation tungsten powder,
2. The extraction of cobalt from the mixture of oxides, which remain after the extraction of tungsten, where following products are obtained:
   - cobalt sulphate monohydrate,
   - cobalt oxide,
   - elemental cobalt powder,
3. The extraction of other metals from the rest of the oxide mixtures, when following products are obtained:
   - tantalum oxide,
   - niobium oxide,
   - a mixture of tantalum oxide and niobium,
   - titanium oxide.

In order to obtain the products based on tungsten the leaching of tungsten from a mixture using NaOH solution is done firstly, which selectively dissolves only the tungsten according to the following reaction:

$$WO_3 + 2NaOH \rightarrow Na_2WO_4 + H_2O \quad (3)$$

Other oxides from the residue remains in the insoluble form and as such they decanted, washed and send to a process for preparing products based on Co, Ti, Ta and Nb. The leaching is carried out with 35-40% solution, at a temperature of 373 to 383 K for about 2 to 4 h with intensive stirring. Initial ratio of the solid and liquid phase is 1:4. Considering the character of solution, the leach container is made of material based on iron, and is required to have a stirrer.

After leaching and decantation into a solution of Na_2WO_4 is introduced concentrated hydrochloric acid (25-30%) to precipitate tungsten acid, H_2WO_4. In this way, a precipitate H_2WO_4 and the solution of an inorganic salt are obtained.

$$Na_2WO_4 + 2HCl \rightarrow H_2WO_4 + 2NaCl \quad (4)$$

The solution of an inorganic salt is decanted and discarded. H_2WO_4 precipitate is washed, filtered, dried and calcined at a temperature of 923 K to obtain a tungsten (VI) oxide:

$$H_2WO_4 \rightarrow WO_3 + H_2O \quad (5)$$

The calcination process is carried out in an electric box furnace. Elementary tungsten obtained by reduction of tungsten carbide with hydrogen at temperature of 1023 K for 3 h. Tungsten carbide powder is obtained by homogenisation mixture of elementary tungsten pure powder and coal powder. The homogenised mixture then is subjected to the process of carbidization. Equipment for reduction, homogenisation and carbidization has the same characteristics as the equipment used for above mentioned processes taking place in processing of obtaining the powder mixture directly applicable for reproduction of a hard metal.

In this way, the obtained powder of tungsten (VI) oxide and tungsten pure elemental powders are classified as coarse powders. In order to obtain fine powders of tungsten (VI) oxide and pure elemental tungsten, precipitate of the tungstic acid, prior to calcination, redissolved with ammonium hydroxide. Then, ammonium paratungstate (APV) crystallize by evaporation and subjected to calcination process, to give a powder of tungsten (VI) oxide fine granulation.

In order to obtain pure powder of elemental tungsten, the obtained tungsten (VI) oxide powder is reduced with hydrogen.

The reduction process of tungsten oxide, because of the low reaction temperature and a high degree of purity of the obtained products, is the subject of many researches [31-34]. The results of researches point to the fact that the properties of the synthesized powder of tungsten depends, above all, of the characteristics of the starting powder, and the parameters of the technological processes, respectively of a manner performing of the reduction process.

It was concluded that by varying the parameters of the technological process, such as temperature and flow of the hydrogen, as well as performing the process in isothermal and non-isothermal conditions by the process of reduction can be obtained ultra-fine, homogeneous and loose powders of tungsten.

Synthesis of ultra fine tungsten powder by reduction of tungsten oxide can be successfully carried out in a vertical tube reactor. The basis of reactor is a vertical electro resistance furnace with a quartz tube.

The reduction process is carried out in the presence of hydrogen, which is moving in the direction opposite to the direction of movement of particles of tungsten (VI) oxide, to give a powder of particle size below 1 μm [35].

The apparatus for the reduction of WO_3 powder with hydrogen in the vertical tube reactor (Figure 3.) consists of:

the gas inlet system,
the gas purifier system,
the aggregate heating system,
the initial powder supply system (vibration supplier),
instruments for process measurement and regulation,
quartz tubes with the diameter of Ø22mm and with the height of h = 540 mm,
the coolers.

