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## ENVIRONMENTALLY SAFE PROCESSING OF NICKEL-CONTAINING WASTE AS A SOURCE OF MATERIALS FOR FOOD PRODUCTION EQUIPMENT

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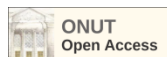
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### Introduction. Formulation of the problem

The modern level of engineering development involves the use of materials capable of satisfying a complex of diverse operational requirements. The leading place among them is occupied by metals and their alloys, which are widely used both in the domestic sphere and in technical systems. At the same time, individual metals, as a rule, do not provide the necessary set of properties for operation in difficult conditions,

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**Abstract.** The object of the research is the process of electrochemical anodic dissolution of heat-resistant nickel superalloy as a method of regeneration of alloying components for food equipment materials. Scrap recycling is carried out in an environmentally friendly way, which consists in low-temperature anodic treatment without the use of energy-consuming and harmful metallurgical methods. The starting material was obtained from spent components of high-temperature equipment. The work investigated the anodic dissolution of the specified alloy in environments based on sulfuric and methanesulfonic acids, and also performed a comparative analysis of the results obtained by cyclic voltammetry and galvanostatic measurements. It is shown that in an electrolyte based on H<sub>2</sub>SO<sub>4</sub>, anodic processes are characterized by higher current density values, which indicates their greater intensity. At the same time, this method records not only currents associated with metal dissolution, but also the contribution of side reactions, such as oxygen evolution and secondary oxidation of ions in the solution. In contrast, galvanostatic experiments, which allow for direct assessment of the mass loss of the alloy, have shown that the system based on methanesulfonic acid with the addition of sodium chloride provides higher dissolution rates, despite the lower electrical conductivity of the electrolyte. This effect is explained by the increased solubility and stability of methanesulfonate complexes of alloying elements, which reduces the likelihood of passivation of the electrode surface. In a sulfuric acid environment, dissolution occurs more evenly, but with less efficiency in terms of mass, which is associated with the formation of poorly soluble sulfate compounds. It has been established that in the electrolyte CH<sub>3</sub>SO<sub>3</sub>H + NaCl in the range of current densities of 1.5–2.5 A·dm<sup>-2</sup> the ratio of nickel, chromium, cobalt, tungsten and rhenium in the solution is as close as possible to the composition of the original alloy. This ensures the transition of rhenium into the solution, while in a sulfuric acid environment it is not detected. The results obtained can be used to optimize the initial stage of processing heat-resistant superalloys, as well as in the development of electrochemical technologies for the extraction of strategically important metals used as alloying components in the creation of food equipment.

**Keywords:** food production equipment materials, methanesulfonate solution, processing of superalloys, electrochemical dissolution, rhenium extraction, nickel-containing superalloy

which determines the predominant use of multicomponent alloys [1]. This is explained by the possibility of purposeful regulation of their characteristics by introducing alloying additives, which allow varying corrosion resistance, hardness, wear resistance, thermal stability, plasticity and other functional parameters [2, 3].

The composition of alloys is formed by a wide range of metallic and non-metallic components. Highly specialized technical applications require materials with

unique properties that can function in conditions that differ significantly from standard operating conditions. In particular, elements of turbine installations must demonstrate increased resistance to oxidation at high temperatures, maintain stability of mechanical and physicochemical characteristics in a wide temperature range, and withstand cyclic thermal loads without structural degradation [4].

An effective solution to such problems has been the creation of heat-resistant superalloys, in particular systems containing rhenium and other alloying components. Their composition may include aluminum, boron, carbon, cobalt, chromium, copper, manganese, molybdenum, nickel, phosphorus, rhenium, sulfur, silicon, tin, tantalum, titanium, vanadium, tungsten and other elements [5, 6].

For Ukraine, a number of these components (in particular, Co, Cr, Ni, Mo, W, Re, Ta, Sn, Bi, B) are critically scarce due to the limited or absence of its own mineral and raw material base [7]. In this regard, meeting the needs for such elements largely depends on imported supplies, which creates risks in terms of resource and technological security. Additionally, the situation is complicated by the instability of world markets and geopolitical factors [8]. These metals are key for the development of high-tech industries and the formation of competitive materials [9]. In particular, Co, Ni, Mo, Cr are necessary for the creation of alloys with increased hardness, corrosion resistance and durability [10, 11]. Such components are necessary for the creation of stainless steels, which are the key material for food production equipment.

