The object of this study is the electrochemical anodic dissolution of a heat-resistant nickel-based superalloy containing rhenium and other alloying elements in acidic electrolytes containing sodium chloride. The investigated alloy was obtained from scrap of high-temperature equipment. The anodic dissolution of the superalloy was studied in two acidic media: sulfuric and methanesulfonic acids. A comparative analysis of cyclic voltammetry and galvanostatic experiments was carried out. In sulfuric acid electrolyte, anodic processes proceed more vigorously, as indicated by higher current densities. However, this method records not only the dissolution currents of metals but also side processes such as anodic oxygen evolution and re-oxidation of dissolved ions. Under galvanostatic conditions, which allow direct determination of alloy mass loss, it was shown that methanesulfonic acid with sodium chloride provides a higher dissolution rate despite the medium's lower conductivity. This effect is explained by the higher solubility and stability of the methanesulfonates of the alloying components (Cr, Al, Nb, Ta, Re), which reduce the tendency of the surface to repassivate. In the H_2SO_4 + NaCl medium, dissolution proceeds more uniformly but at lower mass efficiency, attributed to the formation of poorly soluble sulfates. In the methanesulfonate electrolyte, within the current density range of 1.5–2.5 $A \cdot dm^{-2}$, the ratios of Ni, Cr, Co, W, and Re were closest to those in the original alloy, while rhenium was detected in solution, unlike in the sulfuric medium. The obtained results can be applied to optimize the initial stage of superalloy recycling and to develop electrochemical technologies for the recovery of strategically important metals from industrial waste.

Keywords: superalloy recycling, anodic dissolution, rhenium recovery, nickel-based superalloy

UDC 621.35
DOI: 10.15587/1729-4061.2025.342421

DETERMINATION OF THE EFFICIENCY AND SELECTIVITY OF ANODIC DISSOLUTION OF A HEAT-RESISTANT RHENIUM-CONTAINING SUPERALLOY IN CHLORIDE-CONTAINING MEDIA WITH SULFURIC OR METHANESULFONIC ACIDS

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Received 18.08.2025
Received in revised form 01.10.2025
Accepted date 22.10.2025
Published date 31.10.2025

How to Cite: *Kotok, V., Sknar, Y., Butyrina, T., Sknar, I., Sukha, I., Demchyshyna, O. (2025). Determination of the efficiency and selectivity of anodic dissolution of a heat-resistant rhenium-containing superalloy in chloride-containing media with sulfuric or methanesulfonic acids. Eastern-European Journal of Enterprise Technologies, 5 (6 (137)), 32–40. https://doi.org/10.15587/1729-4061.2025.342421*

1. Introduction

Modern engineering solutions (devices and structural components) require materials that meet a wide range of demanding criteria. Among the most important of these are metals and their alloys, which are widely used in both everyday applications and advanced technologies. Pure metals often lack certain properties required for technical use; therefore, alloys are used much more frequently [1]. This is because the controlled addition of specific elements can significantly modify key characteristics such as corrosion resistance, hardness, wear resistance, heat resistance, and ductility [2, 3].

The basis of alloys includes a wide range of metals and nonmetals. For special-purpose technologies, more complex or "exotic" alloys are often required to ensure the reliable operation of individual components under specific conditions that differ greatly from conventional environments. For example, turbine components must exhibit high corrosion resistance in oxidizing atmospheres at elevated temperatures [4]. They must also maintain stable performance over time and across a wide temperature range, providing sufficient strength both at low and high temperatures. Another critical property is the ability to withstand frequent, sharp temperature fluctuations, which are inherent to turbine operation.

Superalloys have emerged as the answer to these challenges, particularly those containing rhenium and other alloying elements such as Al, B, Bi, C, Co, Cr, Cu, Mn, Mo, Ni, P, Re, S, Si, Sn, Ta, Ti, V, W, and several others [5, 6].

For various reasons, certain elements – Co, Cr, Ni, Mo, W, Re, Ta, Sn, Bi, and B – are particularly problematic for Ukraine [7]. This is due to the limited or complete absence of their natural deposits. Consequently, most of these elements must be imported, which is not a reliable option within the framework of a national security strategy. Moreover, several of these elements are considered difficult to procure because of limited global supply and complex geopolitical conditions [8]. At the same time, many of them are critical for the development of domestic technologies that could provide significant competitive advantages on the global level [9].

For instance, Co, Mn, and Ni are crucial for the production of lithium-ion batteries [10] and other high-energy power sources [11, 12]. Co, Ni, Mo, W, Re, Ta, Sn, and Bi are indispensable for manufacturing various alloys (including superalloys) with enhanced hardness and thermal stability [13, 14].

A possible response to these challenges is the development of deep recycling strategies for alloys with highly selective separation of elements and the creation of a national reserve of valuable metals and materials [15], which could be replenished and used when necessary. Given Ukraine's significant scrap from special-purpose equipment, including turbine components, the study of recycling processes is of utmost importance.

