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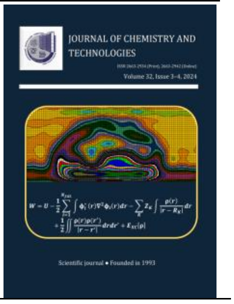

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RECYCLING OF WC-Ni SCRAP TO OBTAIN TUNGSTEN CARBIDE

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Abstract

The paper is devoted to the relevant issue of recycling scrap of the strategic WC-Ni alloy used in the production of armor-piercing shells. The recycling of tungsten and nickel carbide eliminates the problem of shortage and high cost of these components. This paper investigates the effect of the concentration of hydrochloric acid and iron (III) chloride in the leaching solution on the extent of nickel leaching from cemented tungsten carbide. It was found that an increase in the concentration of both components leads to an increase in the process rate. It has been shown that the addition of iron (III) chloride to the acid leaching solution leads to a fivefold increase in the process rate. It has been established that the activation energy of the leaching process in a solution of 4.5 mol/L chloride acid is 50.5 kJ/mol. The activation energy of leaching in a solution containing 4.5 mol/L hydrochloric acid and 2 mol/L iron (III) chloride is 17.9 kJ/mol. When switching from an acid leach solution to a solution containing a mixture of acid and iron (III) chloride, the process moves from the kinetic to the diffusion region. To accelerate leaching under conditions of diffusion limitations, it is proposed to increase the efficiency of surface renewal of raw material pieces by selecting the size and rotation frequency of the grinding drum. It has been shown that the dependence of the leaching degree on the drum rotation frequency passes through a maximum. Increasing the diameter of the drum increases the leaching degree. A new method for leaching a WC-Ni composite to obtain high-quality tungsten carbide powder has been proposed. The process intensification is achieved by organizing leaching under self-grinding conditions with continuous mechanical renewal of the surface that is in contact with the leaching solution.

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

ПЕРЕРОБКА ЛОМУ WC-Ni З ОТРИМАННЯМ КАРБІДУ ВОЛЬФРАМУ

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Анотація

Робота присвячена актуальній темі переробки лому стратегічного сплаву WC-Ni, який використовується у виробництві бронебійних снарядів. Рециклінгове використання карбіду вольфраму та нікелю вирішує проблему дефіциту і дорогоцінності цих компонентів. У даній роботі досліджено вплив концентрації хлоридної кислоти і ферум(III) хлориду як компонентів розчину вилуговування на ступінь вилуговування нікелю з цементованого карбіду вольфраму. Встановлено, що збільшення концентрації обох компонентів призводить до збільшення швидкості процесу. Показано, що додавання ферум(III) хлориду до кислотного розчину вилуговування призводить до п'ятикратного збільшення швидкості процесу. Встановлено, що енергія активації процесу вилуговування в розчині 4.5 моль/л хлоридної кислоти становить 50.5 кДж/моль. Енергія активації вилуговування в розчині, що містить 4.5 моль/л хлоридної кислоти і 2 моль/л ферум(III) хлориду становить 17.9 кДж/моль. Під час переходу від кислотного розчину вилуговування до розчину, що містить суміш кислоти і ферум(III) хлориду відбувається перехід з кінетичної до дифузійної області перебігу процесу. Для прискорення вилуговування в умовах дифузійних обмежень запропоновано збільшити ефективність оновлення поверхні шматочків сировини шляхом підбору розмірів і частоти обертання помольного барабану. Показано, що залежність ступеню вилуговування від частоти обертання барабану проходить через максимум. Збільшення діаметру барабану приводить до збільшення ступеню вилуговування. Запропоновано нову методику вилуговування композиту WC-Ni з отриманням високоякісного порошку карбіду вольфраму. Інтенсифікація процесу досягається організацією вилуговування в умовах самопомелу з безперервним механічним оновленням поверхні, яка контактує з розчином вилуговування.

Ключові слова: порошковий карбід вольфраму; зв'язуюче; сомопомел; рециклінг; ступінь вилуговування.

