

The object of this study was an electrochemical anodic dissolution of a heat-resistant nickel-based superalloy ( $\approx 62$  wt.%), recovered from destroyed components of special-purpose equipment, which contains valuable metals such as Re ( $\approx 4$  wt.%), Co, W, Mo, Ta, Nb, and others. The research addressed the problem of the lack of an effective electrochemical method for selectively extracting these components, particularly rhenium and other valuable elements, from such an alloy in alkaline media. The anodic behavior of the alloy was experimentally studied in 0.5 M NaOH in the presence of various complexing and activating additives (NaCl, citric acid, EDTA salt, and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ). It was shown that none of the additives provided a significant acceleration of anodic dissolution. This was demonstrated by the fact that the increase in the average specific charge calculated for five cyclic voltammetry scans that contributed to alloy dissolution did not exceed 8%. In other cases, the values were significantly lower than in the base solution containing only alkali. It was established that the anodic dissolution process has a surface-selective nature: Ni, Co, Cr, Re, and Al are leached into the electrolyte, while a residual surface layer enriched in W, Ta, Nb, and Mo forms, hindering further dissolution. X-ray fluorescence analysis data confirmed changes in the chemical composition (Ni content decreased to  $\approx 48$  wt.%, W increased from  $\approx 9$  to  $\approx 20$  wt.% on the surface). Theoretical justification of the results is provided, based on the physicochemical properties of compounds that may form during anodic dissolution in the presence of additives. The absence of an activating effect from the additives suggests the need for further studies on pure NaOH. The obtained data are of practical importance for the selective separation of superalloy elements before further processing

**Keywords:** heat-resistant superalloy, electrochemical dissolution, alkaline electrolyte, passivation, selective leaching, rhenium

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# DETERMINATION OF THE ELECTROCHEMICAL DISSOLUTION FEASIBILITY OF A SUPERALLOY USED IN TURBINE COMPONENTS IN ALKALINE SOLUTIONS WITH ADDITIVES

**Valerii Kotok**

*Corresponding author*

PhD, Associate Professor\*

E-mail: valeriykotok@gmail.com

**Tetyana Butyrina**

PhD, Associate Professor

Department of Inorganic Substances and Ecology\*\*

**Yuri Sknar**

Doctor of Chemical Sciences, Head of Department\*

**Oksana Demchyshyna**

PhD, Assistant\*\*\*

**Irina Sknar**

PhD, Associate Professor\*

**Ella Chasova**

PhD, Associate Professor\*\*\*

\*Department of Processes, Apparatus and General Chemical Technology\*\*

\*\*Ukrainian State University of Science and Technologies

Nauky ave., 8, Dnipro, Ukraine, 49005

\*\*\*Department of Mineral Processing and Chemistry

Kryvyi Rih National University

Vitaliya Matusevycha str., 11, Kryvyi Rih, Ukraine, 50027

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## 1. Introduction

Alloys are the foundation of modern engineering progress, playing a key role in constructions, mechanisms, power plants, electronics, aviation, turbomachinery, and many other fields [1, 2]. Their functionality and advanced properties largely depend on their composition and manufacturing technology.

Modern special alloys are multicomponent systems that often include both non-metals (P, C, S, Si, B) and a wide range of metals – Ti, Ta, W, Re, Cu, Co, Ni, Cr, Sn, Mn, Al, Mo, V, Bi, etc. They often contain rare-earth elements, and in some cases even noble metals [3, 4]. A significant portion of

these strategically important materials is absent in Ukraine, and their supply on the international market is limited. In addition, the presence of political or economic restrictions, particularly those related to geopolitical conflicts, may block access to critical resources [5].

An example is the production of high-performance batteries (lithium-ion, nickel-metal hydride, lead-acid, etc.), which requires a number of rare metals unavailable in Ukraine [6, 7]. In the modern militarized world, the availability of domestic raw materials for the production of energy systems becomes of strategic importance.

One of the most promising ways to ensure resource independence is alloy recycling with selective extraction of valu-

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able components. In this case, the important criteria remain the process rate, energy efficiency, and control over the form of the final product.

Electrochemical dissolution is one of the most flexible and controllable methods of such recycling. It provides a high level of selectivity, especially when combined with chemical stages, which makes it possible to accurately control the separation of components depending on their electrode potentials, alloy structure, and electrolyte composition.

In addition to selectivity, electrochemical methods allow direct production of target metals in the desired form – in particular, as high-purity deposits or powders with specified morphological characteristics. This opens possibilities not only for extraction but also for the creation of high-value products – for example, nanopowders for additive manufacturing, electrode materials, or catalysis, where the final form of the product determines its market value. For instance, the price of pure nickel powder can reach up to 500 USD/kg [8] depending on purity and particle size, while the price of compact metal is about 15 USD/kg [9].

When using the electrochemical dissolution stage before subsequent chemical and electrochemical processing, this operation can be carried out in two ways. The first is the complete dissolution of the alloy, followed by the separation of the individual components. The second (if possible) is selective dissolution of individual components, followed by dissolution of the remaining scrap. The latter approach simplifies further processing, since it reduces the number of elements left in the alloy, or decreases the processing cost if the elements in the scrap are cheap and not worth further recovery.