The materials used in turbine blades and disks, as well as in combustion chamber linings, are composed of refractory superalloys based on Ni and Co with various alloying additions [2]. One of the commonly used superalloys is ZhS32-VI, which contains approximately Ni (≈60%), Co (≈9%), W (≈8%), Al (≈6%), Cr (≈5%), Re (≈4%), and Ta (≈4%). Other elements – Nb, C, Mo, B, and Ce – together account for less than 2% [16]. From this composition, it is evident that recycling the waste of such superalloys can yield a considerable quantity of metals that are strategically important for Ukraine.

The main challenge at the initial stage of processing such alloys lies in their high mechanical strength and corrosion resistance in oxidizing environments – the very properties that ensure the long service life of turbine components [17]. On the other hand, the chemical inertness and hardness of these alloys negatively affect processing efficiency, making it essential to carefully choose the conditions of the first treatment stage.

Electrochemical dissolution in aqueous solutions is considered one of the most rational methods, as it combines chemical dissolution with the oxidative action of an applied anodic current. During this process, both soluble components and solid residues are formed, which can subsequently be processed through additional chemical or electrochemical steps. Therefore, selecting the appropriate dissolution parameters and electrolyte composition is crucial for the efficient recycling of superalloys.

2. Literature review and problem statement

In study [18], the electrochemical dissolution of the superalloy VNZh-90, based on tungsten and a nickel-iron binder, was investigated in HCl, HCl + NaCl, and HCl + $FeCl_3$ solutions. The authors demonstrated the possibility of selective dissolution of the metallic binder in 9% HCl with added NaCl. However, the study was limited to voltammetric characterization and concerned an alloy of a different composition.

Another study examined the selective dissolution of superalloys VK20KS, VN8, VNZh, and VNDS [19] in a 9% HCl solution. For VK20KS, selective dissolution was observed at a current density of 15 $A \cdot dm^{-2}$. A gradual decrease in the anodic dissolution rate was recorded due to the dissolution of the metallic binder and accumulation of inert WC. The experiments were limited to voltammetric curve analysis and lacked long-term galvanostatic measurements. Moreover, the composition of these alloys differs significantly from that of ZhS32-VI.

Korean researchers proposed a two-step leaching process for recycling the PWA-1484 alloy [20]. The first step involved grinding the alloy to a particle size of 150 μm through preliminary prometallurgical treatment at 1500°C. Subsequently, acids were used to dissolve Ni, Co, Cr, and Al, while Re remained in the residue. In the next step, rhenium was extracted by oxidation with electro-generated chlorine in HCl. However, this method may be more energy-intensive compared to conventional chemical–electrochemical dissolution techniques.

Another study addressed the recycling of a Ni-based superalloy, CMSX-4, containing 3% Re [21], in a mixture of nitric and hydrochloric acids. The authors found that the use of ultrasound was ineffective, as it did not significantly increase rhenium recovery. Instead, they identified two types of precipitates: at pH ≈5, a mixture of Al, Cr, Mo, and Ti oxides; and at pH ≈7, hydroxides of Co and Ni. Rhenium remained in solution for further processing.

It should be noted that such oxide mixtures have limited commercial value, as they can only be used without separation in a narrow range of applications. Another disadvantage of this method is the use of "aqua regia," which releases carcinogenic nitrogen oxides and toxic chlorine gas.

A separate research group investigated the kinetics of chemical dissolution of crushed (0.063–0.1 mm) heat-resistant nickel alloy waste in individual acids (HNO_3, HCl, H_2SO_4) and their mixtures at various temperatures [22]. The optimal conditions were identified as leaching in 3 M H_2SO_4 at 100°C for 6 hours, resulting in complete nickel dissolution. The limitation of this work is the absence of a combined chemical-electrochemical approach that could accelerate dissolution.

In another study [23], acid leaching and bioleaching of Ni/Co-based superalloys were compared. It was found that H_2SO_4 at 85°C enabled up to 96% recovery of Ni and Co within several hours, while bioleaching with Acidithiobacillus ferrooxidants proceeded more slowly but was environmentally cleaner. The limitation of this research was the absence of a hybrid chemical-electrochemical variant, which might have improved process efficiency.

In article [24], the first stage of superalloy recycling was proposed – sulfurization of the GH4169 superalloy in a sulfur-rich environment at 600–800°C. During this process, Ni, Co, and Cr are converted into sulfides, which are more easily leached by acids. Pyrite and nickel matte were used as sulfurizing agents. This approach is considered an alternative to oxidative roasting to improve the extraction efficiency of Re, W, and Ta. However, the use of sulfur-containing materials at elevated temperatures raises environmental concerns.

