UDC 544.654.2:(669.74+669.719+669.78+669.77) Complex Use of Mineral Resources № 4. 2017.

S. K. KILIBAYEVA, Zh. E. YAKHIYAEVA, L. Ya. AGAPOVA, A. N. ALTENOVA, B. M. SUKUROV*

*Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan, e-mail: *rm.303.imo@mail.ru*

THE ELECTROLYTE COMPOSITION INFLUENCE ON THE STRUCTURE OF DEPOSITED ALLOYS OF NICKEL WITH REFRACTORY RARE METALS

Abstract: The present work provides the results of electrolytic deposition of alloys on the basis of nickel with refractory rare metals (Re, W, Mo) from sulfate fluoride and ammonium-sulfate electrolytes in the conditions of membrane electrolysis. The precipitations analyses of alloys were carried out by X-ray phase and electronic-microscopic methods. Influence of composition of electrolyte on structure, the phase and chemical composition of the deposited alloys is investigated. It is established that from sulfate fluoride solutions powders ternary (Ni-Re-W, Ni-Re-Mo) and quaternary (Ni-Re-W-Mo) alloys of dark gray color with a green shade precipitated; from ammonium-sulfate solutions three-component Ni-Re-Mo alloy in the form of a foil of gray color is deposited. Results of the raster electronic microscopy (REM) have shown that precipitate deposited from fluoride sulfate solutions, consists of alloys of Ni with Re, W and Mo, and their particles generally have mainly layered structure (heavy fraction) and also agglomerate structure (easy fraction). In case of the alloys obtained from ammonium-sulfate electrolytes, the surface of the agglomerated particles becomes smoother. Element composition of the precipitates of Ni-Re-W-Mo alloys deposited from sulfate fluoride solutions, according to electron microscopy is following, wt. %: 57.24 Ni; 2.01 Re; 0.36 W; 1.82 Mo; 5.34 Ti; 32.92 O. For the Ni-Re-Mo alloys deposited from ammonium-sulfate solutions the following element composition is established, wt. %: 58.67 Ni; 22.71 Re; 9.88 Mo; 0.19 Ti; 8.69 O. In the alloy deposited from ammonium-sulfate electrolytes, tungsten isn't found. The presence of titanium in alloys is explained by its transition from cathode material to precipitates of alloys in the course of electrolysis. Heat treatment of alloys slightly reduces the content of oxygen in them and doesn't lead to strong change of composition of alloy. Results of the X-ray phase analysis have shown that after alloys annealing operation, change of phase structure isn't recorded.

Key words: electrolysis, electrolytic alloys, nickel, rhenium, tungsten, molybdenum, titanium, electrolyte, microstructure, electrodeposition

Introduction. Researches in obtaining heat-resistant nickel and rhenium-containing alloys are relevant, since the development of the electronic, aerospace, and energy industries is observed, where these alloys are broadly used [1-4]. Generally, all known methods for obtaining heat-resistant nickel-base alloys are carried out at high temperatures.

However, there are works on the electrolytic deposition of nickel alloys with some refractory metals from aqueous solutions of electrolytes. As an example, studies on the deposition of double alloys with rhenium and other refractory metals from aqueous solutions of nickel are carried out in Russia, Kazakhstan, China, Israel, Japan [5-13].

Electrolytic alloys in comparison with similar foundry alloys possess more pronounced valuable technical characteristics [5, 6]. The content in the electrolytic nickel alloys of refractory rare metals (rhenium, tungsten) in most cases is up to 50 % and higher.

Decrease in the content of refractory rare metals in electrolytic nickel-base alloys within their content in heat-resistant nickel superalloys (0.5-10 %), obtained by thermal methods, will lead to a decrease in the cost of production of electrolytic alloys. Deposition nickel-based alloys with several refractory rare metals (rhenium, tungsten, molybdenum) from aqueous solutions of will enable to obtain materials with high physicochemical and structural properties.

The goal of the present work is the electrolytic deposition of ternary and quaternary nickel-base alloys with refractory rare metals (Re, W, Mo) from sulfuric acid fluoride and ammonium sulfate electrolytes, as well as study of structure, phase and chemical composition of them.

Experimental part. *Research methods*. Experiments on the production of ternary (Ni-Re-W, Ni-Re-Mo) and quaternary (Ni-Re-W-Mo) electrolytic alloys were carried out in a temperature-controlled electrochemical cell with a platinum anode and a titanium cathode under membrane electrolysis. To exclude the mixing of products of the cathode and anode reactions, the interelectrode spaces in the cell were separated by the cation-exchange membrane MK-40. The surface of the titanium cathode was chemically treated in a solution of sulfuric acid with a concentration of 10 g/dm^3. Stirring was carried out due to gases released on the electrodes and by means of a magnetic stirrer.

