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**THERMODYNAMIC EVALUATION OF PROBABILITY
OF DISSOLUTION OF SECONDARY HEAT-RESISTANT
NICKEL-CONTAINING ALLOY GS32-VI
BY MINERAL ACIDS SOLUTIONS**

Abstract. The thermodynamic probability of the transition of the components of the heat-resisting nickel-containing alloy GS32-VI to the aqueous phase under the influence of solutions of hydrochloric, sulfuric and nitric acids is considered in the article. Chemical composition of the alloy GS32-VI, wt. %: Ni - 60,05; Co - 9,3; W - 8,6; Al - 6,0; Cr - 5,0; Re - 4,0; Ta - 4,0; Y - 0,005; Nb - 1,6; Mo - 1,1; C - 0,16; B - 0,15; Ce - 0,025; La - 0,005. The main crystalline phases of the alloy are the compounds $AlNi_3$, $Cr_{0,4}Ni_{0,6}$, $Co_{0,9}W_{0,1}$, $Cr_4Ni_{1,5}W$, $(Al_{0,7}Cr_{0,3})Ni_3$ and C_5Nb_6 , that has been revealed by the means of X-ray phase analysis. The thermodynamic probability of dissolution of GS32-VI alloy components was estimated on values of isobaric and isothermal potential of probable reactions of interaction of the main components and phases with solutions of the specified mineral acids. On the basis of the thermodynamic analysis it is established that the possibility of transition to solution of some main components of alloy depending on type of mineral acid decreases in ranks:

– for nickel, cobalt, aluminum and rhenium: $HNO_3 > H_2SO_4 > HCl$;– for chrome: $H_2SO_4 > HCl > HNO_3$.

It is shown that nickel, cobalt, aluminum, rhenium and chromium can have the greatest probability of transition into the aqueous phase in the acidic pH region. At the same time, niobium, tungsten, tantalum and molybdenum will most likely remain in the cake as insoluble compounds in aqueous solutions.

Keywords: dissolution, heat-resisting nickel-containing alloy, hydrochloric acid, sulfuric acid, nitric acid, thermodynamics, isobaric and isothermal coefficient, equilibrium constant.

Introduction. Heat resisting nickel-containing alloys are used in many branches of the national economy, their main part is applied in aircraft industry, elements of the equipment of combined heat and power plant and thermal power plant. Their basic purpose is working under loading at high temperatures. Now a significant amount of such fulfilled alloys has collected, and need for their processing has ripened. Especially as a significant amount not only non-ferrous metals, but rare and rare-earth elements which need to be returned in production is their part [1, 2].

Hydrometallurgical and electrochemical methods of processing of such alloys with usage of mineral acids solutions [3-5] are considered as perspective methods. These methods, especially electrochemical, allow not only to take and transfer valuable components to solution but to receive almost ready-made products in the form of powders of individual metals and their mixes that makes hydrometallurgical and electrochemical methods of processing of the fulfilled alloys even more attractive [6-8].

The relevance of hydrometallurgical and electrochemical processing of heat-resistant alloys is also contained in the fact that it is possible to separate the elements and obtain concentrates of rare and rare-earth metals that cannot be done by pyrometallurgical processing [9, 10].

To substantiate the probability of dissolution of the secondary heat-resistant nickel-containing alloy GS32-VI with solutions of mineral acids, a thermodynamic analysis of possible dissolution reactions of the components and compounds included in this alloy was considered.

Methods of research and thermodynamic calculations. The object of the research was the heat-resistant nickel-containing alloy GS32-VI the elemental analysis of which was carried out using an ICP mass spectrometer for isotope and elemental analysis of ELAN DRC-e (Perkin Elmer, Canada). The alloy had the following composition, wt. %: Ni - 60.05; Co - 9.3; W = 8.6; Al is 6.0; Cr is 5.0; Re - 4.0; Ta - 4.0; Y = 0.005; Nb = 1.6; Mo - 1.1; C = 0.16; B - 0.15; Ce - 0.025; La is 0.005. That is, the main components of the alloy GS32-VI are nickel, cobalt, tungsten, aluminum, chromium, rhenium, niobium and tantalum.

The phase analysis of alloy was made with use of the Shimadzu XDR 6000 diffractometer (radiation $\text{CuK}\alpha$, rotation of a sample, continuous (1 deg/min.), stepwise (a step 0,02 °, an exposure 10 s) the modes in the range of corners 2Θ 10-90. The phase analysis has shown that the main crystal phases of nickel-containing GS32-VI alloy besides metals (nickel, cobalt, aluminum and chrome) are the compounds AlNi_3 , $\text{Cr}_{0,4}\text{Ni}_{0,6}$, $\text{Co}_{0,9}\text{W}_{0,1}$, $\text{Cr}_4\text{Ni}_{15}\text{W}$, $(\text{Al}_{0,7}\text{Cr}_{0,3})$ of Ni_3 and C_5Nb_6 (figure 1, table 1).