On the one hand, superalloys used in turbine elements under high-temperature and aggressive oxidative environments exhibit enhanced corrosion resistance. In addition, such alloys have high mechanical properties. All this significantly complicates their processing by pyrometallurgical methods. On the other hand, as a result of military actions, a scrap of such alloys is present in large quantities on the territory of Ukraine. It contains some metals absent from Ukrainian deposits, in particular tungsten and rhenium, as well as other metals: Ni, Cr, Co, Al, Ta, and Nb. It should be noted that the most valuable component of these alloys is rhenium, which mining is limited to a few countries, does not exceed 50 tons per year, and which price reaches up to 2500 USD/kg [10]. From this point of view, it would be reasonable to investigate the potential possibility of selective electrochemical dissolution of such alloys.

## 2. Literature review and problem statement

As noted in [10], the average composition of alloys corresponds to a nickel-based superalloy containing Cr, Co, W, Al, Re, Ta, Nb, and Mo. This work indicates that the alloy composition corresponds to ZhS32-VI (USSR), which is also similar to CMSX-4 (USA, Rolls-Royce / GE Aviation) [11], and PWA 1484 (USA, Pratt & Whitney) [12]. The above-mentioned sources report the physicochemical aspects of the behavior of these alloys under various conditions, but information regarding potential processing methods is limited.

In [13], an electrochemical method of dissolving superalloys with Re (1–10%) in an acidic medium (2–6 V, AC/DC, alternating polarity) was described, which allows separation of Re, Ta, W, Hf, and Pt by controlling electrolysis. An inorganic oxygen-free acid was used as the electrolyte. Only an

acidic electrolyte was proposed, which may limit the search for possibilities of selective alloy processing.

In [14], it was established that the electrochemical reactions of different metallic elements in CMSX-4 superalloy scrap during anodic dissolution are similar in three types of acidic media: sulfate, nitrate, and chloride acids. Ni, Co, Cr, Al, and other metals dissolve and remain in solution as ions; W, Ta, and other metals oxidize and accumulate in the slag phase, while Mo, Re, and other elements are dispersed between the solution and the slag. In this study, acidic single-component electrolytes were used, which sets limitations in the search for new electrolytes for selective alloy processing.

Study [15] presents research on the anodic dissolution of a rhenium-containing turbine blade alloy in  $\text{H}_2\text{SO}_4$  with the addition of  $\text{HNO}_3$ . Under these conditions, up to 80–90% of rhenium and 90–95% of nickel, cobalt, chromium, and aluminum pass into solution. Most of the refractory rare metals (tungsten, tantalum, hafnium) are almost completely deposited in the anodic sludge. The study mentions a two-component acidic electrolyte without additional additives. This imposes restrictions on the search for alternative, multicomponent electrolytes for selective dissolution.

In [10], it was shown that for nickel-based superalloys with several percent of rhenium, the most effective dissolution occurs in NaCl or HCl, while sulfate and methanesulfonic acid solutions are less effective. Four single-component electrolytes were used in the work – three acidic and one close to neutral. Among them, there were no alkaline electrolytes or those containing additional activating additives, which narrows the search for promising electrolytes for anodic dissolution of rhenium-containing nickel-based alloys.

Study [16] investigates selective anodic dissolution of tin or zinc in brass under natural conditions (e.g., artificial saliva or saline solutions). The authors found that Zn dissolves faster than Cu, forming a dezincified layer that significantly changes the surface composition. This study illustrates the possibility of selective investigation of electrolytes, but does not provide similar solutions for nickel-based superalloys with rhenium.

In [17], experiments with Cu-Ni alloys in 0.1 M  $\text{Na}_2\text{SO}_4$  were described, showing how Cu and Ni selectively dissolve within a potential range with characteristic peaks. NiO and  $\text{Cu}_2\text{O}$  form at lower anodic potentials, while CuO and  $\text{Ni}_2\text{O}_3$  form at higher potentials. The authors demonstrated the possibility of selective study of nickel-copper alloys. However, nickel-rhenium superalloys with other metals differ significantly in phase composition, elemental composition, and properties, which creates difficulties when using  $\text{Na}_2\text{SO}_4$  solution.

In [18], an anodic etching technique was presented, by which Cu can be completely removed from Cu-Ni alloys, producing a nanoporous Ni structure – an example of morphology control by selective electrochemical etching. The work shows a successful example of selective dissolution, but this technique cannot be applied to nickel-based heat-resistant superalloys due to their different phase composition.

One of the promising but poorly studied directions for multicomponent superalloys containing rhenium is anodic dissolution in alkaline media with the addition of various additives. For example, in [19], the effect of systematically increasing Ni content on the anodic dissolution and passivation of Zn-Ni alloys in KOH solutions of different concentrations (0.1–1 M) was studied using potentiodynamic and potentiostatic methods. It was found that increasing Ni content increases the activation energy and decreases the dissolution rate of alloys in KOH, with the lowest dissolution

rate observed at 10% Ni. The article demonstrates the potential possibility of selective dissolution of nickel-containing alloys, though not for heat-resistant nickel-based superalloys.