The obtained cathode pellets were putified with distilled water, dried at 105 °C to constant weight, and weighed. The precipitates of the alloys were heat treated in a tube furnace in an argon flow at a temperature of 400 °C, and the holding time was 1 hour.

To determine the physicochemical properties of the alloys obtained, x-ray phase and electron-microscopic methods of analysis were used. An electronic raster microscope with a JEOL analyzer and an X-ray diffractometer D8 Advance (BRUKER) with Cu radiation were used.

The studies used solutions of sulfuric acid, nickel sulfate and ammonium, ammonium perrhenate, tungsten and molybdic acid, sodium fluoride. The qualification of acids and salts corresponded to the brands ChP and PFA. Ammonium perrhenate corresponded to the brand AR-0.

Results and discussion. Deposition of nickel alloys with several refractory rare metals from aqueous solutions is a complex process. Our earlier studies [14] on the identification of the kinetic regularities of cathodic reduction of nickel, rhenium, tungsten and molybdenum ions separately and their combined presence from electrolytes of various compositions have shown the possibility of Ni deposition with Re, W and Mo.

Deposition of alloys was carried out from sulfate fluoride solutions of electrolytes of composition, g/dm^3: H_2SO_4 - 40; NaF-10; Ni - 20; Re, W, Mo - 2 (samples 1, 2, 3) and from ammonium sulfate solutions of electrolytes of composition, g/dm^3: H_2SO_4 - 6.6; $(NH_4)_2SO_4$ - 40; Ni - 20; Re, W, Mo - 2 (samples 4, 5, 6) on a titanium electrode with a cathode current density of 600 A/m^2, a temperature of 50 °C, a process time of 4 hours.

The results of experiments on the cathodic deposition of powders of nickel-based alloys have shown that the alloys are precipitated from sulfuric acid fluoride solutions in the form of a loose powder of dark gray color with a green tint, which is well removed from the surface of the electrode. From ammonium sulfate electrolytes, the precipitate of the alloy is deposited in the form of a thin metal foil, which has good adhesion to the electrode, so it is difficult to remove it.

The power yield of nickel in alloys (samples 1, 2, 3), obtained from sulfate fluoride electrolytes, respectively, was 21, 31 and 37 %; the power yield of nickel in alloys (samples 4, 5, 6), precipitated from ammonium-sulfate solutions was 42, 47 and 50 %, respectively.

The results of X-ray phase analysis of alloys without annealing showed that the alloys obtained from sulfate fluoride solutions are amorphous and multiphase, in which phases of metallic nickel, rhenium oxide, tungsten dioxide and trioxide and sodium molybdate are determined. Alloys deposited from ammonium sulfate electrolytes are basically solid solutions based on nickel.

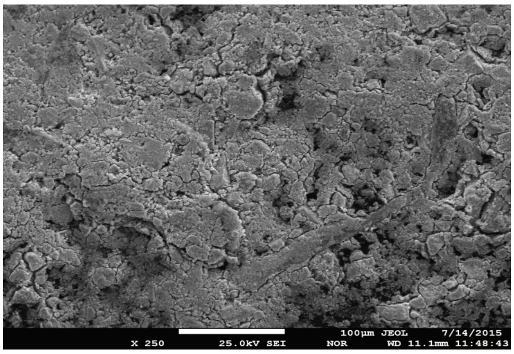
Table 1 – Electrolyte composition influence on the elemental composition of precipitates of nickel-based alloys with Re, W, Mo (before annealing).

Sample No	Electrolyte composition, g/dm^3	Content, wt. %									
		Ni	Re	W	Mo	C	O	Na	Ti	S	F
Sulfuric acid fluoride electrolyte											
1	40 H_2SO_4; 10 NaF; 20 Ni; 2 Re; 2 W	3.05	54.83	25.31	-	-	16.67	-	0.25	0.18	-
2	40 H_2SO_4; 10 NaF; 20 Ni; 2 Re; 2 Mo	32.52	15.11	-	3.69	-	24.72	-	3.59	2.88	1.89
3	40 H_2SO_4; 10 NaF; 20 Ni; 2 Re; 2 W; 2 Mo	57.24	2.01	0.36	1.82	-	32.92	0.33	5.34	0.33	-
Ammonium sulfate electrolyte											
4	6,6 H_2SO_4; 40 $(NH_4)_2SO_4$; 20 Ni; 2 Re; 2 W	58.86	28.66	-	-	2.58	5.96	-	0.05	-	-
5	6,6 H_2SO_4; 40 $(NH_4)_2SO_4$; 20 Ni; 2 Re; 2 Mo	56.17	12.82	-	8.78	2.97	7.29	-	-	-	-
6	6,6 H_2SO_4; 20 Ni; 40 $(NH_4)_2SO_4$; 2 Re; 2 W; 2 Mo	58.67	22.71	-	9.88	-	8.69	-	0.19	-	-

