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Selection of Elements at the Dissolution of Heat Resistant Nickel Alloys in Mineral Acid Solutions

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Abstract

Thermodynamic modeling of the interaction of a heat-resistant nickel alloy containing refractory rare metals with hydrochloric, sulfuric and nitric acids with a temperature change in the range of 20-100 ° C and a concentration of 50 to 150 g / dm^3 at a pressure of 1 atm was carried out. The thermodynamic assessment data were confirmed in experiments on the anodic dissolution of the alloy in sulfate solutions. According to the results of x-ray phase analysis of the sludge, it was revealed that tungsten in the form of a solid solution in nickel passes to this product. Also, tantalum and niobium pass into the slurry in the form of oxides. Mostly, Re, Co, Cr passed into the electrolyte solution. The results of the study can serve as a scientific basis for the development of promising technologies for processing metal waste from heat-resistant alloys.

Keywords: thermodynamic modeling, heat resistant nickel alloy, rare elements, mineral acids, dissolution.

Rare metals to a large extent determine the development of such important areas as electrical vacuum technology, semiconductor electronics, nuclear energy, aircraft and rocket science, as well as the production of special steels, heat-resistant and anti-corrosion alloys. Among the most demanded are rare refractory transition metals, which form alloys with intermetallic compounds and solid solutions, characterized by a high intermolecular bonding of atoms in crystals. High rates of development of the above branches of technology determine a continuously growing demand for rare metals, which provides for further expansion of their output. The solution to this problem can be implemented by maximizing the use of recycled materials, which will significantly reduce the deficit of rare metals in the Russian market. Of the most significant types of secondary raw materials, it should be noted metal waste (for example, from nickel alloys used for the manufacture of gas turbine engine blades) containing W, Nb, Ta, Re. One of the promising directions in the technology for processing such waste is processes based on electrochemical approaches [1], which allow the separation of metals.

Metal selection using the electrolysis method allows the processing of wastes for multicomponent metal alloys with high strength. With the successful selection of the electrolyte, temperature, mixing conditions and electrical parameters, the electrochemical dissolution of the alloys allows the transfer of valuable rare and non-ferrous metals from waste to solution and sludge with the prospect of further processing of these products [1–4]. The relatively low productivity of the method in this case does not matter because of the relatively small volume of waste.

In this work, we performed thermodynamic modeling of the interaction of mineral acids used in electrochemical processes with a nickel alloy containing, by weight. %: 5.0 Cr, 9.3 Co, 1.1 Mo, 8.5 W, 6.0 Al, 4.0 Ta, 1.6 Nb, 4.0 Re, 57.4 Ni.

Modeling was performed to qualitatively evaluate the interaction of the alloy with solutions of sulfuric, hydrochloric and nitric acids using the HSC Chemistry 8 software package [5], its work is based on the principle of minimizing the free energy of the entire system. Previously, this approach was successfully tested in the study of phase formation for the interaction of aluminum with multicomponent oxide systems [6, 7]. Calculations were performed for a temperature range of 20–100 ° C and a pressure of 1 atm for alloys weighing 40 g. The acid concentration in solutions with a volume of 200 cm^3 was varied from 50 to 150 g / dm^3.

As can be seen from Figure 1, when dissolving the alloy in a solution of sulfuric acid with a concentration of 50 g / dm^3, mainly metallic nickel will go into the solid phase (sludge). With an increase in temperature of more than 60 ° C, there is a sharp decrease in the number of complex and simple oxide compounds of cobalt, tungsten and chromium passing into the sludge. The concentration of Ta_2O_5 and Nb_2O_5 practically does not change with temperature. With an increase in the H_2SO_4 concentration to 100 and 150 g / dm^3, a transition of nickel in the solution is observed and, correspondingly, a decrease in its amount in the sludge, the identified trends in the transition to the sludge of other elements are generally preserved.

The data of thermodynamic modeling were confirmed in experiments on the anodic dissolution of the alloy in sulfate solutions [8, 9]. According to the results of X-ray phase analysis of the sludge, it was revealed (Figure 2) that the highest intensity of the diffraction pattern peaks corresponded to a solid solution of tungsten in nickel. Tantalum oxide phases have also been detected.

