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Regeneration of Hard Alloy Wastes by Low Energy Consumption and Environmentally Friendly Hydrothermal Technology

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Hard alloys are indispensable material for many branches of modern industry. However, even with the base composition (WC-Co) they are quite expensive due to the limited natural resources of cobalt and the complexity of their production from the minerals. Therefore, the collection and recycling of hard alloys waste have not only scientific but practical importance, taking into account that the cost of production of 1 ton of alloy from recovered waste comes to 20% cheaper than in the core technology. Existing methods of hard alloys waste treatment have several disadvantages, the main of which are high power consumption and big load on the environment. As a result of this research a high-performance, low-energy consumption, eco-friendly way for recycling of hard alloys waste has been proposed. According to this technology, in a first step the WC powder, and the solution containing cobalt salts were obtained by autoclaving at 230 °C in a mixture of HCl-H₃PO₄-HNO₃ acids, and followed then metal cobalt recovery from hydrothermal solution at temperatures of 110 – 160 °C.

Keywords: hard alloy, waste, regeneration, autoclave, hydrothermal process

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Introduction

Cermets WC-Co often called hard alloy are widely used for industrial tools and construction applications due to their unique mechanical properties [1, 2]. These properties (hardness, strength, toughness and wear resistance) are based on that WC and Co most closely correspond to requirements for components from which composite is made namely complete wetting a refractory component (WC) by easily melted (Co), limited solubility of refractory component in the easily melted and practical insolubility of easily melted component in the refractory portion.

In order to receive the special properties the WC basis of hard alloy is subjected to doping. The most known additives are TiC, TaC, NbC. However, even in basic composition (WC-Co) the hard alloys are very expensive due to limited natural resources of Co in earth and complicated technology of preparation of products from mineral raw materials. On the other hand, 1 ton of products from regenerated hard alloy wastes has 20 % low price [3].

There are several methods, and new methods for utilization of hard alloy wastes are developed from year to year, for example, exotic method based on the dispersion in water by electric discharge has been proposed [4]. At the same time methods that used in practice could be divided on 4 groups:

1) mechanical desintegration [5-6],

2) cobalt extraction by physico-metallurgical technique (Zn method - melting together with Zn, and subsequent sublimation in vacuum) [7-8],

3) cobalt extraction by hydrometallurgical chemical or electrochemical* methods. This group includes a lot of techniques [9-12],

4) chemical desintegration (oxidation-reduction-carbidization) [3, 13,14].

Obvious characters of all processes are:

a – high energy consumption (1,2,3*,4)

b – long duration (3,4)

c – high temperature (2,4)

d – restricted purity of products (1,2)

e – pollution of environment (2,3)

f – expensive reagents (3)

g – processing only for graded wastes (1,4)

Despite the fact that latter process applied only for graded wastes, but it is very efficient in processing of waste generation, that are formed during the production of synthetic diamonds, for example. Generally here two kinds of hard alloys with 6% of Co for press dies and with 15% of Co for supporting plates are used. Wastes from both are easily separated by size dies are small and plates are big. Scheme of such process, which long time has been used at Institute of Superhard Materials NASU is shown in Figure 1.

According to this technology hard alloy wastes after cleaning and washing were subjected to air oxidation and then to reduction/carbidization in hydrogen with

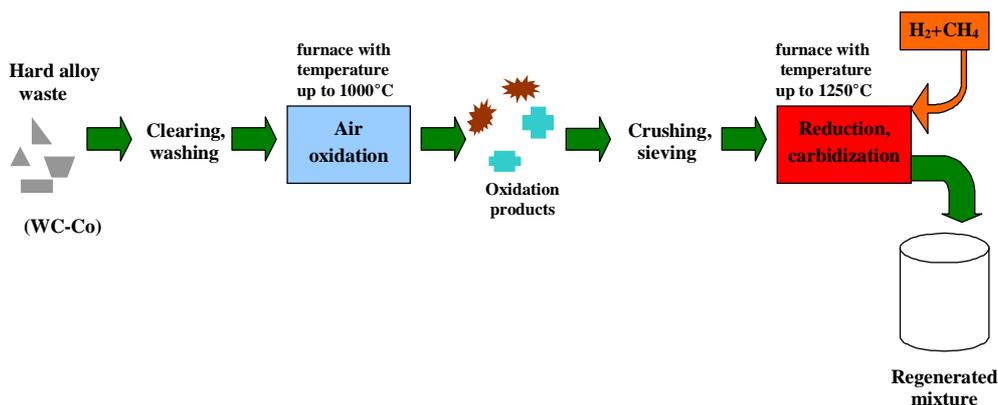


Fig. 1. Scheme of regeneration of WC-Co hard alloys waste.