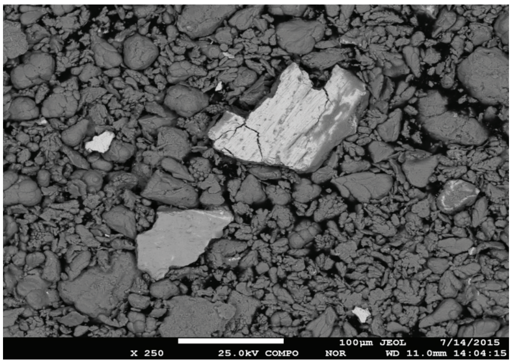
The obtained precipitates of alloys were studied by semiquantitative and quantitative wave-dispersion spectroscopic (WDS) analysis. The results of the analysis are given in Table 1.

It has been established that the oxygen content of alloys deposited from sulfuric acid fluoride solutions is higher than in alloys deposited from ammonium sulfate electrolytes. Also, the presence of titanium in the resulting alloys is established, which is explained by its transition from cathode material to deposited of alloys during electrolysis. The highest content of titanium was found in alloys precipitated from sulfuric acid fluoride solutions, which is associated with greater corrosion of titanium in fluoride solutions.

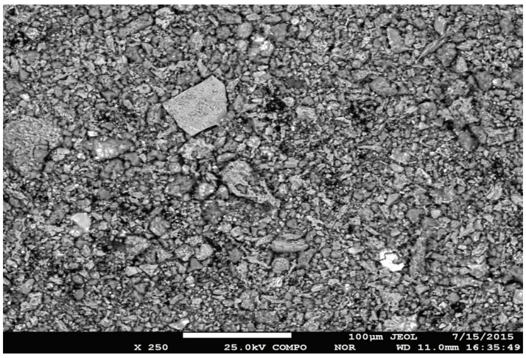
The microstructure of nickel-base alloys with rhenium, tungsten and molybdenum deposited from sulfuric acid fluoride and ammonium-sulphate solutions, without annealing is shown in Figure 1.



