ON APPLICABILITY OF THE TWO-PHASE ALLOYS OF PRASEODYMIUM AND NEODYMIUM WITH INDIUM AND BISMUTH ACTING AS REFERENCE ELECTRODES IN THE GALVANIC CELLS WITH MOLTEN ELECTROLYTE

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It is shown, that liquid two-phase (liquid alloy + intermetallic compound) alloys of praseodymium and neodymium with indium or bismuth can be used as trusty reference electrodes, allowing to study the processes of alloy formation between the mentioned above 4f-elements and individual low-melting metals or their metallic compositions. The dependencies of potential differences between metal electrode (Pr and Nd) and the two-phase alloy, formed by the corresponding rare earth metal and indium or bismuth, are given in the wide temperature range between 573-1073 K. Partial thermodynamic functions ($\Delta\bar{H}, \Delta\bar{S}, \Delta\bar{G}$) of praseodymium and neodymium in the two-phase alloys were calculated.

Introduction

Recently bismuth and its alloys with metals from the 13th and 14th groups of the periodic table increasingly attract attention of engineers and scientists developing new generation of safety nuclear power plants and technologies of spent nuclear fuel (SNF) reprocessing. An interest to bismuth alloys is related with need in designing new engineering solutions in the mentioned field. Bismuth and its alloys can be applied as:

- liquid electrodes for uranium and minor actinides electrowinning [1, 2];

- liquid metal extractants in the "molten salt – liquid metal" systems [3-5];

- media for rare earth metals (REM) reduction from tail-ends of SNF after pyrochemical reprocessing using lithium drawdown [6];

- heat transfer agent of nuclear reactors with molten salt core [7], etc.

Indium and its alloys with other low-melting metals, including REM doped alloys, find applications in technologies of producing composite and lead-free solders [8].

It is evidently, that the lack of the data on thermodynamics of alloys formation between bismuth and indium with lanthanides and actinides does not allow realizing the abovementioned engineering activities. In addition, the alloys of bismuth and indium with 4f-metals are of independent interest since they may be applied for studying thermodynamics of multicomponent alloy formation employing classic electromotive force (emf) method. Application of the two-phase alloys excludes the need to use solid metal rare earth electrodes in the galvanic cells with molten electrolyte. The present work is aimed in generalization of the existing thermodynamic data and experimental study the thermodynamics of alloy formation between lanthanides (Pr and Nd) and indium or bismuth. The necessity for the study is caused by increasing attention to the alloys of rare earth metals with bismuth [9] and indium, as well as there is still a lack of thermodynamic data on the activity of 4f-elements in the binary metal melts [10].

Experimental

In the alloys of praseodymium with indium (with Pr content up to 29 wt.%) forms only one intermetallic compound (IMC) $PrIn_3$. The compound has not phase transformations up to the melting point (1210 °C). On the phase diagram liquidus line of the binary Pr-In alloys is reliably determined. In the alloys Pr-Bi, with praseodymium content up to 25 wt.%, forms intermetallic compound $PrBi_2$. The compound has not phase transitions up to the melting temperature. However, liquidus line of the alloys Pr-Bi on the binary phase diagram is not trustworthy found [11].

In the alloys of neodymium with indium (with Nd content up to 29.5 wt.%) in equilibrium with liquid phase is stable $NdIn_3$ compound. As in case of the Pr-In system, the compound has not phase transformations up to the melting point (1220 °C). Liquidus line of the Nd-In alloys was determined trustworthy for the entire series of alloys. In the Nd-Bi alloys, containing up to 26 wt.% of Nd, forms compound $NdBi_2$. It has no phase transitions up to 1600 °C. Liquidus line of the Nd-Bi alloys is reliably determined only for alloys, containing more than 10 wt.% of Nd [11].