precisely controlled amount of methane. For both main stages a low rate of process is main limitation (every stage requires at least 24 hours of exposure).

At research stage a limiting step was carbidization process of oxidized waste in hydrogen with a controlled amount of methane. However, during exploitation of this technology it is appeared that the limiting stage is the oxidation and the milling of the oxidized product due to low durability of equipment for these operations. In the air oxidation process at the temperature of 1000 °C the pans in which oxidation occurs are rapidly destroyed, and due to the high strength of the resulting oxides, milling equipment quickly became damaged.

On the other hand air oxidation could be replaced by autoclave hydrothermal oxidation [15]. Such process can be referred as thermochemical and has several obvious advantages. Since it is closed process therefore should be environmentally friendly, occurs at relatively low temperatures with high speeds that permits to reduce a processing time. Resulting product does not require significant energy expenses for grinding and has a high purity.

Except for mechanical desintegration process all above-mentioned recycling methods consist of at least two stages. Moreover, it well known that carbidization is most long and power-consuming stage. Elimination of this stage by etching under high pressure it is possible to separate metal matrix from the alloy base using special solutions that is economically favorable. For example, the authors [16] subjected to treatment a WC-20%Co hard alloy in concentrated HCl at 110 °C for 48h in order to separate cobalt and get a highly porous carcass of easily crushed WC. Most used sorts of hard alloy, however, contain the 6 or 15% of cobalt. Their character, in contrast with 20 % grade, is that most cobalt forms a γ -solid solution and few free Co there is at the grain boundaries.

Present research was devoted to recycling of hard alloy with 6% of cobalt (BK-6) (pieces of destroyed pistons of high pressure apparatus, 2-4 g weight). Such parts, after sintering compulsorily are subjected gas-static treatment, which makes them practically nonporous with a minimum amount of defects. Therefore, the recycling of such alloys is completely another problem then model

samples in [16].

I. Experimental procedures

Experiments were performed in a steel autoclave with a modified PTFE insert that had 80 ml volume that secured long exposure at 230 °C. Construction of autoclave is given in [17]. Experiments were performed in the hydrothermal fluid as well as in saturated steam (Fig. 2).

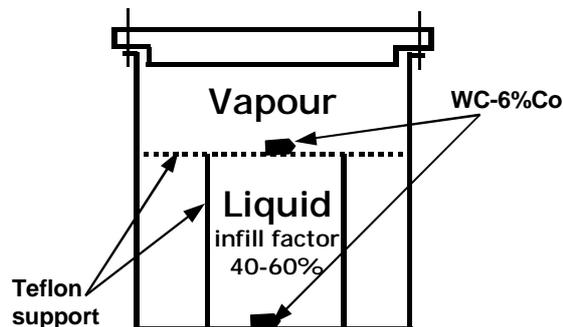


Fig. 2. Scheme of arrangement of samples in Teflon autoclave. Liquid-solid ratio was 4-6.

As source reagents were used ammonium hydroxide NH_4OH (25 % NH_3), hydrogen peroxide 30 % H_2O_2 , muriatic acid 4, 6, 11.2 N and 37 % HCl, nitric acid 30 % HNO_3 , phosphoric acid 85 % H_3PO_4 , phosphorous acid 45 % H_3PO_3 .

After the hydrothermal treatment, the reaction solution with the pieces of hard alloy and detached powder was treated in an ultrasonic bath for 10 min and then settled. Once the solution became clear it was separated from solid portion and studied by X-ray fluorescence analysis (XRF). Powder and solid pieces washed successively with distilled water and alcohol and dried at temperature of 90 °C.