In another study, a nickel-based superalloy was treated with molten Mg-Zn for selective nickel extraction [25]. The authors demonstrated that at 800°C, with a molar Mg/Zn ratio of 9/1, a mass ratio of Mg-Zn/superalloy of 5/1, and a heating time of 240 minutes, a nickel recovery degree of 97.1% was achieved, while the extraction of Fe, Cr, and refractory metals (Nb, Mo, and Ti) remained below 1%. However, the limitation of the study is the lack of an integrated approach for processing the remaining residue to recover individual metals.

Study [26] focused on the ultrasonic leaching of a nickel-based superalloy containing valuable metals, including rhenium. The results showed that the leaching and separation of rare metals from superalloy waste could be achieved by controlling the potential and pH of the leaching solutions. Furthermore, ultrasonic leaching improved the recovery rate of rare metals by approximately 20% compared to conventional leaching. Using a two-step precipitation process, rare metals could be efficiently recovered without generating acid waste. Nevertheless, the economic benefit of ultrasound application was found to be relatively modest.

In work [27], the electrochemical dissolution of the cast superalloy K423A was studied. It was found that the microstructure of K423A – particularly the uneven distribution of carbon and carbides within the matrix and along grain boundaries – significantly affects the stability of the electrochemical dissolution process. The authors demonstrated that a stable and effective dissolution process can be achieved in a 10% $NaNO_3$ solution at 40°C. However, other, more aggressive and potentially more effective electrolytes for electrochemical dissolution were not investigated.

Based on the presented literature review, it can be concluded that most studies are limited either by incomplete experimental data, differences in alloy composition compared to the one used in the present work, or unresolved environmental and energy-related issues. Another important conclusion is that despite the various approaches demonstrated by researchers, little attention has been paid to the dissolution rate during the initial stage of alloy recycling – one of the key techno-economic parameters closely linked to the aforementioned challenges.

In contrast to previously mentioned studies, work [16] justified the selection of sulfuric, hydrochloric, and methanesulfonic acids, as well as sodium chloride, as initial electrolytes for identifying conditions that ensure rapid dissolution of the JS32-VI superalloy. At the same time, these components are more environmentally and economically viable, and their individual physicochemical properties can contribute to reducing energy consumption in industrial applications. The results of that study demonstrated the highest dissolution rate in a 0.5 M NaCl + HCl solution, while the rates in methanesulfonic and sulfuric acids were lower. Therefore, investigating the synergistic effects that could enhance the dissolution rate [21], as well as exploring possible selectivity in the "NaCl + H_2SO_4" and "NaCl + methanesulfonic acid" systems while maintaining environmental and economic advantages, remains an important research task.

3. The aim and objectives of research

The aim of this study is to establish the possibility of increasing the anodic dissolution rate of a heat-resistant superalloy containing rhenium and other valuable metals (Ni, Cr, Co, Al, Ta, Nb, W) in acidic media with the addition of sodium chloride. It is expected that the combination of mineral acids (H_2SO_4 and methanesulfonic acid) with NaCl will improve the dissolution rate and possibly its selectivity, while avoiding the use of highly hazardous components.

To achieve this aim, the following objectives were set:

– to evaluate the effect of different acid-NaCl combinations on the electrochemical anodic dissolution of the superalloy;

– to determine the conditions that ensure an increased anodic dissolution rate and allow for selective dissolution of rhenium or other valuable components.

4. Materials and methods

4. 1. The 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 in acidic electrolytes with the addition of sodium chloride.

The hypothesis assumes the possibility of increasing the anodic dissolution rate of the superalloy due to the combined effect of ions in the acidic medium, which intensifies the process. This approach is based on the depassivating action of chloride ions, the higher solubility of methanesulfonate complexes of certain metals, improved electrolyte conductivity, and the simultaneous occurrence of chemical dissolution at the anode. The choice of such conditions aims to intensify the dissolution process, simplify and reduce the cost of subsequent stages of superalloy recycling with high corrosion resistance. Additionally, it enables control over dissolution selectivity and reduces the cost of further valuable metal recovery steps.

Before the experiments, several assumptions and simplifications were made. During cyclic voltammetry, the working surface area of the specimen (and thus the current density) was assumed to remain nearly constant due to the high potential scan rate. It was also simplified that the main part of the current corresponds to the primary dissolution process.

4. 2. Materials and reagents

Distilled water was used to prepare all solutions. Sodium chloride (NaCl), methanesulfonic acid (CH_3SO_3H), and sulfuric acid (H_2SO_4) were of analytical grade purity.

4. 3. Methods for studying the characteristics of the superalloy

4. 3. 1. Chemical composition analysis

The electrolyte solution obtained after anodic dissolution was analyzed for the following ions: Ni, Co, Cr (total concentration of the three ions), Mo, Ni (separately), Cr (separately), and Re.

