SOV/2o-121-4-31/54

5(4)
AUTHORS: Smirnov, M. V., Ivanovskiy, L. Ye., Loginov, N. A.

TITLE: The Equilibrium Potentials of Titanium in Chloride Melts (Ravnovesnyye potentsialy titana v khloridnykh rasplavakh)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 121, Nr 4, pp 685-688 (USSR)

ABSTRACT: The authors measured the equilibrium potentials in pure argon in a hermetically closed wide test tube of quartz. On the bottom of this tube there was an eutectic mixture of lithium chloride and potassium chloride. An electrode of titanium iodide was fastened to a molybdenum feeder and it was immersed in a salt melt of the same composition. The potential of the titanium electrode was measured with respect to a lead electrode. The results of the measurements, (with respect to a chlorine electrode of comparison) are given in a diagram which demonstrates the dependence of the electromotive force on the temperature for various given concentrations of the titanium in the electrolyte. The experimental points agree well with straight lines. Another diagram shows the isothermal lines deduced from the above-mentioned results for 700, 800,

Card 1/3

The Equilibrium Potentials of Titanium in Chloride Melts

900, and 1000°K. The equilibrium potential of the metallic titanium electrode in chloride melts which contain less than 6 weight % of titanium depends on its molar concentration in the electrolyte according to the following thermodynamical equation:

$$E = E^{o}_{Ti/Ti^{2+}} + (2,3\ RT/2F)\ lg\ \left[Ti^{2+}\right] .$$

This shows that such melts contain ions of divalent titanium and behave as ideal solutions. The quantity $E^{o}_{Ti/Ti^{2+}}$ may be found from the above-mentioned experimental data, $E^{o}_{Ti/Ti^{2+}} = (-2,371 + 6,09.10^{-4}T)V$ is obtained with respect to the chlorine electrode. For the calculation of the isobaric potential for the composition of the liquid titanium dichloride from the elements the equation $\Delta Z = (-109\ 360 + 27,03\ T)$ cal/mol $TiCl_2$ may be used. There are 4 figures and 12 references, 3 of which are Soviet.

Card 2/3

SOV/20-121-4-31/54

The Equilibrium Potentials of Titanium in Chloride Melts

ASSOCIATION: Laboratoriya elektrokhimii Ural'skogo filiala Akademii nauk SSSR
(Laboratory of Electrochemistry of the Ural Branch, AS USSR)

PRESENTED: April 11, 1958, by A. N. Frumkin, Academician

SUBMITTED: March 25, 1958

Card 3/3

SMIRNOV, M.V.

Smirnov, M.V., and L.Ye. Ivanovskiy (Institute of Chemistry, Urals Branch, Academy of Sciences USSR). Electrolysis of a Chloride Bath With Titanium Monoxide Anodes, p. 100. Titan i yego splavy. vyp. II: Metallurgiya titana (Titanium and Its Alloys. No. 2: Metallurgy of Titanium) Moscow, Izd-vo AN SSSR, 1959. 179 p.

This collection of papers deals with sources of titanium; production of titanium dioxide, metallic titanium, and titanium sheet; slag composition; determination of titanium content in slags; and other related matters. The sources of titanium discussed are the complex sillimanite ores of the Kyakhtinskoye Deposit (Buryatskaya ASSR) and certain aluminum ores of Eastern Siberia. One paper explains the advantages of using ilmenite titanium slags for the production of titanium dioxide by the sulfuric acid method. Production of metallic titanium by thermal reduction processes (hydrogen, magnesium, and carbon reduction) is the subject of several papers, while other papers are concerned with the electrolytic production of titanium. Other subjects dealt with are interaction of titanium with water vapor and with hydrogen and the determination of titanium in slags.

SMIRNOV M.V.

~~BAKHCHISA[illegible], N.G.~~

5(4) PHASE I BOOK EXPLOITATION SOV/2216

Soveshchaniye po elektrokhimii. 4th, Moscow, 1956.

Trudy...; [sbornik] (Transactions of the Fourth Conference on Electrochemistry; Collection of Articles) Moscow, Izd-vo AN SSSR, 1959. 868 p. Errata slip inserted. 2,500 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Otdeleniye khimicheskikh nauk.

Editorial Board: A.N. Frumkin (Resp. Ed.) Academician, O.A. Yesin, Professor; S.I. Zhdanov (Resp. Secretary), B.N. Kabanov, Professor, S.I. Zhdanov (Resp. Secretary); B.N. Kabanov, Professor; Ya. M. Kolotyrkin, Doctor of Chemical Sciences; V.V. Losev, P.D. Lukovtsev, Professor; Z.A. Solov'yeva; V.V. Stender, Professor; and G.M. Florianovich; Ed. of Publishing House: N.G. Yegorov; Tech. Ed.: T.A. Prusakova.

PURPOSE: This book is intended for chemical and electrical engineers, physicists, metallurgists and researchers interested in various aspects of electrochemistry.

COVERAGE: The book contains 127 of the 138 reports presented at the Fourth Conference on Electrochemistry sponsored by the Department of Chemical Sciences and the Institute of Physical Chemistry Academy of Sciences, USSR. The collection pertains to different branches of electrochemical kinetics, double layer theories and galvanic processes in metal electrodeposition and industrial electrolysis. Abridged discussions are given at the end of each division. The majority of reports not included here have been published in periodical literature. No personalities are mentioned. References are given at the end of most of the articles.

Card 15/34

Card 16/34

SHIREOV, M.V.

Chemical form of the motion of matter. Part 1: Determination of the chemical form of the motion of matter. Filos. vop. fiz.i khim. no. 1:73-82 '59. (MIRA 14:2)
(Motion) (Chemical affinity) (Matter)

SMIRNOV, M.V.; IVANOVSKIY, L.Ye.

Electrolysis of the chloridizing bath with anodes of titanium oxide. Titan i ego splavy no.2:100-102 '59. (MIRA 13:6)

1. Institut khimii Ural'skogo filiala AN SSSR.
(Titanium--Electrometallurgy)

5(4) SOV/62-59-2-10/40

AUTHORS: Smirnov, M. V., Yushina, L. D.

TITLE: Equilibrium Potentials of Metals in Molten Electrolytes (Ravnovesnyye potentsialy metallov v rasplavlennykh elektrolitakh) Communication 1. Equilibrium Potentials of Thorium in Chloride Melts (Soobshcheniye 1. Ravnovesnyye potentsialy toriya v khloridnykh rasplavakh)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 2, pp 251-258 (USSR)

ABSTRACT: In the present paper the authors present the determination results of equilibrium potentials of thorium in equimolar mixture of sodium- and potassium chlorides both with and without thorium-chloride addition. The equilibrium potential of thorium in chloride melts which contained in the initial state 0.14 up to 78% $ThCl_4$ was measured in the temperature range of 680 - 825° (Fig 2). In order to determine the change of the electromotive force with the varying concentration of $ThCl_2$ in the melt, isothermal lines were drawn (Fig 3).

The molten mixtures of sodium- and potassium chloride with thorium dichloride behave in all concentrations of $ThCl_2$ like

Card 1/3

Equilibrium Potentials of Metals in Molten Electrolytes. Communication 1. Equilibrium Potentials of Thorium in Chloride Melts

ideal solutions. A dependence of the equilibrium potential of thorium on temperature and concentration was found. According to experimental data the oxidation-reduction potential of thorium in chloride melts as well as the equilibrium constant of the reaction was calculated:

$$Th^{4+}(melt) + Th \rightleftarrows 2Th^{2+}(melt).$$

In the temperature range of 680 - 825° the equilibrium constant varies from 51.1 up to 0.91. According to the temperature dependence of the electromotive force of galvanic elements with the melt containing thorium dichloride the quantities of the decomposition voltage of the molten $ThCl_2$ and the variation of the isobaric potential for the following reactions were calculated:

$$Th(solid) + Cl_2(gaseous) = ThCl_2(liquid$$

and $$ThCl_4(liquid) + Th(solid) = 2ThCl_2(liquid)$$

The stationary potential of thorium in the equimolar mixture KCl + NaCl at 700 - 842° was determined (Fig 4). There are

SOV/62-59-2-10/

Equilibrium Potentials of Metals in Molten Electrolytes. Communication 1. Equilibrium Potentials of Thorium in Chloride Melts

4 figures and 12 references, 9 of which are Soviet.