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Introduction

Cemented carbides are a strategically important material that is widely used in the defense and manufacturing industries. Cemented tungsten carbide occupies the leading place in terms of variety of applications among the so-called hard metals due to its unique strength and hardness. The high hardness and strength of tungsten carbide combined with the strength and ductility of the binder metal makes it a critically important engineering material [1; 2]. As compared to other alloys, WC is an ideal material used for the manufacture of wear-resistant tools for rock drilling, metalworking, construction, and the oil and gas industry [3; 4]. The main component of cemented tungsten carbide is tungsten monocarbide (WC), which exhibits hardness comparable to that of diamond. This brittle, refractory carbide phase is combined with a strong binder metal such as cobalt or nickel to form cemented carbides [5; 6]. Such composite materials are characterized by high strength and hardness with moderate ductility and are the most versatile solid material for the manufacture of high-tech tools and machinery in mechanical engineering.

The mechanical properties of cemented tungsten carbide depend on the content of the binder and the grain size of WC. With an increase in the content of the binder, the hardness of the composite decreases but the ductility increases, while an increase in grain size causes the opposite effect. The binder content normally ranges from 6 to 16 %, and the grain size of WC varies from 0.2 to tens of microns [7].

The traditional way to produce tungsten is to process tungsten ores, such as tungstenite, ferberite, or scheelite, which typically contain 0.1–5 % W [6; 8–11]. However, tungsten content is significantly higher in the scrap of hard tungsten-containing alloys. The tungsten content in such alloys is fifteen times higher than in tungstenite or scheelite. Cemented tungsten carbide scrap contains 40–95 % tungsten and the processing of this waste consumes 70 % less energy than the extraction of tungsten from ore [3]. In addition, recycling reduces the environmental impact. Thus, the recycling of cemented tungsten carbide scrap is a strategically important area to obtain its valuable components, given the lower cost and environmental impact compared to the processing of tungsten-containing ores [12].

Cemented tungsten carbide is processed using direct, indirect, and semi-direct methods [12]. The most common direct method is the selective removal of binder additives and the extraction of WC using high-temperature melting [7; 13]. This involves dissolving the scrap in a zinc melt. The scrap is sorted and then packed into graphite boats or crucibles together with zinc. The air is pumped out of the furnace; the furnace is filled with argon and heated to temperatures of 750–960 °C, depending on the scrap, furnace design, etc. The treatment of tungsten carbide and molten zinc at these temperatures results in the formation of a liquid zinc-binder alloy. Zinc is removed by distillation, and the resulting product consists of a mixture of tungsten carbide and a binder metal in which the bond between the components is broken. The resulting tungsten carbide can be easily crushed to a particle size similar to the grain size of the initial microstructure of cemented carbide [14]. Another method of processing cemented tungsten carbide is its electrochemical dissolution in the melt with simultaneous deposition of a binder metal and tungsten on the cathode [15]. Studies of the electrochemical processing of cemented tungsten carbide scrap WC-10 Co in NaF-KF melt at a temperature of 1073 K have shown that electrodeposition of cobalt powder with a diameter of 1 μm occurs at a voltage of ≤ 0.6 V and of tungsten powder with a diameter of 200 nm at a voltage of 1.0 V [16]. It has been shown that cemented carbide scrap can be used as a consumable anode for the selective production of cobalt and tungsten powders [16]. This method provides high W recovery rates for the subsequent production of high-quality WC powder [17].

In the case of indirect methods, chemical transformations in acidic or alkaline environments produce very pure intermediates, such as ammonium tungstate or tungstic acid, which are further processed into pure metal using extraction, ion exchange, crystallization, etc. [12]. Such processing methods are usually more expensive than direct processing. This is due to the need for additional purification steps required to obtain a pure product. However, selective leaching of the binder can reduce the number of steps and make the process more energy efficient. Such leaching is carried out in inorganic and organic acids, aqueous alkaline solutions using chemical or electrochemical methods. The process can be accelerated by using a strong acid or oxidizing agent. In [14], the use of acetic acid as a solvent for cobalt binder in cemented tungsten carbide WC-Co is reported. The process is carried out at 80 °C for 21 days. It is noted that the main disadvantage of this method is the slow process.