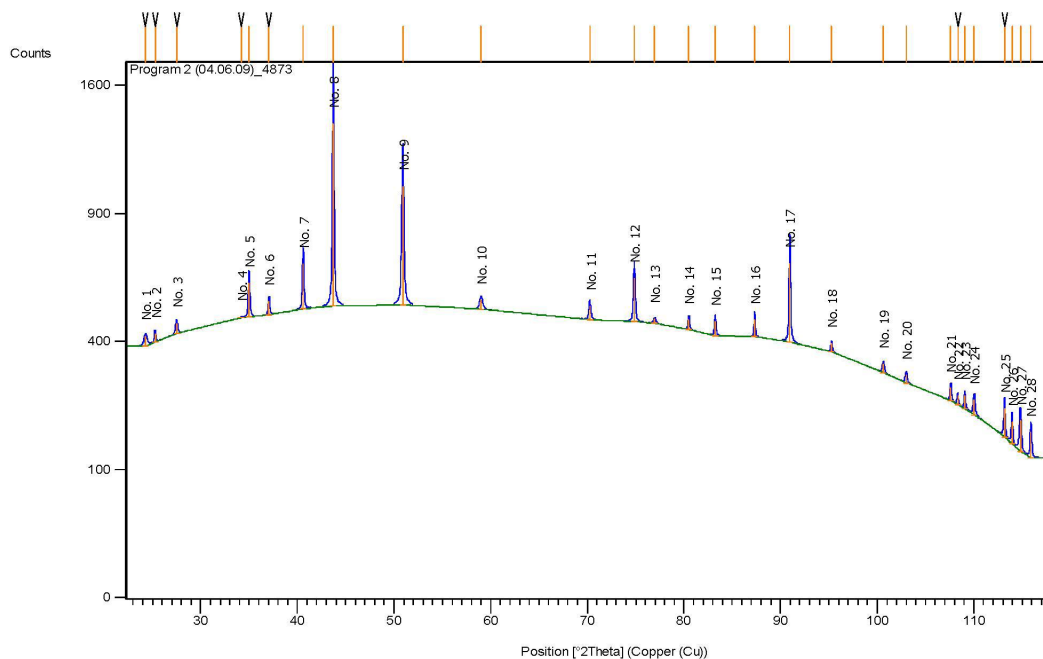


Figure 1 – X-ray diffraction pattern of the nickel-containing alloy GS32-VI

To substantiate the choice of reagents for chemical and electrochemical dissolution of the chosen heat resisting alloy it is necessary to make the thermodynamic analysis of process of conversion in solution of the color, rare and rare-earth elements which are a part of GS32-VI alloy.

Calculation of thermodynamic characteristics (isobaric and isothermal potential and equilibrium constant) of possible reactions of chemical dissolution of components of GS32-VI alloy in solutions of mineral acids was carried out by means of the program of thermodynamic calculations HSC Chemistry 5.11 of the Outokumpu Technology Engineering Research company.

Along with the calculations of Gibbs energy and the equilibrium constant, the possible state of nickel and cobalt, the main components of the alloy, on contact with mineral acids at a temperature of 25 ° C was analyzed, starting from the thermodynamic calculations of the Pourbaix diagrams constructed using the same program.

Thermodynamics of chemical dissolution of components of nickel-containing alloy GS32-VI in solutions of mineral acids. Thermodynamic analysis of possible reactions of dissolution of the main components of the alloy GS32-VI in solutions of mineral acids is carried out for two temperatures of 20

Table 1 – Phase composition of the nickel-containing alloy ZhS32-VI using the Shimadzu XDR 6000 diffractometer database

| Phase | Reference code of the card | Latin name of phase | Chemical formula | Correspondence to the peaks on the roentgenogram | Content, wt. % |
|-------|----------------------------|---------------------------|---|--|----------------|
| 1 | 03-065-1160 | Niobium Carbide | C ₅ Nb ₆ | 5, 7, 9-13,15-21, 23, 24, 26-28 | 7 |
| 2 | 03-065-9928 | Cobalt Tungsten | Co _{0,9} W _{0,1} | 9, 12, 17 | 17 |
| 3 | 01-072-2720 | Aluminum Nickel | AlNi ₃ | 8, 9, 12, 17, 21 | 14 |
| 4 | 03-065-8387 | Rhenium Tungsten | W ₁₃ Re ₇ | 7, 10, 28 | 1 |
| 5 | 01-089-2120 | Niobium Carbide | Nb ₄ C ₃ | 5, 7, 10, 11, 13, 14 | 3 |
| 6 | 01-071-3771 | Molybdenum | Mo | 7, 16, 28 | 1 |
| 7 | 01-071-7326 | Cobalt Molybdenum | (Co _{0,08} Mo _{0,92}) | 7, 10 | 2 |
| 8 | 03-065-5108 | Chromium Nickel Tungsten | Cr ₄ Ni ₁₅ W | 8, 9, 12, 17 | 12 |
| 9 | 01-072-3080 | Rhenium Tungsten | (Re _{0,35} W _{0,65}) | 7, 10, 28 | 1 |
| 10 | 01-071-7596 | Chromium Nickel | (Cr _{0,4} Ni _{0,6}) | 8, 9, 12, 17 | 25 |
| 11 | 01-071-5711 | Aluminum Chromium Nickel | (Al _{0,7} Cr _{0,3})Ni ₃ | 8, 9, 14, 21 | 13 |
| 12 | 01-089-7251 | Chromium Tantalum Carbide | Cr _{0,1} Ta _{0,9} C | 5, 7, 10, 11 | 2 |

Note. The peaks of X-ray diffraction patterns No. 1-4, 6, 22, 25 were not identified.