In [20], the anodic behavior of VR20 alloy in sodium hydroxide solutions was investigated. Using linear voltammetry, the possibility of high-speed electrochemical dissolution of this alloy under direct current was established, with the formation of potassium perrhenate, which separates from the electrolyte as an intermediate product. It is then converted into perrhenic acid. The main parameters of electrodialysis conversion with an electrolyte concentration of 591 g/L were determined. However, some experimental details concerning the dissolution conditions were absent in the article.

Study [21] analyzed the efficiency of rhenium extraction and its separation from molybdenum in an alkaline leaching solution of superalloy waste using methyltriethylammonium chloride (N263). It was found that the concentration of N263 was the main factor influencing rhenium extraction.

To intensify selective anodic dissolution, substances can be added that affect the mechanism of the process through destruction of the passive film, formation of soluble complexes, or salts. Well-soluble citrate complexes of perrhenate  $\text{Re(VII)}$  are known [22]; therefore, the addition of citrate ions could potentially improve the rate of electrochemical dissolution of rhenium. However, the use of citrate as an activating additive during the dissolution of heat-resistant superalloys has not been demonstrated in studies devoted to their processing.

For other metals, such as Sn [23], Zn [24], and others, improved electrochemical dissolution in the presence of EDTA in alkaline solutions has been recorded. Strong complexes of Ni with EDTA are also known [25], even in alkaline media, as well as with Co, Cr, and Al. Thus, the addition of EDTA could improve the solubility of certain superalloy components, facilitating their selective dissolution. However, the addition of EDTA as an activating additive during anodic dissolution of heat-resistant superalloys has not been reported in the literature.

On the other hand, the strategy of selective dissolution of the superalloy described in [10] could be different. For example, dissolution of one or several components can be blocked by the formation of insoluble compounds. The main element in the superalloy – nickel – is poorly soluble in alkaline medium without additional additives, since it forms nickel hydroxide. Addition of, for example, pyrophosphate ions may further reduce the dissolution of certain elements through the formation of poorly soluble compounds such as nickel pyrophosphate [26]. It should be noted that the use of pyrophosphate for facilitating the dissolution of heat-resistant superalloys has not been reported in other studies.

Thus, the majority of works concern the use of single- or two-component acidic or neutral electrolytes without the possibility of selective dissolution. Virtually no studies were found in alkaline solutions with the addition of activating components such as citrate, chloride, pyrophosphate ions, or EDTA. On the other hand, the potential activating effect of these components has been demonstrated; therefore, testing alkaline solutions with the addition of such additives is an interesting research task.

### 3. The aim and objectives of the study

This study aims to establish the possibility of selective anodic dissolution of a heat-resistant superalloy containing rhenium and other valuable metals (Ni, Cr, Co, Al, Ta, Nb, W)

in an alkaline medium with the addition of organic and inorganic compounds. This approach is intended to simplify and reduce the cost of subsequent stages of processing alloys with high corrosion resistance, in particular by intensifying selective dissolution or, conversely, blocking the dissolution of individual components.

To achieve this aim, the following objectives were set:

- to evaluate the effect of different types of additives on the electrochemical anodic dissolution of the superalloy;
- to identify conditions under which selective dissolution of rhenium or other components occurs with minimal loss of other valuable metals, or, conversely, blocking of the dissolution of less important components through the formation of insoluble complexes.

## 4. Materials and methods

### 4.1. Object and hypothesis of the study

The object of this study is the electrochemical anodic dissolution of a heat-resistant nickel-based superalloy containing rhenium and other alloying elements. Particular attention was paid to dissolution in alkaline electrolytes with the addition of complexing agents, in particular citrate, EDTA, and sodium pyrophosphate.

The study hypothesis is the possibility of selective dissolution of superalloy components at the anode when using a specially selected electrolyte. It is assumed that the introduction of additional components will lead either to selective complex formation, selective destruction of the passive film, or the formation of poorly soluble compounds with certain elements of the superalloy. This approach could provide selective transfer of valuable metals such as rhenium into solution, while less valuable or inert components remain on the surface. This would simplify the subsequent stages of metal recovery and reduce processing costs.

### 4.2. Materials and reagents

Distilled water was used for the preparation of solutions. NaOH, NaCl,  $\text{C}_6\text{H}_8\text{O}_7$ , EDTA, and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  were used with analytical grade purity. Parts of the turbine superalloy were carefully cleaned with water, distilled water, acetone, and ethanol.

### 4.3. Methods for superalloy characterization

#### *Chemical composition analysis.*

The elemental composition of the studied superalloy was determined by X-ray fluorescence analysis using the “SPRUT” spectrometer (TD “Ukrintekh”, Ukraine [27]) in energy-dispersive mode. Calibration was performed using certified standard alloy samples to ensure the accuracy of quantitative analysis.