ASSOCIATION: Ural'skiy filial Akademii nauk SSSR (Ural Branch of the Academy of Sciences, USSR)

SUBMITTED: March 18, 1957

Card 3/3

SOV/78-4-1-30/48

5(2), 5(4)
AUTHORS: Tsiovkina, L. A., Smirnov, M. V.

TITLE: The Influence of the Nature of Cations and Anions on the Solubility of Titanium Tetrachloride in Salt Melts (Vliyaniye prirody kationov i anionov na rastvorimost' tetrakhlorida titana v solevykh rasplavakh)

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 1, pp 158-162 (USSR)

ABSTRACT: The solubility of titanium tetrachloride in melts of LiCl, KCl, CsCl, NaCl-KCl, and an equimolar mixture of NaCl-KCl with additions of 10, 15, and 20 wt.% NaF was examined at 650 - 800°. The dependence of the solubility of $TiCl_4$ on the nature of the cations in the melt shows a solubility increase in the direction from LiCl to CsCl. The solubility increase is caused by the formation of complex anions. The complex forming process is indicated by the following reactions:

$$TiCl_{4gas} + Cl^-_{melt} \rightleftarrows TiCl^-_{5melt},$$

$$TiCl^-_{5melt} + Cl^-_{melt} \rightleftarrows TiCl^{2-}_{6melt}.$$

Card 1/2

The Influence of the Nature of Cations and Anions on the Solubility of Titanium Tetrachloride in Salt Melts SOV/78-4-1-30/48

The dependence of the solubility of titanium tetrachloride in the melt of NaCl-KCl(1:1) on the temperature and the dependence of the solubility of the NaF concentration was investigated. In melts with fluorine ions the solubility of $TiCl_4$ increases with the formation of titanium fluorine complex TiF_6^{2-}. The complex ion TiF_6^{2-} has a higher temperature stability than the ion $TiCl_6^{2-}$. There are 6 figures and 13 references, 1 of which is Soviet.

SUBMITTED: October 28, 1957

Card 2/2

05871
SOV/78-4-11-24/50

5(2)
AUTHORS: Smirnov, M. V., Chukreyev, N. Ya.

TITLE: The Behavior of Beryllium in Fused Salt Baths in the Presence of Metallic Beryllium

PERIODICAL: Zhurnal neorganicheskoy khimii, 1959, Vol 4, Nr 11, pp 2536 - 2543 (USSR)

ABSTRACT: Alkaline- earth metals are dissolved in their chlorides under the formation of subchlorides. The authors found also for beryllium (Ref 3) that the Be^{+} ion is present in chloride melts in addition to the Be^{2+} ion. In order to confirm this result, the reaction of metallic Be in alkali-chloride melts is investigated here within the temperature range 351-600°. The reaction $Be^{2+}+Be=2Be^{+}$ is measured by variation of the redox potential of a molybdenum electrode. The redox potential varied by 1.3 v, and thus allowed for the determination of the smallest Be^{+} quantities. To make sure whether this was really a variation of the redox potential of the molybdenum electrode, the authors compared the potentials of the molybdenum electrode and the beryllium electrode with those of a chlorine electrode (Table 1). The Be electrode had a constant potential of -2.44 v

Card 1/3

The Behavior of Beryllium in Fused Salt Baths in the Presence of Metallic Beryllium

whereas the potential of the Mo electrode dropped from -1.13 v to - 1.82 v. Figure 1 shows the course of the redox potential during the experiments which were extended to 30 h. The potentials of the Mo and Be electrode could not be fully compensated because the surface of the latter was passivated. The weight loss of the Be anode was measured for the purpose of determining the equilibrium constant of the reaction $Be^{2+}+Be \rightleftharpoons 2\ Be^{+}$. The scheme of figure 2 shows the apparatus used. A eutectic LiCl-KCl melt served as electrolyte, the anode and cathode space were separated by a BeO pot, and the cathode was made of molybdenum wire. Results of 20 experiments are listed in table 2. As the Be anode corrodes in addition to the anodic dissolution of Be, the authors determined the dissolution rate of Be in chloride melts at the same experimental temperatures (Fig 3). The results corrected in consideration of the corrosion of Be in chloride melts and the equilibrium constant calculated for the experimental temperatures are listed in table 3. Figure 4 shows the temperature dependence of the equilibrium constant which satisfies the empirical equation

SOV/20-127-5-37/58

5(4)

AUTHORS: Smirnov, M. V., Chukreyev, N. Ya.

TITLE: The Redox Potential of the System Be^{+}/Be^{++} in a Melt of Alkali Metal Chlorides

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1066-1069 (USSR)

ABSTRACT: In preceding papers (Refs 1,2) the authors found that in chloride melts which are in contact with metallic beryllium, besides Be^{++}- also Be^{+}-ions are contained. There follows the determination of $E^{o}_{Be/Be^{+}}$, $E^{o}_{Be/Be^{++}}$, and $E^{o}_{Be^{+}/Be^{++}}$ on the basis of the corresponding thermodynamic equations for the equilibrium potentials of Be and its mono- and bivalent ions, and the determination of the redox potential of the system Be^{+}/Be^{++} in salt melts. Measurement of the equilibrium potential was carried out in a temperature interval 380-940° in a measuring cell, which is shown by figure 1. As an electrolyte, an eutectic melt of LiCl and KCl in argon atmosphere was used. Figure 2 shows the variation of the electromotive force of the cell $Be \mid BeCl_2, LiCl, KCl \mid Cl_2C$ with temperature. The isothermal line of the equilibrium potential of the beryllium electrode

Card 1/2

($E - \lg [Be]$, Fig 3) calculated on the basis of the experimental data, confirms that the melt contains Be^{+}-ions, the concentration of which decreases with increasing temperature. Table 1 shows the results of calculation for melts with different beryllium content in the temperature interval 700 - 1200°K. Figure 4 shows the temperature dependence for $E^{o}_{Be/Be^{+}}$ and $E^{o}_{Be/Be^{++}}$.

Empirical equations are written down for this temperature dependence, and the constants of the thermodynamic equation for the redox potential of the system Be^{+}/Be^{++} are calculated. There are 4 figures, 1 table, and 3 Soviet references.

ASSOCIATION: Institut elektrokhimii Ural'skogo filiala Akademii nauk SSSR (Institute of Electrochemistry of the Ural Branch of the Academy of Sciences, USSR)

PRESENTED: April 13, 1959 by A. N. Frumkin, Academician

SUBMITTED: April 13, 1959

S/631/60/000/001/001/014
B101/B147

AUTHOR: Smirnov, M. V.

