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**RECYCLING OF W-Ni-Fe SCRAP TO PRODUCE POWDERED TUNGSTEN**Yuri E. Sknar\*, Oleg V. Kozhura, Irina V. Sknar, Valeriy A. Kotok, Tetyana E. Butyrina,  
Mykola O. Kuznetsov*Ukrainian State University of Science and Technology, str. Lazaryana, 2, Dnipro, 49010, Ukraine.**Received 16 April 2024; accepted 10 June 2024; available online 10 July 2024***Abstract**

The paper addresses the topical issue of recycling of scrap of strategic W-Ni-Fe alloy used in the production of armor-piercing shells. Recovery of tungsten and other alloy components solves the problem of shortage and high cost of these metals. The paper investigates the effect of the concentration of hydrochloric acid and hydrogen peroxide, as components of the leach solution, on the degree of leaching of the binder phase. It has been found that an increase in the concentration of the two components leads to an increase in the rate of both the leaching process and side processes, which results in inappropriate consumption of reagents. The results of the experimental studies show that the most effective is the use of hydrochloric acid with a concentration of 2 mol/L and hydrogen peroxide with a concentration of 2 mol / L. The problem of catalytic decomposition of hydrogen peroxide is solved by performing the leaching process at a low temperature (about -5 °C). A new method of leaching of the W-Ni-Fe alloy to obtain high-quality tungsten powder has been proposed. The intensification of the process is achieved by leaching under self-grinding conditions with continuous mechanical renewal of the surface that is in contact with the acid-oxidizing leach solution.

*Keywords:* powdered tungsten; binder phase; self-grinding; recycling; leaching degree.

**ПЕРЕРОБКА ЛОМУ W-Ni-Fe З ОТРИМАННЯМ ПОРОШКОВОГО ВОЛЬФРАМУ**Юрій Є. Скар, Олег В. Кожура, Ірина В. Скар, Валерій А. Коток, Тетяна Є. Бутиріна,  
Микола О. Кузнецов*Український державний науково-технічний університет, пр. Лазаряна, 2, Дніпро, 49010, Україна***Анотація**

Робота присвячена актуальній темі переробки лому стратегічного сплаву W-Ni-Fe, який використовується у виробництві броньованих снарядів. Рециклінгове використання вольфраму та інших компонентів сплаву вирішує проблему дефіциту і дорожчості цих металів. У даній роботі досліджено вплив концентрації хлоридної кислоти і гідроген пероксиду, як компонентів розчину вилуговування, на ступінь вилуговування зв'язуючої фази. Встановлено, що збільшення концентрації обох компонентів призводить до збільшення швидкості як процесу вилуговування, так і перебігу побічних процесів, які призводять до нецільової витрати реагентів. Результати проведених експериментальних досліджень свідчать, що найбільш ефективним є використання хлоридної кислоти концентрацією 2 моль/л та гідроген пероксиду концентрацією 2 моль/л. Проблема каталітичного розкладання гідроген пероксиду вирішується за рахунок проведення процесу вилуговування за низької температури (близько -5 °C). Запропоновано нову методику вилуговування сплаву W-Ni-Fe з отриманням високоякісного порошку вольфраму. Інтенсифікація процесу досягається організацією вилуговування в умовах самопомелу з безперервним механічним оновленням поверхні, яка контактує з кислотно-окиснювальним розчином вилуговування.

*Ключові слова:* порошковий вольфрам; зв'язуюча фаза; самопомел; рециклінг; ступінь вилуговування.

