



PRODUCING OF SURFACE ALLOYS OF THE ERBIUM-NICKEL SYSTEM IN HALIDE MELTS

Kondrat'ev D. A.¹, Ereemeeva T. V.¹, Kamalov K. O.¹, Kovalenko V. L.^{2,1}, Kotok V. A.^{3,1,5} and Kovalenko I. L.⁴

¹Department of Technologies of Inorganic Substances and Electrochemical Manufacturing, Vyatka State University, Moskovskaya St., Kirov, Russian Federation

²Department of Analytical Chemistry and Chemical Technologies of Food Additives and Cosmetics, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine

³Department of Processes, Apparatus and General Chemical Technology, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine

⁴Department of Inorganic Chemistry, Ukrainian State University of Chemical Technology, Gagarin Ave, Dnipro, Ukraine
E-Mail: Valeriy_e-ch@ukr.net

ABSTRACT

The gravimetric method was used to evaluate the influence of temperature and duration on the specific change in mass of nickel samples ($P = \Delta m / S$, where Δm - mass change, S - surface area) during electroless diffusive saturation with erbium in a molten eutectic mixture of lithium and potassium chlorides with the addition of 5 wt. % erbium chloride. Mathematical dependencies of P on duration in 773 - 973 K temperature range. The composition of alloy-coats prepared with the electroless transfer of erbium on nickel was studied using energy dispersive energy-dispersive X-ray fluorescence spectrometer, X-Ray microanalyzer and scanning electron microscope. Heat resistance of prepared Er-Ni surface alloy has been studied.

Keywords: electroless transfer, erbium, diffusive saturation, nickel, surface alloy.

INTRODUCTION

Alloys and intermetallic compounds (IMC) of rare-earth metal (REM) with nickel possess a range of unique properties: heat resistance, high catalytic and sorption properties [1-3]. One perspective method for preparing REM-nickel alloys is electroless diffusion saturation of nickel with rare-earth metal in salt melts [4-7].

Processes occurring in chloride melts during transfer of REM onto more electropositive metals is studied by authors of papers [8, 9]. Present work describes results of experimental studies of process parameters (temperature and process duration) on kinetic characteristics of alloy formation during electroless diffusive saturation of nickel with erbium in LiCl-KCl-ErCl₃ melt.

MATERIALS AND METHODS

Analytical grade lithium, potassium and erbium chlorides, erbium EpM-I and nickel NP-2 were used in experiments. Dehydrated chlorides of lithium, potassium and eutectic LiCl-KCl mixture were re-melted in a quartz cell, the melt was sparged with dry HCl and kept molten under vacuum for 2 - 3 hours. The cooled down mixture was kept in a desiccator filled with purified argon. Anhydrous erbium chloride was prepared from its crystal hydrate via slow heating under vacuum in excess NH₄Cl. Diffusive saturation of nickel with erbium was conducted in melt LiCl (60 mol.%)–KCl with the addition of 5 wt.% ErCl₃, in presence of metallic erbium plate according to the literature [10]. Experiments were conducted in the closed cell (Figure-1) in an atmosphere of purified argon. 30±2 g of the prepared mixture was placed into barium oxide crucible, which placed inside a stainless steel cell suspended on molybdenum hinge. The cell was heated by

the electric furnace with semi-automatic temperature control. The cell was kept under vacuum until it reached the set temperature after which it was filled with purified argon and nickel and erbium plates with a surface area of 9±2 cm² and 1.4±0.8 cm² respectively, were placed into the melt. The plates were fixed in a way as to avoid contact between each other and the walls of the crucible. After a set time, nickel plates diffusively saturated with erbium were removed and cooled under an inert atmosphere. Change of specific mass of nickel samples in time was used as a qualitative characteristic of alloy formation. Temperature interval for studies was chosen based on analysis of Er-Ni phase diagrams and results of preliminary tests.