In these conditions, the development of effective technologies for processing secondary raw materials, in particular waste alloys, with the provision of highly selective extraction of valuable components is a relevant direction [12]. This opens up the possibility of forming strategic reserves of scarce metals at the national level. Given the presence of significant volumes of scrap specialized equipment, including turbine assemblies, the issue of their comprehensive processing acquires special scientific and practical significance.

The materials used in the manufacture of turbine blades and discs, as well as combustion chamber elements, are usually nickel- and cobalt-containing heat-resistant superalloys alloyed with a number of refractory elements [13]. This chemical composition indicates a significant potential for secondary extraction of strategically important metals in the recycling process.

However, the initial stages of recycling such materials are complicated by their high mechanical strength and chemical inertness, which ensure durability in operating conditions, but at the same time reduce the efficiency of traditional recycling methods [14]. This necessitates the use of specialized approaches to their destruction.

One of the promising methods is electrochemical dissolution in aqueous electrolytes, which combines chemical interaction with anodic oxidation under the action of electric current. As a result, both soluble ionic forms of metals and solid products are formed, suitable for further extraction at subsequent stages of processing. This method of processing secondary materials is energy-saving and more environmentally friendly compared to metallurgical methods of metal regeneration. Therefore, optimization of the electrolyte composition and electrolysis modes is a determining factor in ensuring the efficiency of the superalloy processing process.

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#### Analysis of recent research and publications

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In [15], the electrochemical dissolution process of the superalloy, characterized by a tungsten matrix with a nickel-iron bond, in HCl solutions, as well as in HCl–NaCl and HCl–FeCl<sub>3</sub> systems, was analyzed. It was shown that in a 9% HCl environment with the addition of NaCl, selective dissolution of the metallic bond is possible. At the same time, the study was limited to the analysis of current-voltage dependences and was performed for an alloy with a different chemical composition.

In another work [16], the selective dissolution of a number of superalloys (TC20SA, TN8, TNI, TNSD) in a 9% HCl solution was considered. For the TC20SA alloy, the possibility of selective anodic dissolution at a current density of 15 A/dm<sup>2</sup> was established. A decrease in the process speed was also found due to the depletion of the metallic bond and the accumulation of the inert WC phase. However, the experimental part is limited to the study of current-voltage characteristics without conducting long-term galvanostatic tests, and the chemical composition of the considered materials is significantly different from the ZHS32 alloy.

In the study [17], a two-stage leaching technology was proposed for the processing of the superalloy PWA-1484. In the first stage, pyrometallurgical treatment was carried out at 1500°C with subsequent grinding of the material to a size of about 150 μm. This was followed by acid leaching, during which Ni, Co, Cr and Al went into solution, while rhenium was concentrated in the solid phase. In the next stage, Re was extracted by oxidation with electrogenerated chlorine in an HCl environment. This approach, however, is characterized by increased energy consumption compared to traditional chemical-electrochemical methods.

In [18], the processing of the nickel superalloy CMSX-4 (with a rhenium content of about 3%) in a mixture of HNO<sub>3</sub> and HCl was investigated. It was found that the use of ultrasonication does not lead to an increase in the yield of rhenium. At the same time, the possibility of fractional precipitation was shown: at pH ≈5, a mixture of Al, Cr, Mo, and Ti oxides is formed, and at pH ≈7, Co and Ni hydroxides are formed, while rhenium remains in solution for further extraction.

It should be noted that the formation of multicomponent oxide mixtures reduces the commercial attractiveness of the products due to the need for additional separation. In addition, the use of mixtures of the "aqua regia" type is accompanied by the release of toxic and carcinogenic gaseous products, in particular nitrogen oxides and chlorine.