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## Introduction

Tungsten is a rare earth metal with a high melting point and stable chemical properties. Furthermore, it has excellent mechanical properties at high temperatures, which necessitate its use in the production of alloys with enhanced hardness, heat resistance, and abrasion resistance [1–3]. Due to its unique physical and chemical properties, tungsten is a strategic raw material and has no acceptable substitute. The use of tungsten in hard alloys, in particular, is its most important application. Industrially, tungsten is used in the production of metalworking, mining and stone-cutting tools, high-temperature equipment, catalysts, weapons, and in the aerospace industry [4–8]. Tungsten is also used in the manufacture of rocket nozzles and turbine blades [9]. Tungsten is mostly extracted from the minerals wolframite and scheelite [10–13]. Scarcity of tungsten sources along with environmental considerations is driving manufacturers to reuse tungsten waste. In its vast majority, the scrap contains more tungsten than even ore concentrates. The tungsten content in scrap ranges between 40 and 95 % [14], while scheelite and wolframite concentrates contain 7–60 % of tungsten. Moreover, tungsten recovery from scrap requires less energy and chemicals and produces less waste. Currently, about a third of the world's total tungsten demand is met through recycling of tungsten-containing scrap [15–19]. Tungsten scrap contains other valuable metals such as V, Co, Ni, Cu, Ta, Nb, Ti, Re, Ag, etc., which are also of great value. This encourages the combined processing of this kind of raw material to obtain several valuable metals [20].

The cores of armor-piercing shells used for defense purposes are made using tungsten in the powder metallurgy process. The finely dispersed powder of tungsten, nickel and iron is thoroughly mixed and compacted. The compacted rods are sintered to produce an alloy that can be machined. The initial structure of the alloy consists of tungsten grains and interlayers of the matrix of a solid solution of tungsten in a Ni-Fe base. Iron prevents dissolution of tungsten in nickel. These heavy alloys are ductile and can be easily machined by cutting and pressure. The process of manufacturing military products from W-Ni-Fe hard alloy generates three types of waste: powder scrap from pressing; scrap from

machining (turning); and defective products in the form of solid rods [21]. The production of shells accumulates significant amounts of this type of scrap. Due to the strategic importance of tungsten, as well as nickel, recycling of the scrap is becoming an urgent task these days.

For the recovery of tungsten from the W-Ni-Fe alloy used to manufacture armor-piercing shell cores, electrochemical and chemical processing of the scrap has been proposed. As a result of electrochemical dissolution of this kind of alloy, tungsten passes into solution in the form of sodium tungstate. The next step is to convert it into ammonium paratungstate, from which tungsten oxide is obtained [21]. The chemical method of recycling of W-Ni-Fe scrap is the acid leaching of iron and nickel. The highest dissolution rate of Ni-Fe alloys is observed in nitric acid solutions. This results in the dissolution of the binder and formation of powdered tungsten. The process is complicated by the fact that tungsten contained in the binder changes into the form of  $H_2WO_4$  with the formation of a film on the surface of the tungsten grains [22]. The film leads to significant diffusion complications in the leaching process. As a result, W-Ni-Fe alloy scrap parts that have not been subjected to fine grinding exhibit significant resistance to acid.

Thus, an urgent scientific and technical task is to intensify the processing of W-Ni-Fe alloy scrap by dissolving the binder phase and obtaining powdered tungsten. It is expected to achieve a significant intensification of leaching due to the new method of carrying out this process under self-grinding conditions.

## Materials and methods

The scrap cores of armor-piercing shells with a content of 90 % (wt.) tungsten, 6 % (wt.) nickel, and 4 % (wt.) iron were used as a raw material for the research.

For leaching the W-Ni-Fe alloy scrap parts, a laboratory installation was proposed, the scheme of which is shown in Fig. 1. The volume of the leach solution was 4 liters. 10 kg of scrap parts weighing 300 to 600 g were placed in the drum. The leaching was carried out in a mill under self-grinding conditions. To intensify the leaching of the binder phase, hydrogen peroxide was added to the acid solution.