In the case of complete extraction of Co the solid residue was easily ground in an agate mortar.

The resulting powders after hydrothermal treatment were investigated using scanning electron microscopy combined with energy dispersive analysis (SEM-EDX), X-ray diffraction (XRD) and X-ray fluorescence

analysis.

II. Results and discussion

Despite the fact that hard alloy starts to react with tested solutions even at the room temperature (colour of solutions is changed), but the rate of this process is such low (weight changes are undistinguished), that usually more than one-month exposure is required. The degree of conversion (extraction of cobalt) α was defined as the

$$\text{ratio: } a = \frac{m_o - m_p}{m_1}, \text{ where } m_o - \text{ mass of the sample}$$

before treatment, m_p - mass of the sample after treatment, m_1 - calculated mass of cobalt in the sample on the basis of its 6 % concentration.

The rate of process is increased at 200 °C in the autoclave conditions, but concentrated HCl as well as other tested solutions [18] was found as ineffective. Calculated process end is about 200 h.

Another results were obtained for HCl-HNO₃ mixture. Thus adding to the hydrothermal process oxidant (HNO₃) leads to the appearance of significant amounts of WO₃ (bright yellow powder) on the bottom of the autoclave. This greatly complicates the correct assessment of the degree of conversion (α) or does it even not possible in the case of addition of 5 mL HNO₃. In this case the sample was completely oxidized and destroyed already after three hours at 200 °C. Despite the fact that WO₃ was formed as main solid product, but distinguishable amount of black powder (WC) was also collected on the bottom of autoclave.

Hence the high temperature oxidation process can be replaced by highly efficient autoclave process at 200 °C in a mixture of HCl and HNO₃ acids.

On the other hand the processes of recovery and carbidization of WO₃ are quite energy consumable and prolonged. Therefore further efforts it was reasonable to spend on etching of cobalt phase at maximum possible preservation of WC carcass. Experiments were carried out at 230 °C maximum temperature for given construction of the autoclave.

Beside previously used mixture of HCl-HNO₃ as working solutions were applied also phosphorous acid, possessing strong reducing properties [19] or phosphoric acid, which dissolves a wide range of oxides at boiling [20-21]. Additive of each in the hydrothermal solution must slow down or even stop the formation of WO₃.

It should be noted that even in the case where degree of cobalt extraction (α) come near to 80 % the solid residue remains extremely strong which excludes the possibility of preparation of powder without using of special facilities.

If special reactant solution HCl-H₃PO₄-HNO₃ was used then as a result of hydrothermal interaction the whole cobalt phase (> 99 %) was completely transferred into solution for 30 h at 230 °C, and WC powder and easy destructible solid was collected on the bottom of the autoclave. While degree of extraction in hydrochloric acid at the same conditions was only 66 % and solid residue WC had extremely high strength.

The WC final product was identified by X-ray diffraction, X-ray fluorescence analysis and observed by scanning electron microscope (Fig. 3). In the X-ray spectrum of the powder sample only reflection from