In the study [19], the kinetic patterns of chemical dissolution of crushed waste of heat-resistant nickel alloy (particle size 0.063–0.1 mm) in various acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ) and their mixtures at variable temperatures were studied. The most effective conditions were determined to be leaching in 3 M  $\text{H}_2\text{SO}_4$  at 100°C for 6 hours, which ensures almost complete dissolution of nickel. At the same time, the lack of studies of combined chemical-electrochemical modes limits the possibilities of intensification of the process.

In [20], a comparative analysis of acid and biological leaching of Ni/Co-containing superalloys was conducted. It was found that the use of  $\text{H}_2\text{SO}_4$  at 85°C allows to achieve Ni and Co extraction at a level of up to 96% within a few hours, while bioleaching is much slower, although more environmentally acceptable. In this case, combined schemes with electrochemical activation were not considered.

In the publication [21], a preliminary stage of sulfurization of the superalloy GH4169 in a sulfur environment at 600–800°C was proposed. As a result, Ni, Co, and Cr are converted into sulfide forms characterized by increased solubility in acids. Pyrite and nickel matte were used as sulfurizing agents. This approach is considered as an alternative to oxidative calcination to increase the degree of extraction of refractory elements (Re, W, Ta), but is associated with potential environmental risks due to the use of sulfur-containing materials at high temperatures.

In the study [22], a method of selective nickel extraction by treating a nickel superalloy with a Mg–Zn melt was proposed. Under the conditions of a temperature of 800°C, a molar ratio of Mg/Zn = 9:1, a mass ratio of melt/alloy = 5:1, and a process duration of 240 min, a Ni extraction degree of 97.1% was achieved, while the extraction of Fe, Cr, and refractory components (Nb, Mo, Ti) did not exceed 1%. The disadvantage of the approach is the lack of further comprehensive processing of the residual phase.

In [23], ultrasonic leaching of nickel superalloys containing rare metals, including rhenium, was investigated. It was shown that regulation of electrode potential and pH of the medium allows controlling the leaching and separation processes. The use of ultrasound provides an increase in the degree of extraction by approximately 20% compared to traditional methods, and two-stage precipitation allows for the effective recovery of rare metals without the formation of significant volumes of acid waste. However, the economic feasibility of such an approach is limited.

In [24], the electrochemical dissolution of cast superalloy K423A was investigated. A significant influence of microstructural factors, in particular the distribution of carbon and carbide phases in the matrix and at grain boundaries, on the stability of the process was established. It was shown that effective and stable dissolution can be achieved in a 10%  $\text{NaNO}_3$  solution at a temperature of 40°C. At the same time, more aggressive electrolyte systems were not the subject of the study.

The analysis of the literature data shows that existing approaches are either based on a limited experimental base, or concern materials with different chemical composition, or are accompanied by significant energy and environmental limitations. In addition, most works do not pay enough attention to the speed of the initial stage of processing as one of the key technical and economic indicators of the process.

In contrast, in [25] the use of  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , methanesulfonic acid and  $\text{NaCl}$  as basic electrolyte systems for intensification of dissolution of the ZHS32 alloy is justified. These reagents are characterized by a relatively low environmental load and economic feasibility, and are also able to reduce the energy costs of the process. It was experimentally established that the maximum dissolution rate is achieved in the 0.5 M  $\text{NaCl}$  +  $\text{HCl}$  system, while for sulfuric and methanesulfonic acids this indicator is lower. In this regard, it is relevant to study the synergistic effect of combined electrolytes, in particular the systems " $\text{NaCl}$  +  $\text{H}_2\text{SO}_4$ " and " $\text{NaCl}$  + methanesulfonic acid", in order to increase the dissolution rate while maintaining environmental and economic advantages.

Leaching of superalloys is usually carried out using sulfuric, hydrochloric, or nitric acids [25]. At the same time, the development of modern technologies has ensured the industrial production of methanesulfonic acid, which forms highly water-soluble metal salts [15].