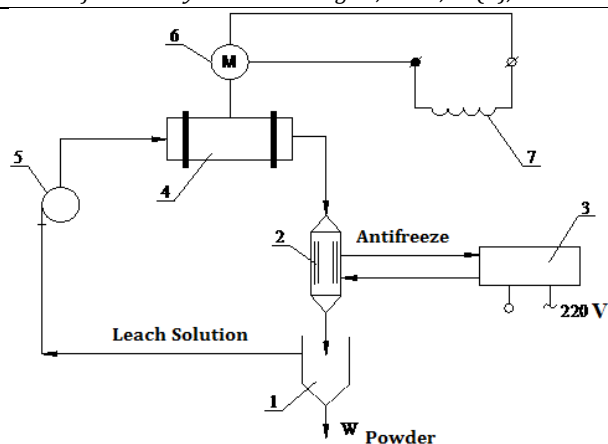


Fig. 1. Laboratory installation for leaching and grinding W-Ni-Fe alloy scrap:

1 - settling tank; 2 - heat exchanger; 3 - refrigeration thermostat; 4 - mill; 5 - pump; 6 - mill motor; 7 - laboratory autotransformer

Hydrogen peroxide is a thermodynamically unstable compound.  $\text{Fe}^{3+}$  ions, the dispersed tungsten phase, and an increase in temperature act as accelerating factors in the decomposition of  $\text{H}_2\text{O}_2$ . To slow down this process, the laboratory installation was equipped with a titanium heat exchanger with antifreeze circulating in the intertubular space. The antifreeze temperature was maintained by a refrigeration thermostat with an accuracy of  $\pm 1$  °C. The leach solution was fed into the pipe space of the heat exchanger using pump 5. The leaching was carried out in the grinding drum 4 with the rotational speed set at 60 rpm and controlled by the transformer 7.

The leach solution was transferred from the heat exchanger to the mill drum to further enter the receiving chamber of the settling tank, where tungsten powder was deposited. A layer of chemically inert organic substance, Freon 113 (boiling point = 47 °C, melting point = -20 °C,  $\rho = 1.5 \text{ g/cm}^3$ ), was placed in the lower part of the settling tank to prevent the tungsten powder contact with the leach solution. The leach solution, freed from dispersed tungsten, flowed by gravity to the heat exchanger and was then pumped to the grinding drum.

The concentration of hydrogen peroxide in the leach solutions was measured by permanganometry.

The content of iron (III) ions in the solutions was analyzed as follows. Into a 250 ml flask, 0.5 ml of the solution was poured, 100 ml of water and 6 ml of hydrochloric acid were added. An aluminum wire was immersed in the solution containing a sample and hydrochloric acid. The solution was held at a temperature of 70 °C for 20 minutes. After the holding time, all iron (III) ions were reduced to iron (II) and the solution was

discolored. After that, a piece of marble was added to the solution and the solution was held for 10 minutes. The carbon dioxide formed by the interaction of marble and acid protected the iron (II) ions from oxidation by air oxygen. 1 ml of orthophosphoric acid was added to the transparent light green solution and titrated with a 0.1 N potassium permanganate solution until the color changed to pink.

The content of nickel (II) ions was measured by trilonometric titration according to the method described in [23].

The degree of the binder leaching was assessed by the change in the mass of iron and nickel that passed from the alloy into the solution during leaching:

$$\alpha = \frac{m_{\text{Fe}} + m_{\text{Ni}}}{m_{\text{Fe}(\text{alloy})} + m_{\text{Ni}(\text{alloy})}}, \quad (1)$$

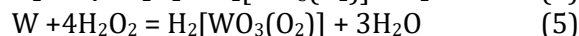
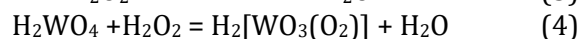
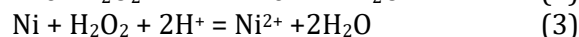
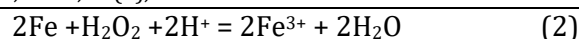
where  $m_{\text{Fe}}$ ,  $m_{\text{Ni}}$  are the masses of iron and nickel that have passed into the leach solution;  $m_{\text{Fe}(\text{alloy})}$ ,  $m_{\text{Ni}(\text{alloy})}$  are the masses of iron and nickel in the source scrap parts that were subjected to leaching.