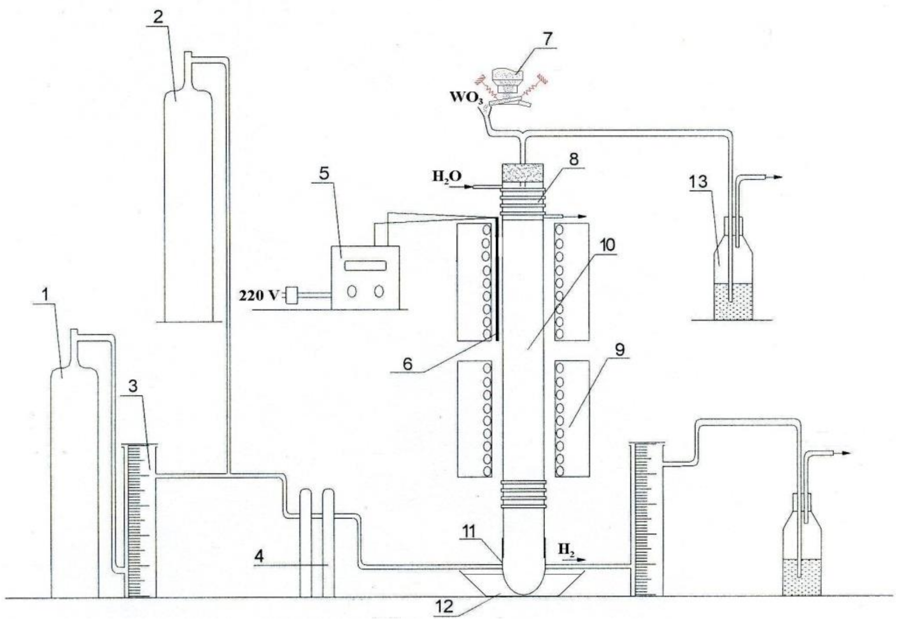

Fig. 3. The scheme of the assembly used for the reduction of WO_3 with hydrogen in the vertical tube reactor [29, 30]: 1. Hydrogen bottle, 2. Nitrogen bottle, 3. Rotameter, 4. Purification columns, 5. Thermoregulator, 6. Thermocouple, 7. Vibration supplier, 8. Radiator, 9. Electro resistant furnace, 10. Quartz tube, 11. Glass supplement, 12. Ice bowl, 13. Cleanser

The reduction of WO_3 with hydrogen in a vertical tube reactor is a new approach to the reduction of tungsten oxide compared to conventional procedures in a stationary layer.

Tungsten powder particles with a size of less than 1 μm were obtained with optimum temperature conditions and flow of hydrogen as result of the stretching and cracking of large particles, first in the reaction zone and then, due to an appropriate temperature shock, outside of this zone. The advantage of the procedure is the intensive contact between the reducing agents and the oxide particles, which results in a higher degree of reduction and a shortening of the reduction time to only a few seconds, while the process in a horizontal tube lasts for several hours and as a result less reduced powder is obtained.

The development of the vertical tube reactor for direct hydrogen reduction has enabled the production of powder and/or powder mixture of the high quality from the aspect of both physical and structural characteristics, high utilization level, and reducing of the process duration to just a few seconds, which has finally resulted in significant energy saving, as well as economic effect.

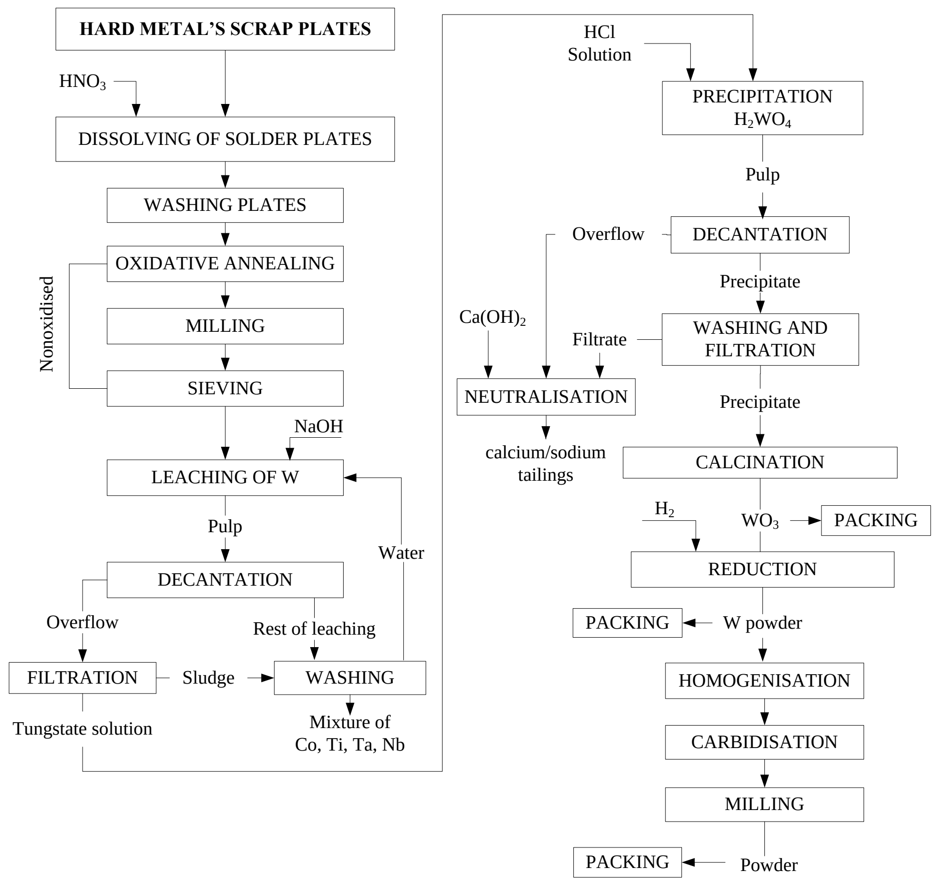

Fig. 4. The technological procedure of processing hard metal's scrap plates to obtain a product based on tungsten (WO_3 powder, a powder of elemental tungsten, tungsten carbide powder) [2,6,29]