Heat resistance of Er-Ni surface alloy was evaluated by thermal cycling in a muffle furnace to 1073 K under air atmosphere. Duration of one cycle was 5 h. Total testing time was 50 hours. Heat resistance was measured as mass increase per surface after each thermal cycle.

RESULTS AND DISCUSSIONS

Experimental results of determining dependence P of nickel samples on duration (τ) of erbium saturation at different temperature are listed in Figure-2. For each studied temperature dependence P on τ was approximated by the following equation:

$$P = k_m \tau^n, \quad (1)$$

where k_m (kg/(m²·hⁿ)) – process rate constant;

n - exponent.



Distribution of empirical values relative to curve (1) was evaluated as a relative error ($\Delta P/P_{\text{calc.}}$, %).

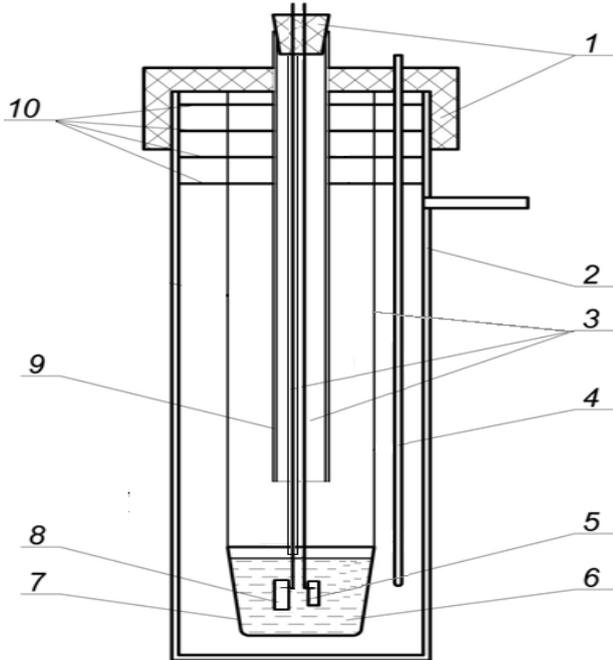


Figure-1. Cell for diffusive saturation experiments: 1 - rubber stoppers; 2- stainless steel cell; 3 - molybdenum hinges; 4 - quartz thermocouple cover; 5 - studied sample, nickel; 6 - electrolyte (melt); 7 - beryllium oxide crucible; 8 - rare-earth metal (erbium); 9 - quartz tube; 10 - aluminum shields.

The obtained experimental data on the dependency of the sample's mass on the duration of process duration in selected temperature ranges are presented in Figure-2.

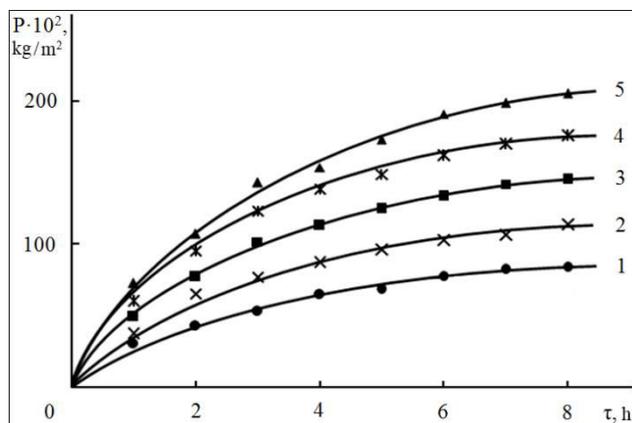


Figure-2. Dependency of specific mass gain (P) of nickel sample on duration (τ) of saturation with erbium: 1- 773 K; 2- 823 K; 3- 873 K; 4- 923 K; 5 - 973 K.

Analysis of obtained graphical dependencies allows concluding that higher process temperature leads to faster alloy formation due to higher diffusion in the solid phase.

Constant k_m in equation (1), which describes the character of dependency of sample's mass gain on the duration of saturation process, is a complex function which included a number of factors affecting the rate of saturation process, such as temperature, nature of substrate metal and saturating element. The calculated constant values are similar to those we have previously obtained for diffusive saturation of nickel with samarium, yttrium, gadolinium [10, 11].