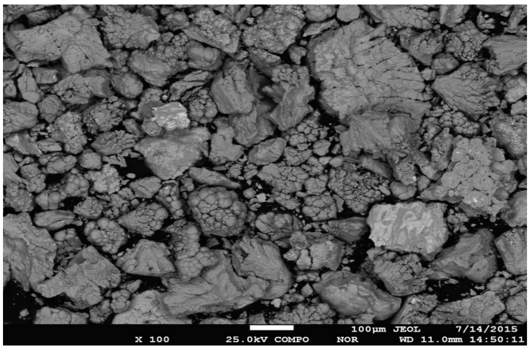
Sample No 1 x250



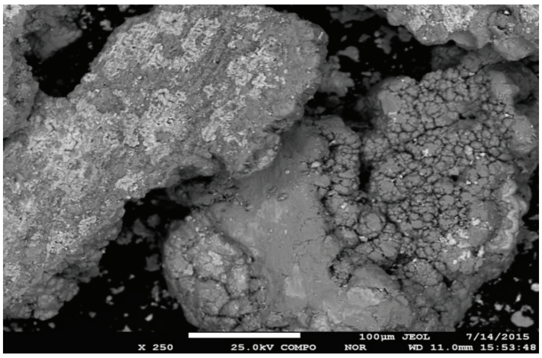
Sample No 4 x250



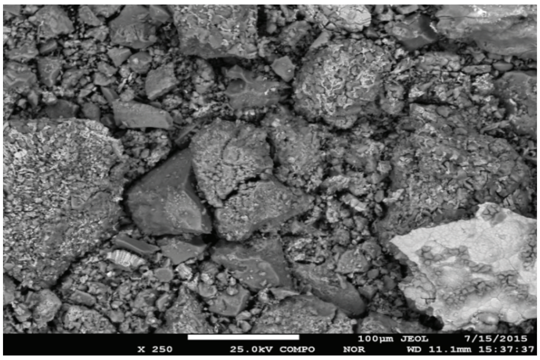
Sample No2 x250



Sample No 5 x100



Sample No 3 x250



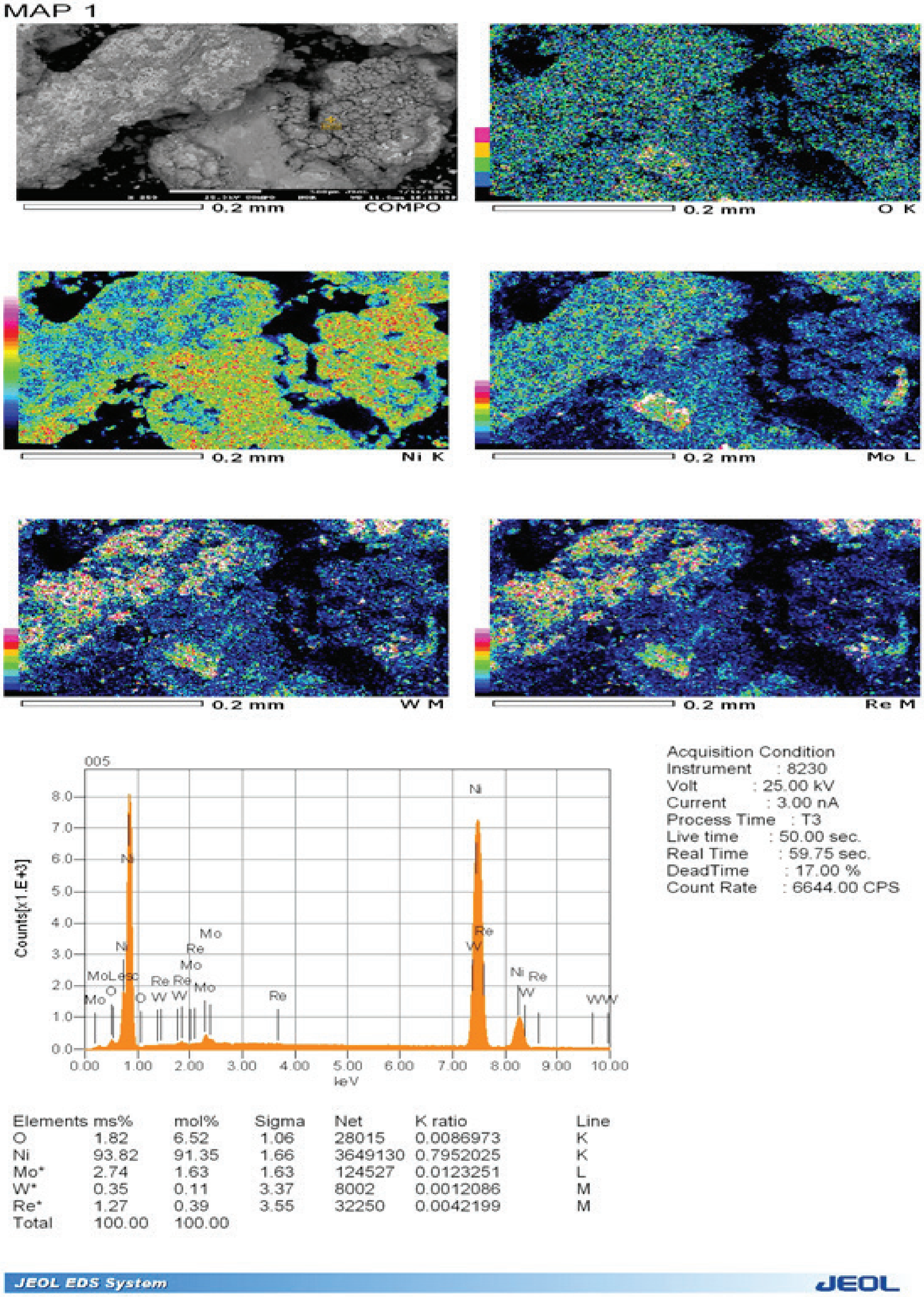
Sample No 6 x250

No 1, 2, 3 – alloys deposited from sulfate fluoride electrolytes.

No 4, 5, 6 – alloys deposited from ammonium sulfate electrolytes

Figure 1 - Microstructure of nickel-based alloys with refractory rare metals, depending on the composition of electrolytes before annealing (in backscattered electrons)

Results of the raster electronic microscopy (REM) have shown that alloys depending on structure have particles of different character. The sample precipitated from fluoride sulfate solutions consist of Ni alloys with Re, W and Mo, and their particles generally have mainly layered structure (heavy fraction) and also agglomerate structure (easy fraction). The heavy fraction represents connection of a type of Ni-Re-Mo-W with insignificant impurity O and Ti.



Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 3.00 nA
Process Time : T3
Live time : 50.00 sec.
Real Time : 59.75 sec.
DeadTime : 17.00 %
Count Rate : 6644.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	1.82	6.52	1.06	28015	0.0086973	K
Ni	93.82	91.35	1.66	3649130	0.7952025	K
Mo*	2.74	1.63	1.63	124527	0.0123251	L
W*	0.35	0.11	3.37	8002	0.0012086	M
Re*	1.27	0.39	3.55	32250	0.0042199	M
Total	100.00	100.00				

Figure 2 - PDS mapping of sample No. 3 precipitated from fluoride sulphate electrolyte, an increase of x250.