Mixture of oxides Co, Ti, Ta and Nb, remained in insoluble form after leaching of tungsten with NaOH is subjected to a sulphatisation annealing which is carried out by addition of concentrated H_2SO_4 at a temperature of 615 K. Sulphatisation annealing is carried out for 3 to 6 h, depending on the thickness of batch layer and amount of added acid in the die-cast made of stainless steel vessel, which is heated in an electric box furnace. The required amount of concentrated H_2SO_4 is 4 to 5 times greater than the stoichiometric amounts.

The sulphatisation process lasting until white SO_3 fumes are developed. This process takes place according to the following reactions:

$$Co_3O_4 + 4H_2SO_4 \rightarrow CoSO_4 + Co_2(SO_4)_3 + 3H_2O \qquad 6$$

$$H_2SO_4 \rightarrow SO_3 + H_2O \qquad 7$$

Two-phase system is obtained by described method. One phase is precipitate of Ti, Ta and Nb oxides, and the second one is aqueous solution of $CoSO_4$. The obtained phases are separated by decantation.

Cobalt (II) sulphate is leached by warm water in acidly resistant container (e.g., enamel pot), at a temperature of 333 K for 1-2 h, with vigorous stirring.

In order to obtain cobalt sulfate, as the commercial product, a solution of cobalt sulfate is evaporated and then crystallized by cooling $CoSO_4 \cdot H_2O$. In the production of cobalt oxide and pure elemental cobalt powder, the precipitation of the mixture of cobalt carbonate and cobalt hydroxide with a solution of Na_2CO_3 at a temperature of 343-353 K is performed.

The cobalt carbonate is separate by decantation and washing, then calcinated at a temperature of 973-1173 K in an electric box furnace and finaly Co_3O_4 was prepared according to the following reaction:

$$2CoCO_3 + Co(OH)_2 + \tfrac{1}{2}O_2 \rightarrow Co_3O_4 + 2CO_2 + H_2O \qquad 8$$

The synthesis of pure elemental cobalt powder is carried out in an electric resistance tube furnace by reduction of Co_3O_4 with hydrogen at a temperature of 773 to 823 K for a period of 3 to 4 h. In the aim of synthesis of ultra fine powder of cobalt, shortening of the reduction time and an increasing the degree of reduction, for the reduction process is very well can be used vertical pipe reactor.

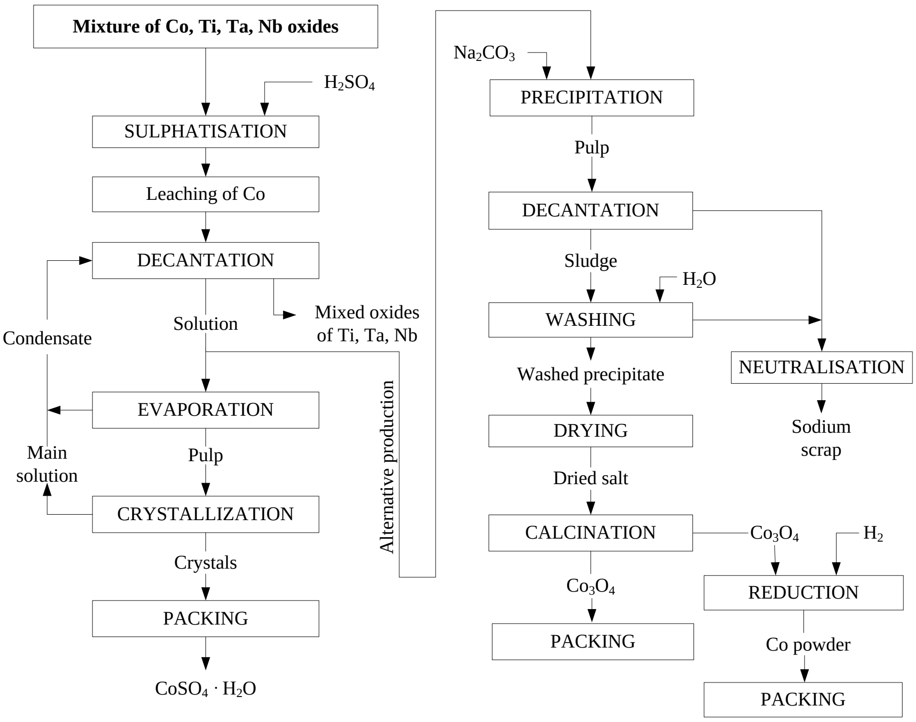

Fig. 5. The technological procedure of processing hard metal's scrap to obtain a product based on cobalt ($CoSO_4 \cdot H_2O$, and Co_3O_4 powder of elemental cobalt) [2, 6]