## Results and discussion

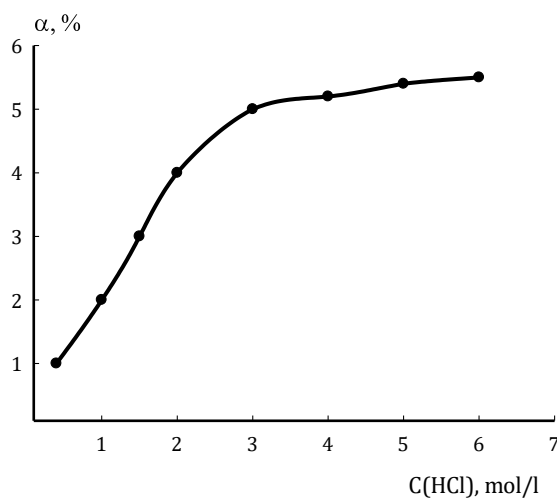
Preliminary studies on the selection of the type of acid for leaching the binder in the W-Ni-Fe alloy have shown that within one hour, no noticeable dissolution of the alloy occurs under self-grinding conditions in either nitric acid or sulfuric acid solutions in the presence of hydrogen peroxide. The study of the leaching process of the raw material in nitric acid 2–4 mol/l and sulfuric acid 2 mol/l solutions in the presence of 2 mol/l of  $\text{H}_2\text{O}_2$  showed that the change in the mass of the processed material did not exceed 1%. However, the use of a mixture of

hydrochloric acid and hydrogen peroxide results in active dissolution of the material.

To destroy the binder phase, we propose to use acidic solutions of hydrogen peroxide. When dissolved in such solutions, hydrogen peroxide acts not only as an oxidizer of all alloy components, but also as a complexing agent for tungstic acid. The finely dispersed tungsten particles in the Ni-Fe binder phase have an extended surface and, unlike large tungsten crystals, are easily oxidized and pass into solution. The leaching process occurs through the following reactions:

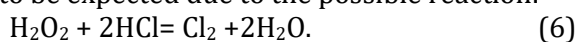


A 1 h study of the effect of hydrochloric acid concentration on the degree of binder leaching (Fig. 2) showed that an increase in acid concentration from 0.5 to 3 mol/l leads to a significant acceleration of the process. A further increase in the acid concentration to 6 mol / l only leads to a small increase in the degree of conversion.



**Fig. 2. Dependence of the degree of binder leaching for 1 hour on the hydrochloric acid concentration in the presence of 2 mol/l hydrogen peroxide in the leach solution**

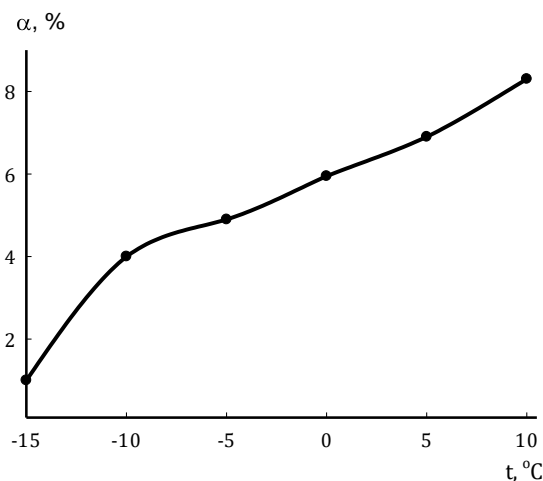
It should be noted that an increase in the hydrochloric acid concentration above 3 mol / l led to a noticeable release of chlorine. This effect is to be expected due to the possible reaction:



The rate of this reaction increases with an increase in the concentration of H<sup>+</sup> ions. In this case, chlorine is released into the gas phase and does not participate in the leaching process.