The cobalt concentration was determined as the difference between the total (Ni + Co + Cr) and the individual Ni and Cr contents.

Analysis of Ni, Co, and Cr (*total concentration of three ions*).

2 ml of the analyzed solution was transferred into a flask, followed by the addition of 50 ml of distilled water, 10 ml of buffer solution, and a few drops of murexide indicator [28].

Titration was carried out with 0.1 N Trilon B (EDTA) solution from a 25 ml burette until a violet-blue color appeared. The exact concentration and total mass of dissolved metals were calculated according to the law of equivalents, considering the solution volume.

Analysis of W.

100 ml of the anodic solution was taken, and 5 g of $CaCl_2$ was added. The beaker with the mixture was left at room temperature until calcium tungstate crystals precipitated. The precipitate was filtered, dried, and weighed to determine the mass of the formed crystals.

Separate analysis of Ni.

0.1 ml of the analyzed solution was transferred into a 100 ml volumetric flask. Sequentially, 20 ml of distilled water, 2 ml of $(NH_4)_2S_2O_8$, 20 drops of ammonia, and 1 ml of 5% KOH solution containing 1% dimethylglyoxime were added. After 10 minutes, the solution was diluted to the mark with distilled water. The optical density was measured at a wavelength of 490 nm using a photoelectric colorimeter (PEC). The nickel ion concentration was determined from a pre-calibrated optical density-concentration graph.

Separate analysis of Cr.

15 ml of 0.1 N Trilon B (EDTA) was placed into a heat-resistant 50 ml beaker, followed by the addition of 2 ml of concentrated acetic acid (HAc) and 2 ml of the analyzed solution. The mixture was boiled for five minutes, cooled, quantitatively transferred into a 50 ml volumetric flask, and diluted to volume with distilled water. The optical density was measured at a wavelength of 540 nm using a PEC, and the chromium concentration was determined from a pre-constructed calibration curve of optical density versus concentration.

Analysis of Re.

100 ml of the anodic solution was transferred into a beaker, and 5 g of KCl was added. The beaker was then placed in an ice bath until potassium perrhenate crystals precipitated. The precipitate was filtered, dried, and weighed, and the mass of rhenium was calculated accordingly.

4. 3. 2. Electrochemical studies

Cyclic voltammetry.

The electrochemical behavior of the alloy was studied using an MTech SPG-500fast potentiostat (“MTech,” Ukraine). In the measurement setup, a graphite electrode was used as the counter electrode, and an Ag|AgCl reference electrode (in 3.5 M KCl) was employed. All measurements were conducted at a temperature of 20°C. Cyclic voltammetric curves (CVA) were recorded at a scan rate of 50 mV/s within a selected potential window, typically from +0.9 V to −0.2 V. Each curve included five complete cycles.

Fragments of the turbine superalloy were thoroughly cleaned with running water, followed by distilled water. Before each measurement, the surface was renewed using 80 μm sandpaper and degreased sequentially in acetone and ethanol.

To determine the specific electrochemical activity, the exposed electrode area was standardized by partially covering the surface with PTFE tape, leaving only a defined active zone.

Evaluation of specific electrochemical dissolution rate.

Fig. 1 illustrates a typical CVA curve, where four characteristic zones are identified — two anodic and two cathodic – which were used to calculate the corresponding quantities of electric charge.

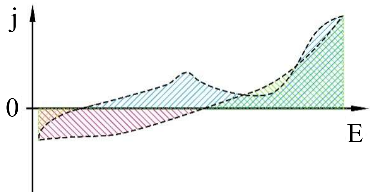

Fig. 1. Calculation of the electric charge from cyclic voltammetry data: an example of a cyclic voltammogram with the designated zones used for charge determination

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

Data processing.

To quantitatively evaluate the dissolution and reduction processes, the current density was integrated within each of the designated zones. The experimental data were processed using a custom Python script [10] developed by the authors, employing the open-source Pandas and Matplotlib libraries.

Integration was performed using the trapezoidal rule separately for anodic and cathodic directions, according to the following criteria for defining integration boundaries:

1. A change in the sign of the current density.
2. A change in the potential scan direction.

When one of these conditions was met, the calculation of the charge for the corresponding zone was completed, and a new integration cycle began. This approach ensured accurate determination of the electrochemical reaction activity in each potential cycle.

The trapezoidal method, widely used in numerical integration, approximates the area under a curve as the sum of the areas of trapezoids formed between adjacent data points.

Galvanostatic measurements.

A divided electrochemical cell with a membrane separating the anode and cathode compartments was filled with 500 ml of the corresponding electrolyte, for example, 0.5 M H_2SO_4 + 0.5 M NaCl. The superalloy sample was placed in the anode compartment, while a copper electrode served as the cathode.