#### *Phase composition of the surface.*

X-ray diffraction (XRD) analysis was carried out on a DRON-3 diffractometer using monochromatized  $\text{Co-K}\alpha$  radiation ( $\lambda = 1.7902 \text{ \AA}$ ). Phase identification was performed by comparing interplanar spacings ( $d$ ,  $\text{\AA}$ ) and relative intensities of the experimental pattern with the PCPDFWIN electronic database. Measurements were taken at angles between  $10\text{--}90^\circ$ . For phase analysis, a resolution of  $0.1^\circ$  was used with a signal accumulation time of 5 s for each step. The anode voltage was 30 kV.

#### *Electrochemical studies.*

The electrochemical behavior of the alloy was studied using a potentiostat MTech SPG-500fast (“MTech”, Ukraine). In the measurement setup, a graphite electrode was used as

a counter electrode, and an Ag|AgCl electrode in 3.5 M KCl was used as a reference electrode. Measurements were performed at 18°C. Cyclic voltammetry (CVA) curves were recorded at a scan rate of 50 mV/s within a specified potential window. Each curve included 5 full cycles.

Before each experiment, the sample surface was polished with sandpaper of 80  $\mu\text{m}$  grit size and degreased. To determine the specific electrochemical activity, the open electrode area was standardized by partial coverage with PTFE film, leaving only a defined active area exposed.

*Evaluation of the specific electrochemical dissolution rate.*

Fig. 1 illustrates a typical example of a CVA curve, where four characteristic zones – two anodic and two cathodic – are highlighted and used for calculating the corresponding charge values.

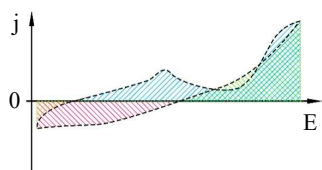


Fig. 1. Calculation of the charge based on cyclic voltammetry results: an example of a cyclic voltammetry curve with highlighted zones for charge calculation

This makes it possible to evaluate the intensity of dissolution and reduction processes within a single cycle.

*Data processing.*

For quantitative evaluation of dissolution and reduction processes, the current density was integrated within each of the indicated zones. Experimental data were processed using a custom Python code [10] (Python Software Foundation) with the open-source libraries Pandas and Matplotlib. Integration was performed by the trapezoidal method separately for each direction (anodic and cathodic), taking into account the following criteria for dividing the integral zones:

1. Change of the current density sign.
2. Change of the potential scan direction.

When one of these conditions was met, the charge calculation for the corresponding zone was completed, and a new calculation was started. This approach allowed precise determination of the electrochemical reaction activity in each cycle.

## 5. Results of anodic dissolution of the heat-resistant superalloy in alkaline medium

### 5.1. Evaluation of electrochemical characteristics of the studied alloy and the effect of different additives on electrochemical anodic dissolution

A series of experiments was carried out to investigate the anodic dissolution

of the nickel-based superalloy in 0.5 M NaOH (alkaline medium) with the addition of various substances. The effect of the following additives was studied (concentration of each – 0.1 M):

- 1) no additives (pure 0.5 M NaOH, control case);
- 2) EDTA salt – complexing agent;
- 3) NaCl – sodium chloride (source of  $\text{Cl}^-$  ions, which are strong depassivators);
- 4) citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) – organic complexing agent;
- 5)  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  – source of pyrophosphate ion.

Cyclic voltammetry (CVA) curves of the alloy obtained for each case are presented in Fig. 2. In addition, for comparison of the electrochemical characteristics of the nickel-based superalloy in alkaline medium with pure nickel, a CVA was additionally recorded in a wider potential window in 0.5 M NaOH on a nickel electrode – Fig. 2.