TITLE: Residual currents and cathodic current yield in the electrolysis of salt melts

SOURCE: Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov, no. 1, 1960, 3-6

TEXT: Previous studies on the electrodeposition of Be (ZhFKh, 32, 2174, 1958), Th (Izv. AN SSSR, OKhN, 1285, 1956), Ti (Izv. Sibirskogo otd. AN SSSR, 1960), Zr and Hf have shown that a charge reversal of ions to subions occurs: $Me^{z+} + ne = Me^{(z-n)+}$. The metal deposition sets in as soon as the concentration of these ions in the electrolyte layer close to the cathode corresponds to the equilibrium between them and the salt melt. The charge reversal produces a residual current. The cathodic potential φ is given by $\varphi = E^{o}_{Me^{(z-n)+}/Me^{z+}} + (RT/nF)\ln\left\{nFD_{Me^{(z-n)+}}[Me^{z+}]/\delta i\right.$

Card 1/3

Residual currents and cathodic...

$- D_{Me^{(z-n)+}}/D_{Me^{z+}}\}$, where $E^{o}_{Me^{(z-n)+}/Me^{z+}}$ is a constant of the thermodynamical equation of the redox potential, $D_{Me^{z+}}$, $D_{Me^{(z-n)+}}$ are the diffusion constants of the ions in the melt, δ is the thickness of the diffusion layer on the cathode, $[Me^{z+}]$ is the molar part concentration of the metal ion with ordinary valence in the melt. The residual current caused by the cathodic charge reversal can now be written as

$$i_{res} = nFD_{Me^{(z-n)+}}[Me^{z+}]/\delta\left\{\exp\left[(nF/RT)(\varphi - E^{o}_{Me^{(z-n)+}/Me^{z+}})\right] + D_{Me^{(z-n)+}}/D_{Me^{z+}}\right\}.$$

i_{res} reaches a limit when the deposition of the metal begins ($\varphi = E^{equ}_{Me}$ = const). The ratio of the molar part concentration of the ions remains also constant: $[Me^{(z-n)+}]_s/[Me^{z+}]_s^{(z-n)/z} = K$. If no metal is lost by side reactions on the cathode the current yield is given by $\eta = 1 - i_{res}/i$. If the accumulation of ions of low valency is prevented by

Card 2/3

BARABOSHKIN, A.N.; SMIRNOV, M.V.

Time necessary to attain a steady state in electrolysis with a constant current intensity. Trudy Inst.elektrokhim.UFAN SSSR no.17-16 '60. (MIRA 15:2)

(Salts)
(Electrolysis)

S/631/60/000/001/002/014
B101/B147

AUTHORS: Komarov, V. Ye., Smirnov, M. V., Baraboshkin, A. N.

TITLE: Equilibrium potentials of zirconium in a fused equimolar mixture of sodium chloride and potassium chloride

SOURCE: Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov, no. 1, 1960, 17-22

TEXT: Measurements were made at 687-978°C in an equimolar NaCl + KCl melt with 0.16-6.8 % by weight of Zr in an argon atmosphere in order to determine the temperature coefficient of the equilibrium potentials of Zr with respect to the chlorine electrode and to clarify the effect of cations on this coefficient. The emf between Zr and Cl was found to be
$\varepsilon_1 = 2.560 - 3.62 \cdot 10^{-4}T \pm 0.005$ v for 0.16 % by weight of Zr;
$\varepsilon_2 = 2.587 - 4.72 \cdot 10^{-4}T \pm 0.002$ v for 1.24 % by weight of Zr;
$\varepsilon_3 = 2.600 - 5.43 \cdot 10^{-4}T \pm 0.003$ v for 6.8 % by weight of Zr. Taking into account the thermo-emf between the carbon current lead to the chlorine

Card 1/4

Equilibrium potentials of zirconium in...

electrode and the molybdenum lead to the zirconium electrode, the following equilibrium potentials are obtained: $E_1 = -2.552 + 3.45 \cdot 10^{-4} T$ v; $E_2 = -2.579 + 4.55 \cdot 10^{-4} T$ v; $E_3 = -2.592 + 5.26 \cdot 10^{-4} T$ v. Owing to the reaction $Zr^{4+}_{melt} + Zr \rightleftharpoons 2Zr^{2+}_{melt}$ (1) the isothermal lines are not linear. At low Zr concentrations, the equilibrium constant of this reaction is given by $K = (1-x)^2 [Zr]/x$, where x = molar part of the Zr^{4+} ions, and [Zr] = total concentration of Zr. 1 - x = molar part of the Zr^{2+} ions. The average valency of Zr at $[Zr] = 5.83 \cdot 10^{-4}$ is approximately 2. For $[Zr] = 2.46 \cdot 10^{-2}$ it is 2.36 at 1000°K and 2.28 at 1200°K. $\Delta H^o_{ZrCl_2} = -112.3$ kcal/mole was found in an LiCl + KCl melt, whereas $\Delta H^o_{ZrCl_2}$ amounts to -117.7 kcal/mole for the NaCl + KCl melt. This difference is due to the interaction of Zr^{2+} with chlorine ions in the

Card 2/4

Equilibrium potentials of zirconium in...

Assuming a latent heat of fusion of $ZrCl_4$ equal to 9.0 kcal/mole, the heat of formation of $ZrCl_6^{2-}$ ions in the melt is found to be -16 kcal/mole.

A paper of I. S. Morozov, D. Ya. Toptygin (Izv. AN SSSR, OKhN, 1920, 1959) is mentioned. There are 4 figures, 1 table, and 10 references: 6 Soviet and 4 non-Soviet. The four references to English-language publications read as follows: E. M. Larsen, J. J. Leddy, J. Am. Chem. Soc., 78, 5983, 1956; P. Gross, C. Hayman, D. L. Levi, Trans. Farad. Soc., 53, 1285, 1957; A. A. Palko, A. D. Ryon, D. W. Kuhn, J. Phys. Chem. 62, 319, 1958; L. Jang, R. G. Hudson, Trans. Metallurg. Soc. AIME, 215, 589, 1959.

Card 4/4

Thermodynamics of formation of the ...

$\Delta\mathcal{E}>0$, the greater part of titanium is bound to the fluorine complex, with $\Delta\mathcal{E}<0$, to the chlorine complex. TiO_2 - C electrodes were produced from pure TiO_2 for the experiment. TiO_2 was mixed with concentrated, aqueous glucose solution. The mixture was evaporated and the residue pulverized. Cylindrical electrodes were molded from the powder and heated at 800°C with exclusion of air. The pyrolysis of glucose yielded carbon forming a homogeneous mixture with the oxide. An analysis of the electrode yielded 52.39% Ti and 11.64% C. The following reaction proceeeded on this electrode: $TiO_2 + C - 3e \rightarrow Ti^{3+}$. Ti^{3+} ion saturation in the electrolytic layer near the cathode gives a constant potential. At first, an equimolecular NaCl and KCl mixture was used as electrolyte. 0.50% by weight NaF was added in a second series of experiments. With higher NaF content, the TiO_2 - C electrode was destroyed. The melt was subjected to reduced pressure for 1 hr, and the gas room filled with CO_2 and CO to fix a constant oxygen activity in the system. The chlorine electrode was

Card 2/4

$\Delta Z = -27\,190 - 27.513\,(1.694 + \log [F^-]).T + 550$ cal/g-ion;
$\Delta H = -27.2$ kcal/g-ion; $\Delta S = 27.513\,(1.694 + \log [F^-])$. ΔS changes its sign at $[F^-] = 2{,}07 \cdot 10^{-3}$. For a lower concentration, $\Delta S < 0$. For a higher, $\Delta S > 0$. The decrease in entropy with decreasing fluorine ion concentration may be explained by the arrangement of fluorine ions around titanium cations. There are 2 figures and 12 references: 7 Soviet and 5 non-Soviet. The three references to English-language publications read as follows: N. F. H. Bright, J. F. Rowland, R. H. Lake. Can. Dept. Mines and Tech. Surveys, Mines Branch Rept. N MD 196; J. G. Wurm, L. Gravel, R. J. A. Potvin. J. Electrochem. Soc., 104, 301, 1957; W. C. Kreye, H. H. Kellog, J. Electrochem. Soc., 104, 504, 1957.