The cell was connected to a regulated DC power source (VSA-5K, USSR) in series with a copper coulometer, which was used to determine the total electric charge (Q). The mass of the dissolved alloy was determined as the difference between the sample mass before and after dissolution, measured on analytical balances with an accuracy of four decimal places in grams.

The current density was calculated based on the exposed anode area and the measured current, which was recorded using a UNI-T UT60 (China) multimeter.

5. Results of anodic dissolution studies of the heat-resistant superalloy in a combined electrolyte

5. 1. Evaluation of the electrochemical characteristics of the alloy and overall dissolution efficiency

Fig. 2, 3 show the cyclic voltammetry results obtained for the superalloy in two electrolytes – 0.5 M NaCl + 0.5 M H_2SO_4 and 0.5 M NaCl + 0.5 M CH_3SO_3H.

In the electrolyte containing sulfuric acid, the anodic processes proceed more intensively, which is reflected by higher current densities compared to the methanesulfonic acid system. On the forward scan of the curve in the H_2SO_4-containing electrolyte, several distinct peaks appear (Fig. 2).

These peaks are likely associated with the oxidation of surface species that are progressively consumed during successive cycles, as their intensity decreases almost to zero. A similar trend is observed for the electrolyte containing methanesulfonic acid.

This behavior can be explained by the presence of oxide films or other adsorbed ions (or molecules) on the metal surface that undergo irreversible oxidation during anodic dissolution and are not reduced within the selected potential window [29].

Fig. 4 presents the integrated anodic sections of the cyclic voltammograms, illustrating the total charge associated with anodic processes. In the sulfuric acid electrolyte, the total anodic charge initially decreases and then stabilizes. In contrast, for the methanesulfonic acid electrolyte, the anodic charge gradually increases before reaching a steady-state level. The difference between the stabilized values for the two systems is approximately 23% higher for the methanesulfonic acid electrolyte compared to the sulfuric acid one.

It should be noted that CVA data reflect the total current, which includes both metal dissolution and parasitic reactions such as oxygen evolution and further oxidation of dissolved species. Therefore, the interpretation of CVA alone provides only partial insight into the anodic process.

For this reason, galvanostatic experiments were conducted to determine the actual mass losses of the superalloy at various current densities. These experiments allow for a more accurate evaluation of the anodic dissolution efficiency and the selectivity of individual component transfer into the electrolyte. The results of these experiments are presented in Fig. 5, 6.

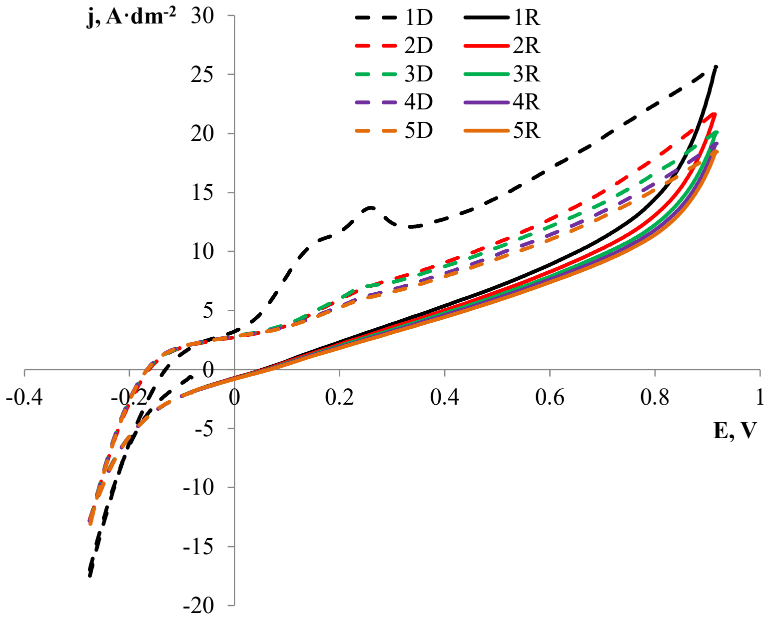

Fig. 2. Cyclic voltammogram of the superalloy obtained in a solution of 0.5 M NaCl + 0.5 M H_2SO_4, where *j* (A·dm^{-2}) is the current density and *E* (V) is the potential. The numbers on the curve indicate the cycle number, while the letters D and R denote the direct and reverse scan directions, respectively