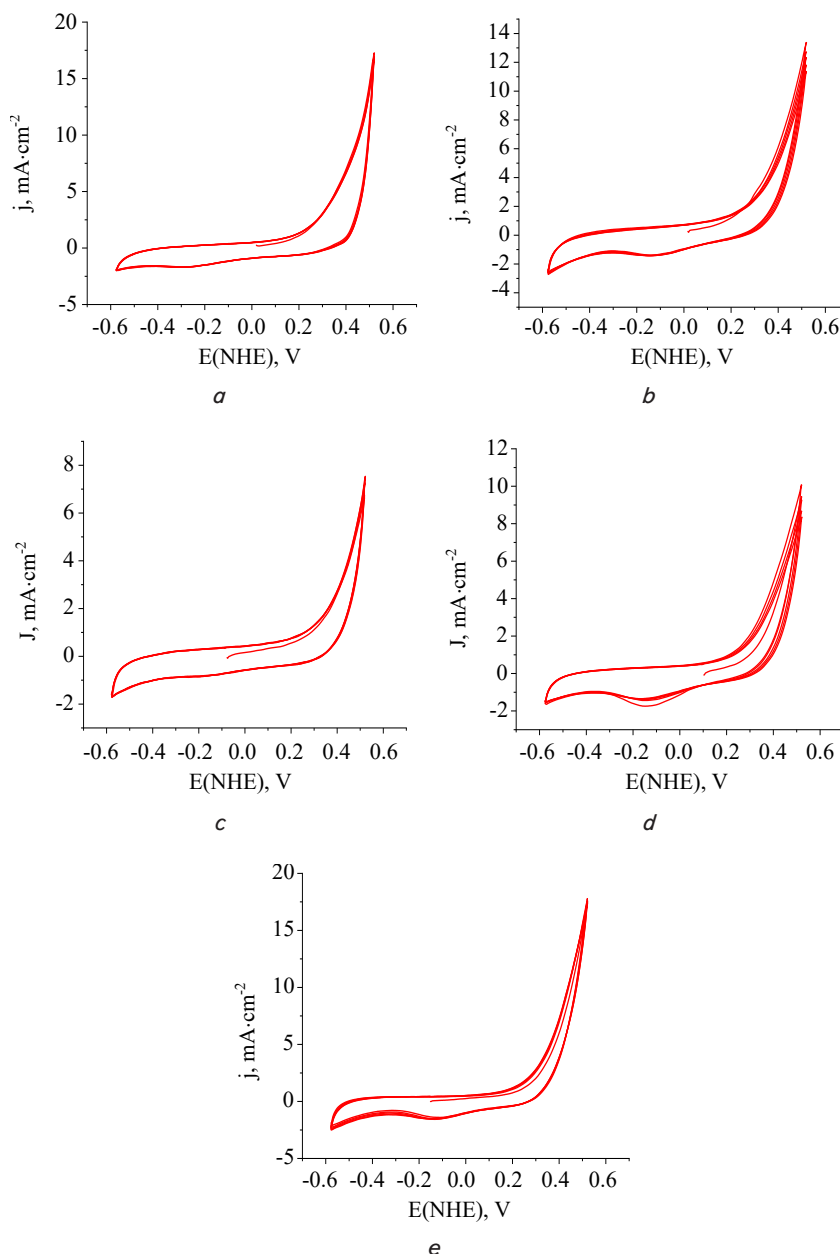


Fig. 2. Cyclic voltammetry curves, where the current density  $j$ ,  $\text{mA}\cdot\text{cm}^{-2}$ , and potential  $E$ , V, were obtained for the superalloy in 0.5 M NaOH solution with the addition of 0.1 M of each additive: *a* – without additives; *b* – EDTA; *c* – NaCl; *d* –  $\text{C}_6\text{H}_8\text{O}_7$ ; *e* –  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$



All voltammetry curves for the alloy have a similar general shape, characteristic of anodic behavior of nickel alloys in alkaline medium: at the beginning, no active dissolution is observed, then with increasing potential, the current increases – Fig. 2, *a–d*. The addition of each of the mentioned substances does not lead to a drastic change in the curve shape: no new pronounced anodic dissolution peaks or significant increase in maximum current were observed compared with the base electrolyte curve without additives.

Fig. 3 illustrates the CVA for pure nickel in 0.5 M NaOH (without additives and in a wider potential range). The behavior of pure Ni in alkaline solution demonstrates typical passivation with the formation of surface  $\text{Ni}(\text{OH})_2$  [28], which transforms into  $\text{NiOOH}$  at higher potentials. When the potential decreases, nickel oxyhydroxide ( $\text{NiOOH}$ ) converts back to nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ), producing a cathodic peak (between 0.3–0.6 V). The use of the alloy instead of nickel modifies the voltammetry curve, but the general character of the CVA remains similar to that of pure nickel.

Fig. 4 shows the dynamics of changes in the specific charge consumed for alloy dissolution during each of the successive 5 CVA cycles in different solutions. It can be seen that in the second cycle, anodic dissolution is more intensive for all solutions (higher charge). After that, in the following cycles, the charge consumed for dissolution decreases and stabilizes – this may be associated with the formation of a passivating layer on the alloy surface or with changes in surface composition after initial dissolution.

Fig. 5 summarizes these data, showing the average values of the specific dissolution charge over 5 cycles for each case.

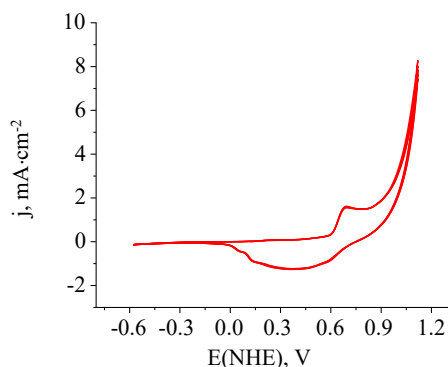


Fig. 3. Cyclic voltammogram, where the current density  $j$ ,  $\text{mA}\cdot\text{cm}^{-2}$ , and potential  $E$ , V, were obtained for metallic nickel in 0.5 M NaOH solution without additives

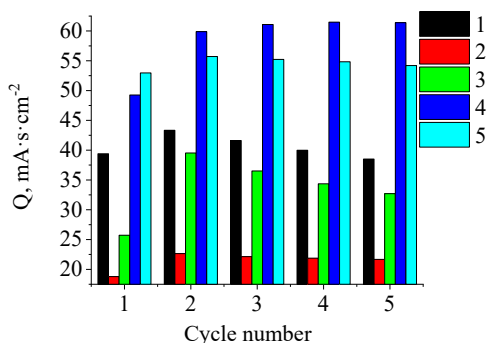


Fig. 4. Dynamics of changes in specific charge over 5 cycles of cyclic voltammogram curves, corresponding to alloy dissolution in 0.5 M NaOH solution with the addition of 0.1 M of each additive: 1 – EDTA; 2 – NaCl; 3 –  $\text{C}_6\text{H}_8\text{O}_7$ ; 4 –  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ; 5 – without additives