Table 2 - Weight of nickel alloys obtained with refractory rare metals before and after annealing

Sample No	Alloy weight, g		Sample No	Alloy weight, g	
	before annealing	after annealing		before annealing	after annealing
	Sulfurous fluoride electrolyte			Ammonium sulfate electrolyte	
1	0.118	0.113	4	0.832	0.832
2	0.629	0.574	5	0.933	0.932
3	0.870	0,718	6	0.768	0.766

The alloy No. 1 deposited from sulfate fluoride electrolyte has particles of the large and small extent of irregular shape in which existence of W, Re and O in a large number is established. Concentration of Ni, Ti and S significantly differ from zero.

It is remarkable that in case of sulfate fluoride electrolytes (test No. 1, No. 2 and No. 3), the agglomerated particles become covered by a layer of heavy fraction. While in case of ammonium-sulfate electrolytes (test No. 4, No. 5 and No. 6) the surface of the agglomerated particles becomes more smooth.

Methods of mapping of elements in the mode of the power-dispersive spectrometry (PDS) have established uneven distribution (figure 2) of the entered elements (Ni with Re, W and Mo) in material.

The mass values of the obtained alloys before and after the heat treatment are given in Table 2.

After annealing, the color of the precipitation of alloys precipitated from sulfate fluoride electrolytes, regardless of the composition of the solutions, has changed rom dark gray with a green shade to gray with a brown shade. Also the noticeable decrease of mass of precipitation was observed. In case of alloys precipitated from ammonium-sulphate electrolytes, the heat treatment does not particularly influence neither the change in the mass of the alloys nor on the appearance of precipitation.

The chemical composition of the cathode deposites obtained after annealing according to electron microscopic analysis is demonstrated in Table 3.

As appears from the Table 3 the annealing operation reduces the oxygen content in the alloys a little.

Based on the results of X-ray phase analysis of alloys after annealing, the phase composition changes in them have not been recorded.

Conclusions. During the process of electrolytic deposition, multiphase alloys based on nickel with refractory rare metals were obtained from sulfate fluoride and ammonium sulfate electrolytes. It is established that alloys in the form of loose powders are precipitated from sulfuric acid fluoride solutions. Alloys from ammonium-sulfate solutions were deposited in the form of a foil.

According to electron microscopy, ternary (Ni-Re-W, Ni-Re-Mo) and quaternary (Ni-Re-W-Mo) alloys are precipitated from sulfate fluoride electrolytes. From ammonium sulfate electrolytes, a Ni-Re-Mo ternary alloy is precipitated under these conditions.

The results of raster electron microscopy (REM) have demonstrated that precipitates from fluoride sulfuric solutions of deposition of alloys consist of Ni with Re, W and Mo, and their particles mainly have a predominantly layered structure (heavy fraction), and also an agglomerate structure (light fraction). In the case of alloys obtained from ammonium sulfate electrolytes, the surface of the agglomerated particles becomes more smooth.

The elemental composition of the precipitates of Ni-Re-W-Mo alloys deposited from sulfuric acid fluoride solutions, according to electron microscopy, is

Table 3 - Effect of the electrolyte composition on the elemental composition of precipitates of nickel-base alloys with Re, W, Mo (after annealing)

Sample No	Content, wt. %									
	Ni	Re	W	Mo	C	O	Na	Ti	S	F
Sulfurous fluoride electrolyte										
1.1	1.67	42.85	37.70	-	-	15.00	-	0.32	0.14	-
2.1	34.62	18.40	-	12.69	-	27.72	-	3.99	-	-
3.1	55.61	2.14	0.35	2.66	5.83	24.72	0.46	5.95	-	-
Ammonium sulfate electrolyte										
4.1	62.77	17.15	-	-	4.23	5.76	-	0.02	-	-
5.1	71.31	18.42	-	3.69	-	3.93	-	0.16	-	-
6.1	56.12	15.19	-	6.01	-	6.53	-	8.67	-	-

the following, %: 57.24 Ni; 2.01 Re; 0.36 W; 1.82 Mo; 5.34 Ti; 32.92 O. For Ni-Re-Mo alloys deposited from ammonium-sulphate solutions, wt. %: 58.67 Ni; 22.71 Re; 9.88 Mo; 0.19 Ti; 8.69 O. In the alloy obtained from ammonium sulfate electrolytes, tungsten isn't found.

The process of heat treatment of alloys fractionally reduces the oxygen content in the alloy and does not lead to a strong change in the composition of the alloy. The results of X-ray phase analysis have shown that after the annealing operation of alloys, the change in the phase composition isn't recorded.