Chlorination of Ti, Ta and Nb oxides mixture is base for generating products which are further processed. First, Ti, Ta and Nb oxides are mixed with powdered coal and briquetted, and then chlorinated. Chlorination process is carried out in an electro resistance furnace in which the tube of stainless steel is placed. The obtained product is mixture of chlorides, except that the $TiCl_4$ is separated by condensation due to its volatility. Titanium chloride is converted to H_2TiO_3 by process of hydrolysis. Thereafter, TiO_2 is obtained by process of calcination. Also, mixture of $TaCl_5$ and $NbCl_5$ are subjected to hydrolysis to give a mixture of Ta and Nb oxides. If it is wanted to separately obtain tantalum oxide and niobium oxide as commercial product, then the mixture of $TiCl_5$ and $NbCl_5$ are first separated by fractional distillation and then converted by hydrolysis in the separated oxides (Ta oxide and Nb oxide).

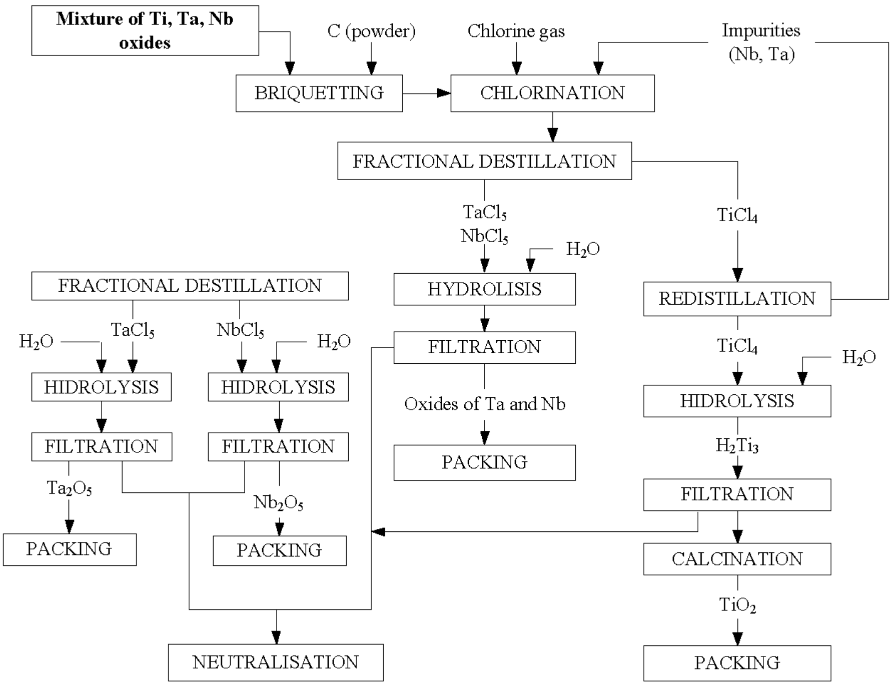

Fig. 6. The technological procedures of processing hard metal's scrap to obtain powder based on titanium, tantalum and niobium [2, 6]

Conclusion

The wide range of uses of hard metals in various fields of industry, as well as their increasing consumption, high cost and scarcity of their constituent elements has resulted in the need for recycling and valorisation of useful components from secondary raw materials based on hard metals. On the basis of previous studies, technological procedure of integrated processing of hard metal's scrap is developed and two directions are defined.

The first direction includes the processing and bringing the waste into such condition that can be immediately returned to the production process of hard metals. The second direction relates to the technology of processing of scrap materials to metal powders, either as oxides, carbides, salts, or in the elemental form, which is further processed depending on their purposes.

In accordance with the requirements for predicted synthesis of materials with required, improved properties, the integrated processing of hard metal's scrap provides obtaining of fine grained powders in a higher degree of reduction and a shortening of the reduction time to only a few seconds by using a vertical tubular reactor which has finally resulted in significant energy saving, as well as economic effect.

Finally, besides conservation of natural resources, there are also significantly economic and energetic benefits because the technological procedure of integrated processing of hard metal's scrap provides obtaining of wide range of powders with the required properties, a high efficiency and reduce the durations of individual stages of procedures for processing. Also, the developed technological procedure is in service of sustainable development.

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