The use of hydrochloric acid with a concentration of 50 g / dm^3 as an electrolyte showed that here into the sludge mostly transition nickel as a pure metal or Ni_4W compound, the concentration of oxides Ta_2O_5, Nb_2O_5, MoO_2, and WO_2 practically does not change with temperature. With an increase in temperature of more than 60 ° C, there is a sharp decrease in the amount of the complex oxide compound $CoO*Cr_2O_3$ passing into the sludge and an increase in the amount of chromium (III) oxide. When using hydrochloric acid with a concentration of 100 and 150 g / dm^3, the amount of nickel

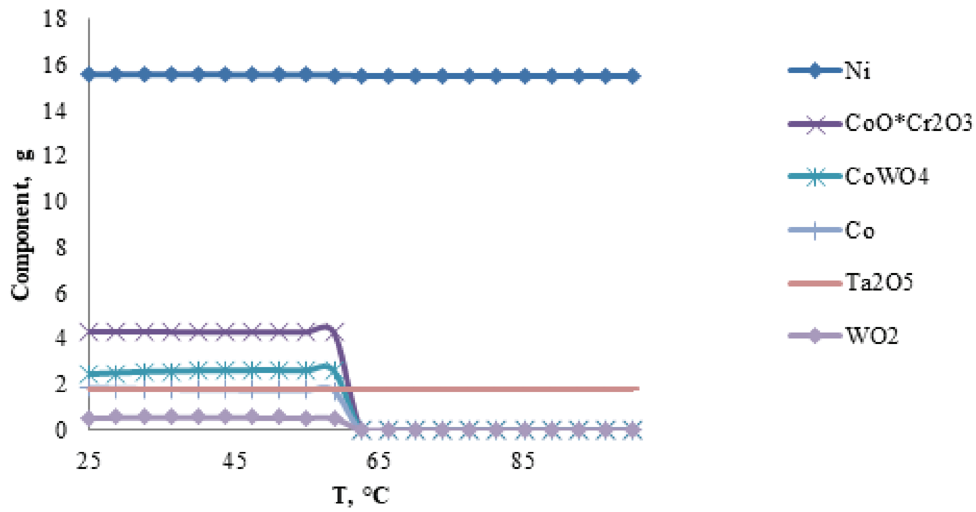

Figure 1: The effect of temperature on the transition to the sludge of components during the dissolution of a nickel alloy in a solution of sulfuric acid with a concentration of 50 g / dm^3

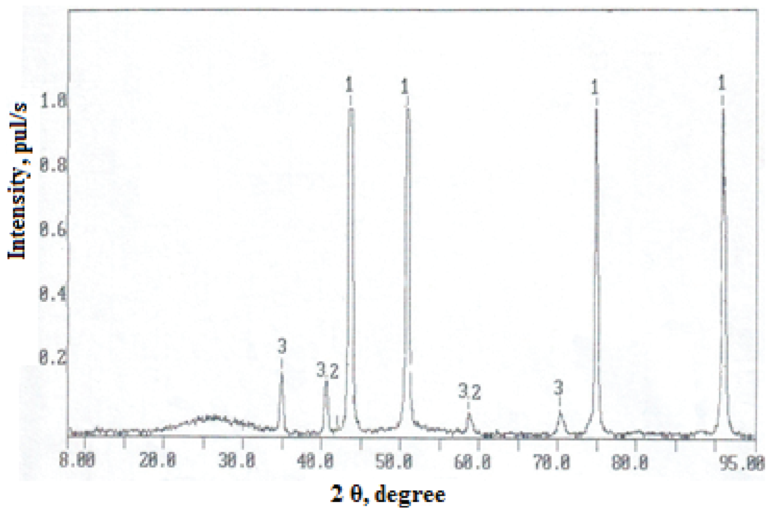

Figure 2: The results of x-ray phase analysis of sludge: 1 – $Ni_{0.92}W_{0.08}$, 2 – Mo, 3 – TaO

released into the solid phase is significantly reduced. The sludge content of Ni_4W is still high and does not change. For other elements with an increase in the HCl concentration to 100 and 150 g / dm^3, no changes in their behavior were noticed.