ASSOCIATION: Institut elektrokhimii Ural'skogo filiala AN SSSR
(Institute of Electrochemistry of the Ural Branch AS USSR)

Card 4/4

Behavior of anodes of an intimate ...

low current density ($1 \cdot 10^{-4}$ - $1 \cdot 10^{-3}$ a/cm^2), the potential changes little, but it rises quickly at higher current densities. The redox potential of Ti^{4+}/Ti^{3+} in the chloride melt is -0.8 v. Hence, it is concluded that Ti^{3+} passes into the electrolyte since $\left[Ti^{4+}\right]/\left[Ti^{3+}\right] \approx 10^{-2}$. The following reaction takes place: $TiO_2 + C - 3e = Ti^{3+}_{(m)} + CO_2$ (m = melt). The Ti ions enter the melt, like the low Ti oxides. Anodic dissolution depends on O_2 diffusion from the electrolyte to the TiO_2 - C electrode. The anode current density can only be increased when the discharged chlorine ions react with the TiO_2 - C electrode. 11,000 TiO_2 particles fall to 1 cm^2 of electrode surface. The effective cross section of the oxide layer was $3.22 \cdot 10^{-3}$ cm, its resistance $R \approx 1$ ohm. The high polarization observed is due to the change in O_2 concentration on the surface of oxide particles in contact with the melt, and in the concentration of Ti ions

Card 2/4

S/631/60/000/001/004/014
B140/B110

Behavior of anodes of an intimate ...

1 non-Soviet.

ASSOCIATION: Institut elektrokhimii Ural'skogo filiala Akademii nauk SSSR (Institute of Electrochemistry of the Ural Branch of the Academy of Sciences USSR)

SUBMITTED: 1960

Card 4/4

S/631/60/000/001/005/014
B117/B147

AUTHORS: Smirnov, M. V., Krasnov, Yu. N.

TITLE: Oxide - carbon anodes with lowest titanium oxides in electrolysis of chloride melts

SOURCE: Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov, no. 1, 1960, 35-41

TEXT: The behavior of oxide - carbon anodes with lowest metal oxides was investigated. For this purpose, the polarization of titanium monoxide and titanium sesquioxide - carbon anodes was studied, and the products of electrolysis at various current densities were determined. An equimolar melt of sodium and potassium chlorides was used as electrolyte. The polarization of titanium monoxide - carbon anodes was measured at 740 and 830°C, that of titanium sesquioxide - carbon anodes at 730 and 805°C. The authors found that the potentials of oxide - carbon anodes and the corresponding oxide anodes at current densities below 1 a/cm^2 (with

Oxide - carbon anodes with lowest ...

TiO+C) and 0.5 a/cm^2 (with Ti_2O_3+C) were similar. The only difference is that the former potential increases with the current density much more rapidly than the latter. It is also characteristic that the precipitation of carbon dioxide on oxide - carbon anodes with TiO and Ti_2O_3 sets in not at the beginning of electrolysis as with TiO_2+C, but later, and the more so the lower the current density. Gas separation sets in more rapidly on anodes with Ti_2O_3 under otherwise equal conditions.

Experimental data allow definite conclusions on processes during the electrolysis of salt melts on oxide - carbon anodes with TiO and Ti_2O_3. These anodes first dissolve like oxide anodes without carbon participation which only supplies oxide particles with current:

$$3TiO_{(solid)} - ne \rightarrow Ti_2O_3\ (solid) + Ti^{n+}\ (melt)$$

$$2Ti_2O_{3(solid)} - me \rightarrow 3TiO_{2(solid)} + Ti^{m+}\ (melt).$$

Card 2/4

Oxide - carbon anodes with lowest ...

In the case of electrodes with TiO, the first electrode reaction takes place at current densities not higher than 0.2 - 0.3 a/cm^2 if their potential is more negative than -1.5 v. At higher current densities and more positive potentials, a new phase of changing Ti_2O_3 composition forms which yields titanium ions in the melt corresponding to the second electrode reaction. The fact that carbon does not participate in electrode reactions agrees with thermodynamical calculations. Summary: Electrolysis with Ti_2O_3+C anodes, without gas separation at its beginning suggests that carbon does not participate in the dissolution which proceeds therefore like that with a pure Ti_2O_3 anode. If the oxygen content of the surface layer of sesquioxide approaches its maximum (the anode potential reaching -1.3 to -1.2 v referring to the chlorine electrode), carbon starts participating in the process. If the current density is increased, the second reaction prevails. The polarization curve shows a salient point and a new wave. The latter lies in the same potential range as with TiO_2+C anodes but at a higher current density.

Card 3/4

At maximum diffusion current, further increase of anodic current density is only possible at the expense of a discharge of chlorine ions, which are adsorbed on carbon particles and then participate in the chlorination of the oxide - carbon mixture. An ever-increasing portion of tetravalent titanium passes over into the electrolyte as the anode potential increases. The ratio of tri- and tetravalent titanium is determined by the redox potential according to the thermodynamic equation

$$E = E^{o}_{Ti^{3+}/Ti^{4+}} + RT/F \ln (Ti^{4+})/(Ti^{3+})$$

There are 4 figures and 5 Soviet references.

dependence between the current yield for titanium on the current density D_a at 500°C. With $D_a > 0.1$ a/cm^2 mainly $TiCl_4$ is formed, which is sublimated from the melt. Fig. 2 represents the polarization of the titanium carbide anode at 530, 650, and 800° ($D_a = 5 \cdot 10^{-4}$ to 1 a/cm^2) in the coordinates log i_a, φ (φ = potential referred to a chlorine electrode). The authors discuss the low polarization at small D_a, which they ascribe to diffusion of titanium from the interior of the electrode toward the surface. The respective equations are written down. The decomposition of the carbide anode starts at potentials which, depending on D_a and temperature, are 0.5 - 1.4 v more negative than the potentials of chlorine separation, and are accompanied by a polarization of 0.5 - 0.65 v. Fig. 3 shows the temperature dependence of the potential of the TiC-C electrode with respect to a Cl electrode. Moreover, the authors discuss the system Ti - C, which below 900°C consists of the metallic α-phase with less than 1 per cent of C and the δ-carbide phase with 13 - 20 per cent of C. The emf of the cell $Ti/TiCl_2, TiCl_3, LiCl, KCl_{melt}/Ti_{1+x}C$ between 425 and 725°C and its

Card 2/3

67945

S/020/60/130/03/027/065
B004/B011

5.4700
5.2200(A)

~~5(4)~~

AUTHORS: Smirnov, M. V., Nichkov, I. F., ~~Raspopin, S. P.~~, Perfil'yev, M. V.