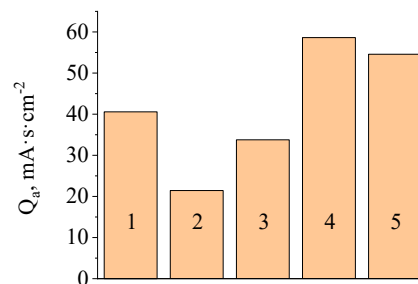


Fig. 5. Average values of specific charge for 5 cycles of cyclic voltammogram curves corresponding to alloy dissolution in 0.5 M NaOH solution with the addition of 0.1 M of each additive: 1 – EDTA; 2 – NaCl; 3 –  $\text{C}_6\text{H}_8\text{O}_7$ ; 4 –  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ; 5 – without additives

According to the graph, none of the added substances provides a significant increase in the amount of dissolved metal compared to the pure alkaline electrolyte. In this graph (Fig. 5), all values for EDTA, NaCl, citric acid, and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  are of the same order of magnitude as in the case without additives. This indicates that the anodic dissolution rate of the superalloy practically does not increase due to the introduction of these additives, at least under the given conditions, in particular at a concentration of 0.1 M.

## 5. 2. Identification of conditions for selective alloy dissolution

After cyclic anodic polarization of the alloy in alkaline solution without additives, an analysis of changes on the alloy surface was carried out. X-ray diffraction of the samples before and after anodic treatment (Fig. 6, 7) showed no appearance of new phase peaks. The diffractograms of the alloy before treatment and after 5 cycles in 0.5 M NaOH are similar, meaning that the crystalline structure of the alloy remained unchanged – no new crystalline oxides or other compounds were detected within the sensitivity of the method. This indicates that anodic dissolution did not lead to the formation of thick layers of new phases on the surface or to internal structural changes in the bulk of the material, and the changes are limited to the surface layer.

For quantitative determination of chemical transformations, elemental analysis of the alloy composition was performed before and after anodic dissolution in alkaline solution (Table 1). The main changes in the concentration of elements in the near-surface layer of the alloy (the upper layer affected by dissolution was analyzed after treatment) are summarized below:

- decrease (leaching) of easily soluble components: Ni (from ~62.4% to ~48.3%), Cr (from ~4.62% to ~1.85%), Co (from ~9.3% to ~4.7%), Al (from ~2.4% to ~0.8%), and Re (from ~3.98% to ~0%). Thus, nickel and other more active metals largely passed into solution, while rhenium was completely removed from the surface layer. Clearly, leaching occurs only on the surface, and metals such as nickel, chromium, and cobalt are removed in the form of oxides and hydroxides, which may detach from the surface, especially when oxygen evolution occurs at high potentials;

- increase (accumulation) of refractory, less active elements: W (from ~9.1% to ~20.0%), Ta (from ~4.15% to ~9.38%), Nb (from ~1.68% to ~3.42%), Mo (from ~1.2% to ~1.76%), and Si (from ~0.98% to ~7.93%). These elements either do not dissolve under the given conditions or they form stable surface compounds, which is why their relative fraction on the surface increases after selective leaching of Ni, Co, Cr, etc.

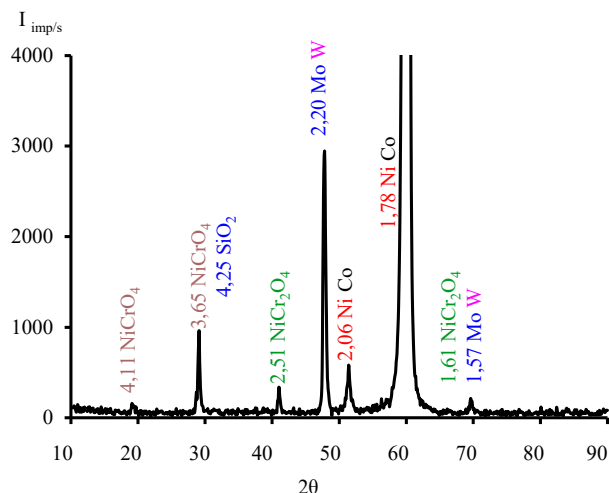


Fig. 6. X-ray diffraction pattern of the alloy before treatment

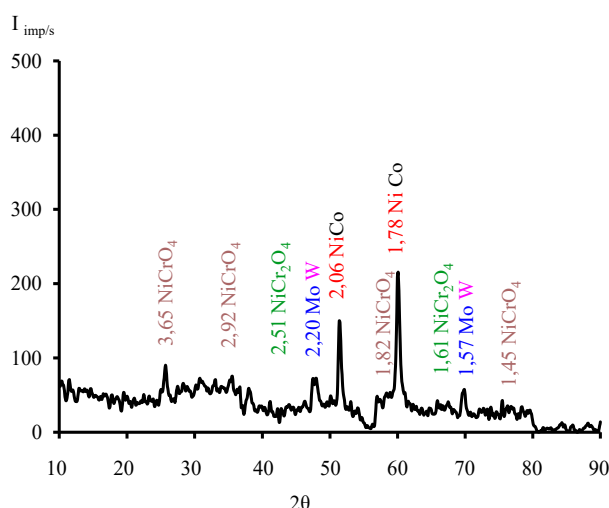


Fig. 7. X-ray diffraction pattern of the alloy after treatment in 0.5 M NaOH solution