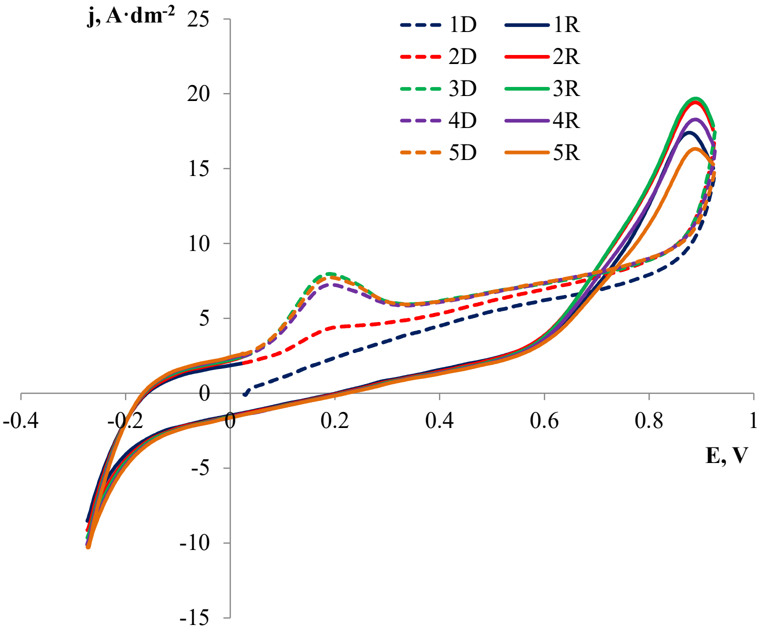

Fig. 3. Cyclic voltammogram of the superalloy obtained in a solution of 0.5 M NaCl + 0.5 M CH_3SO_3H, where *j* (A·dm^{-2}) represents current density and *E* (V) the potential. The numbers on the curve correspond to the cycle number, while the letters D and R indicate the direct and reverse scan directions, respectively

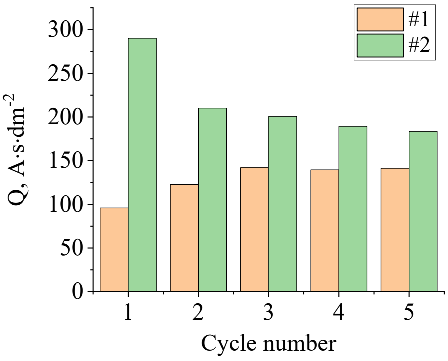

Fig. 4. Dynamics of changes in the specific electric charge (*Q*, A·s·dm^{-2}) over five cycles of the cyclic voltammogram corresponding to the anodic dissolution of the superalloy in the following electrolytes:
1 – 0.5 M NaCl + 0.5 M H_2SO_4;
2 – 0.5 M NaCl + 0.5 M CH_3SO_3H

Fig. 5 shows the specific dissolution rates (g/A·h), calculated from the measured mass losses and the total electric charge passed. At low current densities, the specific dissolution rates are relatively high, which can be attributed to a smaller fraction of side reactions. As the current density increases, the specific rates decrease and eventually reach a plateau. Comparison of the two electrolytes demonstrates that the dissolution intensity is higher in the medium containing methanesulfonic acid than in the system with sulfuric acid and NaCl.

Fig. 6 presents the absolute dissolution rates (g·dm^{-2}·h^{-1}). At low current densities, the dissolution rates for both electrolytes are similar. However, with increasing current density, dissolution in the methanesulfonic acid + NaCl electrolyte becomes more intense and exceeds the corresponding values for the sulfuric acid + NaCl system. Thus, within the current density range of approximately 1.5–3.5 A·dm^{-2}, the methanesulfonic acid with NaCl proves to be a more efficient electrolyte for the anodic dissolution of the investigated superalloy.

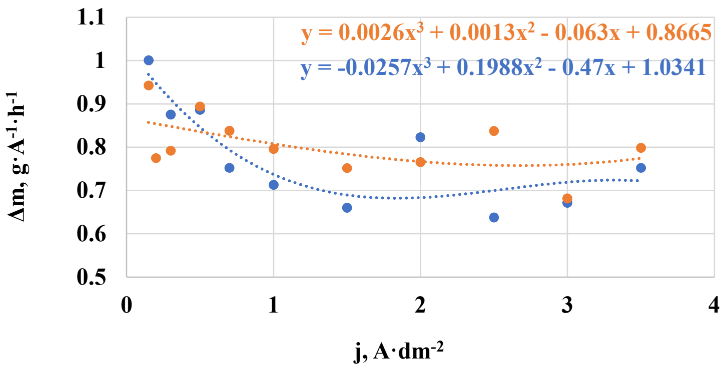

Fig. 5. Dependence of the specific mass loss of the alloy during dissolution (Δm, g·A^{-1}·h^{-1}) on the current density (*j*, A·dm^{-2}): blue line — solution 0.5 M NaCl + 0.5 M H_2SO_4; orange line — solution 0.5 M NaCl + 0.5 M CH_3SO_3H. Dashed lines represent the polynomial approximation curves, with colors corresponding to the respective electrolytes