For praseodymium and neodymium activity determination in the alloys with indium or bismuth it is necessary to measure potential difference between the poles of galvanic cells (1) and (2) respectively:

$$(-)\ Ln^0\ |\ LiCl\text{-}KCl\text{-}CsCl + 0.1\ mol.\%LnCl_3\ |\ L + LnIn_3\ (+), \qquad (1)$$

$$(-)\ Ln^0\ |\ LiCl\text{-}KCl\text{-}CsCl + 0.1\ mol.\%LnCl_3\ |\ L + LnBi_2\ (+), \qquad (2)$$

where Ln = Pr or Nd.

A salt electrolyte preparation method, a scheme of experimental cell and the electromotive force (emf) measurements procedure are described in paper [12] in details. Weighted indium or bismuth with REM addition (around 10-14 wt.%) were introduced into crucibles of beryllium oxide. The crucibles with weighted metals (up to 8 pieces) were placed into BeO container, then molybdenum current leads were introduced into crucibles and, finally, hot (at 500 °C) ternary LiCl-KCl-CsCl melt completely filled the container and covered the crucibles. The described above container was installed into preliminarily assembled holder. The holder with BeO container was very quickly transferred into the stainless steel cell. After that, the cell was sealed, evacuated and refilled for 3 times with purified argon in order to exclude air moisture capturing by the salt melt. The required amounts of rare earth metal chlorides were introduced into the salt melt by electrolysis at the beginning of the experiment at 600-650 K. Hereafter the cell was heated in the furnace to 1073 K for Ln-In (Ln-Bi) alloys homogenization. After exposure for 3-4 hours we believed that homogenization of alloys was reached and then the potential difference measurements were started. Varying temperature inside the experimental cell in increments of 50 degrees, the whole interval of measurements was passed. At each fixed temperature the equilibrium potential between the electrodes of the galvanic cell was recorded, upon condition that the measured value did not changed by more than 0.5 mV for 1 hour. The studied temperature range was passed for several times from high to low temperatures and inversely.

The REM electrodes (a negative pole of the galvanic cell) were held on molybdenum current lead. The metal electrodes were immersed into BeO container after salt melting. In case of employing REM electrodes experiment was conducted rather fast (within 24 hours). During whole experiment the cell was filled with argon, argon pressure was kept constant a little bit higher than equal to atmospheric.

In the experiments the following reagents and substances were used: praseodymium (PrM-1 ($\geq$ 99.8%), TU 48-1-215-72), neodymium (NM-1 ($\geq$ 99.9% Nd) TU 48-4-205-72), indium (In-000 ($\geq$ 99.9996% In) GOST 10297–75), bismuth (Bi-000 ($\geq$ 99.999 Bi), lithium chloride (ROTH ($\geq$ 99%)), potassium chloride (OSCH 5-4), cesium chloride (OSCH 17-2), high purity argon (GOST 10157–79).

Fundamentals
Activity (*a*), activity coefficients (γ) and solubility (X) of metal in the alloy are bound to each other by simple expression (3):

$$\log a = \log \gamma + \log X. \qquad (3)$$

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For determination the activity of any metal in the alloy it is necessary to measure difference of potentials between individual metal and its alloy employing the emf method. Relations between activity and potential differences can be easily found from the following simple dependencies (4-6):

$$\Delta\overline{G} = -n\,F\,E; \tag{4}$$

$$\Delta\overline{G} = 2.303R\,T\,\log a; \tag{5}$$

$$\Delta\overline{G} = \Delta\overline{H} - T\cdot\Delta\overline{S}, \tag{6}$$

where n is a number of electrons, acting in the exchange process between salt melt and metal electrode, $F = 96484.56$ C/mol – Faraday constant, E – the measured value of potential difference, V, R = 8.31441 J/(mol×K) – universal gas constant, T – temperature given in Kelvin degrees, $\Delta\overline{H}$, $\Delta\overline{S}$, $\Delta\overline{G}$ the change of partial enthalpy, entropy and free Gibbs energy of the metal during the alloy formation process.