Dissolution of cobalt from cemented carbide scrap with high efficiency (91.5 %) was achieved using 0.5 M HNO_3 for 2 hours at 25 °C [18]. The authors of [19] proposed to use malic acid to leach cobalt from the WC-Co composite. The process is intensified by using wet grinding in a ball mill and adding hydrogen peroxide. The leaching of cobalt from WC-Co in a ball mill was carried out using sulfuric acid with a concentration of 0.5–2 mol/L [20]. The obtained tungsten carbide and cobalt powders had a purity of more than 98% and the WC-Co composite formed from them demonstrated hardness similar to the initial cemented tungsten carbide. The efficiency of the leaching process can be improved by mechanochemical processing of raw materials. When particles are crushed in a high-energy mill during leaching, it leads to an increase in the reactivity of the dissolved substance. The increased reactivity of solid mineral particles is due to an increase in internal and surface energy, an increase in surface area, and a decrease in coherence energy [21]. Mechanical activation in high-energy mills is achieved by impact (stroke or collision), abrasion (shear) and compression. In such systems, several factors affect the grinding process and the leaching process. The grinding factors include the degree of filling of the grinding chamber, the ratio of ball to powder volumes, grinding speed and time, while the leaching factors are temperature, reagent concentration, stirring speed and leaching time [22; 23]. It was shown in [24] that the use of mechanical activation can reduce the leaching temperature and the concentration of the active ingredient in the leaching solution, i.e., sodium hydroxide. An increase in the mixing speed and a decrease in the liquid/solid ratio led to an increase in the efficiency of the leaching process.

Thus, a topical scientific and technical task is to improve the ways of processing cemented tungsten carbide scrap to produce high-purity composite components. The least energy-intensive technology is hydrometallurgical leaching of the binding component of cemented tungsten carbide. Important tasks that require special attention when developing such a technology include determining the composition of the solution, process parameters, and leaching kinetics.

Research methods

The material under study was cemented tungsten carbide, which is used to make armor-piercing shell cores. The tungsten content was 86 % and the nickel content was 8 %.

The estimated composition of the composite was determined by the X-ray fluorescence method [25] using an X-ray energy dispersive spectrometer CEF-01-M-1 "SPRUT".

To process this material, it is necessary to ensure the selective dissolution of the binding component and the destruction of the base material layer formed on the surface. When nickel dissolves from cemented tungsten carbide, it forms a layer of strong WC skeleton, which creates a significant intra-diffusion resistance to the nickel leaching process. Significant leaching rates can only be achieved when the WC surface layer is destroyed. This can be achieved by using a grinding mill. Given the extreme hardness of tungsten carbide, which is second only to that of diamond, the use of ceramic balls in the grinding drum is impractical. This is due to the undesirable contamination of the reaction mixture with ceramic particles that form when the balls rub against tungsten carbide. Therefore, in this paper, it is proposed to organize the leaching process of cemented tungsten carbide under self-grinding conditions.

For this study, the leaching process was carried out on a plant that ensured temperature control with an accuracy of 1 °C and allowed grinding at different mill drum rotation speeds. The grinding drum was designed to circulate the leaching solution. The leaching solution was pumped into the grinding drum via a heat exchanger. After the grinding drum, the suspension of tungsten carbide in the leaching solution flowed into a sump and from there, through a heat exchanger, to the pump intake chamber. With a total solution volume of 4 liters and a mill rotation speed of 60 rpm, the leaching solution consumption was 2 liters/min. The diameter of the drum was 150 mm.

To achieve the selective dissolution of nickel with the chemical constancy of the main component of the WC-Ni composite, chloride acid and a mixture of chloride acid and iron (III) chloride were chosen as solvents.