#### **Purpose and objectives of the study**

The purpose of this work is to investigate the possibilities of intensifying the anodic dissolution of a heat-resistant superalloy containing rhenium and associated valuable metals (Ni, Cr, Co, Al, Ta, Nb, W) in acidic electrolytes in the presence of sodium chloride. It is assumed that the use of combined systems based on mineral acids (in particular  $\text{H}_2\text{SO}_4$  and methanesulfonic acid) in combination with  $\text{NaCl}$  will contribute to increasing the kinetics of the process, and can also ensure the selectivity of dissolution of individual components without the use of environmentally hazardous reagents.

To achieve the goal, the following tasks were formulated:

- to investigate the effect of combining selected acidic media with  $\text{NaCl}$  on the course of electrochemical anodic dissolution of the superalloy;
- to determine the optimal conditions that ensure the intensification of the process and create the

prerequisites for the selective extraction of rhenium and/or other valuable elements.

### Research materials and methods

All reagents used in the work were of a grade not lower than analytical grade.

The electrochemical characteristics of the alloy were studied using an MTech SPG-500fast potentiostat. Graphite was used as an auxiliary electrode in the measuring cell, and the Ag|AgCl system in 3.5 M KCl solution was used as a reference electrode. The experiments were performed at a temperature of 20°C. Cyclic current-voltage dependences were recorded at a potential scan rate of 50 mV/s in a given interval, which, as a rule, ranged from +0.9 to -0.2 V. Each series of measurements included five consecutive cycles.

Superalloy samples obtained from turbine elements were previously thoroughly cleaned with running and distilled water. Immediately before measurements, the electrode surface was mechanically renewed using abrasive paper with a grain size of 80 µm, after which degreasing was carried out by sequential treatment with acetone and alcohol. For correct determination of the specific electrochemical activity, the area of the working electrode was standardized by partially insulating the surface with a PTFE film, leaving only the controlled active area open.

Galvanostatic studies were carried out in an electrolytic cell with a membrane separation of the anode and cathode spaces. The working volume of the electrolyte was 500 ml. A sample of the alloy under study was placed in the anode compartment, while a copper electrode was placed in the cathode compartment.

The electrochemical cell was connected to a BVP Electronics Home Tools regulated DC power supply, in series with a copper coulometer, which was used to determine the amount of electricity passed (Q). The loss of alloy mass due to dissolution was estimated by the difference in sample mass before and after the experiment, using an analytical balance with an accuracy of 10<sup>-4</sup> g.

After electrochemical dissolution, the resulting solutions were subjected to analytical control for the content of Ni, Co, Cr ions (total concentration), as well as Mo, Ni, Cr (separately) and Re. The cobalt concentration was determined by calculation as the difference between the total content of Ni, Co, Cr and individually determined concentrations of Ni and Cr.

Determination of the total concentration of Ni, Co, Cr. A 2 ml aliquot was transferred to a conical flask, 50 ml of distilled water, 10 ml of buffer solution and murexide indicator were added [26]. Titration was carried out with a 0.1 N solution of Trilon B using a 25 ml burette until a characteristic violet-blue color appeared. The calculation of the concentrations and masses of dissolved metals was carried out based on the

law of equivalents, taking into account the consumption of the titrant.

Determination of tungsten. A 100 ml sample of the anode solution was treated with 5 g of CaCl<sub>2</sub>. The system was kept at room temperature until a calcium tungstate precipitate formed. The precipitate was filtered, dried and weighed, after which the tungsten content was calculated from the data obtained.

Individual determination of nickel. An aliquot of 0.1 ml was placed in a 100 ml volumetric flask, 20 ml of distilled water, 2 ml of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, about 20 drops of ammonia and 1 ml of 5% KOH solution with 1% dimethylglyoxime were added sequentially. After standing for 10 min, the volume was brought to the mark with distilled water. The optical density was measured on a photoelectrocolorimeter at a wavelength of 490 nm. The nickel concentration was determined according to the previously constructed calibration dependence "optical density – concentration".

Individual determination of chromium. 15 ml of 0.1 N Trilon B solution was added to a 50 ml heat-resistant glass, 2 ml of concentrated acetic acid and 2 ml of the analyzed solution were added. The mixture was boiled for 5 min, cooled, quantitatively transferred to a 50 ml volumetric flask and made up to volume with water. Optical density measurements were performed at a wavelength of 540 nm, and the concentration was determined according to the calibration graph.