Table-1 shows the coefficient of equation (1) calculated from experimental values of P , and also maximum $\Delta P/P_{\text{calc.}}$ values at studied temperatures. From Table-1 it can be seen that values of exponent n are close to 0.5, which indicated that limiting stage is diffusion in the solid phase.

Table-1. Coefficient values for equation (1).

T, K	k_m	n	$\Delta P/P_{\text{calc.}}, \%$
773	0.30	0.51	5.1
823	0.42	0.50	4.8
873	0.53	0.52	3.2
923	0.65	0.51	4.7
973	0.76	0.50	4.5

Thus, understudied conditions the electroless REM transfer is realized at a rate that satisfies condition [12]:

$$\beta \gg D, \quad (2)$$

where

- β - mass transfer coefficient in salt media;
- D - diffusion coefficient in solid phase.

Structure and phase composition of obtained erbium-nickel surface alloys were studied by means energy dispersive energy-dispersive X-ray fluorescence spectrometer EDX-720, X-Ray microanalyzer COMEBAX and scanning electron microscope JEOL JSM-6510 LV. The results of analyzing surface alloys and conditions of diffusive saturation of nickel with erbium in LiCl-KCl-ErCl_3 melt are presented in Tables 2, 3, 4 and on Figure-3.

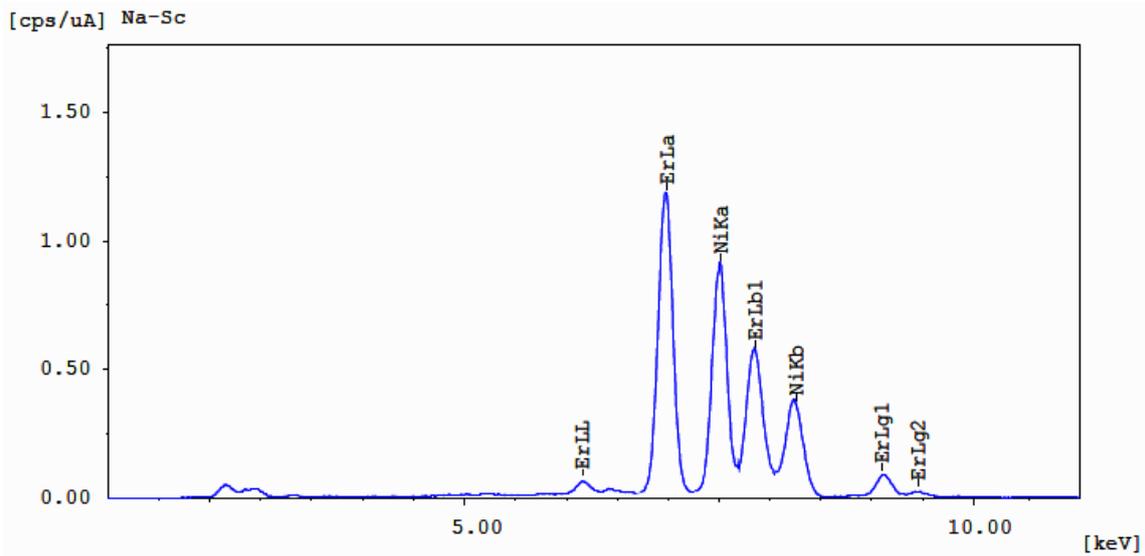


Table-2. Surface composition of samples Er-Ni ($\tau=2$ h, $T=873$ K, $P=0.77$ kg/m²).

