

Study of dissolution of technogenic waste of heat-resistant nickel alloys in acid solutions

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Heat-resistant nickel alloys take the lead among other materials used in machinery, aircraft and other industries. The recycling of disused products consisting of heat-resistant alloys as well as grinding waste from their production is a relevant task, due to the high cost of the components contained in these alloys and the need to return them to production. In addition to nickel, the alloy contains such valuable elements as rhenium, tantalum, cobalt. The hydrometallurgical method of converting alloy components into a solution (usually with acid) followed by their separation allows to solve this problem but it is the acid digestion that constitutes the main problem of the processing. The paper studies the process of acid digestion of grinding waste heat resistant nickel alloy depending on the composition of the acid solution (H_2SO_4 , HCl , HNO_3 and their mixtures), temperature (in the range from room to boiling), the acid concentration (from 150 to 300 g/dm^3) and the ratio of solid to liquid phases. By mass spectrometry and X-ray fluorescence, sieve method, as well as by scanning electron microscopy, elemental, dispersive and morphological analysis of the waste powder was carried out, respectively. The composition of the solution and conditions of acid digestion of grinding waste with the highest degree of extraction of metals in the solution were determined: the treatment should be carried out in sulfuric acid solution with a concentration of 300 g/dm^3 at a temperature of 60–70 °C for 6 hours with solid-to-liquid ratio at 1 : 10. Preliminary heat treatment of the waste powder allows to reduce the amount of organic substances in the material by more than 3 times, thereby reducing the contamination of the solution. It was found that 95–99% of nickel is transferred into solution during the dissolution of the waste powder, and valuable rare-earth elements remain in the undissolved sediment, which is important for the technology of their further separation.

Key words: man-made waste, heat-resistant nickel alloys, grinding waste, chemical processing, acid digestion, leaching.

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Introduction

Heat-resistant materials are used in various industries: mechanical engineering, aircraft engineering, heat power engineering, etc. One of the leading places in this segment of industry is occupied by heat-resistant nickel alloys. To date, the world has accumulated a large number of end-of-life products consisting of them. The high cost of components contained in the alloys (rhenium, tantalum, nickel, cobalt, etc.) necessitates their return to the sphere of industrial production [1, 2].

Based on literature data, the main methods of processing waste heat-resistant nickel alloys are pyrometallurgical (roasting, sintering, oxidation), hydrometallurgical (leaching, electrolysis, liquid extraction, sorption, precipitation) and their combinations [3]. Pyrometallurgical methods are quite complicated, expensive to maintain, require large amounts of energy, and have significant losses of alloying elements. [4, 5]. The main hydrometallurgical methods include alkaline or acid leaching, often in the presence of an oxidizer [5–7], and electrochemical decomposition of scrap or lumpy waste [8–11].

There are two approaches to the processing of high-temperature alloys: one is the stage-by-stage extraction of alloy components in the electrolyte solution followed

by their extraction from the solution; the other involves the combined conversion of all valuable alloy components into the solution and their subsequent selective extraction as low-soluble compounds with pH adjustments of solutions followed by filtration, sorption or extraction. The second approach is the easiest to perform technologically.

Analysis of the literature on the processing of waste heat-resistant nickel alloys showed that the main problem is the disclosure of these wastes. Electrochemical methods of recycling such waste are the most promising because, given the right choice of electrolyzer and electrolyte design, they allow metals to be converted into a solution with sufficiently high technological indicators. However, it is advisable to use reagent dissolution for powder-type grinding waste, since the size of their fractions can have a positive effect on the kinetics of conversion of nickel, the base of the grinding waste, into solution.

Nickel is soluble under certain conditions in solutions of sulfuric, hydrochloric and nitric acids. Its dissolution rate regardless of the dissolution method (chemical or electrochemical) increases with solution temperature and acid concentration up to some values at which passivation is observed.

Due to the heterogeneity and differences in the chemical composition of waste heat-resistant alloys, the choice of methodology, conditions of their dissection and further separation of the main components is determined experimentally for a particular waste.

The purpose of this work was to study the chemical dissolution of a heat-resistant nickel alloy in acid solutions, as well as to select the process parameters at which the maximum yield of metals in the solution is observed.

Methodological part

The process of chemical dissolution of grinding waste of heat-resistant nickel alloy in the form of a powder was investigated in this work. Granulometric composition of the powder under study was determined by sieve analysis according to GOST 18318–94 “Metal powders. Determination of particle size by dry sieving”. Sieve analysis was performed by sieving the sample through a standard set of sieves and weighing the remaining material on each sieve. For sieving we used a set of sieves with the diameter of holes: 0.5; 0.2; 0.1; 0.063; 0.05 and 0.04 mm.