Table 2 – Thermodynamic analysis of possible dissolution reactions of the main components of GS32-VI alloy with solutions of sulfuric acid

| Reaction | ΔG^0 , KJ / mol | | $\lg K_p$ | |
|---|-------------------------|-----------|-----------|---------|
| | 20°C | 60°C | 20°C | 60°C |
| 1 Ni + H ₂ SO ₄ = NiSO ₄ + H ₂ ↑ | -72,190 | -73,927 | 12,864 | 11,592 |
| 2 Ni ₃ Al + 4,5H ₂ SO ₄ + 2,25O ₂ ↑ = 3NiSO ₄ + 0,5Al ₂ (SO ₄) ₃ + 4,5H ₂ O | -1402,929 | -1409,306 | 249,834 | 220,836 |
| 3 Al + 1,5H ₂ SO ₄ = Al ₂ (SO ₄) ₃ + 1,5H ₂ ↑ | -514,646 | -516,615 | 91,709 | 81,007 |
| 4 Co + H ₂ SO ₄ = CoSO ₄ + H ₂ ↑ | -92,183 | -94,565 | 16,427 | 14,828 |
| 5 Co + H ₂ SO ₄ + 0,5O ₂ = CoSO ₄ + H ₂ O | -275,207 | -277,375 | 49,009 | 43,464 |
| 6 Co + H ₂ SO ₄ = CoO↓ + H ₂ O + SO ₂ ↑ | -5,480 | -19,121 | 0,976 | 2,996 |
| 7 Cr + 1,5H ₂ SO ₄ = Cr ₂ (SO ₄) ₃ + 1,5H ₂ ↑ | -253,917 | -256,485 | 45,248 | 40,218 |

and 60 °C. To perform a comparison of the energy indices of chemical reactions, calculations are made for 1 mole of the soluble component. The most technological acid is sulfuric acid, so the thermodynamic calculations of the dissolution of the alloy GS32-VI with the participation of sulfuric acid were performed in the first place. The results of thermodynamic calculations are presented in Table 2.

As follows from Table 2, the dissolution of the intermetallic compound Ni₃Al is the most probable, and its dissolution will be more active in the presence of an oxidizer, which was conventionally taken as oxygen. It is also probable that reactions 3, 5 and 7 will occur. Less possibly – 1 and 4. Reaction 6 is the least probable at dissolution of nickel-containing GS32-VI alloy solutions of sulfuric acid. Based on the above analysis and the composition of the GS32-VI alloy, it can be concluded that all the components listed in Table 2 will pass into the solution upon contact with sulfuric acid.

There is information about the dissolution of nickel-containing alloys with solutions of hydrochloric and nitric acids [3-5]. Table 3 presents the thermodynamic analysis of possible dissolution reactions of the main components of the alloy GS32-VI in hydrochloric and nitric acids.

Thus, the greatest likelihood of dissolution in hydrochloric and nitric acids is observed for the intermetallic compound Ni₃Al, which increases when the oxidant is added to the system. If we compare the effect of all acids, the thermodynamic probability of the reaction of dissolving Ni₃Al in nitric acid is higher than in hydrochloric and sulfuric. At the same time, comparing the values of Gibbs energy for

Table 3 – Thermodynamic analysis of possible dissolution reactions of the main components of GS32-VI alloy with solutions of hydrochloric and nitric acids