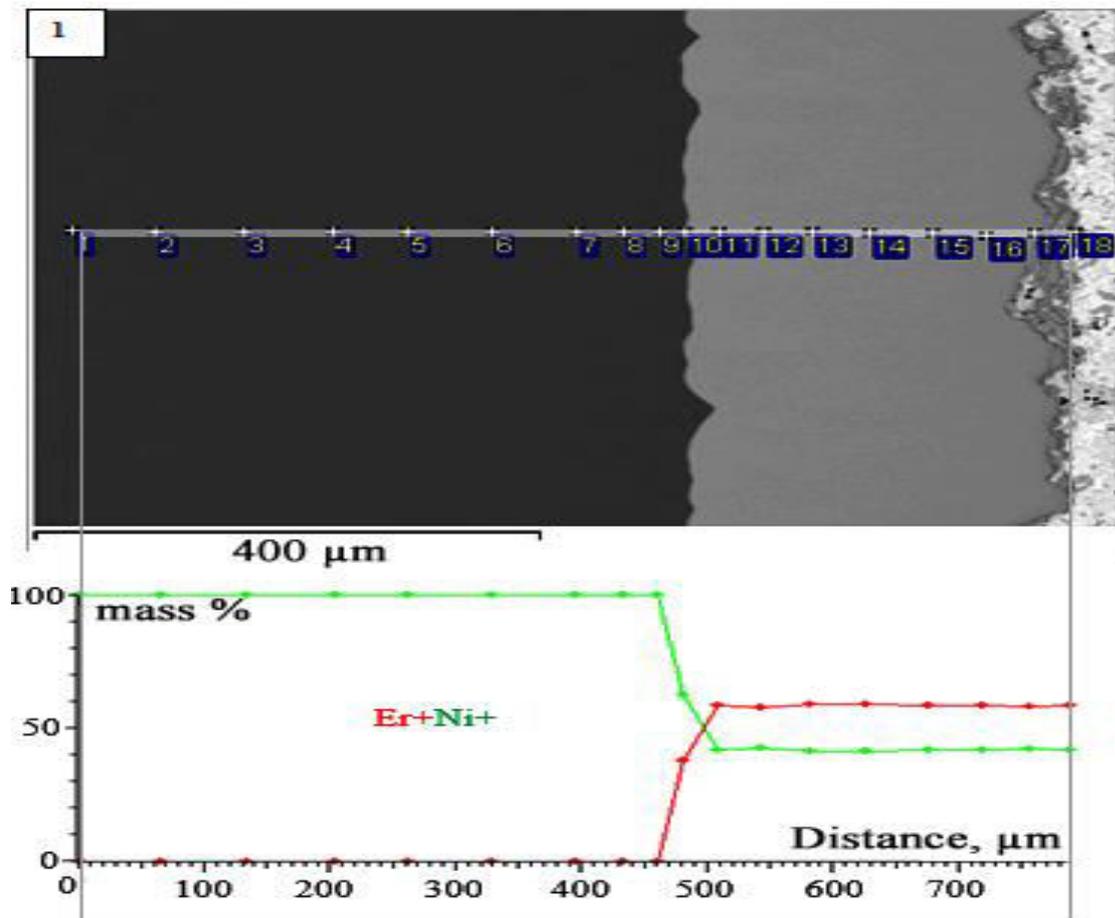
Measurement parameter: apparatus (EDX-720); atmosphere (air); collimator (10 mm); rotation (off.)				
Qualitative result				
Element	Er	Ni		
Quantitative result				
Element	Result, macc. %	Static deviation	Line	Intensity, s/mkA
Er	58.029	0.178	ErLa	217.6599
Ni	41.971	0.059	NiKa	137.8556

Table-3. Microdistribution of the component in coat surface Er-Ni ($\tau=2$ h, $T=873$ K, $P=0.77$ kg/m²).