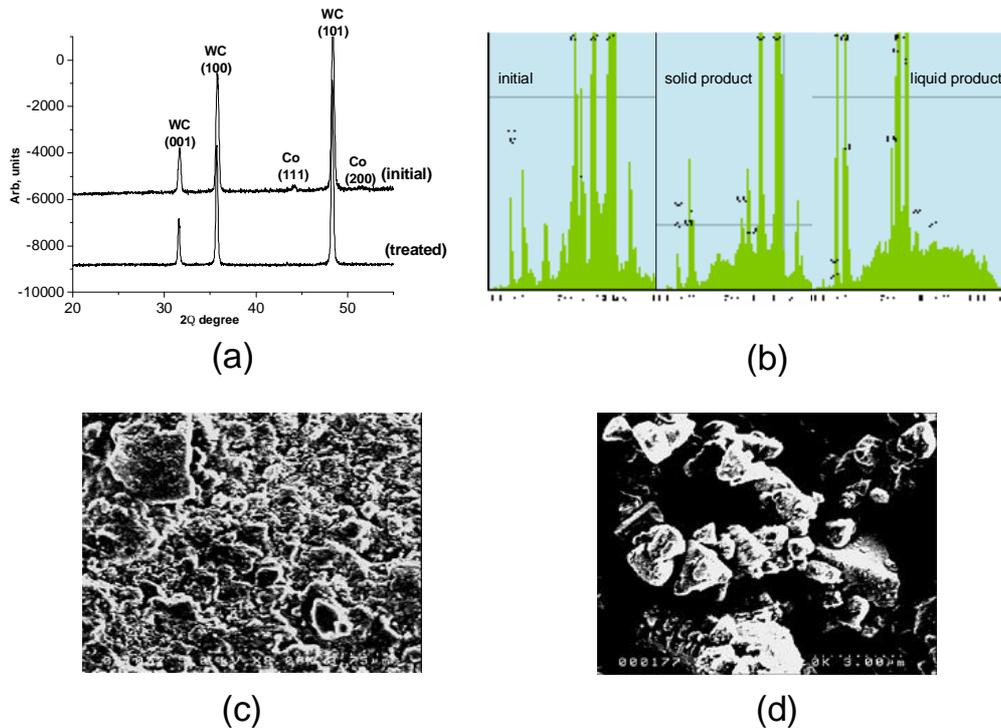


Fig. 3. Results of XRD analysis (a), X-ray fluorescence (b) of initial WC - 6% Co and extracted WC shown in SEM images (c) and (d) respectively.

tungsten carbide WC are visible (Fig. 3,a). A typical XRF spectrum of initial alloy, solid residue after the treatment and reaction solution after 100 % extraction of the cobalt corresponding mixture of phosphate and chloride of cobalt ($\text{CoCl}_3 + \text{Co}_3(\text{PO}_4)_2$ - 98.421 %) are shown in Figure 3,b. Morphological features of the original structure of the initial alloy and the processed product were studied using scanning electron microscopy (Fig. 3,c). It is seen that the alloy BK-6 had very fine grain structure and extracted grains have typical for tungsten carbide shape and size that varying from 300 nm to 3 microns (Fig. 3,d).

Taking into account that even when hydrothermal oxidation to WO_3 occurred, the cobalt phase is transferred into solution containing cobalt chlorides and it is known that cobalt salts solutions can be readily converted to metallic cobalt by hydrothermal recovery

conditions at 160 °C [22, 23] or even at 110 °C [24], then regeneration method of hard alloys waste based on autoclave processes and allowing to process not sorted waste such as destroyed press dies and supporting plates after diamond synthesis has been developed.

Conclusion

As a result of this research highly effective, energy-saving and environmentally friendly autoclave process that allows recycling of not sorted waste of WC - Co hard alloys was developed.

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С.Ф. Корабльов

Переробка відходів твердих сплавів WC-Co за допомогою екологічно чистого автоклавного методу при помірному споживанні енергії.

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Тверді сплави є незамінним матеріалом в багатьох галузях сучасної промисловості. Проте, навіть у базовій композиції (WC-Co) вони досить дорогі через обмеженість природних ресурсів кобальту і складності їх виробництва з мінеральної сировини. Тому питання збору та переробки відходів твердих сплавів мають як наукове так і практичне значення, беручи до уваги, що вартість виробництва 1 тонни сплаву з відновлених відходів обходиться на 20 % дешевше, ніж по основній технології. Існуючі методи переробки відходів твердих сплавів мають ряд недоліків, основними з яких є високе енергоспоживання і велике навантаження на екологію. В результаті проведених досліджень був запропонований високоефективний, енергетично низькозатратний, екологічно чистий спосіб переробки відходів твердих сплавів. Відповідно до цієї технології на першій стадії порошок WC і розчин який містить солі кобальту був отриманий в результаті автоклавної обробки при 230 °C в суміші HCl-H₃PO₄-HNO₃ кислот, після чого металевий кобальт може бути легко виділений з розчину за допомогою гідротермального відновлення при температурах 110 - 160 °C.

Ключові слова: твердий сплав, відходи, регенерація, автоклав, гідротермальний процес.