Table 1

Composition of the alloy before and after treatment in 0.5 M NaOH solution

Before treatment			After treatment		
Element	Content, %	Error, %	Element	Content, %	Error, %
Ni	62.41	± 0.189	Ni	48.35	± 0.161
Cr	4.62	± 0.046	Cr	1.85	± 0.034
Co	9.28	± 0.057	Co	4.74	± 0.041
W	9.07	± 0.095	W	19.95	± 0.11
Al	2.41	± 0.228	Al	0.79	± 0.226
Re	3.98	± 0.058	Re	0	± 0
Ta	4.15	± 0.077	Ta	9.38	± 0.087
Nb	1.68	± 0.015	Nb	3.42	± 0.023
Mo	1.2	± 0.013	Mo	1.76	± 0.016
Si	0.98	± 0.077	Si	7.93	± 0.115
V	0.07	± 0.019	V	0.12	± 0.019
Fe	0.15	± 0.010	Fe	0.17	± 0.011
Si	–	–	Si	0.93	± 0.115
P	–	–	P	0.23	± 0.052
S	–	–	S	0.3	± 0.027
Au	–	–	Au	0.04	± 0.037
Ga	–	–	Ga	0.04	± 0.035
Total	100	–	Total	100	–

Thus, the experimental results show that anodic dissolution in 0.5 M NaOH can occur selectively. Rhenium and aluminum, as well as other reactive components, are predominantly removed from the alloy, while refractory elements accumulate in the residual surface layer. Importantly, the addition of NaCl, EDTA, citric acid, or  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  to the electrolyte did not result in a noticeable increase in the amount of dissolved metal, which is proportional to the specific charge – all graphs and quantitative indicators demonstrate values close to those of the base alkaline solution without additives.

## 6. Discussion of the results on the processing conditions of the heat-resistant superalloy

The CVA curves presented in Fig. 2 show the absence of distinct anodic peaks. This may indicate the absence of selective dissolution of individual metals or the simultaneous dissolution of several metals. The latter may be reflected in the presence of plateaus, which result from the overlap of several peaks. It should be noted that the CVA curve in Fig. 3 for nickel in alkaline electrolyte without additives differs significantly from that of the superalloy (with and without additives), indicating differences in dissolution behavior. This is primarily related to the phase composition and structure of pure metal versus alloy. Pure nickel in alkaline medium is completely passivated, and the peaks are the result of oxidation and reduction of  $\text{Ni}(\text{OH})_2$ .

The summarized data of alloy anodic dissolution (Fig. 4, 5) show that none of the added reagents caused a significant acceleration of anodic dissolution. This result may seem unexpected, since each of the tested additives could theoretically influence the dissolution process. In particular, EDTA (a complexing agent), citric acid, and the pyrophosphate ion are ligand-type complexing agents, which could chelate metal cations and thus prevent the formation of a passive film on the anode. It is known, for example, that the addition of EDTA effectively suppresses the formation of passive hydroxide films on metals by binding cations in solution, as shown previously. For aluminum in alkaline solutions, EDTA addition even leads to a sharp increase in the anodic dissolution rate, since  $\text{Al}^{3+}$  complexation disrupts passivation by  $\text{Al}(\text{OH})_3$  oxide. However, in the case of the nickel-based superalloy in concentrated NaOH, the action of complexing agents proved ineffective. The likely reason is that the main passivating barrier consists of  $\text{Ni}(\text{II})/\text{Ni}(\text{III})$  hydroxides and chromium oxides on the surface, which form very quickly and have low solubility in a strongly alkaline medium [29, 30]. EDTA and other compounds either do not act fast enough or are unable to remove these solid oxide-hydroxide films from the surface; they can only chelate metal ions already in solution. Neither nickel oxide nor chromium(III) oxide ( $\text{Cr}_2\text{O}_3/\text{Cr}(\text{OH})_3$ ) significantly complex or dissolve under the action of these reagents. As a result, despite the presence of strong chelators, a passive film still forms.