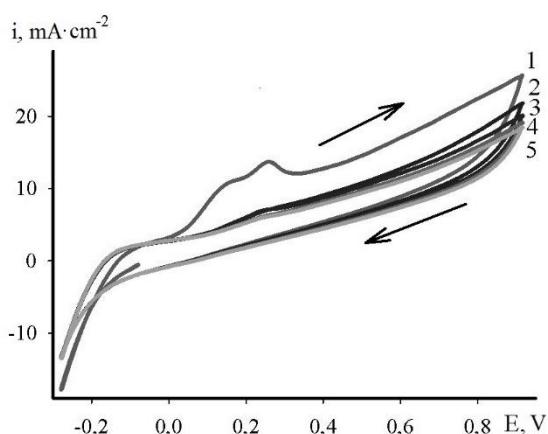
Rhenium determination. A 100 ml aliquot of the anode solution was treated with 5 g of KCl, after which the system was cooled in an ice bath until potassium perrhenate crystallized. The precipitate was filtered, dried, and weighed, after which the rhenium content in the starting solution was calculated from the mass of the precipitate.

### Results of the research and their discussion

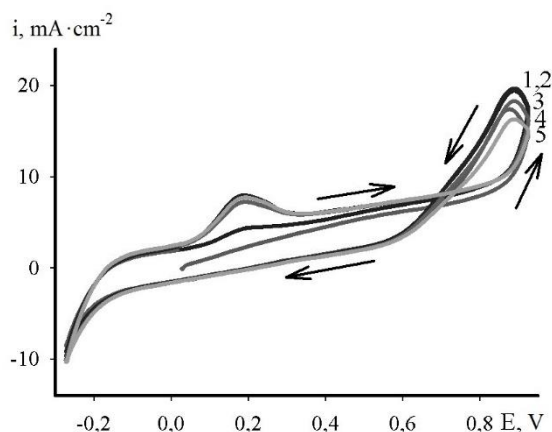
Fig. 1 and 2 present the results of cyclic voltammetry of the superalloy in the electrolyte systems 0.3 M NaCl + 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.3 M NaCl + 0.5 M CH<sub>3</sub>SO<sub>3</sub>H. It was found that in the environment with the addition of sulfuric acid, the anodic processes are characterized by higher intensity, which is manifested in increased current density values compared to the electrolyte based on methanesulfonic acid.

On the anodic branch of the current-voltage curves for the system with H<sub>2</sub>SO<sub>4</sub>, there are several peaks, which are probably associated with the oxidation of components present at the initial stage of the process. The intensity of these peaks is maximum during the first cycle and gradually decreases during subsequent scans, practically disappearing. A similar trend is observed for the electrolyte containing methanesulfonic acid.

This phenomenon can be explained by the presence of oxide films or adsorbed particles (ions or molecules) on the electrode surface, which undergo irreversible oxidation during anodic polarization and are not restored within the studied potential interval [27].



**Fig. 1. Cyclic current-voltage curves obtained for the superalloy in a solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.3 M NaCl. 1-5 – cycle number**

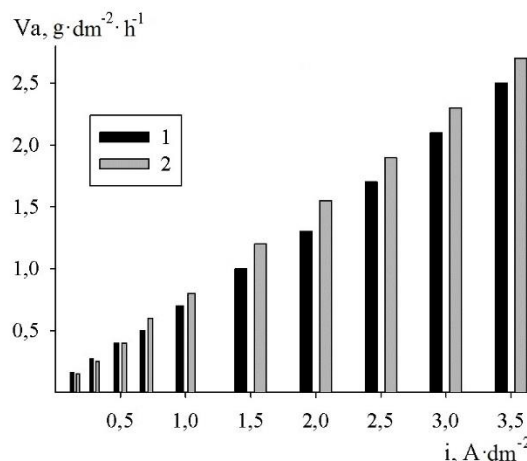


**Fig. 2. Cyclic current-voltage curves obtained for the superalloy in a solution of 0.5 M CH<sub>3</sub>SO<sub>3</sub>H + 0.3 M NaCl. 1-5 – cycle number**

It should be emphasized that the results of cyclic voltammetry reflect the total current response, which includes both the processes of anodic metal dissolution and the contribution of side reactions, in particular oxygen evolution and further oxidation of already dissolved components. In this regard, the interpretation of the electrochemical behavior solely on the basis of CVA is limited.