Spectrum	Content, wt. %		
	Ni	Er	Total
1	100.00	0.00	100.00
2	100.00	0.00	100.00
3	100.00	0.00	100.00
4	100.00	0.00	100.00
5	100.00	0.00	100.00
6	100.00	0.00	100.00
7	100.00	0.00	100.00
8	100.00	0.00	100.00
9	100.00	0.00	100.00
10	62.55	37.45	100.00
11	41.58	58.41	100.00
12	42.54	57.46	100.00
13	41.19	58.81	100.00
14	41.41	58.59	100.00
15	41.70	58.30	100.00
16	41.68	58.32	100.00
17	41.85	58.15	100.00
18	41.80	58.20	100.00



(a)



(b)

Figure-3. Result of X-Ray fluorescence (a) and X-Ray spectral (b) analysis of *Er-Ni* surface alloy ($\tau=2$ h, $T=873$ K, $P=0.77$ kg/m²).

**Table-4.** Structure and phase composition of erbium-nickel layers.

Diffusive saturation parameters		P , kg/m^2	Coat thickness, μm	Erbium content X-Ray fluorescence analysis, mass. %	Coat composition according to X-ray spectral analysis
T , K	τ , h				
773	2.00	0.43	155	57.6	ErNi_2
823	2.00	0.65	230	57.8	ErNi_2
873	2.00	0.77	275	58.2	ErNi_2

The result of complex analyses of erbium-nickel alloy allows concluding that experimental conditions lead to the formation of the single structural zone, which corresponds to Laves ErNi_2 , with narrow homogeneity region [13]. The obtained result is in agreement with paper [10], which described that during galvanodiffusion saturation under potentiostatic conditions and electroless transfer of diffusant in salt melts, the formation condition of diffusion coating containing IMC are similar to each other.

Figure-4 shows the results of heat resistance tests diffusion-saturated nickel with erbium. For comparison, it also shows uncoated nickel sample and results of similar tests for Gd-Ni surface alloy, prepared by authors of paper [10].

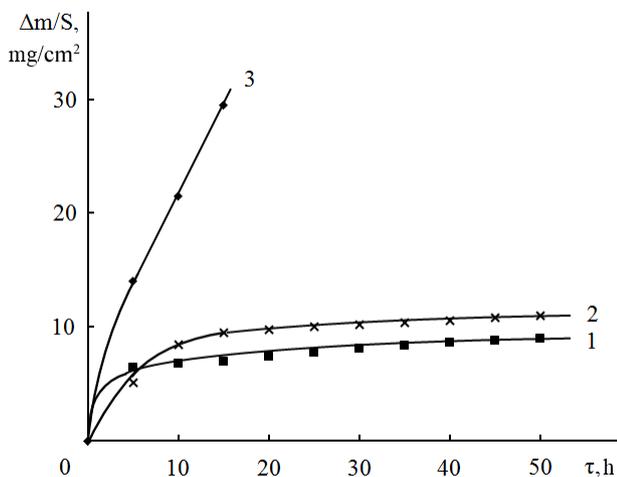


Figure-4. Kinetic curves of sample oxidation at $T=1073$ K: 1-Er-Ni ($T=773$ K, $\tau=1.5$ h, $P=0.29$ kg/m^2); 2- Gd-Ni ($T=873$ K, $\tau=5$ h, $P=0.32$ kg/m^2) [10]; 3-uncoated nickel.

It can be seen from Fig. 4 that during the first 10 hours of testing, the oxidation of erbium-coated sample occurs at a significant rate of about $0.6\text{--}0.8$ $\text{mg/cm}^2\cdot\text{h}$. However, during consequent tests (more than 10 hours) the oxidation rate remained almost constant, while for uncoated nickel (curve 3) the corrosion occurs at a high rate through testing. A significant decrease in the corrosion rate of the coated sample can be attributed to the protective oxide layer, which resists cyclic high-temperature oxidation. Similar shape of curve shape of $\Delta m/S$ dependency on duration of thermocycling heat resistance tests is observed for sample Gd-Ni (curve 2) [11], which was prepared in by diffusive saturation of

nickel with gadolinium in расплаве LiCl (60 mol.%)–KCl + 5 wt.% GdCl_3 melt.