The analysis of solutions for the content of ferric ions was performed as follows. A 0.5 ml solution was taken into a 250 ml flask, 100 ml of water and 6 ml of hydrochloric acid were added. An aluminum wire was immersed in the solution containing the sample and hydrochloric acid. The solution was kept at 70 °C for 20 minutes. As a result, 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 left for 10 minutes. The carbon dioxide formed by the interaction of marble and acid protected the iron (II) ions from oxidation by air oxygen. Then 1 mL of orthophosphoric acid was added to the clear light green solution and titrated with 0.1 N potassium permanganate solution until the color turned pink.

The content of nickel (II) ions was determined according to the method described in [26].

The degree of the binder leaching was determined by the change in the nickel mass that passed from the composite to the solution during leaching:

$$\alpha = \frac{m_{Ni}}{m_{Ni(comp)}} , \qquad (1)$$

where m_{Ni} is the mass of nickel that has been transferred to the leaching solution; $m_{Ni(comp)}$ is the mass of nickel in the starting parts that were subjected to leaching.

The mass of nickel in the starting parts was determined after separation from tungsten carbide and its conversion to ionic form. A sample of the starting material was sintered with sodium hydroxide in a platinum crucible with air in a mass ratio of 1 : 2 to produce sodium tungstate and nickel powder. The suspension was transferred to a glass beaker containing a mixture of chloride and nitric acids. The chloride acid was taken with a 10 % (mol.) excess relative to the alkali. The amount of nitric acid was 20 % (mol.) of the amount of chloride acid. The suspension was brought to a boil to produce a yellow form of tungstic acid and dissolve nickel. The tungstic acid was filtered off and the resulting solution was analyzed for nickel (II) ions.

Results and discussion

The results of the study of the effect of the hydrochloric acid concentration on the degree of nickel leaching from cemented tungsten carbide achieved in one hour were obtained at a process temperature of 50 °C. An increase in the acid concentration from 1 to 7 mol/L leads to a linear increase in the leaching degree (Fig. 1).

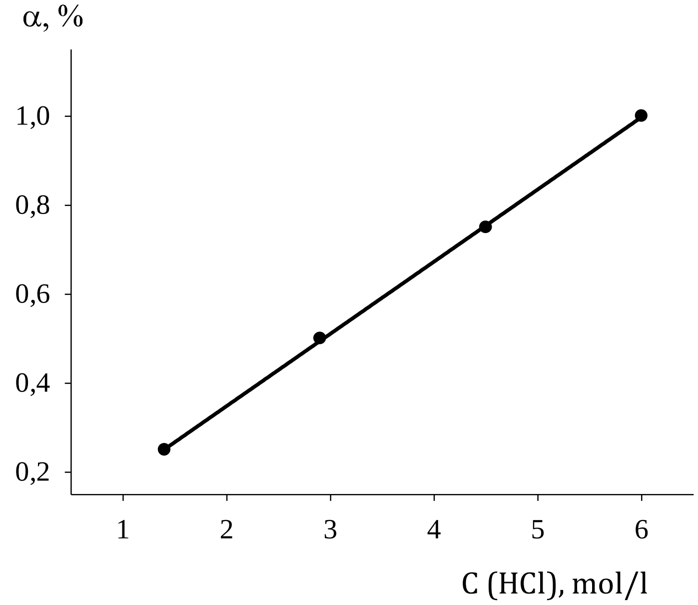

Fig. 1. Dependence of the degree of 1-hour leaching at 50 °C on the concentration of hydrochloric acid

Obviously, to intensify the process, it is advisable to increase the concentration of hydrochloric acid. However, a more concentrated acid solution corresponds to a higher HCI partial pressure, which imposes certain limitations on the use of overly concentrated acid. For technological reasons, the concentration of hydrochloric acid equal to 4.5 mol/L can be considered acceptable for the leaching process. Therefore, this acid concentration value was used for further research.

The temperature effect on the degree of nickel leaching from cemented tungsten carbide in a hydrochloric acid solution is exponential (Fig. 2). Since the leaching degree values are obtained for one hour of the process, these values are proportional to the leaching rate.