Taking $n = 3$ [13, 14] (as a stable oxidation state of Pr and Nd in chloride melts) and equating the expressions (4) and (5) it is easily to find relations between temperature dependencies of emf and activity of metal in the alloy. Equating left sides of formulas (5) and (6) and presenting the temperature dependence of activity as (7):

$$\log a = c + d/T, \tag{7}$$

simple equations (8) can be obtained for calculating thermodynamic parameters $\Delta\overline{H}$ and $\Delta\overline{S}$:

$$\Delta\overline{H} = 2.303\text{R}\cdot d, \quad \Delta\overline{S} = -2.303\text{R}\cdot c. \tag{8}$$

Results and discussion

In case of rare earth metal electrodes application in the galvanic cells with molten electrolyte the secondary processes may take place. It is known that in the electrochemical series, potentials of REM are very close to the potentials of the alkali metals forming salt electrolytes. Firstly, this leads to reducing alkali metals (lithium) from their chloride melts by REM. Secondary, corrosion (dissolution) of metal REM in the electrolyte may occurs. In its turn, reduced alkali metals can dissolve in their own chloride melts. After contact between salt melts containing reduced metals of the 1st group and liquid metal electrodes an uncontrolled alloy formation of metal melt components with alkali metals takes place. The latter process starts depletion of salt melt by REM ions and changes

composition of liquid electrodes. It is especially critical when diluted by REM alloys are under investigation. Moreover, a currentless metal transport from one electrode to another is also possible in the studied electrochemical cells.

The described secondary processes cannot be quantified and determine errors of the emf method. The errors are particularly defined by gradient of potential-determining ion concentrations in the volume of salt electrolyte. Therefore lack of metal electrodes corrosion is an indicator of measurements correctness. For inhibiting corrosion processes it is necessary to pay attention to the preparation quality of the salt electrolyte, as well as taking readings of potential difference fast, and, if it is possible, avoid using the rare earth metal electrodes. As an alternative to the metal electrodes the binary two-phase (L+IMC) alloys of REM with some low-melting metals can be applied. In the described alloys thermodynamic activity of REM is decreased in 8-10 orders by magnitude, providing absence of corrosion processes. An exchange of metal REM electrodes to the two-phase alloys (L+LnIn$_3$ or L+LnBi$_2$), acting as reference electrodes, is possible if emf temperature dependencies of the galvanic cells (1) and (2) are known. Then applying the emf addition rule i.e. summarizing both values of potential differences between the investigated alloy and the reference electrode and values of potential differences between the metal electrode and the reference electrode it is possible to calculate the potential difference between the studied alloy and the metal REM electrode.

An alloy, forming the reference electrode, should meet the following requirements: 1) thermodynamic properties of reference electrode alloy should be surely determined by independent groups of researchers; 2) the dissolved in the alloy rare earth metal should be in equilibrium only with one type of intermetallic compound with well-known phase structure; 3) the reference electrode and its components should not have phase transitions in the entire studied temperature range; 4) it is desirable that the emf temperature dependence of the reference electrode should described by linear equation in the entire temperature range. According to the binary phase diagrams [11] the alloys of praseodymium and neodymium with indium and bismuth satisfy the given above requirements. Therefore it has caused an interest in their study.

The emf temperature dependence of L+PrIn$_3$ alloys is described by equation (9) between 573-1073 K. At temperatures above the phase transition α-Pr→β-Pr (T=1069 K) [10] a thermodynamic amendment of emf $\Delta E_{\alpha\text{-Pr}\to\beta\text{-Pr}} = -0{,}011 + 1.0\times10^{-5}\,T$ was added. The temperature dependence of praseodymium activity in alloys (L + PrIn$_3$) is approximated by equation (10) in terms of "compact form of experimental data representation":

$$E_{L+Pr\,In_3} = (833.2 - 0.303T) \pm 1.98\sqrt{75.4\ (\frac{1}{110} + \frac{(T-800.7)^2}{1.5\cdot10^6})},\,mV \quad (9)$$

$$\log a_{\alpha-Pr(In)} = (4.58 - 12600\,/\,T) \pm 1.98\sqrt{0.010\ (\frac{1}{110} + \frac{1000\,/\,T-1.276)^2}{4.1})}. \quad (10)$$