| Reaction | | ΔG^0 , KJ / mol | | $\lg K_p$ | |
|----------------------------------|---|-------------------------|-----------|-----------|---------|
| | | 20°C | 60°C | 20°C | 60°C |
| Dissolution in hydrochloric acid | | | | | |
| 1 | $\text{Ni} + 2\text{HCl} = \text{NiCl}_2 + \text{H}_2\uparrow$ | -45,825 | -44,630 | 8,166 | 6,998 |
| 2 | $\text{Ni}_3\text{Al} + 9\text{HCl} = 3\text{NiCl}_2 + \text{AlCl}_3 + 4,5\text{H}_2\uparrow$ | -473,810 | -481,330 | 84,432 | 72,652 |
| 3 | $\text{Ni}_3\text{Al} + 9\text{HCl} + 2,25\text{O}_2 = 3\text{NiCl}_2 + \text{AlCl}_3 + 4,5\text{H}_2\text{O}$ | -1143,67 | -1131,83 | 203,665 | 177,357 |
| 4 | $\text{Co} + 2\text{HCl} = \text{CoCl}_2 + \text{H}_2\uparrow$ | 61,773 | 62,310 | -11,080 | -9,770 |
| 5 | $\text{Co} + 3\text{HCl} = \text{CoCl}_3 + 1,5\text{H}_2\uparrow$ | 132,930 | 138,655 | -23,689 | -21,742 |
| 6 | $\text{Al} + 3\text{HCl} = \text{AlCl}_3 + 1,5\text{H}_2\uparrow$ | -488,330 | -481,280 | 73,520 | 75,466 |
| 7 | $\text{Cr} + 2\text{HCl} = \text{CrCl}_2 + \text{H}_2\uparrow$ | -164,900 | -165,098 | 29,385 | 25,888 |
| 8 | $\text{Cr} + 3\text{HCl} = \text{CrCl}_3 + 1,5\text{H}_2\uparrow$ | -207,155 | -201,039 | 36,915 | 31,535 |
| 9 | $\text{Cr} + \text{HCl} + \text{H}_2\text{O} = 0,5\text{H}_2\text{CrO}_4 + 0,5\text{CrCl}_2 + 2\text{H}_2\uparrow$ | 64,137 | 59,332 | -11,429 | -9,304 |
| Dissolution in nitric acid | | | | | |
| 10 | $\text{Ni} + 2,4\text{HNO}_3 = \text{Ni}(\text{NO}_3)_2 + 0,2\text{N}_2\uparrow + 1,2\text{H}_2\text{O}$ | -313,954 | -310,019 | 55,946 | 48,612 |
| 11 | $\text{Ni} + 2,5\text{HNO}_3 = \text{Ni}(\text{NO}_3)_2 + 0,25\text{N}_2\text{O}\uparrow + 1,25\text{H}_2\text{O}$ | -291,784 | -288,026 | 51,995 | 45,163 |
| 12 | $\text{Ni} + 2\text{HNO}_3 + 0,5\text{O}_2 = \text{Ni}(\text{NO}_3)_2 + \text{H}_2\text{O}$ | -283,784 | -276,118 | 50,750 | 43,296 |
| 13 | $\text{Ni}_3\text{Al} + 9\text{HNO}_3 + 2,25\text{O}_2 = 3\text{Ni}(\text{NO}_3)_2 + \text{Al}(\text{NO}_3)_3 + \text{H}_2\text{O}$ | -1544,620 | -1550,026 | 275,250 | 235,993 |
| 14 | $\text{Co} + 2,5\text{HNO}_3 = \text{Co}(\text{NO}_3)_2 + 0,25\text{N}_2\text{O}\uparrow + 1,25\text{H}_2\text{O}$ | -293,851 | -289,789 | 52,364 | 45,440 |
| 15 | $\text{Co} + 2\text{HNO}_3 + 0,5\text{O}_2 = \text{Co}(\text{NO}_3)_2 + \text{H}_2\text{O}$ | -176,300 | -169,290 | 31,396 | 26,528 |
| 16 | $\text{Al} + 3,6\text{HNO}_3 = \text{Al}(\text{NO}_3)_3 + 0,3\text{N}_2\uparrow + 1,8\text{H}_2\text{O}$ | -958,387 | -945,912 | 170,784 | 148,322 |
| 17 | $\text{Cr} + 6\text{HNO}_3 = \text{CrO}_3\downarrow + 6\text{NO}_2\uparrow + 3\text{H}_2\text{O}$ | -410,456 | -440,432 | 73,143 | 69,061 |
| 18 | $\text{Cr} + 4\text{HNO}_3 = \text{CrO}_2\downarrow + 4\text{NO}_2\uparrow + 2\text{H}_2\text{O}$ | -468,826 | -488,911 | 83,544 | 76,663 |

nickel and cobalt, it should be said that the probability of dissolution of these metals in nitric acid is much higher than in hydrochloric and sulfuric. The behavior of chromium in solutions of these acids is special. In nitric acid, in addition to soluble chromium (III) nitrate, which is formed in dilute nitric acid solutions [11], chromium (II) and (III) oxides are formed, which can inhibit the dissolution of the alloy. In hydrochloric and sulfuric acids, chromium forms soluble salts with acids, and the thermodynamic probability of chromium dissolution with the formation of chromium (II) sulfate in the solution of sulfuric acid is somewhat higher than the formation of chromium (II) chloride. Concentrated sulfuric and nitric acids passivate chromium [12].

In addition to the behavior of the main components of the GS32-VI alloy with dissolution by mineral acids, the possibility of transferring rare and rare-earth elements to the aqueous phase is considered: tungsten (8.6 wt%), Rhenium (4.0 wt%), Tantalum (4.0 wt%), niobium (1.6 wt%), molybdenum (1.1 wt%).

The results of the thermodynamic analysis of possible reactions of mineral acids with rare and rare-earth elements that are part of GS32-VI alloy are given in Table 4.