TITLE: Investigation of the Thermodynamics of the Reaction $UO_2(s) + \frac{1}{2}C(gr) + Cl_2(g) = UOCl_2(s) + \frac{1}{2}CO_2(g)$ by Means of the Method of Electromotive Forces

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 3, pp 581-584 (USSR)

ABSTRACT: It had been stated in earlier papers (Refs 1-3) that electrodes pressed from metal oxides and carbon are reversible with respect to the corresponding cation in chloride melts. This allows their utilization for investigating the thermodynamic processes and some reactions by measuring the emf. The authors had found in reference 1 that $ThOCl_2$ in melts of chlorides or chlorides and fluorides are practically insoluble. They accepted this for $UOCl_2$ as well and investigated the reaction between uranium dioxide carbon electrodes and melts of alkali chlorides containing UCl_4. By measuring the temperature de-

Card 1/4

Investigation of the Thermodynamics of the Reaction $UO_2(s) + \frac{1}{2}C(gr) + Cl_2(g) = UOCl_2(s) + \frac{1}{2}CO_2(g)$ by Means of the Method of Electromotive Forces

occurred the earlier, the higher the temperature and the UCl_4 content in the melt (Fig 2). With high UCl_4 content in the melt, the electrode is destroyed. The appearance of the equilibrium potential corresponds to the reaction $UO_2(s) + UCl_4(melt) \rightleftharpoons 2UOCl_2(s)$. Experimental data are on the straight line $\varepsilon = (0.713 + 4.8.10^{-4}T)v$ (Fig 3). Herefrom, the authors calculated for the reaction

$UO_2(s) + \frac{1}{2}C(gr) + Cl_2(g) = UOCl_2(s) + \frac{1}{2}CO_2(g)$

$\Delta Z = (-32900 - 2.2T)$ cal/mol $UOCl_2$, and the heat effect $\Delta H = -32.9$ kcal/mol $UOCl_2$ as well as the entropy $\Delta S = 2.2$ cal/degree.mol $UOCl_2$. The formation heat and the entropy of the $UOCl_2$ were calculated on the strength of the thermodynamic data offered in reference 9: $\Delta H^o_{UOCl_2}$ = - 255.9 kcal/mol, $S^o_{UOCl_2}$ = 49.2 cal/degree.mol [illegible] The

Smirnov, M V.

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B004/B064

5.4600

AUTHORS: Smirnov, M. V., Komarov, V. Ye., Baraboshkin, A. N.

TITLE: Equilibrium Potentials of Zirconium in Mixed Fluoride - Chloride Melts

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 2, pp. 409 - 412

TEXT: The authors carried out their investigations in equivalent mixtures from KCl + NaCl under addition of different amounts of fluorides at 700 - 950°C. The melt was produced from chemically pure salts, the zirconium being introduced by means of anodic dissolution of its iodide into the melt directly in the test cell (Fig. 1). Argon served as protective atmosphere. The potentials of melts 0.17 up to 1.05 wt% Zr and up to 15.82 wt% F were measured. The molar ratio of concentration $[F]/[Zr]$ was varied between 9 and 75. The experiments showed that the potential of Zr is more strongly influenced by the concentration of fluorine than by its own concentration. A reaction equation is written down for the formation of the zirconium - fluoride complexes, in which

Card 1/3

81869
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Equilibrium Potentials of Zirconium in Mixed Fluoride - Chloride Melts

the number of F ions that are bound to Zr as complexes is designated with m, the avarage valency of Zr with n. The equation

$E = \text{const} - 1.984 \cdot 10^{-4} T \log [F^-]$ is set up for the dependence of the potential on the concentration of the free fluorine ions. It was checked at 770°C, variation of the fluorine content of 2.04 to 15.82 wt% and constant Zr concentration of 1.05 ± 0.2 wt%. The graphical representation of the experimental data (Fig. 2) yields for m = 6,5,4 straight line, for which empirical equations are written down. The change of m and n is discussed and the following found: $4 \geq n > 2,5$. Formation of different ions at $[F]/[Zr] > 10$ and $[F]/[Zr] < 10$. Fig. 3 shows the results of experiments at temperatures of from 500 to 1250°K for five melts with $[F]/[Zr]$ from 45 to 9, for which also empirical equations were written down. Assuming that in the case of 10 - 15 wt% Zr the fluoride - chloride melts behave in a similar way as if thorium were added (Ref. 3), the equation is written down for the equilibrium potential. In the case of an excessive quantity of fluorine $75 > [F]/[Zr] > 10$ as occurs in the practical electrolysis of fluorine zirconate, it holds that $4 > n > 3$ and $6 > m > 4$. For approximative

Card 2/3

SMIRNOV, M. V.

report to be submitted for the IUPAC 21st Conference and 18th Intl. Congress of Pure and Applied Chemistry, Montreal, Canada, 2-12 August 1961

GORODISKIY, G. V., Academy of Sciences UkSSR, Kiev - "The oscillographic investigation of the electrochemical kinetics in fused salts" (Section A.3,c.2 - Session I, 11 Aug 61, afternoon)
GURVICH, L. V., Academy of Sciences USSR, Moscow - "The calculation of thermodynamic functions of gases in a wide temperature range" (Section A.3,c,(1), Session II - 8 Aug 61, afternoon)
KARGIN, V. A., Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "Vitrification phenomena in crystallin polymers" (Section B.4 - 7 Aug 61, afternoon)
KISELEV, A. V., Moscow State University imeni M. V. Lomonosov - "The influence of surface heterogeneity and adsorbate-adsorbate interaction on the adsorption properties of solid surfaces" (Joint Session, Sections A.2 and B.1 - 8 Aug 61, morning)
KONDRAT'YEV, V. N., Institute of Chemical Physics, Academy of Sciences USSR, Moscow - "The HO_2 radical" (Section A.1, Session I - 11 Aug 61, morning) (Also, Section A.1, Chairman, Session I - 8 Aug 61, morning)
KUZNETSOV, V. I., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "A novelty in the use of organic co-precipitants for concentration of small amounts of the elements" (To be presented in Russian) (Section C.2 - 11 Aug 61, morning)
LAVRUKHINA, A. K., RAKOVSKIY, E. E., and MOSKALEVA, L. P., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "New data on radiochemical investigations of the processes of fission and fragmentation induced by high energy protons" (Section A.4 - 8 Aug 61, afternoon)
LOVACHEV, L. A., Academy of Sciences USSR, Moscow - "Determination of rate constants of elementary processes from flame velocities as a function of temperature, pressure, and molecular transfer coefficients" (Section A.3,b,(2) - 7 Aug 61, afternoon)
MUNDIATH, S. (Probably MUNDYATH, S.) and GERASIMOV, Y. I., Moscow State University imeni M. V. Lomonosov - "Study of the thermodynamic properties of the system iron-latinum" (Section A.3,c,(3), Session II(A) - 11 Aug 61, morning)
PANCHENKOV, G. M., KOLCHIN, A. M., HALANOV, V. F., and SEEYI, Ya., Moscow State University imeni M. V. Lomonosov - "Emission of complex ions in solid-phase reactions" (Joint Session, Sections A.2 and B.1, 8 Aug 61, morning)
SEMENOV, N. N., Institute of Chemical Physics, Academy of Sciences USSR, Moscow - "Certain chemical reactions at reduced temperatures and related problems of energy transfer" (To be presented in Russian) (Plenary lecture - Saturday, 12 Aug 61)
SHILOV, Ye. A., Academy of Sciences UkSSR, Kiev - "The active agents and the intermediary complexes in the heterolytic reactions of halogenation of the organic compounds" (Section A.1, Session II - 11 Aug 61, morning)
SMIRNOV, M. V., Electrochemistry Institute, Sverdlovsk - "The equilibrium between the titanium subgroup metals and the salt melts" (Section B.3 - 7 Aug 61, afternoon)
TAL'ROZE, V. L., Institute of Chemical Physics, Academy of Sciences USSR - "Reactions of ions and molecules in the gas phase" (Section A.1, Session I - 9 Aug 61, afternoon)
TERENIN, Aleksandr N., Leningrad State University imeni A. A. Zhdanov - (Section A.1, Chairman, Session I - 8 Aug 61, afternoon Session) (Also on program for Section A.1, Session I - 9 Aug 61, afternoon)
TERENIN, Aleksandr N., VILESOV, F. I., KURBATOV, B., and DODONOVA, N., Leningrad State University imeni A. A. Zhdanov - "Mass-spectrometry and luminescence of radicals in the photodissociation and photoionization of molecules by vacuum ultra-violet radiation" (Section A.1, Session I - 9 Aug 61 - afternoon)
TUNITSKIY, N. N., Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov - "On the dissociation of molecules on electron impact and the early states of radiation-chemical processes" (Section A.1, Session I - 8 Aug 61, afternoon)
VAYNSHTEYN, Emanuil Ye., and KOROLEV, V. V., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Moscow - "The plasma generator and its use for spectral analysis of alloys and rocks" (Section C.1 - 8 Aug 61, morning)
VINOGRADOV, A. P., LAVRUKHINA, A. K., and REVINA, L. D., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "The study of nuclear reactions in iron meteorites under the action of high energy protons" (Section A.4 - 8 Aug 61, afternoon)
YAKOVLEV, Yu. V., and ALIMARIN, I. P., Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR - "The determination of trace impurities in some materials for semiconductor techniques by radio-activation analysis" (To be presented in Russian) (Section C.1 - 8 Aug 61, afternoon)

