ABSTRACT
of the thesis for the degree of Doctor of Philosophy (PhD)
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Behavior of components of heat-resisting alloys during electrochemical processing of secondary metal-containing raw materials

General description of work. The thesis is devoted to studying of process of anodic dissolution of spent heat-resisting nickel alloy GS32-VI and the behavior of the components of this alloy during electrochemical processing using acidic reagents.

Relevance of research. At present, one of the most important tasks of metallurgy, chemistry and chemical technology is the rational and effective use of secondary resources that are formed and accumulated in virtually all spheres of human activity. Among secondary resources, waste and scrap of rare and non-ferrous metals and alloys have long occupied a special place, the volume of which is constantly growing and is estimated at hundreds of thousands of tons per year. In addition, natural ore sources of metals are gradually being developed and processing of secondary raw materials is becoming increasingly in demand. The problems of rational and integrated use of secondary raw materials are becoming increasingly important in the overall balance of production of metals both in the world and in the Republic of Kazakhstan.

In recent years, due to the development of various fields of technology, heat-resisting alloys have been widely used as a special kind of structural materials, which do not lose their properties for a long time under conditions of high temperatures and complex stresses. At present such alloys are produced on aluminum, titanium, iron, copper, cobalt and nickel bases. Their diversity is associated with the application conditions and the operating temperature range.

Of particular importance are heat-resistant alloys on a nickel base that contain rare and scattered elements: rhenium, tungsten, molybdenum and tantalum, which are widely used in the aerospace industry, nuclear and heat power engineering, engineering and petrochemistry. They are used as a structural material for parts of internal combustion engines, steam and gas turbines, jet engines, nuclear power plants and so on.

Thus, the alloy GS32-VI, alloyed with rhenium, is serially manufactured in VIAM, including up to 100% waste, at a certified ARMAK production site equipped with modern automated melting, analytical and testing equipment, under the supervision of military acceptance. Due to the stability of the chemical composition, the purity of impurities, the quality of the surface of the preforms and the properties, the alloy GS32-VI fully corresponds to TU 1-92-177-91 and the level of the requirements of world standards. The alloy GS32-VI can be used as a freshly melted alloy at engine plants for the manufacture of turbine blades of GTE for various purposes.

It was found that rhenium most effectively increases the long-term strength of heat-resisting nickel alloys from all the alloying elements in the late 80-ies of the twentieth century.. And the heat resistant nickel alloys of the last generation, containing 5-9% Re, are able to maintain their performance at temperatures up to 1700-1800 °C.

Now in the world a large number of heat-resisting nickel alloys have accumulated, the service life of which has expired. The high cost of nickel refractory alloys containing expensive metals (rhenium, tantalum, cobalt, etc.) required solving the problem of rational and complex processing of these materials.

The most economically significant are waste of GS32heat-resisting nickel alloys, with thetypical composition,%: Ni~60, W, Co 5-10; Re, Ta 2-4; Nb 1.5-2; Mo, Cr, Al to 5. Based on the chemical composition of the alloy, it follows that the accumulated waste of such alloys must be processed with the extraction of non-ferrous and rare metals, with special attention paid to the recovery of elements: Re, Ta, Mo, W and Nb.

Existing technologies for processing waste heat-resisting nickel alloys can be divided into 4 groups:

- direct pyrometallurgical processing of wastes of heat-resisting alloys on a nickel base;
- Oxidation-thermal technologies (the basis is pyrometallurgical processing of raw materials with the purpose of transferring alloy components, including rhenium, into a water-soluble form with further separation of metals by hydrometallurgical methods);
- hydrochemical technologies (the basis is direct leaching);
- electrochemical technologies (basis - electrochemical oxidation and dissolution of alloy components, including rhenium).

From the list of the indicated areas of processing of wastes of nickel-containing alloys doped with rare and scattered elements, and in particular rhenium, electrochemical methods have been increasingly used in recent years.

Thus, the choice of the direction of research for this dissertation work is topical, and the results obtained in the course of the work are of scientific and practical importance, since they are devoted to the study of the behavior of the components of a heat-resistant alloy when it is anodically dissolved, which will allow the creation of a promising technology for processing heat-resisting nickel alloy waste.

The aim of the work is to study the behavior of the components of heat-resisting alloys and to study the composition of the products obtained during the electrochemical processing of heat-resistant alloys on a nickel basis.