In view of this, it is advisable to conduct galvanostatic experiments with direct determination of mass losses of the alloy at different values of current density. This approach allows us to quantitatively assess the efficiency of anodic dissolution depending on the electrolysis mode, as well as analyze the selectivity of the transition of individual components into the solution. Fig. 3 presents the values of absolute dissolution rates ( $\text{g}\cdot\text{dm}^{-2}\cdot\text{h}^{-1}$ ). It was found that at low current densities the process speed for both electrolyte systems is comparable. However, with increasing current density, the dissolution intensity in the

methanesulfonic acid medium with the addition of NaCl increases significantly and exceeds the corresponding indicators for the system based on H<sub>2</sub>SO<sub>4</sub> + NaCl. Therefore, in the range of current densities of approximately 1.5–3.5 A·dm<sup>-2</sup>, the CH<sub>3</sub>SO<sub>3</sub>H + NaCl electrolyte demonstrates higher efficiency of anodic dissolution of the studied superalloy.



**Fig. 3. Dependence of the absolute rate of dissolution of the alloy on the current density: 1 – 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.3 M NaCl; 2 – 0.5 M CH<sub>3</sub>SO<sub>3</sub>H + 0.3 M NaCl**

Analysis of the anolyte composition by the content of dissolved ions allowed us to establish a number of characteristic patterns. In particular, it was found that the ratio of Ni, Co and Cr significantly depends on the current density and for both electrolytes studied deviates from the initial composition of the superalloy (Table 1). The most pronounced changes are observed in the methanesulfonic acid-based system at low current densities.

At the same time, when the current density increases to the range of 1.5–2.5 A·dm<sup>-2</sup> in this electrolyte, the composition of the anolyte approaches the composition of the starting material (Ni ≈ 60.7%, Cr ≈ 4.5%, Co ≈ 8.9%), while a significant content of rhenium is recorded in the solution (within 4.69–12.29%). This behavior can be used in cases where almost complete dissolution of the alloy is required. However, in the range of current densities of 0.15–0.3 A·dm<sup>-2</sup>, preferential dissolution of chromium compared to other components is observed, which indicates the unevenness of the process and the presence of selectivity of dissolution in this electrolyte.

For the sulfuric acid-based electrolyte, the dependence between current density and the change in the ratio of Ni, Co, and Cr is less pronounced, and the composition of the anolyte is generally closer to the composition of the original alloy. The largest deviation from the initial ratio of components in this case is recorded at the minimum current density (0.15 A dm<sup>-2</sup>)

Table 1 – Ratio of elements in the anolyte listed in %

Composition i, A/ dm <sup>2</sup>	CH <sub>3</sub> SO <sub>3</sub> H + NaCl			H <sub>2</sub> SO <sub>4</sub> + NaCl		
	Ni	Cr	Co	Ni	Cr	Co
0,15	30,09	26,04	11,71	39,26	18,50	18,10
0,30	47,98	25,66	4,56	61,15	3,5	9,59
0,50	55,86	5,30	16,10	55,90	6,57	6,82
0,70	52,45	5,23	22,30	76,68	4,35	7,79
1,00	56,44	5,17	9,64	64,89	8,65	9,50
1,50	62,68	4,15	13,90	62,33	9,60	12,27
2,00	62,21	3,50	15,99	66,13	5,12	5,10
2,50	62,00	4,40	8,40	62,35	13,8	9,36
3,00	57,42	8,55	18,52	58,56	9,50	12,59
3,50	52,60	13,84	0,37	68,79	8,92	10,60

It should be noted that rhenium was not detected in the solution containing H<sub>2</sub>SO<sub>4</sub>. The probable reason for this is the limited or practically insolubility of rhenium in the specified medium under the studied conditions.