YEROFEYEV, Boris V., Institute of Physical-Organic Chemistry, Minsk - "The effect of donor and acceptor admixtures on the decomposition rate of solids" (Section A.2 - 8 Aug 61, afternoon)

Equilibrium between hafnium metal and...

scale versus equilibrium Hf potentials, are not straight lines. The bending of isotherms is caused by the presence of ions of different valences in the commensurable quantities. The magnitude of mean Hf valence in the electrolyte at different concentrations is determined from the inclination of tangents to the isotherms. Equations are found for the temperature dependence of equilibrium constants of the reaction $Hf^{+}_{(melt)} + Hf = 2Hf^{2+}_{(melt)}$ and standard values of electrode potentials:

$$\lg K = -0.329 - 2820\ T,$$

$E^{o}_{Hf/Hf^{2+}} = -2.51 + 6.3 \cdot 10^{-4}\ Tb$; $E^{o}_{Hf/Hf^{4+}} = -2.65 + 6.2 \cdot 10^{-4}\ Tb$; $E^{o}_{Hf^{2+}/Hf^{4+}} = -2.79 + 6.0 \cdot 10^{-4}\ Tb$. The authors calculated changes in the isobaric potential Δz at reactions of $HfCl_4$ and $HfCl_2$ formation and $HfCl_4$ reduction in $HfCl_2$ by hafnium metal.

$$Hf(solid) + 2Cl_2(gas) = HfCl_4(melt);$$

$$\Delta z = -245{,}000 + 55.0\ T\ cal/mole$$

$$Hf(solid) + Cl_2(gas) = HfCl_2(melt);$$

Card 2/3

40820

S/631/61/000/002/001/013
I003/I203

21.4100

AUTHORS: Skiba, O. V., and Smirnov, M. V.

TITLE: Equilibrium potentials of uranium in fused NaCl-KCl mixtures

SOURCE: Akademiya nauk SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no. 2, 1961, Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov.3–9

TEXT: None of the recent papers on the equilibrium potentials of uranium in fused chloride salts mention its temperature dependence. Equilibrium potentials of uranium in equimolar NaCl–KCl mixtures containing from 0.5 to 27.2 wt % of UCl_3 were measured against a chlorine reference electrode in the temperature range from 700 to 930°C. Within the concentration limits investigated it was found that the equilibrium potential of uranium may be calculated from the Nernst equation: $E = E°_{U/U^{3+}} + \frac{2.3RT}{3F}\log[U^{3+}]$. The temperature dependence of the value $E°_{U/U^{3+}}$ measured against a chlorine reference electrode is expressed by the equation: $E°_{U/U^{3+}} = 3.010 + 6.65.10^{-4}T$. The temperature dependence of the equilibrium constant of the reaction $2U + 3Th^{2+}_{soln} \leftrightharpoons 3Th + 2U^{3+}_{soln}$ is expressed by $\log K = \log \frac{[U^{3+}]^2}{[Th^{2+}]^3} = 11{,}342 - \frac{5564}{T}$. There are 3 figures.

Card 1/1

40822

S/631/61/000/002/003/013
I003/I203

5.4700

AUTHORS: Komarov, V., and Smirnov, M. V. 1/

TITLE: Equilibrium potentials of hafnium in mixed fluoride-chloride melts

SOURCE: Akademiya nauk SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no. 1961, Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov. 19-22

TEXT: The formation of stable hafnium-fluorine complexes in the above salts can be deduced from the results of equilibrium potential measurements of hafnium and from the fact that no solid phase of any hafnium compound containing fluorine is formed when NaCl-KCl fused salts containing up to 3.4 wt % of Hf and up to 35 wt % of NaF are heated between 700 and 900°C. The equilibrium potentials of hafnium were measured against a chlorine reference electrode in NaCl-KCl fused salts containing from 0.99 to 3.4 wt % of Hf and 1.36 to 15.8 wt % of fluorine at 700, 800, and 900°C. Formulas representing the temperature dependence of the equilibrium potential and of the instability coefficent of the HfF_6^{2-} ion are given. There are 2 figures.

Card (1/1) 11 REFERENCE S/631/61/002/002/013

S/137/62/000/008/008/065
A006/A101

AUTHORS: Smirnov, M. V., Loginov, N. A., Tsiovkina, L. A.

TITLE: Behavior and equilibrium potentials of titanium in mixed fluoride-chloride melts

PERIODICAL: Referativnyy zhurnal, Metallurgiya, no. 8, 1962, 21 - 22, abstract 8G160 ("Tr. In-ta elektrokhimii. Ural'skiy fil. AN SSSR", 1961, no. 2, 29 - 40)

TEXT: The authors studied interaction of Ti metal with fluoride-chloride melts containing Ti in 3- and 4-valent state. It is shown that in the presence of an excessive amount of alkali-metal fluoride, a Ti^{2+} compound is being formed whose composition is Me_2TiF_4 and which is poorly soluble in molten mixtures of alkali-metal chlorides and fluorides. It is found that the behavior of a Ti-electrode in mixed fluoride-chloride melts is like the behavior of a second-type electrode; its potential does not depend upon the nominal Ti content in the electrolyte and is wholly determined by the concentration of fluor ions $[F^-]$ according to equation $E = - 2.66 - 4.10 \cdot 10^{-4} T - 3.97 \cdot 10^{-4} T \lg [F^-]^b$ in relation

Card 1/2

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S/631/61/000/002/005/013
I003/I203

5.4700

AUTHORS Smirnov, M. V., Baraboshkin, A. N., Saltykova, N. A., and Komarov, V. Ye

SOURCE: Akademiya nauk SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no 2. 1961. Elektrohimiya rasplavlennykh solevykh i tverdykh elektrolitov. 63-69

TITLE: Cathodic processes during deposition of hafnium from chloride and hloride-fluoride fused salts

TEXT: There are no published data on the electrode processes of the electrolysis of fused salts containing hafnium. The cathodic polarization of molybdenum and tungsten in chloride and and chloride-fluoride fused salts containing hafnium was invastigated by measuring their electrode potentials against a chlorine reference electrode. Current densities were from 10^{-4} to 2 amp/cm^2 and the temperature range from 700 to 900°C. Hafnium was introduced into the fused salts by addition of hafnium tetrachloride or by anodic dissolution of the pure metal in the bath. The presence of fluorine ions in fused chloride salts decreases the deposition potentials of hafnium and decreases the concentration polarization, particularly when the F/Hf molar ratio is 6. There are 5 figures

Card 1/1

40826

S/631/61/000/002/008/013
I003/I203

21.4100

AUTHORS: Nichkov, I. F., Raspopin, S. P., and Smirnov, M. V.