By processing this dependence with the Arrhenius equation (2), we achieve linearization of this dependence in semi logarithmic coordinates (Fig. 3) and we can calculate the activation energy of the process from the tangent of the slope of the line.

$$\alpha = A \cdot e^{-\frac{E_a}{RT}} . \qquad (2)$$

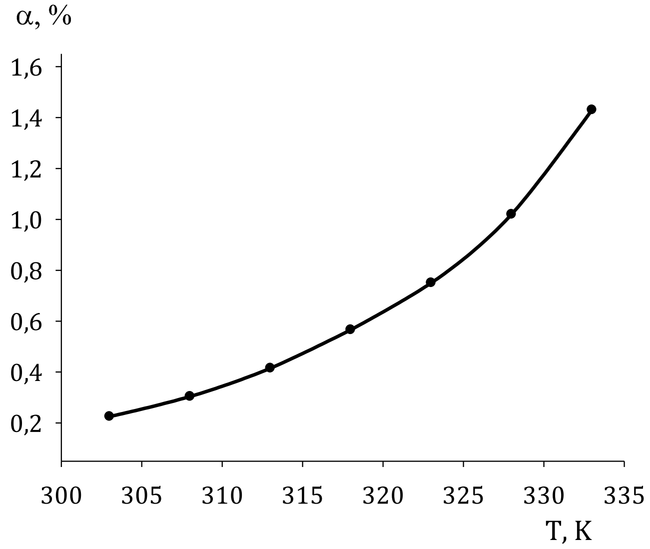

Fig. 2. Dependence of the degree of 1-hour leaching in a solution of hydrochloric acid with a concentration of 4.5 mol/L on the process temperature

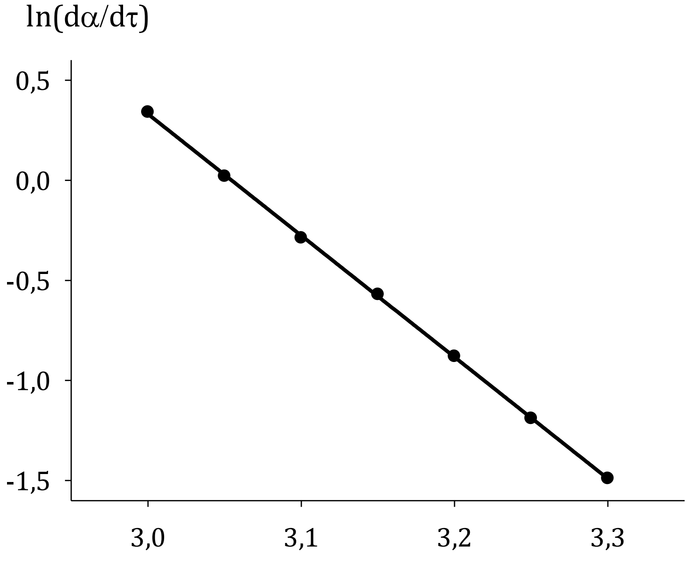

Fig. 3. Temperature dependence of the degree of 1-hour leaching in a solution of hydrochloric acid with a concentration of 4.5 mol/L in semi-logarithmic Arrhenius coordinates

The obtained value of activation energy is 50.5 kJ/mol, which corresponds to the kinetic region of the process that is not complicated by diffusion limitations. Indeed, the surface of the samples subjected to 1-hour leaching in hydrochloric acid solution was silvery, with no visible traces of the tungsten carbide surface layer, which could impede the penetration of the leaching solution to the composite surface.

The data presented indicate a rather slow leaching of cemented tungsten carbide in a hydrochloric acid solution. The rate of nickel dissolution, which corresponds to about 1 % per 1 hour, is unsatisfactory for technological reasons. Therefore, it is advisable to accelerate the process by introducing an additional reagent into the leaching solution, which will selectively transfer nickel from the composite to the solution in ionic form. Since the processing of cemented tungsten carbide scrap should result in the production of tungsten carbide powder by selective dissolution of the binder, it is necessary to select an oxidizer that is active against nickel and does not convert tungsten to oxoanions. Iron (III) chloride is an active oxidizer of nickel in an acidic environment. Therefore, it is advisable to study the kinetics of nickel leaching from cemented tungsten carbide in a solution containing hydrochloric acid and iron (III) chloride.