The present work has been carried out under the grant No. 4997/GF4 for 2015 - 2017 with the financial support of the Science Committee of the Ministry of Education and Science of Republic Kazakhstan.

REFERENCES

1 Kablov E.N., Toloraiya V.N., Orekhov N.G. *Monokristallicheskiye nikelevyye reniy soderzhashchiye splavy dlya turbinnykh lopatok GTD* (Single-crystal nickel rhenium containing alloys for turbine blades). *Metallovedenie i termicheskaya obrabotka metallov = Metal conducting and heat treatment of metals.* **2002.** *7*, 7-11 (in Russ.).

2 Kablov E.N., Petrushin N.V., Svetlov I.L., Demonis I.M. *Liteynyye zharoprochnyye nikelevyye splavy dlya perspektivnykh aviatsionnykh GTD* (Foundry heat-resistant nickel alloys for advanced aviation GTE*). Tehnologiya legkikh splavov = Technology of light alloys*. **2007**. 2, 6-16 (in Russ.).

3 Luo Yushi, Li Jia-rong, Liu Shi-zhong, Sun Feng-li, Han Mei, Cao Chun-xiao. *Vliyaniye Re na dlitel'nuyu prochnost' monokristallicheskikh supersplavov pri povyshennoy temperature i vysokikh napryazheniyakh* (Effect of Re on the long-term strength of single-crystal superalloys at elevated temperature and high stresses). *Tsvetnye metally = Non-ferrous metals*. **2005**. *15, 11*. 1518 (in Chinese: abstract in Eng.).

4 Sakurai Shingo, Mabruri Efendi, Murata Yoshinori, Koyama Toshiyuki, Morinaga Masahiko. Diffusion of refractory elements in ternary Ni-X-Y alloys (X, Y = Co, Re, Ru, W). *Defect and Diffus. Forum.* **2008**. *273-276*, 572-576. (in Eng.)

5 Gamburg Yu.D. *Gal'vanicheskiye pokrytiya. Spravochnik po primeneniyu* (Galvanic coating. The reference book on application). Moscow: Technosphere. **2006**, 216. (in Russ.).

6 Povetkin V.V., Kovenskiy I.M., Ustinovschikov YU.I. *Struktura i svoystva ehlektroliticheskikh splavov* (Structure and properties of electrolytic alloys). Moscow: Nauka. **1992,** 255. (in Russ.).

7 Cesiulis H., Podlaha-Murphy E. J. lectrolyte considerations of electrodeposited Ni-W alloys for microdevice fabrication. *Materials science*. **2003.** *4, 329-333*, 448. (in Eng.).

8 Kukushkina K.V., Yarlyikov M.M., Kudryavtsev V.N., Palatova S.V., Anufriev N.G. *O stabilizatsii protsessa splava Ni-W* (On stabilization of the Ni-W alloy process). *Gal'vanotekhnika i obrabotka poverkhnosti = Electroplating and surface treatment.* **2003.** *1*, 25-32. (in Russ.).

9 Wang Jun-li, Xu Rui-dong, Long Jin-ming, Guo Zhong-cheng. *Issledovaniye svoystv ehlektroosazhdennykh Re-Ni-W-B kompozitsionnykh pokrytiy* (Investigation of properties of the electrodeposited Re-Ni-W-B composite coatings). *Diandu yu tushi = Electroplat. and Finish.* **2005.** *1*, 6-9. (in Chinese: abstract in Eng.).

10 Wang Jian-li, Li Guangqiang, Zhu Cheng-yi. *Vliyaniye soderzhaniya v vanne limonnoj kisloty na svoystva ehlektroosazhdennogo pokrytiya Re-Ni-W-P-SiC* (Influence of the content in the citric acid bath on the properties of the electrodeposited Re-Ni-W-P-SiC coating). *Fushi yu fanghu=Corros. and Prot. Wuhan.* **2006.** *27. 8,* 408-411. (in Chinese: abstract in Eng.)

11 Pat. 7368048 USA. Method for Rhenium Alloy Coating Film Plating by Electrodeposition. Japan Sci. and Tech. Agency, Ebara Corp.; Sapporo Electroplating Industrial Co., Ltd, Narita Toshio / Hayashi Shigenari, Yoshioka Takayuki, Yakuwa Hiroshi, Souma Michiaki, Fukumoto Michihisa; publ. 06.05.**2008.** (in Eng.).

12 Naora A., Eliaz N., Gileadib E. Electrodeposition of rhenium–nickel alloys from aqueous solutions. Electrochimica Acta. **2009.** *54,* 6028–6035. (in Eng.).

13 Vagramyan A.T., Zhamagortsyants M.A. *Osobennosti ehlektroosazhdeniya reniya i ego splavov* (Features of electrodeposition of rhenium and its alloys) Moscow: Science. **1969**, 197. (in Russ.).