TITLE: The polarization of carbon-dioxide uranium anodes in melts of alkali metals chlorides

SOURCE: Akademiya nauk SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no. 2, 1961, Elektro-khimiya rasplavlennykh solevykh i tverdykh elektrolitov. 91-95

TEXT: This work was undertaken to determine the highest current density at which $UOCl_2$ forms and to find the products of the anodic dissolution of carbon dioxide uranium anodes at higher current densities. The polarization of these anodes in an equimolar mixture of fused sodium and potassium chlorides at current densities from 10^{+4} to 10 a/cm^2 was investigated at 700 and 800°C. The electrolytic processes change with increasing current density in the following order: 1) formation of $UOCl_2$; 2) dissolution of uranium oxychloride and uranium dioxide or their chlorination, resulting in the passage of U^{4+} ions into the solution; 3) dissolution of uranium dioxide and the passage of UO_2^{2+} ions into the solution without the participation of carbon, and finally; 4) the evolution of gaseous chlorine. There is 1 figure.

Card 1/1

21119

S/149/61/000/003/002/004
A006/A106

18 1215 1087, 1521 also 1208, 1160

AUTHORS: Nichkov, I. F., Smirnov, M. V.

TITLE: Electrolytic preparation of beryllium-zinc alloys at temperatures below 1,000°C

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy, Tsvetnaya metallurgiya, no. 3, 1961, 104 - 107

TEXT: Literature data indicate the possibility of obtaining beryllium-zinc alloys, but there is no information available on the nature of interaction of these elements and on the properties of their alloys. The authors studied the nature of interaction of berryllium and zinc at temperatures up to 1,000°C. Alloys of these elements were obtained by electrolysis of berryllium-containing melts with liquid zinc cathode permitting the accurate regulation of the alloy composition and of the rate of supplying one component to the surface of the other one. Alloys from a molten chloride bath were obtained in a closed electrolytic cell (Figure 1) with a molten zinc cathode. The electrolyte temperature was 700 ± 10°C. Prior to electrolysis the melt was blown through with dry hydrogen chloride. After termination of the experiment the alloy was cooled either together with the electrolyte,

Card 1/3

... of zinc-beryllium sublimated in a vacuum and ... are 6 figures and 9 references: 4 [English references: A. R. Kaufman, P. Gordon ... Soc. Metal, 42, 1950; J. G. Beach, C. L. Faust, J.

21119
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A006/A106

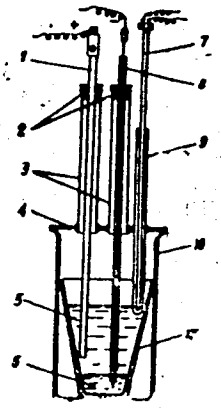
Electrolytic preparation of beryllium-zinc ...

Electrochem. Soc., 100 (6), 276 (1953); G. V. Raynor, J. of the Royal Aeronautical Soc., 50, 390 (1946)]

ASSOCIATION: Ural'skiy politekhnicheskiy institut (Ural Polytechnic Institute)
Fiziko-tekhnicheskiy fakultet (Physicotechnical Division)

SUBMITTED: January 11, 1961

Figure 1:



Schematic drawing of a closed electrolytic cell. 1 - graphite anode; 2 - rubber seals; 3 - glass tubes; 4 - cover; 5 - electrolyte; 6 - zinc cathode; 7 - thermocouple; 8 - molybdenum power connection to the cathode; 9 - thermocouple housing; 10 - porcelain bucket; 11 - alundum crucible.

Card 3/3

Effect of the nature of alkali-metal ...

cylindrical Be electrode with a diameter of 5-10 mm contained only 0.01% electronegative impurities. A carbon-chlorine electrode served as reference electrode. Under equal working conditions (constant temperature and rate of introduction of chlorine), the potentials of the chlorine electrode and the Be electrode were almost equal in the electrolytes LiCl, KCl and CsCl. The emf measurements with various electrolytes (Fig. 2) correspond to the following empirical equations:

2,00 mol % $BeCl_2 + LiCl$ at 649—905°: $E_1 = 2{,}527 - 3{,}73 \cdot 10^{-4} \cdot T \pm 0{,}003$ v
0,46 mol % $BeCl_2 + LiCl$ at 620—889°: $E_2 = 2{,}522 - 277 \cdot 10^{-4} \cdot T \pm 0{,}004$ v
8,17 mol % $BeCl_2 + 3LiCl + 2KCl$ at 421—755°: $E_3 = 2{,}703 - 4{,}97 \cdot 10^{-4} \cdot T \pm 0{,}008$ v
1,2 mol % $BeCl_2 + 3LiCl + 2KCl$ at 393—940°: $E_4 = 2{,}658 - 3{,}56 \cdot 10^{-4} \cdot T \pm 0{,}005$ v
9,77 mol % $BeCl_2 + KCl$ at 779—1007°: $E_5 = 2{,}692 - 3{,}62 \cdot 10^{-4} \cdot T \pm 0{,}002$ v
0,60 mol % $BeCl_2 + KCl$ at 796—1023°: $E_6 = 2{,}637 - 1{,}86 \cdot 10^{-4} \cdot T \pm 0{,}003$ v
10,1 mol % $BeCl_2 + CsCl$ at 666—930°: $E_7 = 2{,}807 - 4{,}43 \cdot 10^{-4} \cdot T \pm 0{,}005$ v
0,47 mol % $BeCl_2 + CsCl$ at 695—950°: $E_8 = 2{,}790 - 2{,}91 \cdot 10^{-4} \cdot T \pm 0{,}005$ v

and agreed well with the values by L. Jang and R. G. Hudson (Trans Metallurg. Soc. AIME, 215, 589 (1959). If the thermo emf $E_T = (-0.0076 + 0.174 \cdot 10^{-4}\ T) \pm 0.001$ v is inserted, the following is obtained:

Card 2/7

Effect of the nature of alkali-metal ...

potential: $E = E^{o}_{Be/Be^{2+}} + (2.3\ RT/2F) \cdot lg\ [Be^{2+}]$. The following equations hold: LiCl melt: $E^{o}_{Be/Be^{2+}} = -2.538 + 5.7 \cdot 10^{-4} \cdot T$ v; 3 LiCl + 2 KCl melt: $E^{o}_{Be/Be^{2+}} = -2.702 + 6.4 \cdot 10^{-4} \cdot T$ v; KCl melt: $E^{o}_{Be/Be^{2+}} = -2.727 + 5.3 \cdot 10^{-4} \cdot T$v; CsCl melt: $E^{o}_{Be/Be^{2+}} = -2.834 + 5.9 \cdot 10^{-4} \cdot T$ v. The effect of the metal cations gets evident through the difference of LiCl and CsCl which amounts to 0.276 v at 1000°K. The effective cation radius r_{ef} in the equimolecular sodium- and potassium chloride is $r_{ef.} = (r_{Na^+} + r_{K^+})/2$ = (0.98 + 1.33)/2 = 1.16. The ion-potential is then: e/r = 1/1.16 = 0.862 and $E^{o}_{Be/Be^{2+}} = -2.718 + 5.83 \cdot 10^{-4} \cdot T$ v. The difference between the E^{o} values in different melts equals the emf: $E = E^{o}_{Be'/Be^{2+}} - E^{o}_{Be''/Be^{2+}}$ of the galvanic element $Be/BeCl_2$, Me'Cl//$BeCl_2$, Me"Cl/Be. It is a direct measure for the change of the isobaric potential at a transition of the Be^{2+} ions from the melt with lower bond energy to the chlorine anion in

Card 4/7

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Effect of the nature of alkali-metal ...

with the ion potential e"/r' is: $\Delta Z = 19833 \left[(e''/r'') - (e'/r')\right]$ cal/g ion

$BeCl_2$. There are 8 figures and 27 references: 21 Soviet-bloc and 6 non-Soviet-bloc. The references to the English-language publications read as follows: Ref. 5: K. K. Stern, J. Phys. Chem., 60, 679 (1956); Ref. 11: L. Jang, R. G. Hudson, J. Electrochem. Soc., 106, 986 (1959); Ref. 10: H. Laitinen, T. W. Pankey, J. Amer. Chem. Soc., 81, 1053 (1959).