The addition of 0.1 M sodium chloride also did not result in a significant increase in dissolution, although chloride ions are usually known as aggressive disruptors of passive oxide layers. In the electrochemical treatment of nickel alloys and steels, chloride can accelerate dissolution. Literature reports indicate that  $\text{Cl}^-$  addition can increase the rates of both active and transpassive dissolution of metals, since interaction at the metal-oxide and oxide-solution interfaces is accelerated. For nickel-based superalloys, chloride addition

increases current at transanodic potentials and improves dissolution efficiency by weakening the protective action of the passive film. In the experiments, however, the chloride concentration and polarization regime were such that dissolution acceleration did not manifest. It can be assumed that 0.1 M NaCl in 0.5 M NaOH caused only minor local destabilization of the passive layer (possibly micro-pitting), which was insufficient to significantly increase the integral anodic current. In addition, after the first cycle, a layer depleted in Ni and enriched in refractory elements (W, Ta, etc.) formed on the surface, which is less susceptible to chloride attack. It is known that selective dissolution of multicomponent alloys can lead to the formation of protective residual phases or layers. For example, in NaCl environments, selective corrosion of nickel-based superalloys occurs mainly through the  $\gamma'$ -phase, while the  $\gamma$ -phase enriched with Cr and W remains as a skeletal framework. The obtained data agree with this picture: tungsten and other components accumulate in the surface layer, forming a barrier for further dissolution. Such a layer may be a mixture of residual alloy matrix and corrosion products (hydroxides/oxides of W, Ta, Nb, Si), which have low conductivity and permeability [31]. This also increases the diffusion path of ions to and from the electrode, further slowing down the process. As a result, after the initial active dissolution in the 1st cycle, the current decreases in subsequent cycles – as observed in Fig. 4. Similar phenomena have been described in the literature for superalloy scrap dissolution: first, the reactive component dissolves, and a porous layer enriched in chromium (or other refractory elements) forms, which hinders further dissolution until it detaches. In this case, the role of chromium may be played by tungsten: Table 1 shows that its surface concentration increased the most, meaning it forms a concentrated residual layer. Notably, rhenium (present in the initial alloy) completely disappeared from the surface layer after anodic dissolution – it likely transferred into solution as perrhenate ion ( $\text{ReO}_4^-$ ) or another soluble species at high anodic potentials. Nickel, cobalt, and aluminum partially entered the solution, while a significant portion of tungsten, tantalum, niobium, molybdenum, and silicon remained in the undissolved state on the anode. All this indicates that chemical and structural changes due to anodic polarization occur only in the thin surface layer of the alloy, while deeper in the material, the original composition and phase structure remain unchanged. The X-ray diffraction pattern after dissolution is practically identical to the initial one, confirming the absence of bulk changes – no new phases crystallized in sufficient amounts to be detected by this method. Thus, the anodic etching process has a purely surface character: essentially, selective leaching of active components occurs, forming a refractory-element-enriched surface layer that limits further dissolution.

Considering that neither complexing agents nor halide ions demonstrated the expected accelerating effect, it was concluded that further research on anodic dissolution of the superalloy in pure alkaline medium without additives is reasonable. Firstly, the use of NaOH alone simplifies the chemical composition of the electrolyte and the subsequent disposal of spent solutions (there is no need to separate or neutralize costly complexing agents). Secondly, the absence of additives ensures that dissolution is controlled by the intrinsic properties of the alloy and the passive film formed on it, without side reactions of complexation in the bulk solution. This allows a deeper understanding of the mechanism of selective dissolution and passivation: as the experiments showed, even

in pure NaOH, an interesting phenomenon of surface layer formation of different composition occurs, which deserves detailed investigation. Thus, from both practical and scientific perspectives, an alkaline electrolyte without additives is a rational choice for further studies of controlled anodic dissolution of this superalloy, especially for selective leaching of rhenium as the most valuable component.

As a limitation of this study, it should be noted that the duration of anodic and cathodic currents acting on the alloy was relatively short. On the one hand, a relatively high potential sweep rate is required to ensure that the electrode area (and hence the real current density) does not change significantly. On the other hand, a slower sweep rate could provide a more detailed picture of electrode processes.

Another drawback of this study is the absence of long-term dissolution experiments in the selected solutions under galvanostatic conditions. This could be done in future work, and the information obtained in such experiments would be valuable for analyzing deep dissolution processes under regimes typically used in industry.

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## 7. Conclusions

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1. It was established that the addition of 0.1 M EDTA, NaCl, citric acid, and  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  does not cause a significant increase in the anodic dissolution rate of the nickel-based superalloy in 0.5 M NaOH. Anodic currents and the amount of dissolved metal with additives remain at levels close to those of the base alkaline solution without additives.

2. It was found that changes in the alloy composition occur only on its surface. After anodic treatment in NaOH, the surface layer of the alloy is depleted in Ni, Co, Cr, Re, and Al, while enriched in W, Ta, Nb, and Mo. This indicates selective leaching of active components with the formation of a refractory-element-enriched residual surface layer. Meanwhile, the phase composition and structure in the bulk of the material remain unchanged, as confirmed by the similarity of the X-ray diffraction patterns of the alloy before and after dissolution.

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## Conflict of interest

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The authors declare that they have no conflict of interest regarding this study, including financial, personal, authorship-related, or other factors that could affect the study and its results presented in this article.

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## Data availability

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This manuscript has no associated data.

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## Use of artificial intelligence tools

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The authors confirm that no artificial intelligence technologies were used in the preparation of this work.

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