As can be seen from Fig. 4, the degree of leaching increases with an increase in the concentration of iron (III) chloride from 0.5 to 2.5 mol/L at a constant concentration of hydrochloric acid in the leaching solution. In the presence of $FeCI_3$ in the hydrochloric acid solution, a significant increase in the leaching degree obtained in a one-hour process was observed. The dissolution of nickel under the action of iron (III) ions in combination with hydrogen ions is more than five times faster than in a pure solution of hydrochloric acid. This effect is explained by the fact that the electrode potential for the reduction of iron (III) ions to iron (II) is 0.78 V more positive than the potential for the reduction of hydrogen ions to hydrogen. The results of the experiment showed that the use of iron (III) chloride as an oxidizing agent in the leaching solution does not lead to the dissolution of tungsten carbide, i.e. this oxidizing agent is selective to nickel and meets the requirements.

A significant increase in the concentration of iron (III) chloride leads to an increase in the viscosity of solutions. In viscous solutions, the efficiency of settling the tungsten carbide precipitate decreases and the filtration of the resulting suspension is slowed down. Therefore, further studies were conducted using leaching solutions containing 2 mol/L iron (III) chloride.

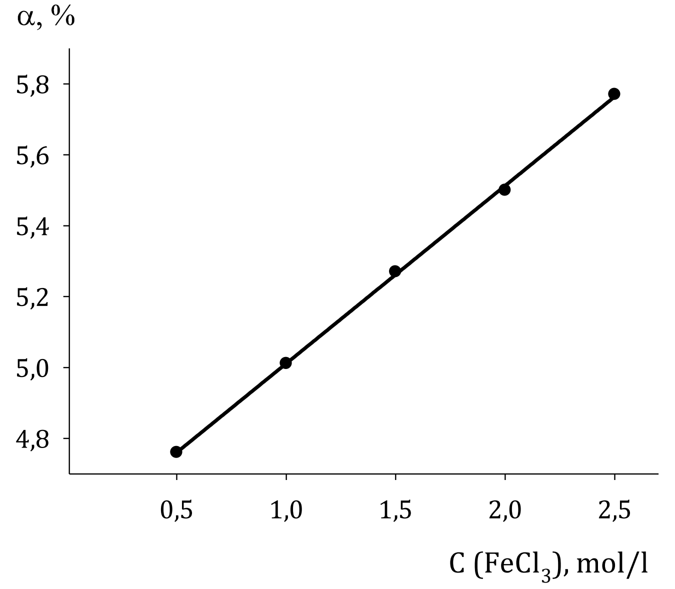

Fig. 4. Dependence of the degree of one-hour leaching in a 4.5 M HCI solution at a temperature of 50 °C on the concentration of $FeCI_3$

To determine the effective activation energy for the process of nickel leaching from cemented tungsten carbide in a solution containing 4.5 mol/L hydrochloric acid and 2 mol/L iron (III) chloride, the temperature dependence of the leaching degree was obtained.