The results of cyclic voltammetry indicate that in the H<sub>2</sub>SO<sub>4</sub>-based electrolyte with the addition of NaCl, anodic processes occur more intensively, which is manifested in increased current density values and the presence of clearly pronounced peaks. At the same time, it should be taken into account that the CVA reflects the total current, which includes both the contribution of metal dissolution and side processes, in particular, anodic oxygen evolution and subsequent oxidation of already dissolved components. The decrease or disappearance of peaks in subsequent cycles can be associated with the initial destruction of the passive film, which during the oxidation process is transformed into a more stable inert layer that is not restored within the studied potential interval. An alternative explanation is the oxidation of particles adsorbed on the surface, which is irreversible. Higher current values in the sulfuric acid medium are probably due to its higher electrical conductivity and a more uniform distribution of current density over microirregularities of the electrode surface [28].

Galvanostatic studies allowed us to obtain more objective characteristics of the process, in particular to estimate the mass losses of the alloy. It was found that the specific dissolution rates (g·dm<sup>-2</sup>·h<sup>-1</sup>) reach maximum values at low current densities, after which they decrease and reach a plateau. This dependence is characteristic of both electrolytes. The decrease in efficiency at high current densities is associated with an increase in the proportion of side processes. Comparative analysis showed that in the CH<sub>3</sub>SO<sub>3</sub>H + NaCl medium, both the specific and absolute dissolution rates are higher than in the H<sub>2</sub>SO<sub>4</sub> + NaCl system, especially in the range of 1.5–3.5 A·dm<sup>-2</sup> (Fig. 3).

At first glance, this result contradicts the CVA data, since sulfuric acid solutions are characterized by higher electrical conductivity and lower ohmic losses. However, this difference can be explained by the higher

solubility of metal methanesulfonates or the formation of more stable soluble complexes with Cr, Al, Nb, Ta and Re. This, in turn, reduces the probability of surface re-passivation and precipitation of dissolution products. In contrast, in a sulfuric acid environment, the formation of poorly soluble sulfates is possible, which promotes re-passivation of the anode at increased current densities and limits mass transfer, despite the better conductivity of the electrolyte. This effect corresponds to the phenomenon of the so-called “salt passivation”.

Analysis of the anolyte composition showed that for the CH<sub>3</sub>SO<sub>3</sub>H + NaCl system in the range of current densities of 1.5–2.5 A·dm<sup>-2</sup> the ratio of Ni, Cr, Co, W and Re (62.68; 4.15; 13.9; 4.82; 12.29%) is closest to the composition of the original alloy (Ni 60.7%; Cr 4.5%; Co 8.9%; W 8.22%; Re 3.5%), which indicates a relatively uniform nature of dissolution. In contrast, in the H<sub>2</sub>SO<sub>4</sub> + NaCl electrolyte, the solution composition is less stable, and rhenium is not detected in it, which indicates the limited ability of this medium to ensure its transition into solution.

The sulfuric acid electrolyte is characterized by a more stable ratio of Ni, Co, and Cr, close to the alloy composition, and the dependence on current density is less pronounced than in the case of methanesulfonic acid.

Therefore, despite the higher conductivity of sulfuric acid solutions, the methanesulfonic acid-based electrolyte demonstrates better results due to the increased solubility of dissolution products and lower susceptibility to passivation. This allows us to consider the CH<sub>3</sub>SO<sub>3</sub>H + NaCl system as more effective for the initial stage of electrochemical processing of heat-resistant superalloys.

The proposed approach to electrolyte selection provides the opportunity to optimize the first stage of processing of spent turbine equipment materials, increasing the efficiency of extracting target components without the use of toxic or environmentally hazardous reagents.

The results also open up possibilities for process control: the use of CH<sub>3</sub>SO<sub>3</sub>H + NaCl is appropriate for

intensifying the dissolution and transfer of rhenium into solution, while the use of  $\text{H}_2\text{SO}_4 + \text{NaCl}$  can be justified in cases where it is necessary to ensure a more uniform dissolution of the matrix with a rhenium concentration in the solid phase. Both approaches are characterized by relative environmental safety and the absence of the formation of toxic gaseous products at the initial stages of the process.