The mass fraction of the powder fraction was calculated as a percentage by the formula:

$$Q = \frac{\text{mass of residue on the sieve, g}}{\text{initial mass of powder, g}} \cdot 100\%$$

The morphology and dispersity of the powders were studied using a “JEOL JSM-6510” scanning electron microscope (Japan). Microphotographs of the sample surface were obtained at an accelerating voltage of 15 kV using a secondary electron detector.

The elemental composition of the samples was studied by X-ray fluorescence analysis on the Oxford Instruments INCA Energy analyzer, as well as by inductively coupled plasma mass spectrometry with microwave sample preparation in the “Multiwave Go Plus” system. The research was carried out using the equipment of the D. I. Mendeleev Center for Collective Use.

The waste was dissolved in acids (H_2SO_4 , HCl , HNO_3 and their mixtures) at a temperature of 20 to 105 °C with continuous stirring of the solution in a heat-resistant flask with a reflux condenser to prevent solution evaporation. The transfer of nickel ions into solution was monitored by titrimetric method using Trilon B, as well as by inductively coupled plasma mass spectrometry. Dissolution at 60–70 °C was carried out with intensive stirring on an orbital shaker, to put the grinding waste in a suspended state. Studies were performed at the following phase ratios — solid waste : acid solution ($S : L$) = 1 : 10, 2 : 10 and 3 : 10.

Determination of organic impurities (chemical oxygen demand — COD) in solutions after acid treatment of waste was carried out according to GOST 31859–2012 using photometry.

Results and discussion

The particle size distribution of the grinding waste based on the sieve analysis is shown in Fig. 1.

The data obtained show that the powder in its main mass consists of two fractions in the size range of 0.2–0.5 and 0.1–0.2 mm.

The morphology and dispersive composition of grinding waste obtained by scanning electron microscopy are shown in Fig. 2. From the obtained microphotographs it is clear that the studied powder is heterogeneous in disperse and morphological composition and contains mainly irregular-shaped particles sized in the range of 10–100 microns with a friable surface that is clearly visible with a magnification of the image at 5000 and 15000 times.

The results of elemental analysis of the samples obtained by the X-ray fluorescence method are presented in Table 1.

The data obtained show that the main element in the original sample is nickel, the following elements also prevail: chromium, tungsten, molybdenum. In addition, aluminum, titanium and cobalt are present in insignificant amounts.

Table 1
Elemental composition of the surface of the investigated grinding waste powder

Element	C	O	Al	Ti	Cr	Co	Ni	Mo	W
wt. %	14.92	12.5	2.33	2.88	14.57	1.15	36.74	5.13	9.78

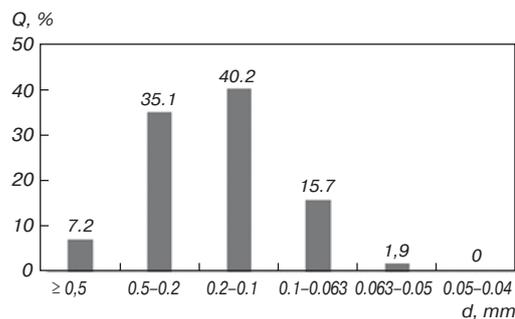


Fig. 1. Powder particle size distributions

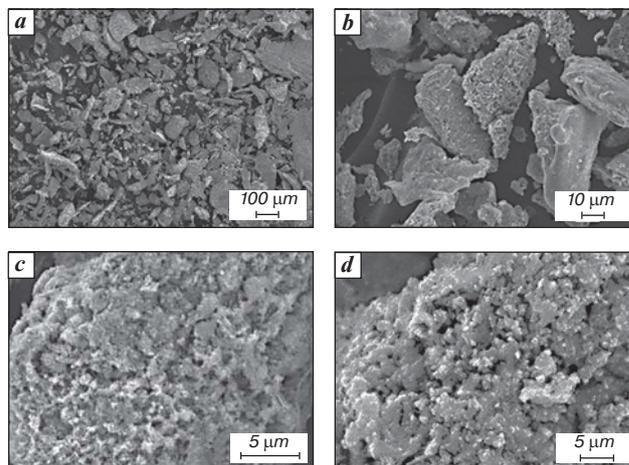


Fig. 2. Microphotographs of grinding waste powder at magnification: a – at 100 times; b – at 1000 times; c – at 5000 times (scale of 5 μm); d – at 15000 times (scale of 1 μm)

Carbon in the powder indicates the presence of carbides of these metals and organic impurities, the presence of oxygen is due to the presence of oxidized forms of metals. The method used is an evaluation method and allows to determine the elemental composition of individual areas of the sample surface, so for a more complete analysis of the powder we used the method of mass spectrometry with inductively coupled plasma with microwave sample preparation in the "Multiwave Go Plus" system.