From the results of the thermodynamic analysis given in Table 4, it follows that rhenium (in solutions of sulfuric and nitric acids) and tungsten (in solutions of sulfuric and hydrochloric acids) can be detected in aqueous solution in dissolved form (in the form of mono- and dibasic acids). Some experimental data indicate that in hydrochloric and sulfuric acid solutions hexavalent molybdenum is in the form of polymerized cations [12]. Tantalum and niobium do not pass into an aqueous solution when dissolved with acids under any conditions [11]. Along with soluble compounds, mineral acids can form a number of insoluble compounds with rare and rare-earth elements, some of which are presented in Table 4.

If we analyze the Gibbs energy values for the dissolution processes in mineral acids of each component separately, we can easily find the following decrease in the thermodynamic probability of formation of water-soluble compounds in the series:

- for nickel, cobalt, aluminum and rhenium: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$;

- for chromium $-\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$.

Table 4 – Thermodynamic analysis of possible reactions of solutions of mineral acids with rare and rare-earth elements that make up the alloy GS32-VI

| Reaction | | $\Delta G^0, \Delta G^0, \text{KJ}$ | | $\lg K_p$ | |
|-------------------|---|-------------------------------------|----------|-----------|---------|
| | | 20°C | 60°C | 20°C | 60°C |
| Sulfuric acid | | | | | |
| 1 | $W + H_2SO_4 + 1,5O_2 = WO_3\downarrow + SO_3\uparrow + H_2O$ | -628,070 | -630,530 | 111,848 | 98,803 |
| 2 | $W + H_2SO_4 = H_2WO_4 + S\downarrow$ | -172,440 | -173,420 | 30,708 | 27,175 |
| 3 | $Mo + 2H_2SO_4 = MoO_2\downarrow + 2SO_2\uparrow + 2H_2O$ | -116,183 | -142,278 | 20,704 | 22,310 |
| 4 | $Mo + 3H_2SO_4 = MoO_3\downarrow + 3SO_2\uparrow + 3H_2O$ | -41,450 | -81,510 | 7,382 | 12,773 |
| Hydrochloric acid | | | | | |
| 5 | $W + 3HCl = WCl_3\downarrow + 1,5H_2\uparrow$ | 154,241 | 147,617 | -27,486 | -23,147 |
| 6 | $W + 2HCl + 2O_2 = H_2WO_4 + Cl_2\uparrow$ | -656,18 | -644,48 | 116,851 | 100,989 |
| 7 | $Re + 4/3HCl + 8/3H_2O = 2/3HReO_4 + 3H_2\uparrow + 1/3ReCl_4\downarrow$ | 289,205 | 277,206 | -51,536 | -65,200 |
| 8 | $Re + HCl + 2O_2 = HReO_4 + 0,5Cl_2\uparrow$ | -564,820 | -557,280 | 100,583 | 87,325 |
| 9 | $Ta + 3HCl = TaCl_3\downarrow + 1,5H_2\uparrow$ | -92,688 | -99,134 | 16,517 | 15,545 |
| 10 | $Ta + 5HCl = TaCl_5\downarrow + 2,5H_2\uparrow$ | -89,063 | -99,479 | 15,871 | 15,599 |
| 11 | $Nb + 3HCl = NbCl_3\downarrow + 1,5H_2\uparrow$ | -120,466 | -126,822 | 21,467 | 19,886 |
| 12 | $Nb + 4HCl = NbCl_4\downarrow + 2H_2\uparrow$ | -76,677 | -88,152 | 14,198 | 13,822 |
| 13 | $NbC_{0,83} + 4HCl + 1,83O_2 = NbCl_4\downarrow + 2H_2O + 0,83CO_2\uparrow$ | -761,520 | -757,470 | 135,612 | 118,694 |
| 14 | $Mo + 2HCl = MoCl_2\downarrow + H_2\uparrow$ | 19,624 | 15,688 | -3,497 | -2,460 |
| 15 | $Mo + HCl + H_2O = 0,5MoCl_2\downarrow + 0,5MoO_2\downarrow + 1,5H_2\uparrow$ | -19,441 | -24,140 | 3,465 | 3,785 |
| Nitric acid | | | | | |
| 16 | $W + 4/3HNO_3 = WO_2\downarrow + 4/3NO\uparrow + 2/3H_2O$ | -467,086 | -472,561 | 83,234 | 74,099 |
| 17 | $Re + HNO_3 + O_2 = HReO_4 + NO\uparrow$ | -496,540 | -497,550 | 88,424 | 77,965 |
| 18 | $Re + 7/3HNO_3 = HReO_4 + 7/3NO\uparrow + 2/3H_2O$ | -420,228 | -431,785 | 74,884 | 67,705 |
| 19 | $Ta + 5HNO_3 = 0,5Ta_2O_5\downarrow + 5NO_2\uparrow + 2,5H_2O$ | -881,197 | -906,025 | 157,028 | 142,068 |
| 20 | $Nb + 5HNO_3 = 0,5Nb_2O_5\downarrow + 5NO_2\uparrow + 2,5H_2O$ | -807,329 | -832,272 | 143,865 | 130,503 |
| 21 | $NbC_{0,83} + HNO_3 + 1,83O_2\uparrow = HNbO_3\downarrow + NO_2\uparrow + 0,83CO_2\uparrow$ | -993,850 | -988,660 | 176,983 | 154,921 |
| 22 | $NbC_{0,75} + HNO_3 + 1,75O_2\uparrow = HNbO_3\downarrow + NO_2\uparrow + 0,75CO_2\uparrow$ | -958,410 | -953,030 | 170,674 | 149,339 |