14 Kilibaeva S.K., Yakhiyayeva Zh.E., Agapova L.Ya., Abisheva Z.S., Altenova A.N. *Kinetika katodnogo vosstanovleniya ionov nikelya, reniya, vol'frama i molibdena iz sernokislykh ehlektrolitov* (Kinetics of cathodic reduction of nickel, rhenium, tungsten and molybdenum ions from sulphate electrolytes). *Kompleksnoye ispol'zovaniye mineral'nogo syr'ya = Complex use of mineral resources.* **2016.** *1,* 71-79. (in Russ.)

ЛИТЕРАТУРА

1 Каблов Е. Н., Толораия В. Н., Орехов Н. Г. Монокристаллические никелевые ренийсодержащие сплавы для турбинных лопаток ГТД // Металловедение и термическая обработка металлов. – 2002 – № 7. – С. 7-11.

2 Каблов Е.Н., Петрушин Н.В., Светлов И.Л., Демонис И.М. Литейные жаропрочные никелевые сплавы для перспективных авиационных ГТД // Технология легких сплавов. – 2007. – № 2. – С. 6-16.

3 Luo Yushi, Li Jia-rong, Liu Shi-zhong, Sun Feng-li, Han Mei, Cao Chun-xiao. Влияние Re на длительную прочность монокристаллических суперсплавов при повышенной температуре и высоких напряжениях // Nonferrous Metals. – 2005. – Т. 15. № 11. – P. 1518.

4 Sakurai Shingo, Mabruri Efendi, Murata Yoshinori, Koyama Toshiyuki, Morinaga Masahiko.Диффузия тугоплавких элементов в тройных сплавах Ni-X-Y (X, Y=Co, Re, Ru, W) // Defect and Diffus. Forum. – 2008.– № 273-276.– С. 572-576.

5 Гамбург Ю.Д. Гальванические покрытия. Справочник по применению. – М.: Техносфера, 2006. – 216 с.

6 Поветкин В.В., Ковенский И.М., Устиновщиков Ю.И. Структура и свойства электролитических сплавов. – М.: Наука, 1992. – С. 255

7 Cesiulis H., Podlaha-Murphy E. J. Electrolyte considerations of electrodeposited Ni-W alloys for microdevice fabrication //Mater. sci. – 2003. – Т.9. № 4. – С. 329-333, 448.

8 Кукушкина К.В., Ярлыков М.М., Кудрявцев В.Н., Палатова С.В., Ануфриев Н.Г. О стабилизации процесса сплава Ni-W // Гальванотехника и обработка поверхности. – 2003. – № 1. – С. 25-32.

9 Wang Jun-li, Xu Rui-dong, Long Jin-ming, Guo Zhongcheng. Исследование свойств электроосажденных Re-Ni-W-B композитных покрытий // Diandu yu tushi =Electroplate and Finish. – 2005. – № 1. – С. 6-9.

10 Wang Jian-li, Li Guangqiang, Zhu Cheng-yi. Влияние содержания в ванне лимонной кислоты на свойства электроосажденного покрытия Re-Ni-W-P-SiC. // Fushi yu fanghu=Corros. and Prot. Wuhan. – 2006. – Т.27. № 8. – С. 408-411.

11 Pat. 7368048 USA. Method for Rhenium Alloy Coating Film Plating by Electrodeposition. Japan Sci. and Tech. Agency, Ebara Corp.; Sapporo Electroplating Industrial Co., Ltd, Narita Toshio / Hayashi Shigenari, Yoshioka Takayuki, Yakuwa Hiroshi, Souma Michiaki, Fukumoto Michihisa; publ. 06.05.2008.

12 Naora A., Eliaz N., Gileadib E. Electrodeposition of rhenium–nickel alloys from aqueous solutions // Electrochimica Acta. – 2009. – N 54. – P. 6028–6035.

13 Ваграмян А.Т., Жамагорцянц М.А. Особенности электроосаждения рения и его сплавов // Электроосаждение металлов и ингибирующая адсорбция. – М.: Наука, 1969. – 197 с.