The data obtained (Table 2) show that, in addition to the main elements (nickel, cobalt, chromium), the powder contains valuable rare-earth elements: rhenium, iridium, and vanadium.

According to the literature [12, 13], acid solutions with a concentration of 100–150 g/dm³ have been proposed for powder dissolution. However, studies have shown that with

Table 2
Metal content in the sample obtained by inductively coupled plasma mass spectrometry

Element	C, mg/kg	ΔC, mg/kg	ω, %
Ca	682.45	5.16	0.068
Co	68716	317	6.87
Cr	70421	407	7.04
Fe	6767	39	0.68
Ir	1977	11	0.19
Mg	35.54	0.59	0,0036
Mo	12665	94	1.27
Ni	501999	2657	50.2
Re	5934	12	0.59
Ru	844	26	0.084
S	< 900	0	0
Ti	15365	72	1.54
V	1364.7	9.7	0.14
W	420.6	6.8	0.042

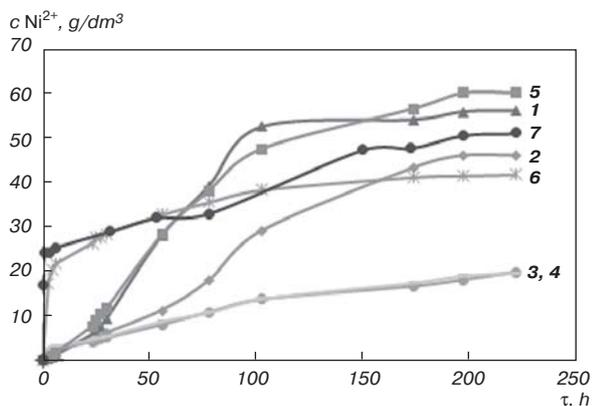


Fig. 3. Dependence of the concentration of nickel ions in the solution on the duration of acid treatment of the powder and the composition of the medium at room temperature ($t = 24\text{--}27\text{ }^{\circ}\text{C}$): 1 – 300 g/dm³ H₂SO₄; 2 – 300 g/dm³ HCl; 3 – 300 g/dm³ HNO₃; 4 – 300 g/dm³ H₂SO₄ + 15 g/dm³ HNO₃; 5 – 300 g/dm³ H₂SO₄ + 15 g/dm³ HCl; 6 – 300 g/dm³ HNO₃ + 15 g/dm³ HCl; 7 – 300 g/dm³ HCl + 15 g/dm³ HNO₃

a sulfuric acid concentration of 150 g/dm³, the concentration of nickel ions in the solution after 10 hours is 50 g/dm³, while increasing the concentration of sulfuric acid to 300 g/dm³ increases the concentration of nickel ions to 64 g/l. It should be noted that the complete transition of the basic elements in the solution does not occur, even when increasing the duration of treatment in a boiling solution up to 20 hours. Therefore, further studies were carried out in more concentrated acid solutions.

To study the chemical dissolution of the grinding powder, seven solutions were selected, including sulfuric, hydrochloric, nitric acid and their mixtures. Due to the fact that the base of the grinding waste is nickel, the control of its dissolution was analyzed by the concentration of nickel (II) ions in the solution. The data obtained by dissolving the powder at room temperature are shown in Fig. 3.

It was found that in solutions "6" and "7" containing nitric and hydrochloric acids, in the first hours of treatment the speed of the powder dissolution process is maximum. The mixture of hydrochloric and nitric acids used is a diluted solution of "aqua regia" whose high oxidizing power, according to the literature, is due to the release of chlorine and nitrosyl chloride as a result of reactions:



However, after 100 h, the rate slows down and the dissolution curve falls into a plateau, with the concentration of nickel in solution "6" not exceeding 42 g/dm³, and in solution "7" – 51 g/dm³. In solutions "3" and "4" containing nitric acid the dissolution process is extremely slow, which is probably due to passivation of the powder surface, as a result of which the dissolution of the base metal occurs through the pores of the passive film, the concentration of nickel in solution does not exceed 20 g/dm³ even after 220 hours of treatment. These compositions were not used in further studies.