Analysis of the Pourbaix diagrams constructed for the main components of the alloy GS32-VI. In this paper, an analysis of the Pourbaix diagram at 25 °C is given only for nickel and cobalt, the content of which in the alloy is 60.05 and 9.3 wt. %, respectively (Figures 2 and 3). The diagrams of the state of nickel and cobalt in aqueous solutions in the presence of chlorine, sulfur and nitrogen in the system are constructed for clarity by imposing individual phase diagrams. Since the article considers the possibility of dissolution of a nickel-containing alloy by acid solutions, we were interested in the acidic pH range of the combined diagram.

On the combined diagram of the state of nickel (Figure 2), the same regions of existence for all types of acids are observed only for the following nickel forms: NiO^*OH , Ni , $NiH_{0,68}$.

In the presence of hydrochloric acid, along with the nickel Ni^{2+} ion in the acidic pH range, undissociated nickel chloride- $NiCl^2$ is stable. These water-soluble forms are stable up to $pH = 5$. In the presence of sulfuric acid there is a wide range of existence of the four-water nickel sulfate crystal hydrate, which extends up to $pH = 9$. The presence of nitric acid in the aqueous solution expands the region of existence of the Ni^{2+} nickel cation by the values of the oxidation potential. It should be noted that the water-soluble forms of nickel are stable only in the region of oxidation potentials and the pH of the aqueous phase is less than 5.

As can be seen from the combined diagram of the cobalt state (Figure 3), the same regions of existence for all types of acids are characteristic only of $Co(OH)_3$ and metallic Co . All other areas have features depending on the type of acid. In the solution of hydrochloric acid, the presence of the $CoCl^+$ ion