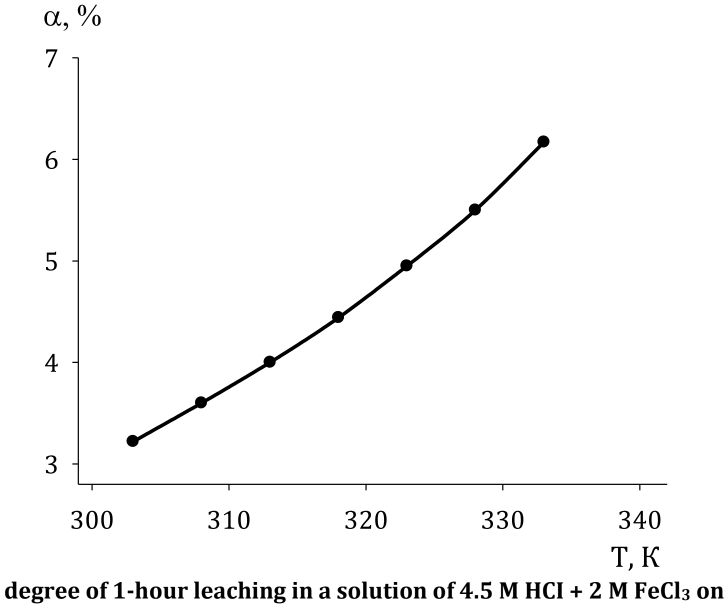

Fig. 5. Dependence of the degree of 1-hour leaching in a solution of 4.5 M HCI + 2 M $FeCl_3$ on the process temperature

As can be seen from Fig. 5, the obtained dependence is exponential and can be calculated in the coordinates of the Arrhenius equation (2). The calculated data presented in semi-logarithmic coordinates are shown in Fig. 6. As we can see, the dependence is linear and the activation energy of the leaching process can be calculated from the tangent of the slope. The activation energy is 17.9 kJ/mol, which corresponds to the diffusion control of the studied process.

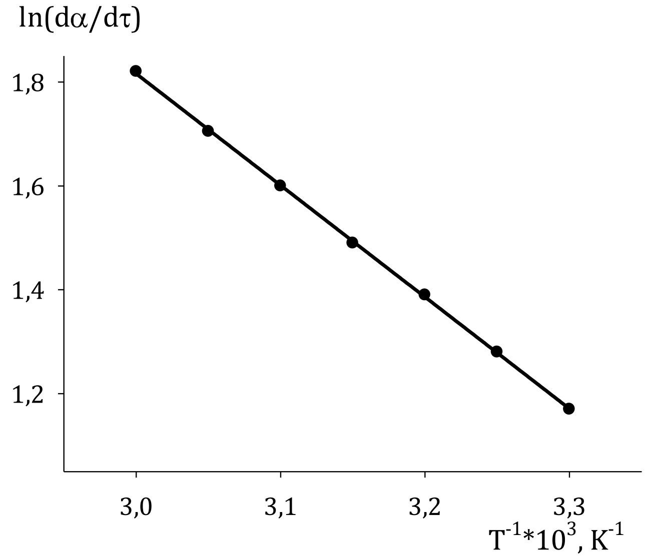

Fig. 6. Temperature dependence of the degree of 1-hour leaching in a solution of 4.5 M HCl + 2 M $FeCl_3$ in semi-logarithmic Arrhenius coordinates

Thus, when iron (III) chloride is added to the acid leaching solution, the limiting stage of the process changes and the transition from the kinetic to the diffusion region occurs. Visual assessment of the surface of the cemented tungsten carbide samples subjected to leaching showed the presence of a continuous black layer. That is, the rate of surface renewal of tungsten carbide-free parts is insufficient, and during leaching, the WC layer constantly covers the treated samples.

Obviously, in order to accelerate the process that is limited by the diffusion of reagents through the tungsten carbide framework, it is necessary to organize the process of mechanical extraction of tungsten carbide from the surface of the studied samples as efficiently as possible. In these conditions, an important factor in increasing the process rate is to ensure a rational grinding regime.

It should be noted that in order to obtain high-purity components of the cemented tungsten carbide composite, we propose not to use ceramic balls as grinding elements and to carry out leaching in the self-grinding mode. Tungsten carbide is one of the hardest but most brittle materials. Therefore, the elements that subject the feedstock to abrasion and grinding are the cemented tungsten carbide samples themselves. In such conditions, the factors that affect the grinding efficiency are the rotation speed and the diameter of the grinding drum.

As can be seen from Fig. 7, the dependence of the leaching degree on the drum rotation speed is extreme and passes through the maximum value. For a drum with a diameter of 150 mm, this maximum is 80 rpm. An increase in drum diameter leads to an acceleration of leaching. Under these conditions, the maximum leaching rate corresponds to a drum speed of 60 rpm.