The maximum concentration of nickel ions in the solution is observed after processing the metal powder in a solution of 300 g/dm³ H₂SO₄ and 15 g/dm³ HCl and is 60 g/dm³. A slightly reduced content of 56 g/dm³ of nickel ions was obtained in a solution of 300 g/dm³ H₂SO₄.

Process temperature is an important parameter to improve dissolution efficiency. On the one hand, increasing it positively contributes to increasing the recovery rate, but on the other hand, too much of it can lead to increased energy consumption. Experiments to find the optimal process temperature were carried out using a sulfuric acid solution with a concentration of 300 g/dm³, the results are shown in Fig. 4.

From the data obtained it is clear that when solutions are heated from room temperature to 60–70 °C for the first 6 hours the concentration of nickel in the solution increases from 2–3 g/dm³ to 30–50 g/dm³. From the data obtained it is clear that when solutions are heated from room temperature to 60–70 °C for the first 6 hours the

Table 3

Distribution of elements between solution and insoluble precipitate after acid treatment of grinding waste in H_2SO_4 with a concentration of 300 g/dm^3 at room temperature related to kg of waste after 96 h from the beginning of the process

Element	Ni	Cr	Co	Mo	Ti	W	Fe	Re	Ir	V	Ru	Ca	Mg
Solution g/kg	451	75.1	56.9	17.23	1.62	1.21	7.59	0.09	0	0	0	0	0
Precipitate g/kg	309.8	44.8	36.9	9.79	7.7	0.35	3.84	4.41	1.22	0.6	0.57	0.36	0.04

concentration of nickel in the solution increases from $2\text{--}3\text{ g/dm}^3$ to $30\text{--}50\text{ g/dm}^3$.

The elemental composition of the solution and undissolved sediment obtained by mass spectrometry is presented in **Table 3**.

It should be noted that after dissolution, valuable rare elements such as ruthenium, iridium, vanadium, most of the rhenium, as well as titanium remain in the sediment, which is important in separation technology.

Grinding waste always contains a coolant-cutting fluid (CCF), which includes an organic component that complicates the access of the reagent to digested components and if it is not fully removed, the increased content of residual carbon will significantly degrade the quality of the final product.

To remove the organic impurities initial powder was subjected to thermal treatment at $600\text{ }^\circ\text{C}$ during 2 hours. It is known from the literature that organic compounds contained in CCF, such as oleic acid, decompose at higher processing temperatures. However, calcining the grinding waste at higher temperatures will result in the formation of non-recoverable carbon. In work [14] it was noted that the use of hot sulfuric acid solves the problem of simultaneous removal of coolant and grinding waste stripping without the use of separate reagents and the formation of additional liquid waste.

Comparative studies were carried out to determine the chemical oxygen consumption (COD) in solutions after dissolution with sulfuric acid 300 g/dm^3 depending on the temperature: at room temperature and at boiling, as well as using a pre-treatment of the sample in order to remove organic impurities (**Table 4**).

From the data obtained it is clear that dissolving the powder by boiling in sulfuric acid does not affect the content of organic impurities in the sample, while heat treatment can reduce the amount of organic matter by more than 3 times. However, further dissolution of the heat-treated powder in 300 g/l sulfuric acid solution does not affect the degree of nickel extraction into the solution. The effect of $S:L$ ratio on the dissolution process of the heat-treated powder was investigated, the analysis was carried out for the main elements present in the powder (**Fig. 5**).

It is clear from the data obtained that an excess of acid and boiling of the solution results in dissolving a larger mass of the sample and, accordingly, releasing more metals into solution. Thus, it is possible to return filtrate for dissolution of a new batch of powder during control of acid content after separation of undissolved deposit.

Table 4

COD indicator in solutions after dissolution with $300\text{ g/l } H_2SO_4$

COD, g/l	Treatment in $300\text{ g/l } H_2SO_4$ solution		
	Initial powder		Heat-treated powder
	$t = 24\text{--}27\text{ }^\circ\text{C}$	$t = 100\text{--}102\text{ }^\circ\text{C}$	$t = 100\text{--}102\text{ }^\circ\text{C}$
	40	40	12