When an aqueous solution of nitric acid with a concentration of 50 g / dm^3 is used as an electrolyte (Figure 4), the content in the sludge of complex oxides of cobalt, tungsten, aluminum, and chromium sharply decreases with an increase in temperature over 60 ° C. The same trend is observed for the oxide compound $NiMoO_4$. The amounts of Ta_2O_5 and Nb_2O_5 do not change with temperature. With an increase in the concentration of HNO_3 to 150 g / dm^3, nickel passes into the solid phase both in the form of $NiMoO_4$and $NiO*WO_3$. Cobalt to a greater extent passes into solution.

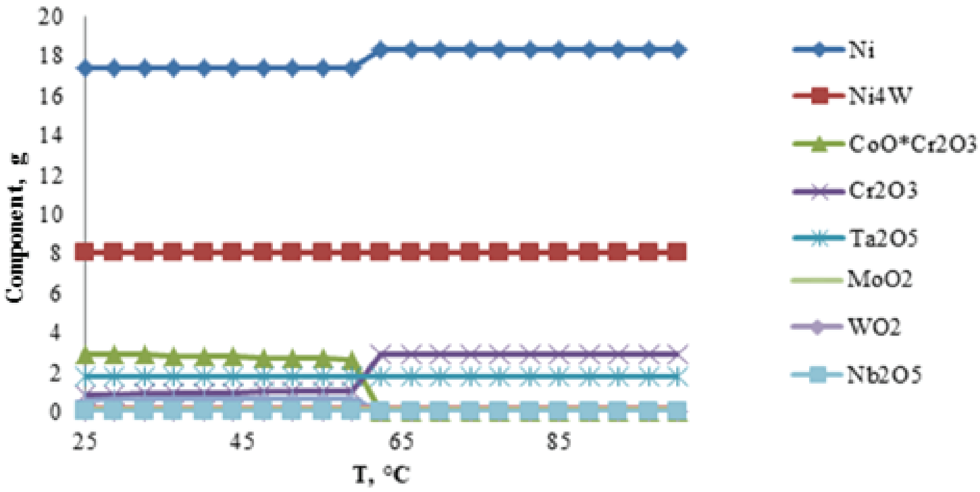

Figure 3: The temperature effect on the transition of components to the sludge during dissolution of a nickel alloy in a solution of hydrochloric acid with a concentration of 50 g / dm^3

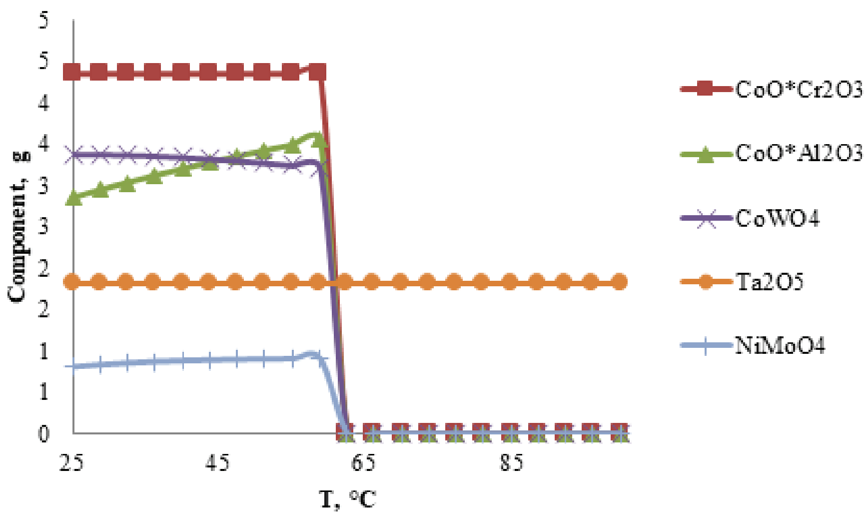

Figure 4: The temperature effect on the transition of components to the sludge during the dissolution of a nickel alloy in a solution of nitric acid with a concentration of 50 g / dm^3

Thus, thermodynamic modeling has shown that when dissolving a heat-resistant nickel alloy in solutions of mineral acids, refractory rare elements pass mainly to the sludge in oxide form. Nickel passes into the sludge both in the form of a metal and of the Ni_4W compound, which is more resistant to acids. An increase in temperature over 60 ° C and acid concentration from 50 to 150 g / dm^3 does not affect the predominant distribution of tantalum and niobium pentoxides into the sludge and facilitates the transition to the non-ferrous metal solution.

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