CONCLUSIONS

- A series nickel samples have been subjected to electroless diffusive saturation with erbium in eutectic LiCl–KCl melts with the addition of erbium chloride (5 wt. %) in the temperature range of 773–973 K, from 1 to 8 hours.
- It was discovered that mathematical dependencies of specific mass change P on process duration τ , in studied temperature range can be described by $P=k_m\tau^n$. Based analysis of obtained equations, it was established that limiting stage of electroless diffusion of erbium onto nickel substrate is diffusion in the solid phase.
- Results of Er– Ni surface alloys, prepared under differed regimes, revealed that given experimental conditions result in the formation of a single structural zone– intermetallic ErNi_2 .
- Heat resistance of Er-Ni coat has been studied at 1073 K under an air atmosphere in thermocycling regime. It was discovered that initial oxidation rate is close to that of uncoated nickel. However, the resistance to heat oxidation increased with further testing, which explained by the formation of the protective oxide layer.

REFERENCES

- Kuznetsov S.A. 2007. Electrochemistry of rare-earth, rare metals in salt melts and synthesis of new compounds and materials of functional purpose on their basis. Proc. XIV National Conference on Physical Chemistry and Electrochemistry of ionic melts and solid electrolytes. Ekaterinburg: Institute of High-Temperature Electrochemistry, Ural Branch of Russian Academy of Sciences. 1: 110.
- Verbetsky V.N., Velikorodniy Y.A., Lushchekina S.V. 2002. Synthesis of hydride based on the



- intermetallic compound YbNi_2 . Bulletin of the Moscow-Univ. Series 2 "Chemistry". 1(43): 58.
- [3] Azhazha V.M., Bortz B.V., Vanja A.V., Rybal'chenko N.D., Shevyakova E.P. 2008. Possibilities of using rare-earth elements in creating structural materials for the nuclear industry of Ukraine. In the requests of Nuclear Science and Technology. 1: 195-201.
- [4] Kushkhov H.B., Vindizheva M.K., Mukozhev R.A., Tlenkopachev M.R., Abazova A.H. 2013. Electroreduction of cerium (III) ions on a silver electrode in a chloride melt at 823 K. Electrochemistry. 4 (49): 411-415.
- [5] Kushkhov H.B., Vindizheva M.K., Mukozhev R.A., Tlenkopachev M.R., Nafonova M.N. 2012. Study of the electroreduction of lanthanum ions on a tungsten electrode in halide melts at $T = 823$ K. Melts. 1: 50-59.
- [6] Novoselova A.V., Smolenskii V.V. 2013. Electrochemical and thermodynamic properties of lanthanides Radiochemistry. 3(55): 243-256.
- [7] Novoselova A.V., Smolenskii V.V. 2012. Electrochemical study of the reduction of Tm (III) ions in a molten NaCl-2CsCl eutectic. Russ. J. Appl. Chem. 2(85): 218-224.
- [8] Ilyushchenko N.G., Anfinogenov A.I., N.I. 1991. Shurov Interaction of metals in ionic melts. Moscow: Nauka.
- [9] Kondratyev D.A., Kovalevsky A.V., Chebykin V.V. 2013. Alloy formation during the current-free diffusion saturation of nickel with dysprosium in the melt of LiCl-KCl-DyCl₃. Melts. 6: 47-52.
- [10] Elkin O.V., Chebykin V.V., Kovalevsky A.V. 2009. The kinetics of the alloying-tion when currentless transfer of ytterbium, samarium and gadolinium nickel in chloride melts. Melts. 4: 20-26.
- [11] Kovalevsky A.V., Elkin O.V., Chebykin V.V. 2011. Current-free diffusion saturation of nickel with gadolinium in a melt LiCl-KCl-GdCl₃. Izv. vuzov. tevet. metallurgija. 5: 35-39.
- [12] Baraboshkin A.N. 1986. On conditions for a smooth diffusion coatings are dead and electrodeposition transfer. Temperature Electrochemistry: Kinetics: Coll. -hundred children. Sverdlovsk, USSR ounces. 1: 36-41.
- [13] Gshneyder K.A. 1965. Alloys of rare earth metals. M.: Mir.