Based on the experimental data obtained, a leach solution containing 2 mol/l of hydrochloric acid was used in further studies.

The temperature effect on the leaching degree was studied during one hour of treatment of W-Ni-Fe alloy scrap. Fig. 3 shows that the leaching degree increases with an increase in the solution temperature. A decrease in the temperature below -15 °C leads to the leach solution freezing.



**Fig. 3. Effect of temperature on the leaching degree within one hour**

It should be noted that the rate of hydrogen peroxide decomposition is largely dependent on the temperature. Therefore, it is necessary to consider this dependence for a corresponding leach solution prior to selecting the temperature

regime of the process of leaching of the binder in a W-Ni-Fe alloy.

Fig. 4 shows that in the studied temperature range, the rate of the reaction



is minimal in the range of  $-15$  to  $0$  °C.

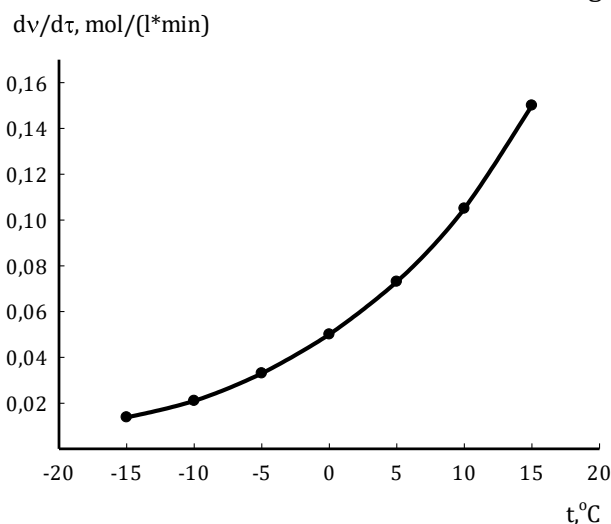


Fig. 4. Dependence of the rate of  $\text{H}_2\text{O}_2$  decomposition on the temperature of the solution: 2 mol/l  $\text{H}_2\text{O}_2$  + 2 mol/l HCl

Deep cooling requires significant energy consumption for the operation of the refrigeration unit. Therefore, the optimal level of leaching temperature is set taking into account the costs of operating the refrigeration unit and maintaining the required concentration of hydrogen peroxide. Under laboratory conditions,

the leaching temperature was maintained at  $-5$  °C.

A key parameter that affects the leaching rate is the concentration of hydrogen peroxide in the solution. With an increase in the concentration of hydrogen peroxide, the leaching rate, represented as a time differential of the leaching degree, increases (Fig. 5).

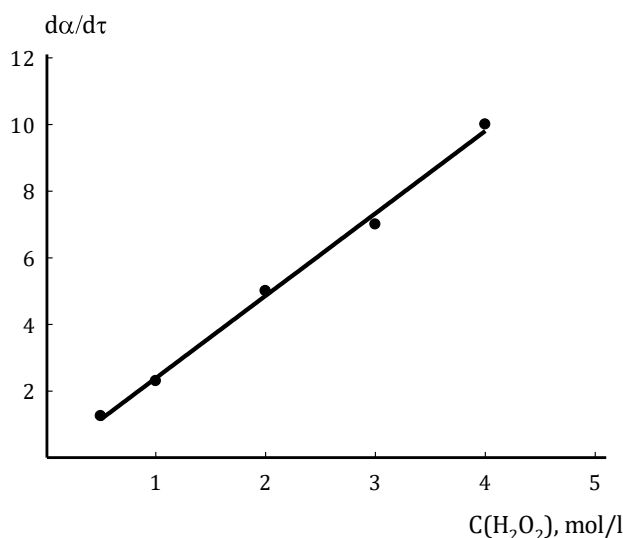


Fig. 5 Effect of hydrogen peroxide concentration on the leaching rate at  $t = -5$  °C in a solution containing 2 mol/l of hydrochloric acid