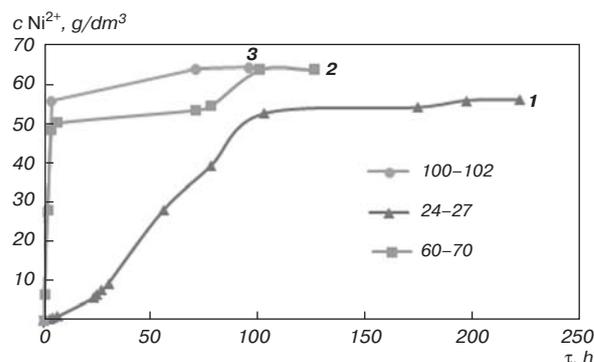


Fig. 4. Dependence of the concentration of nickel ions in the solution on the duration of acid treatment of the powder in H_2SO_4 medium with a concentration of 300 g/dm^3 and on the solution temperature: 1 – $24\text{--}27\text{ }^\circ\text{C}$; 2 – $60\text{--}70\text{ }^\circ\text{C}$; 3 – $100\text{--}102\text{ }^\circ\text{C}$

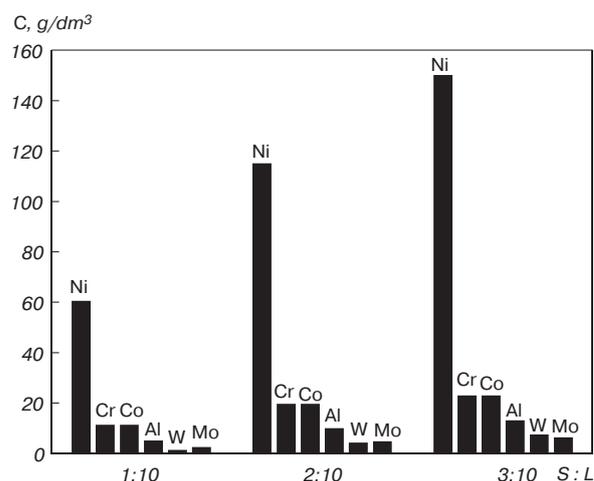


Fig. 5. Dependence of element concentration in $300\text{ g/l } H_2SO_4$ solution on the solid-to-liquid ratio during dissolution of heat-treated powder ($t = 100\text{--}102\text{ }^\circ\text{C}$)

Conclusion

In present work, the qualitative and quantitative composition and morphology of grinding waste heat-resistant nickel alloy of metallurgical production was determined, the optimal composition and concentration of the solution for its digestion was identified.

The maximum rate of the process in the first hours of treatment is observed in solutions containing nitric and

hydrochloric acids, due to their high oxidative capacity. However, these solutions are of the least practical interest in terms of their subsequent processing by reagent method and obtaining commercial products of the base metal (nickel), which will contain chloride ions that are difficult to separate.

Leaching should be carried out in sulfuric acid solution with a concentration of 300 g/dm^3 at a temperature of $60\text{--}70 \text{ }^\circ\text{C}$ and at a phase ratio of solid waste : acid solution ($S : L$) = 1 : 10.

It should be noted that when the waste is dissolved in a 300 g/dm^3 solution of sulfuric acid, valuable rare elements such as ruthenium, iridium, vanadium, most of the rhenium, and titanium remain in the undissolved precipitate, which is obviously important in the technology of element separation.

Increasing the temperature of the treated solution accelerates the dissolution process, as evidenced by the increase in the concentration of the base metal by more than 10 times from $2\text{--}3 \text{ g/dm}^3$ ($t = 24\text{--}27 \text{ }^\circ\text{C}$) to $30\text{--}50 \text{ g/dm}^3$ ($t = 60\text{--}70 \text{ }^\circ\text{C}$). However, as the temperature of the solution increases further to $100 \text{ }^\circ\text{C}$, the concentration of nickel ions in the solution increases by only 6 g/dm^3 during the first 4 hours from the start of the process. Thus, it is not advisable to conduct the process in a boiling solution, due to the increased energy consumption.

It was found that pretreatment of waste at $600 \text{ }^\circ\text{C}$ reduces its content of organic impurities by 3 times, which in turn reduces their concentration in the solution after acid treatment of powder. At the same time, it was found that preheating of the powder does not affect the degree of nickel extraction into the solution. As the mass of the dissolved powder increases in relation to the volume of the digestion solution, there is an increase in the concentration of major elements in the solution; however, only 85% of nickel passes into the solution when the waste powder is dissolved. In this case, the solution with a higher concentration of elements in the further processing is poorly filtered and crystallization of the saturated solution on the filter is observed. After separation of undissolved sludge with control of solution acidity it is possible to return filtrate for leaching.

Thus, the data obtained are of practical interest for industrial enterprises engaged in the production of metals and processing of man-made waste. The data obtained will intensify the process of waste acid digestion in the technology of its processing, which is an important economic component of the technological process of recycling.

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