The main research tasks:

- theoretical and thermodynamic justification of the possibility and prospects of electrochemical processing of heat-resisting alloys on a nickel basis;
- choice of methods for research and analysis of products;
- study of the influence of technological factors on the process of electrochemical processing of heat-resisting alloys;

- identification of the behavior of the components of heat-resisting alloys during their electrochemical processing;

- study of the physicochemical properties of products of electrochemical processing;

- development of technology for processing secondary heat-resisting alloys based on electrochemical processes.

Scientific novelty of the results: the possibility of obtaining an electrolytic nickel-containing powder of the predicted composition and dispersion is established based on the choice of the anodic dissolution regime, the nature of the electrolyte, and the use of an organic surface-active polarizing compound, sulfosalicylic acid, as an additive to an electrolyte promoting the formation of a plurality of crystallization centers and so the greatest increase in the dispersion of the resulting powder, which is related to the property of the sulfosalicylic acid screen surface of formed crystal and cause the need for new crystallization centers.

The following research results were obtained:

- the behavior of the components of a heat-resisting alloy is shown depending on the regimes and the choice of the nature of the electrolyte: in the anode slurry, mainly rare and rare-earth elements are concentrated, and nickel, cobalt, rhenium and aluminum are distributed between the electrolyte and the cathode deposit;

- the possibility of obtaining cathode deposits of various qualitiesis established, depending on the choice of the anode dissolution regime and the nature of the electrolyte:

a) fromsulphate electrolyte - a nickel-containing powder with a nickel content of about 95%;

b) from a nitric acid electrolyte, a nickel-containing powder of Ni: Re: Co: Al = 3: 1: 1: 1 and Ni: Re: Co: Al = 10: 1: 1: 1;

c) from hydrochloric acid electrolyte - nickel-containing powder of composition Ni: Co: Al = 4: 1: 1;

- Based on the performed galvanostatic studies, it is established that the composition of the resulting cathode deposit can be varied during the anodic dissolution of the heat-resistant nickel-containing alloy in the nitrate electrolyte;

- the effect of sulfosalicylic acid on the dispersion of the resulting nickel-containing powder was established, in particular, its addition to the electrolyte in an amount of 10 g/l increases the yield of the fine powder fraction (less than 0.1 μm) to 99.5-99.7%.

The objects of research are samples of the heat-resisting nickel alloy GS32-VI and the products of electrochemical processing of this alloy: electrolytes, cathodicdeposits and anode sludge. The alloy GS32-VI is a bright representative of the group of heat-resisting nickel alloys, since it contains practically all the alloying elements that make up other alloys, in addition, rhenium is included in its composition, the extraction of which is interesting for scientists at the Zhezkazgan University.

The subject of the study is the anodic dissolution of the heat-resistant nickel alloy GS32-VI, the cathodic deposition of metals forming part of the

electrolyte produced, as well as the composition and some physicochemical properties of the resulting products of electrochemical processing.

Methods of research and analysis:

- Calculation of the thermodynamic characteristics (isobaric-isothermal potential and equilibrium constant) of possible chemical dissolution reactions of the components of the GS32-VI alloy in mineral acid solutions was carried out using the program of thermodynamic calculations of HSC Chemistry 5.11 of Outokumpu Technology Engineering Research;
- Potentiodynamic studies of the electrochemical dissolution of the alloy GS32-VI were carried out using the PCI4/750/ZRA potentiostat in the potentiodynamic mode with coverage of the anode and cathode potential regions (from minus 2 to 3 V) with the automatic current detection setting;
- electrochemical dissolution was carried out using the electrochemical technological complex EHK-1012 (developed by Tetran LLC) using an uncompensated method for measuring the potential;
- Elemental analysis was carried out using an ICP mass spectrometer for isotope and elemental analysis of ELAN DRC-e (PerkinElmer, Canada);
- particle size determination by dynamic light scattering measurement was carried out on a submicron particle size analyzer and the Delsa ™ Nano zeta potential, PN A54412AA;
- X-ray powder studies - on a Shimadzu XDR 6000 diffractometer (CuKα radiation, sample rotation, continuous (1 de/min), stepwise (step 0.02 °, exposure 10 s) modes in the angle range 2Θ10-90.