The emf of the galvanic cell (2) is described by equation (11) between 633-973 K, applied for the Pr-Bi alloys (in equilibrium L+PrBi$_2$):

$$E_{(L+Pr\,Bi_2)} = (928.5 - 0.238\ T) \pm 1.98\sqrt{0.017\ (\frac{1}{156} + \frac{(T-807.0)^2}{1.4\cdot10^6})},\,mV. \quad (11)$$

Activity of α-praseodymium in alloys with bismuth is adequately approximated by the linear equation (12):

$$\log a_{\alpha-Pr(Bi)} = (3.59 - 14040\,/\,T) \pm 1.98\sqrt{0.017\ (\frac{1}{156} + \frac{(1000\,/\,T-1.257)^2}{3.7})}. \quad (12)$$

The emf temperature dependence of (L+NdIn$_3$) alloys and the temperature dependence of activity of neodymium in the two-phase alloy with indium can be expressed by equations (13) and (14) between 623-973 K respectively:

$$E_{(L+NdIn_3)} = (848.6 - 0.340\ T) \pm 2.00\sqrt{40.64\ (\frac{1}{58} + \frac{(1000\,/\,T-1.25)^2}{1.35})},\ mV. \quad (13)$$

$$\log a_{\alpha-Nd(In)} = (5.14 - 12830\,/\,T) \pm 2.00\sqrt{0.016(\frac{1}{58} + \frac{(1000\,/\,T-1.25)^2}{1.35})}. \quad (14)$$

In the range of 573-1073 K the dependence $E = f(T)$ of the galvanic cell (2) of alloys (L+NdBi$_2$) and the temperature dependence of α-neodymium in the two-phase alloy with bismuth are approximated by equations (15) and (16) respectively:

$$E_{(L+NdBi_2)} = (875.4 - 0.194T) \pm 1.98\sqrt{68.3\ (\frac{1}{110} + \frac{(T-843.1)^2}{1.95\cdot10^6})},\,mV \quad (15)$$

$$\log a_{\alpha-Nd(Bi)} = (2.93 - 13235/T) \pm 1.98 \sqrt{0.023 \left(\frac{1}{110} + \frac{(1000/T - 1.218)^2}{4.5}\right)}. (16)$$

A thermodynamic amendment for neodymium phase transitions was not added. In the studied temperature ranges the first phase transition temperature of neodymium ($T_{\alpha-Nd \to \beta-Nd}$= 1128 K) was not reached [10].

In Fig. 1 and 2 are shown the emf temperature dependencies of the two-phase alloys (L + IMC) of lanthanides with indium and bismuth in the studied temperature interval and the same dependencies obtained by another groups of researchers in narrower temperature ranges. It is evidently that the emf values received by independent researchers for alloys (L+PrIn$_3$ and L+PrBi$_2$) are almost identical.

Partial thermodynamic characteristics of α-praseodymium and α-neodymium in the two-phase alloys with indium and bismuth are given in the table.

Partial thermodynamic characteristics of α-praseodymium and α-neodymium in the two-phase alloys with bismuth and indium

Alloy	$-\Delta \overline{H}_{Ln}$, kJ/mol	$-\Delta \overline{S}_{Ln}$, J/mol·K	$-\Delta \overline{G}_{Ln}$, kJ/mol			Re-fe-rence
			675 K	775 K	973 K	
L+PrBi$_2$	268.8±2.6	68.8±3.2	222.3±0.5	215.4±0.3	201.8±0.6	P.w.*
	259.4±2.6	61.9±3.1	217.6±0.6	211.4±0.3	199.2±0.5	[15]
L+PrIn$_3$	241.2±2.0	87.7±2.5	182.0±0.4	173.2±0.3	155.9±0.5	P.w.
	242.6±3.1	90.4±3.7	181.6±0.6	172.6±0.4	154.7±0.7	[15]
	243.7	91.3	-	172.9	154.9	[16]
L+NdBi$_2$	253.4±2.9	56.1±3.4	215.5±0.7	209.9±0.5	198.8±0.6	P.w.
	262.5±4.9	65.3±5.8	218.4±1.1	211.9±0.7	198.9±1.0	[17]
L+NdIn$_3$	245.6±4.2	98.3±5.1	179.3±0.8	169.4±0.5	150.0±0.9	P.w.
	233.9±7.8	81.7±9.2	178.7±1.8	170.5±1.1	154.3±1.4	[17]
	241.2	89.6	180.5	171.6	153.8	[18]