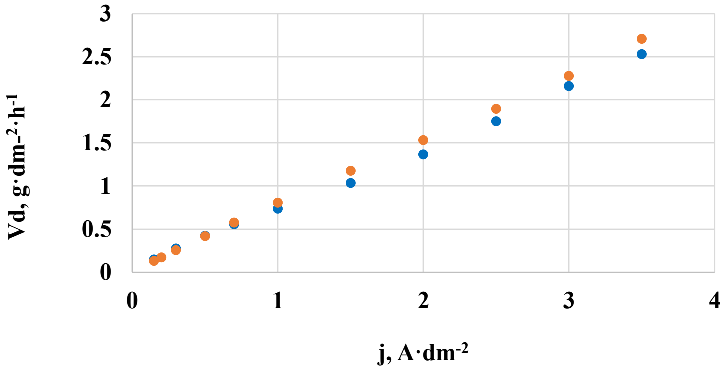

Fig. 6. Dependence of the specific dissolution rate of the alloy (*Vd*, g·dm^{-2}·h^{-1}) on the current density (*j*, A·dm^{-2}): blue line — solution 0.5 M NaCl + 0.5 M H_2SO_4; orange line — solution 0.5 M NaCl + 0.5 M CH_3SO_3H

5. 2. Identification of conditions for selective alloy dissolution

Analysis of the dissolved ion composition in the anolyte revealed several noteworthy observations.

Firstly, the ratio of Ni, Co, and Cr varies with current density in both electrolytes relative to the initial alloy composition (Table 1). This effect is especially pronounced for the methanesulfonic acid electrolyte at lower current densities. At higher current densities, within the range of 1.5–2.5 A·dm^{-2}, the anolyte composition for this electrolyte becomes the closest to that of the original alloy (Ni 60.7%, Cr 4.5%, Co 8.9%), with a significant amount of Re (4.69–12.29%) detected in solution. This regime could be useful when complete alloy dissolution is desired.

For example, at lower current densities (0.15–0.3 A·dm^{-2}), chromium dissolves much more readily than the other elements, indicating that the superalloy does not dissolve uniformly in this electrolyte and exhibits a certain degree of selectivity during anodic dissolution.

Secondly, in the electrolyte containing sulfuric acid, the relationship between the current density and the variation in the Ni-Co-Cr ratio is less pronounced and generally remains closer to the composition of the alloy. The largest deviation in metal ratios between the dissolved phase and the base alloy in the sulfuric acid electrolyte was observed at the lowest current density – 0.15 A·dm^{-2}.

Table 1

Elemental ratios in the anolyte, recalculated as percentages (%)

Composition	NaCl + CH_3SO_3H			NaCl + H_2SO_4		
j, A/dm^2	Ni	Cr	Co	Ni	Cr	Co
0.15	30.09	26.04	11.71	39.26	18.5	18.1
0.3	47.98	25.66	4.56	61.15	3.5	9.59
0.5	55.86	5.3	16.1	55.9	6.57	6.82
0.7	52.45	5.23	22.3	76.68	4.35	7.79
1	56.44	5.165	9.64	64.89	8.65	9.5
1.5	62.68	4.15	13.9	62.33	9.6	12.27
2	62.21	3.5	15.99	66.13	5.12	5.1
2.5	62	4.4	8.4	62.35	13.8	9.36
3	57.42	8.55	18.52	58.56	9.5	12.59
3.5	52.6	13.84	0.37	68.79	8.92	10.6

Thirdly, rhenium could not be detected in the electrolyte containing H_2SO_4, most likely due to its poor solubility in this medium.

6. Discussion of the conditions for processing the heat-resistant superalloy

The cyclic voltammetry results (Fig. 2, 3) demonstrated that in the H_2SO_4 + NaCl electrolyte, anodic processes proceed more intensively, which is reflected in higher current densities and the presence of pronounced peaks. However, it should be noted that CVA records the total current, which includes both metal dissolution and secondary processes – such as oxygen evolution and oxidation of already dissolved species.

The disappearance of peaks in subsequent cycles can be explained by the fact that the initial breakdown of the passive film is accompanied by its oxidation and transformation into a more inert layer that does not regenerate in later cycles. Another possible explanation is the presence of adsorbed ions or molecules that undergo irreversible oxidation. The higher currents observed in the sulfuric acid electrolyte are likely related to its better electrical conductivity and thus a more uniform current distribution across the microscopic surface irregularities of the metal [30].

The galvanostatic experiments (Fig. 4, 5) provided more reliable data on the actual mass loss of the superalloy during dissolution. The specific dissolution rates (g·dm^{-2}·h^{-1}) are highest at low current densities, after which they decrease and reach a plateau – a trend observed for both electrolytes, as shown by the fitted curves in Fig. 4. The obtained equations for the fitted dependencies are also indicated in the figure. This behavior in both systems is explained by an increased contribution of side reactions at higher current densities.