Practical significance of the work is the creation of an electrochemical technology for the processing of heat-resisting nickel alloy GS32-VI waste to produce nickel-cobalt powder doped with rhenium, which can be used to produce a number of composite materials with improved physical and mechanical properties

Provisions to be defended:

- results of thermodynamic analysis of the probability of electrochemical processing of heat-resistant alloys on a nickel base;
- justification of the choice of the object of research, reagents, methods of research and analysis of the products obtained;
- results of studying the influence of technological factors on the process of electrochemical processing of selected heat-resisting alloys;
- experimental substantiation of the behavior of components of heat-resisting alloys during their electrochemical processing;
- results of studying the physical and chemical properties of products of electrochemical processing;
- results of balance experiments on electrochemical processing of secondary heat-resistant alloys on the basis of electrochemical processes.

The work was carried out at the department "Metallurgical processes, heat engineering and technology of special materials "KazNRTUn.a. K.I. Satpayev and at the “K.A. Bolshakov Department of Chemistry and Technology of Rare and Scattered Elements” of Moscow Technological University (Moscow, Russian Federation).

Personal contribution of the author: the author plays a decisive role in setting research tasks, performing experimental works, processing data and generalizing the results obtained.

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Approbation of the work: The main provisions of the thesis were reported and discussed at four international conferences, including the XIV International Congress "Machines, Technologies, Materials" (Bulgaria, 2017), X CIS Congress of mineral processing engineers(RF, 2015), VIII All-Russian (with international participation) scientific conference "Modern methods in theoretical and experimental electrochemistry" (RF, 2016) and International Satpaev Readings "Competitiveness of Engineering Science and Education" (RK, 2016).

Publications: Based on the results of the work, 9 scientific papers have been published, including 4 reports at conferences, 1 article in the journal cited in Scopus database, 3 articles in journals recommended by Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan.

The structure and scope of the thesis. The thesis includes the following elements: "Normative references", "Designations and abbreviations", "Introduction", a review on the problems of processing of heat-resisting nickel alloys, the experimental part of 5 parts, "Conclusion", references and appendixes.

The first chapter of the thesis is devoted to the analysis of the current state of the process of electrochemical processing of heat-resisting alloys on a nickel basis.

The second chapter describes the methods of research and analysis, the starting materials and reagents, instruments and equipment used in the performance of the thesis. X-ray phase and element analysis of the alloy chosen as the object of the studies was performed. It is shown that the main components of the initial heat-resisting alloy are nickel, cobalt, tungsten, aluminum, chromium, rhenium, niobium and tantalum, which are present in the alloy both in the form of metals and in the form of intermetallic compounds. It is shown that in addition to the crystalline component, amorphous is present in the alloy, the origin of which directly depends on the conditions of storage and operation of the alloy.

The third chapter is devoted to the thermodynamic analysis of possible reactions, systems and processes in the electrochemical processing of heat-resistant alloys on a nickel basis. It is shown that nickel, cobalt, aluminum, chromium, rhenium and, possibly, tungsten can pass into the aqueous solution; rare and rare-earth elements (except rhenium) basically either form insoluble compounds with acids, or remain unchanged.

The fourth chapter is devoted to the selection of the initial conditions for studying the electrochemical process of processing the heat-resisting alloy GS32-VI. Based on potentiodynamic studies, it is concluded that the polarizability of electrodes is affected by both the nature and concentration of acids in the

electrolyte. The results of the same search for electrochemical dissolution of the alloy GS32-VI at the choice of electrolyte showed the efficiency of using as electrolyte solutions of nitric acid.

The fifth and sixth chapters are the main sections devoted to a detailed study of the process of electrochemical processing of the heat-resisting nickel alloy GS32-VI. The distribution of metals by products formed during electrochemical processing is shown. The compositions of the products obtained are established, in particular, during electrochemical processing, a nickel-containing powder with a nickel content of about 95% is precipitated from the electrolyte sulphate on the cathode, nickel-containing powder of Ni: Re: Co: Al = 3: 1: 1: 1 and Ni : Re: Co: Al = 10: 1: 1: 1, from hydrochloric acid electrolyte is a nickel-containing powder of the composition Ni: Co: Al = 4: 1: 1. A special place in the work was occupied by the studies devoted to the electrochemical dissolution of the alloy GS32-VI by acid electrolytes, which included organic acids, which are inherently polarizing agents. The result of the research was the recommendation of the use of sulfosalicylic acid, the presence of which in the electrolyte causes an improvement in technological parameters and an increase in the dispersity of the resulting nickel-containing powder.