* Data obtained in the present work.

Values of partial thermodynamic functions of studied lanthanides in the alloys with indium and bismuth are in a good agreement with the same values obtained by other researchers. A good agreement of partial thermodynamic parameters confirms the possibility of applying the binary alloys (L+PrIn$_3$) and (L+NdIn$_3$) as reliable reference electrodes for use in the emf method.
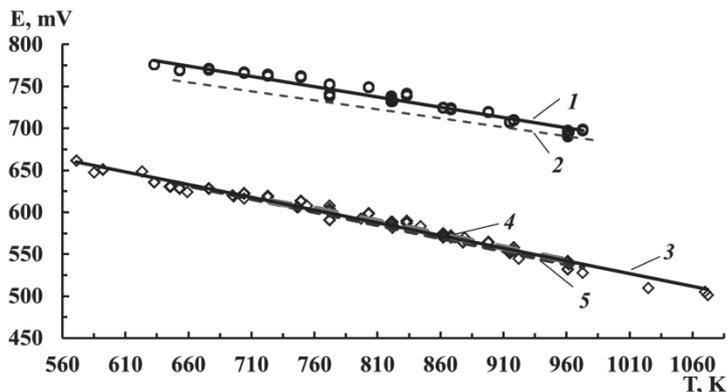

Fig. 1. Emf temperature dependencies of alloys formed by praseodymium with bismuth: 1 – present work, 2 – [15], with indium (lines are practically coincide), 3 – present work (573–1073 K), 4 – [15] (723–973 K), 5 – [16] (648–970 K)
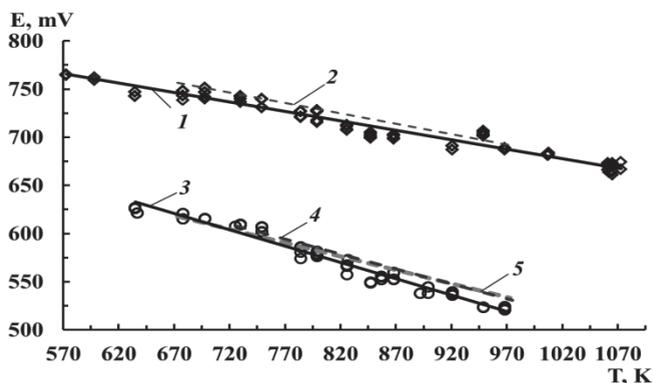

Fig. 2. Emf temperature dependencies of alloys formed by neodymium with bismuth: 1 – present work, 2 – [17]; with indium: 3 – present work (623–973 K), 4 – [18] (763–973 K), 5 – [17] (673–973 K)

Conclusions

Thermodynamic activity of REM in alloys with In and Bi is reduced by 6-16 orders in magnitude in the range of 573-1073 K. Alloys of indium and bismuth saturated by praseodymium or neodymium (up to 12 wt.%) can be applied as reliable reference electrodes in the galvanic cell with salt electrolyte. Studied two-phase electrodes are suitable for the emf measurements of rare earth containing alloys acting as alternative to the metal electrodes. The obtained temperature dependencies of emf and activity of REM in the alloys with indium and bismuth are in a good agreement with data provided by another groups of researchers that have measured the same dependencies in narrower temperature ranges.

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