14 Килибаева С.К., Яхияева Ж.Е., Агапова Л.Я., Абишева З.С., Алтенова А.Н. Кинетика катодного восстановления ионов никеля, рения, вольфрама и молибдена из сернокислых электролитов // Комплексное использование минерального сырья. – 2016. – № 1. – С. 71-79

ТҮЙІНДЕМЕ

Жұмыста фторид күкіртқышқылды және сульфат-аммонийлі электролиттерден мембраналы электролиз жағдайында сирек қиын балқитын (Re, W, Mo) металдармен тұндырылатын никельді қорытпаларының нәтижелері жазылған. Қорытпа тұнбаларына электронды-микроскопиялы және рентгенофазалы әдістермен талдау жүргізілді. Электролит құрамының тұндырылатын қорытпалардың құрылысына, химиялық және фазалық құрамына әсері зерттелген. Фторид күкіртқышқылды ерітінділерден үштік (Ni-Re-W, Ni-Re-Mo) және төрттік (Ni-Re-W-Mo) қорытпа ұнтақтары қанық-сүр түсті жасил реңімен алынады; сульфат-аммонийлі ерітіндісінен үштік Ni-Re-Mo қорытпасы сүр түсті фольга түрінде тұндырылатыны анықталды. Электронды раст микроскопиясының (ЭРМ) нәтижесі фторид күкіртқышқылды ерітінділердің тұнбасы Ni Re, W және Mo-мен қорытпаларынан және олардың бөлшектері негізінен қатпарлы құрылымнан (ауыр фракция), сонымен бірге агломератты құрылымынан (жеңіл фракция) турады. Сульфат-аммонийлі электролиттерден алынған қорытпалар жағдайында агломератті бөлшектерінің беткі қабаты тегістеу болады. Фторид күкіртқышқылды ерітінділерден тұндырылған Ni-Re-W-Mo қорытпалар тұнбасының элементтік құрамы электронды микроскопия деректері бойынша келесідей берілген, мас. %: 57,24 Ni; 2,01 Re; 0,36 W; 1,82 Mo; 5,34 Ti; 32,92 O. Сульфат-аммоний-лі ерітінділерден тұндырылған Ni-Re-Mo қорытпалары үшін , мас. %: 58,67 Ni; 22,71 Re; 9,88 Mo; 0,19 Ti; 8,69 O. Сульфат-аммонийлі электролитінен тұндырылған қорытпада вольфрам анықталмады. Қорытпадағы титанның болуы электролиз үрдісінде оның катод материалынан тұнбаға өтуімен түсіндіріледі. Қорытпаларды термиялық қайта өңдеуде олардағы оттегі құрамының төмендеуіне және қорытпа құрамының өзгеруіне көп өзгеріс келтірілмейді. Рентгенофазалық талдау қорытпаларды күйдіру операциясынан кейін фазалық құрамының өзгермейтінін көрсетті.

Түйін сөздер: электролиз, электролиттік қорытпалар, никель, рений, вольфрам, молибден, электролит, микроқұрылыс

РЕЗЮМЕ

В работе изложены результаты электролитического осаждения сплавов на основе никеля с тугоплавкими редкими металлами (Re, W, Mo) из сернокислых фторидных и аммонийно-сульфатных электролитов в условиях мембранного электролиза. Анализ осадков сплавов проводили рентгенофазовым и электронно-микроскопическим методами. Исследовано влияние состава электролита на структуру, фазовый и химический состав осаждаемых сплавов. Установлено, что из сернокислых фторидных растворов получаются порошки тройных (Ni-Re-W, Ni-Re-Mo) и четверных (Ni-Re-W-Mo) сплавов темно-серого цвета с зеленым оттенком; из аммонийно-сульфатных растворов осаждается тройной сплав Ni-Re-Mo в виде фольги серого цвета. Результаты растровой электронной микроскопии (РЭМ) показали, что осажденные из фторидных сернокислых растворов осадки состоят из сплавов Ni с Re, W и Mo, и их частицы в основном имеют преимущественно слоистую структуру (тяжелая фракция), а также агломератную структуру (легкая фракция). В случае сплавов, полученных из аммонийно-сульфатных электролитов, поверхность агломерированных частиц становится более гладкой. Элементный состав осадков сплавов Ni-Re-W-Mo, осажденных из сернокислых фторидных растворов, по данным электронной микроскопии, следующий, мас. %: 57,24 Ni; 2,01 Re; 0,36 W; 1,82 Mo; 5,34 Ti; 32,92 O. Для сплавов Ni-Re-Mo, осажденных из аммонийно-сульфатных растворов, установлен следующий состав, мас. %: 58,67 Ni; 22,71 Re; 9,88 Mo; 0,19 Ti; 8,69 O. В сплаве, осажденном из аммонийно-сульфатных электролитов, вольфрам не обнаружен. Наличие титана в сплавах объясняется его переходом из материала катода в осадки сплавов в процессе электролиза. Термическая обработка сплавов незначительно снижает содержание кислорода в них и не приводит к сильному изменению состава сплава. Результаты рентгенофазового анализа показали, что после операции отжига сплавов, изменение фазового состава не зафиксировано.

Ключевые слова: электролиз, электролитические сплавы, никель, рений, вольфрам, молибден, титан, электролит, микроструктура, электроосаждение

Received 17.10.2017.