That is, the most effective renewal of the sample surface from the tungsten carbide sponge and reduction of diffusion limitations of the leaching process are achieved under conditions of the strongest impact of scrap pieces. This happens when they rise to the maximum possible height and fall under the gravity. Therefore, it is possible to intensify the process of leaching the binder from cemented tungsten carbide under self-grinding conditions during the process in the diffusion region by selecting the optimal geometric parameters and rotation frequency of the grinding drum.

According to the results of the study, it is recommended to carry out the leaching of scrap of the WC-Ni composite in a solution containing 4.5 mol/L hydrochloric acid and 2 mol/L iron (III) chloride. The process temperature is 50 °C. The process is performed under self-grinding conditions. The tungsten carbide powder obtained by the above method is a finely dispersed material ready for reuse in strategic powder metallurgy (Fig. 8).

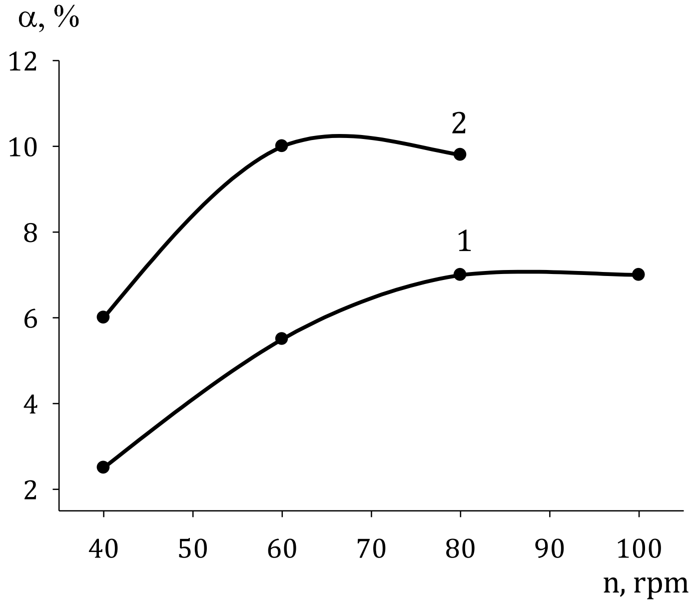

Fig. 7 Dependence of the degree of 1-hour leaching in a solution of 4.5 M HCl + 2 M $FeCl_3$ at 50 °C on the rotation frequency of a drum dia., mm: 1 – 150; 2 – 230

Fig. 8 Tungsten carbide powder obtained as a result of leaching of WC-Ni

Conclusions

1. The paper investigates the degree of leaching of the binder metal, nickel, in a WC-Ni composite in order to obtain powdered tungsten carbide, depending on the process conditions. The kinetic characteristics of the process of nickel leaching from cemented tungsten carbide under self-grinding conditions in a hydrochloric acid solution have been obtained. It has been found that the activation energy is 50.5 kJ/mol and the process proceeds in the kinetic region.

2. It has been shown that the intensification of the process of nickel leaching from cemented tungsten carbide is possible using a solution of hydrochloric acid with the addition of iron (III) chloride. It has been found that the activation energy of the process under these conditions is 17.9 kJ/mol and the process proceeds in the diffusion region. It has been shown that it is possible to accelerate the process, which is limited by the rate of reagent transport through the surface layer of tungsten carbide, by optimizing the self-grinding process. This is achieved by selecting the optimal values of the rotational speed and diameter of the grinding drum. It was found that the dependence of the leaching degree on the drum rotation speed passes through the maximum. An increase in the diameter of the drum leads to an increase in the degree of leaching. The organizational aspect of self-grinding is to achieve the collisions of the raw material pieces with maximum force.

3. A new method of leaching the WC-Ni composite to obtain high-quality tungsten carbide powder has been recommended, which involves the use of a leaching solution containing 4.5 mol/L of hydrochloric acid and 2 mol/L of iron (III) chloride. The process is carried out under self-grinding conditions, which ensures simultaneous surface renewal and its chemical interaction with the leaching solution.

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