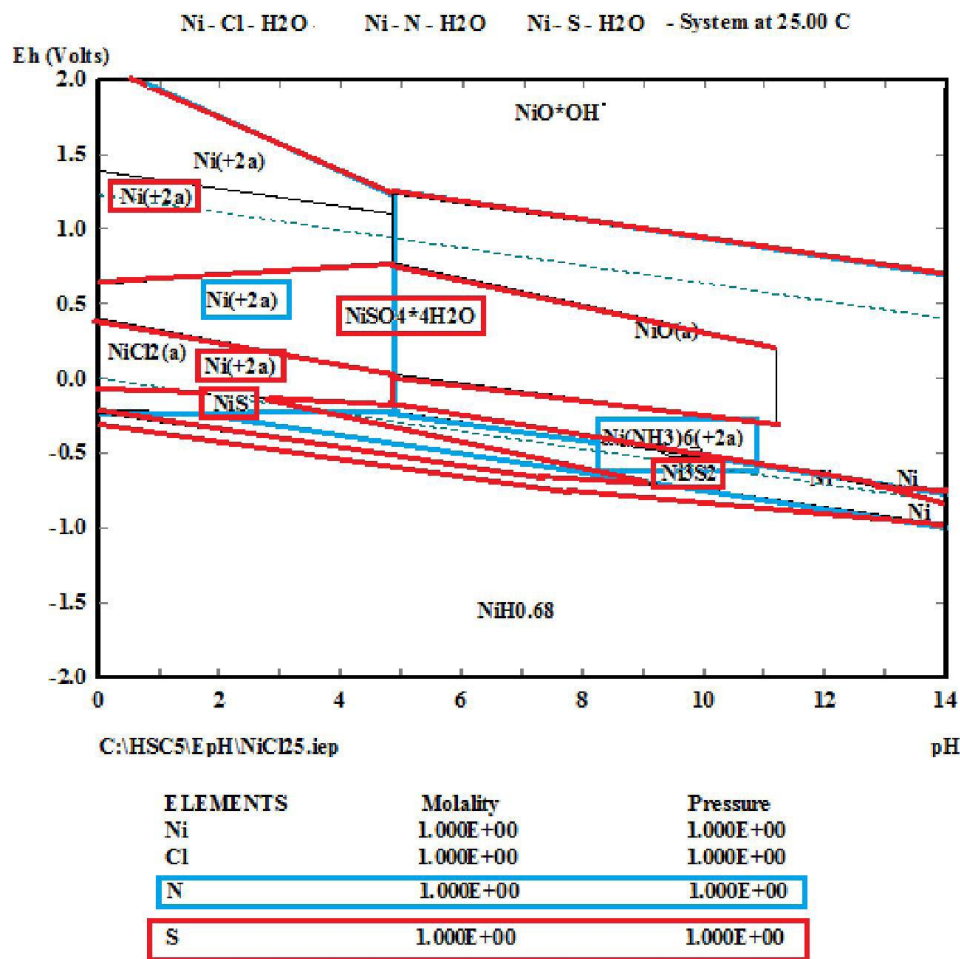


Figure 2 –
Combined diagram
of Ni-Cl-N-S-H₂O nickel state
in aqueous solutions

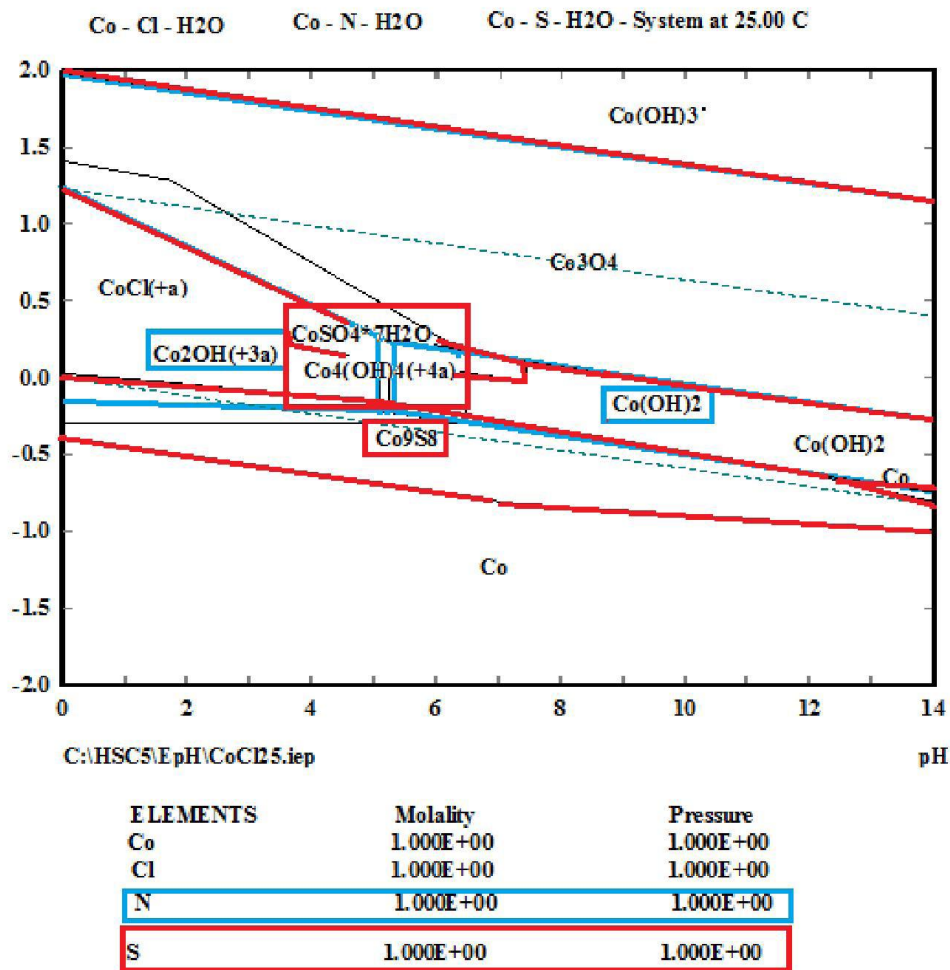


Figure 3 –
Combined diagram
of the Co-Cl-N-S-H₂O cobalt state
in aqueous solutions

should be predicted, whose existence range extends up to pH = 7. In the presence of nitric acid, up to pH = 5, the formation of a complex cobalt ion $[\text{Co}_2\text{OH}]^{3+}$ is possible, which then passes into the $[\text{Co}_4(\text{OH})_4]^{4+}$. The presence of sulfuric acid in the aqueous solution, like that of nitric acid, leads to the formation of $[\text{Co}_2\text{OH}]^{3+}$, which then, depending on the potential in the system, can either go to the $[\text{Co}_4(\text{OH})_4]^{4+}$ state, or to the seven-hydrate sulphatecobalt crystal hydrate. Thus, the presence of acids in the aqueous solution promotes the conversion of cobalt into water-soluble forms.

Conclusions:

- thermodynamic analysis of possible dissolution reactions of nickel-containing alloy GS32-VI with solutions of mineral acids showed that the following components will pass into the aqueous solution: nickel, cobalt, aluminum, chromium, rhenium and, possibly, tungsten;

- rare and rare-earth elements (except rhenium) basically either form insoluble compounds with acids, or remain unchanged;

- a decrease in the thermodynamic probability of formation of water-soluble compounds in the series was established: for nickel, cobalt, aluminum and rhenium: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$; for chromium - $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$;

- analysis of the state of nickel and cobalt in aqueous solutions showed that the main amount of water-soluble compounds of these metals is stable in the acidic pH range.