It is expected that the implementation of the proposed solutions will contribute to increasing the efficiency of the extraction of strategically important metals, reducing energy and environmental costs, as well as creating a scientific and technological base for the development of industrial processes for the processing of spent superalloys.

### Conclusion

The use of solutions based on methanesulfonic acid with the addition of NaCl provides higher

efficiency of anodic dissolution of the superalloy compared to a sulfuric acid medium of similar composition, despite lower values of electrical conductivity. This advantage is probably due to the increased solubility of metal methanesulfonates and a lower susceptibility of the anode surface to salt passivation phenomena.

In the range of current densities of  $1.5\text{--}2.5 \text{ A}\cdot\text{dm}^{-2}$  for the electrolyte  $0.5 \text{ M CH}_3\text{SO}_3\text{H} + 0.3 \text{ M NaCl}$ , the composition of the anolyte is as close as possible to the chemical composition of the original alloy and is characterized by a significant content of rhenium. This indicates a relatively uniform nature of dissolution and creates favorable conditions for further effective extraction of strategically important components. The proposed method of extracting alloying components of stainless steels from secondary raw materials allows for eco-friendly and cheaper production of food equipment materials and increases the competitiveness of domestic food production.

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## ЕКОЛОГІЧНО БЕЗПЕЧНА ПЕРЕРОБКА НІКЕЛЬВМІСНИХ ВІДХОДІВ ЯК ДЖЕРЕЛО МАТЕРІАЛІВ ОБЛАДНАННЯ ХАРЧОВИХ ВИРОБНИЦТВ

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### Анотація

Об'єктом дослідження виступає процес електрохімічного анодного розчинення жароміцного нікелевого суперсплаву, як спосіб регенерації легуючих компонентів для матеріалів харчового обладнання. Переробка лому проводиться екологічним способом, що полягає у низькотемпературній анодній обробці без використання енергозатратних та шкідливих металургійних методів. Вихідний матеріал отримано з відпрацьованих компонентів високотемпературного обладнання. У роботі проведено дослідження анодного розчинення зазначеного сплаву в середовищах на основі сірчаної та метансульфонові кислот, а також виконано порівняльний аналіз результатів, отриманих методами циклічної вольтамперометрії та гальваностатичних вимірювань. Показано, що в електроліті на основі H<sub>2</sub>SO<sub>4</sub> анодні процеси характеризуються вищими значеннями густини струму, що свідчить про їх більшу інтенсивність. Разом з тим, даний метод реєструє не лише струми, пов'язані з розчиненням металу, але й внесок побічних реакцій, таких як виділення кисню та доокиснення іонів у розчині. Натомість гальваностатичні експерименти, які дозволяють безпосередньо оцінити масові втрати сплаву, показали, що система на основі метансульфонові кислоти з додаванням натрій хлориду забезпечує вищі швидкості розчинення, незважаючи на нижчу електропровідність електроліту. Такий ефект пояснюється підвищеною розчинністю та стабільністю метансульфонатних комплексів легувальних елементів, що знижує ймовірність пасивації поверхні електрода. У сірчанокиислому середовищі розчинення відбувається більш рівномірно, однак із меншою ефективністю за масовими показниками, що пов'язано з утворенням малорозчинних сульфатних сполук. Встановлено, що в електроліті CH<sub>3</sub>SO<sub>3</sub>H + NaCl у діапазоні густин струму 1,5–2,5 А·дм<sup>-2</sup> співвідношення нікелю, хрому, кобальту, вольфраму та ренію у розчині є максимально наближеним до складу вихідного сплаву. При цьому забезпечується перехід ренію у розчин, тоді як у сірчанокиислому середовищі він не виявляється. Отримані результати можуть бути використані для оптимізації початкової стадії переробки жароміцних суперсплавів, а також при розробці електрохімічних технологій вилучення стратегічно важливих металів, що використовуються в якості легуючих компонентів при створенні харчового обладнання.

**Ключові слова:** матеріали обладнання харчових виробництв, метансульфонатний розчин, перероблення суперсплавів, електрохімічне розчинення, нікельвмісний суперсплав

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