However, an increase in  $\text{H}_2\text{O}_2$  concentration will also accelerate its decomposition. Thus, an important process indicator is the ratio of  $\text{H}_2\text{O}_2$  consumption for the side and target processes. To conduct this study, a laboratory installation was used to measure the volume of oxygen released

during the leaching process. The installation consisted of a sealed titanium cylinder with a gas outlet. The gas outlet was connected to the gas collection cylinder by a flexible hose. Upon completion of the experiment, the volume of oxygen released, the concentration of nickel and

iron leached, and the residual amounts of hydrogen peroxide were measured. The processing of the data obtained allowed constructing the dependence of the ratio of hydrogen peroxide consumption for the side process to the hydrogen peroxide consumption

$$v(\text{H}_2\text{O}_2)_{\text{O}_2}/v(\text{H}_2\text{O}_2)$$

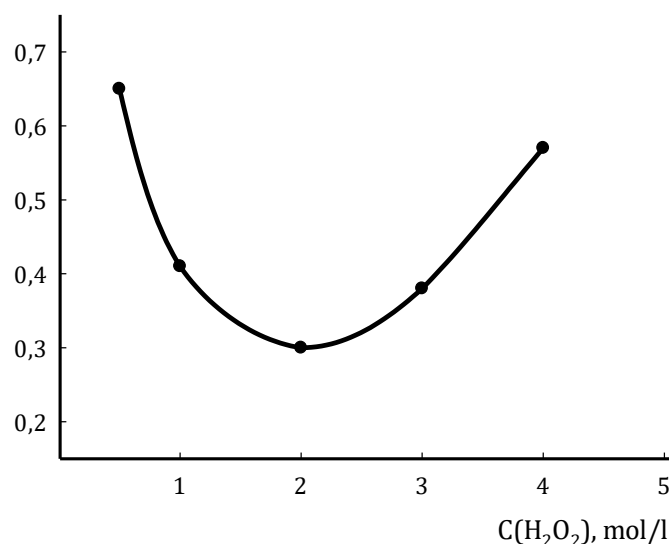


Fig. 6. Dependence of the ratio of H<sub>2</sub>O<sub>2</sub> consumption for the side and target processes on the concentration of hydrogen peroxide in the leach solution

Based on the research results, it is proposed to leach W-Ni-Fe alloy scrap in a solution containing 2 mol/l hydrochloric acid and 2 mol/l hydrogen peroxide. The process temperature is -5 °C. The process is performed

for the target process on the concentration of hydrogen peroxide in the leach solution (Fig. 6). As can be seen from the figure, the dependence has an extreme nature with a minimum at a concentration of 2 mol/l H<sub>2</sub>O<sub>2</sub>.

under self-grinding conditions. The tungsten powder obtained by the above method is a finely dispersed material ready for reuse in strategic powder metallurgy (Fig. 7).



Fig. 7 Tungsten powder obtained by the W-Ni-Fe alloy leaching

## Conclusions

1. The paper investigates the degree of leaching of the binder phase of the W-Ni-Fe alloy to obtain powdered tungsten, depending on the process conditions. It has been found that the dissolution of the binder phase occurs in a leach solution containing a mixture of hydrochloric acid and hydrogen peroxide. An increase in the concentration of hydrochloric acid and hydrogen

peroxide leads to an acceleration of the process. It has been shown that the course of side reactions determines the choice of the most effective concentrations of both chloride acid and hydrogen peroxide.

2. It has been found that the technologically feasible leaching temperature is about -5 °C, which provides the least loss of hydrogen peroxide through the decomposition reaction. A

new method of leaching of the W-Ni-Fe alloy to obtain high-quality tungsten powder has been proposed, which involves the use of a leach solution containing 2 mol/l of hydrochloric acid

and 2 mol/l of hydrogen peroxide. The process is carried out under self-grinding conditions, which ensures simultaneous surface renewal and its chemical interaction with the leach solution.

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