Comparison of the two systems showed that in the methanesulfonic acid medium, both the specific and absolute dissolution rates are higher than in the H_2SO_4 + NaCl electrolyte, especially within the 1.5–3.5 A·dm^{-2} range (Fig. 5).

At first glance, this result seems to contradict the CVA data, since sulfuric acid possesses higher conductivity and therefore lower ohmic losses. However, this can be explained by the higher solubility of methanesulfonate salts and the possible formation of more soluble complexes with Cr, Al, Nb, Ta, and Re. These effects can prevent the re-passivation of the surface and inhibit the precipitation of insoluble products on the anode.

This phenomenon is known as “salt passivation”, in which, at high current densities, the precipitation of poorly soluble metal salts partially or completely blocks the anodic surface. In contrast, in sulfuric acid media, the formation of less soluble sulfates promotes surface re-passivation at elevated current densities, which reduces mass transfer efficiency, even despite the better conductivity of the medium.

This explains why the absolute dissolution rates in CH_3SO_3H + NaCl are higher than in H_2SO_4 + NaCl.

Special attention should be given to the behavior of individual alloy components and how their dissolution ratios vary with current density. For CH_3SO_3H + NaCl, in the range of 1.5–2.5 A·dm^{-2}, the ratio of Ni, Cr, Co, W, and Re (62.68%, 4.15%, 13.9%, 4.82%, 12.29%) closely matches the original alloy composition (Ni 60.7%, Cr 4.5%, Co 8.9%, W 8.22%, Re 3.5%). This indicates relatively uniform dissolution without pronounced selectivity.

Meanwhile, in the H_2SO_4 + NaCl electrolyte, the solution composition was less reproducible, and rhenium was not detected at all, confirming that methanesulfonic acid creates conditions for effective Re dissolution into the electrolyte.

For the sulfuric acid solution, the Ni–Co–Cr ratio remained closer to that of the original alloy composition. Moreover, this ratio was less sensitive to variations in current density compared with the electrolyte containing methanesulfonic acid.

Thus, although sulfuric acid provides higher conductivity, methanesulfonic acid exhibits superior efficiency due to the higher solubility of its salts and a lower tendency toward passivation. This makes CH_3SO_3H + NaCl a more suitable electrolyte for the anodic dissolution of heat-resistant superalloys at the first stage of their recycling.

The developed electrolyte selection approach enables optimization of the initial stage of recycling processes for turbine high-temperature equipment waste, ensuring more efficient recovery of target components without the need for aggressive or toxic reagents.

The obtained results make it possible to flexibly control the process: methanesulfonic acid with sodium chloride can be used as an electrolyte when a high dissolution rate and efficient transition of rhenium into solution are desired. Conversely, if uniform dissolution of alloy components and the accumulation of rhenium in the undissolved residue are preferred, a sulfuric acid-based electrolyte should be applied. Both electrolytes, in contrast to those reported in [20, 21, 24], are relatively safe and do not generate toxic gaseous products during the first stage of processing.

The expected outcomes of implementing these findings include increased efficiency of electrochemical recovery of strategic metals, reduced energy and environmental costs compared with previously reported methods, and the establishment of a scientific foundation for developing industrial recycling technologies for spent superalloys.

Additionally, a comprehensive analysis of the electrolyte composition – for instance, using ion-selective electrodes for corresponding metal ions – would be highly valuable. Even more informative would be in operando surface analysis of the superalloy (e.g., ICP-MS, Raman spectroscopy, FTIR, or SEM with elemental mapping), which would logically extend the current research. Such investigations could provide insight into the need for regime adjustments, process dynamics, and thus facilitate control and optimization, possibly suggesting adaptive or dynamic dissolution modes.

It should also be noted that broadening the range of dissolution conditions could yield further valuable data. This could be achieved by increasing the electrolyte temperature, introducing gas bubbling, applying high-power ultrasound, or organizing intensive flow near the anode, among other techniques.

The future development of this study involves the construction of a mathematical model based on the obtained dependencies. Such a model could help elucidate the mechanism and details of the anodic dissolution process and additionally allow the prediction not only of effective dissolution behavior but also of the corrosion properties of the material.

7. Conclusions

1. Methanesulfonic acid with NaCl provides more efficient anodic dissolution of the superalloy than sulfuric acid with NaCl, despite its lower electrical conductivity. This can be explained by the higher solubility of methanesulfonate salts and the reduced tendency of the surface to salt passivation.

2. In the current density range of 1.5–2.5 A·dm^{-2} in 0.5 M CH_3SO_3H + 0.5 M NaCl, the composition of the anolyte is closest to that of the original alloy and contains significant amounts of rhenium, indicating uniform dissolution and creating favorable conditions for the further efficient recovery of strategically important components.

Conflict of interest

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

Financing

This study was carried out within the framework of R&D project No. NDDKR 0124U000611 (НДДКР 0124U000611).

Data availability

This manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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