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ТЕРМОДИНАМИЧЕСКАЯ ОЦЕНКА ВЕРОЯТНОСТИ РАСТВОРЕНИЯ ВТОРИЧНОГО ЖАРОПРОЧНОГО НИКЕЛЬСОДЕРЖАЩЕГО СПЛАВА ЖС32-ВИ РАСТВОРАМИ МИНЕРАЛЬНЫХ КИСЛОТ

Аннотация. Рассмотрена термодинамическая вероятность перехода компонентов жаропрочного никельсодержащего сплава ЖС32-ВИ в водную фазу при воздействии на сплав растворов соляной, серной и азотной кислот. Химический состав сплава ЖС32-ВИ, масс. %: Ni - 60,05; Co - 9,3; W - 8,6; Al - 6,0; Cr - 5,0; Re - 4,0; Ta - 4,0; Y - 0,005; Nb - 1,6; Mo - 1,1; C - 0,16; B - 0,15; Ce - 0,025; La - 0,005. Основными кристал-

лическими фазами сплава являются соединения AlNi_3 , $\text{Cr}_{0,4}\text{Ni}_{0,6}$, $\text{Co}_{0,9}\text{W}_{0,1}$, $\text{Cr}_4\text{Ni}_{1,5}\text{W}$, $(\text{Al}_{0,7}\text{Cr}_{0,3})\text{Ni}_3$ и C_5Nb_6 , что было выявлено с помощью рентгенофазового анализа. Термодинамическая вероятность растворения компонентов сплава ЖС32-ВИ оценивалась по значениям изобарно-изотермического потенциала вероятных реакций взаимодействия основных компонентов и фаз с растворами указанных минеральных кислот. На основании термодинамического анализа установлено, что возможность перехода в раствор некоторых основных компонентов сплава в зависимости от типа минеральной кислоты уменьшается в рядах:

- для никеля, кобальта, алюминия и рения: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$;
- для хрома: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$.

Показано, что наибольшую вероятность перехода в водную фазу в кислой области pH могут иметь никель, кобальт, алюминий, рений и хром. В то же время ниобий, вольфрам, тантал и молибден, скорее всего, будут оставаться в кеке в виде нерастворимых в водных растворах соединений.

Ключевые слова: растворение, жаропрочный никельсодержащий сплав, соляная кислота, серная кислота, азотная кислота, термодинамика, изобарно-изотермический коэффициент, константа равновесия.

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МИНЕРАЛДЫ ҚЫШҚЫЛДАР ЕРІТІНДІЛЕРІМЕН ЖС32-ВИ НИКЕЛЬҚҰРАМДЫ ҚАЙТАЛАМА ҚЫЗУҒА БЕРІК ҚОРЫТПАСЫ ЕРУ ЫҚТИМАЛДЫЛЫҒЫНЫҢ ТЕРМОДИНАМИКАЛЫҚ БАҒАСЫ

Аннотация. Мақалада ЖС32-ВИ никельқұрамды қызуға берік қорытпаға тұз, күкірт және азот қышқылдары ерітінділерінің әсері кезінде қорытпа компоненттерінің сулы фазаға өтуінің термодинамикалық мүмкіншілігі қарастырылған. ЖС32-ВИ қорытпасының химиялық құрамы, масс. %: Ni - 60,05; Co - 9,3; W - 8,6; Al - 6,0; Cr - 5,0; Re - 4,0; Ta - 4,0; Y - 0,005; Nb - 1,6; Mo - 1,1; C - 0,16; B - 0,15; Se - 0,025; La - 0,005. Қорытпаның негізгі кристалдық фазалары, рентгенофазалық талдау көмегімен анықталған AlNi_3 , $\text{Cr}_{0,4}\text{Ni}_{0,6}$, $\text{Co}_{0,9}\text{W}_{0,1}$, $\text{Cr}_4\text{Ni}_{1,5}\text{W}$, $(\text{Al}_{0,7}\text{Cr}_{0,3})\text{Ni}_3$ және C_5Nb_6 қосылыстары болып табылады. ЖС32-ВИ қорытпа компоненттерінің еру термодинамикалық ықтималдылығы негізгі компоненттер мен фазалардың көрсетілген минералды қышқылдар ерітінділерімен ықтималды өзара әрекеттесу реакциялардың изобарлы-изотермиялық потенциалдар мәні бойынша бағаланған. Термодинамикалық талдау негізінде ерітіндіге қорытпаның кейбір негізгі компоненттерінің өту мүмкіншілігі минералды қышқыл түріне байланысты кемітіні анықталған:

- никель, кобальт, алюминий мен рений үшін: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$;
- хром үшін: $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$.

pH қышқыл облысында никель, кобальт, алюминий, рений мен хром сулы фазаға өту ықтималдылығы жоғары екендігі көрсетілген. Сол мезетте ниобий, вольфрам, тантал және молибден кекте сулы ерітінділерде ерімейтін қосылыстар түрінде қалады.

Түйін сөздер: еру, никельқұрамды қызуға берік қорытпа, тұз қышқылы, күкірт қышқылы, азот қышқылы, термодинамика, изобарлы-изотермиялық коэффициент, тепе-теңдік константасы.

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