ASSOCIATION: Ural'skiy filial Akademii nauk SSSR. Institut elektrokhimii (Ural Branch of the Academy of Sciences USSR. Institute of Electrochemistry)

SUBMITTED: May 4, 1960

Card 6/7

Redox potential of the system...

conclude that in the potentiometric titration with hydrogen not $E^{o}_{Ti^{2+}/Ti^{3+}}$ was measured, but only the potential which corresponds to the equilibrium in the system $TiCl_3$ melt $+ 0.5H_{gas} \rightleftarrows TiCl_2$ melt $+ HCl_{gas}$. To obtain the value $E^{o}_{Ti^{2+}/Ti^{3+}}$, the authors conducted the potentiometric titration with metallic titanium. The initial salt solution was prepared by blowing $TiCl_4$ vapor through an equimolar mixture of NaCl and KCl. The redox potential was measured by a molybdenum electrode referred to a chlorine electrode. For a rapid balancing of the concentration of Ti^{2+} and Ti^{3+} in the melt, the molybdenum electrode rotated at 60 rpm. The potentiometric curves of Fig. 3 were obtained. Their course depends on experimental conditions (temperature, concentration, intermixture). But all of them show the typical salient point which corresponds to the redox potential $E^{o}_{Ti^{2+}/Ti^{3+}} = 1.726 \pm 0.005$ v (referred to chlorine electrode). On the basis of the earlier established $E^{o}_{Ti/Ti^{2+}} = (-2.371+6.09 \cdot 10^{-4}T)$ v,

Card 2/3

the authors calculate $E^{\circ}_{Ti/Ti^{3+}} = (-2.156+3.82\cdot10^{-4}T)$ v, and find $\log K = -2.888 + 3.251/T$ for the equilibrium constant. The resulting K values are: 2.82 at 700°C; 1.35 at 800°C; 0.76 at 900°C; and 0.46 at 1000°C. Thus, the equilibrium of reaction (1) is displaced to the left with rising temperature. In contrast to other researchers, the authors could not establish a dependence of the redox potential on the titanium concentration. There are 3 figures, 2 tables, and 7 references: 3 Soviet-bloc and 4 non-Soviet-bloc.

ASSOCIATION: Institut elektrokhimii Ural'skogo filiala Akademii nauk SSSR (Institute of Electrochemistry of the Ural Branch of the Academy of Sciences USSR)

PRESENTED: September 5, 1960, by A. N. Frumkin, Academician

SUBMITTED: August 31, 1960

Card 3/3

LOGINOV, N.A.; SMIRNOV, M.V.

Oxidation-reduction potential of Ti^{3+} / Ti^{4+} and equilibrium constant of the reaction $3Ti^{4+} + Ti \rightleftarrows 4Ti^{3+}$ in an equimolar mixture of sodium and potassium chloride melts. Trudy Inst. elektrokhim. UFAN SSSR no.3:17-24 '62. (MIRA 16:6)

(Electrodes, Titanium)
(Oxidation-reduction reaction)
(Fused salts)

KOMAROV, V.Ye.; SMIRNOV, M.V.; BARABOSHKIN, A.N.

Anodic solution of zirconium and hafnium in fused salts. Trudy Inst. elektrokhim. UFAN SSSR no.3:25-39 '62. (MIRA 16:6)

(Zirconium) (Hafnium)
(Fused salts—Electric properties)

SKIBA, O.V.; SMIRNOV, M.V.; RYZHIK, O.A.

Polarization of the uranium anode in the electrolysis of a mixture of potassium and sodium chlorides. Trudy Inst. elektrokhim. UFAN SSSR no.3:41-48 '62. (MIRA 16:6)

(Electrodes, Uranium)
(Alkali metal chlorides)
(Polarization(Electricity))

SMIRNOV, M.V.; BAYEVA, T.F.; KOMAROV, V.Ya.

Chronopotentiometric method of measuring the diffusion coefficients of tetravalent hafnium in chloride and fluoride-chloride melts. Trudy Inst. elektrokhim. UFAN SSSR no.3: 59-64 '62. (MIRA 16:6)

(Hafnium compounds) (Diffusion)
(Fused salts) (Potentiometric analysis)

ANFINOGENOV, A.I.; SMIRNOV, M.V.; ILYUSHCHENKO, N.G.; BELYAYEVA, G.I.

Study of the thermodynamics of the beryllium - copper system by the electromotive force method. Trudy Inst. elektrokhim. UFAN SSSR no.3:83-100 '62. (MIRA 16:6)

(Beryllium-copper alloys—Thermodynamic properties)
(Electromotive force)

S/200/62/000/004/001/002
D204/D307

AUTHORS: Smirnov, M.V., and Loginov, N.A.

TITLE: Study of the equilibrium between metallic titanium and its di- and trivalent ions in molten NaCl-KCl, by the method of equilibrium potentials

PERIODICAL: Akademiya nauk SSSR. Sibirskoye otdeleniye. Izvestiya, no. 4, 1962, 64 - 72

TEXT: The authors studied the reaction $2Ti^{3+}_{(melt)} + Ti_{(solid)} \rightleftharpoons 3Ti^{2+}_{(melt)}$, to demonstrate the usefulness of the method of equilibium potentials, in an equimolar melt of NaCl-KCl containing 0.23, 0.7, 1.4 and 5.64 % Ti, between 701 and 975°C. The theoretical background is given. Equilibrium potentials of the Ti electrode were measured under argon against a comparison chlorine electrode, with an accuracy of ± 1 mv, at a series of temperatures maintained within ± 1.5°C. The temperature dependence is of standard electrode potentials were found to be $E^{o}_{Ti/Ti^{2+}} = - 2.382 + 4.83 \times 10^{-4}T$, $E^{o}_{Ti/Ti^{3+}} = - 2.158 +$

Card 1/2

43055

S/826/62/000/000/005/007
D408/D307

5.4700

AUTHORS: Smirnov, M.V., Baraboshkin, A.N., Komarov, V.Ye. and Saltykova, N.A.

TITLE: Cathodic and anodic processes during the electrolysis of chloride and fluoride-chloride containing zirconium and hafnium.

SOURCE: Fizicheskaya khimiya rasplavlennykh soley i shlakov; trudy Vses. soveshch. po fiz.khimii raspl. soley i shlakov, 22 - 25 noyabrya 1960 g., Moscow, Metallurgizdat, 1962, 257 - 265

TEXT: A continuation of previous investigations of electrode processes during the electrolysis of chloride and fluoride-chloride melts containing other polyvalent transition metals. Anodic and cathodic polarization curves were obtained by measuring the electrode potentials at the moment of switching on the polarizing current. Polarization curves are presented for e.g. the anodic solution of Zr and Hf in molten equimolar mixtures

Card 1/5

Cathodic and anodic processes ...

but partly to change in the diffusion coefficient of the ions in the high concentration region and, thus, to change in the thickness of the diffusion layer. The anodic polarization curves shift to the side of more positive potentials with increase in temperature, but the general character of the dependence of the anodic potential on current density does not change substantially. The following expression was derived for the average valency of the metal ions passing into solution at potential φ:

$$\varphi = E^{o}_{Me^{4+}/Me^{2+}} + 0.992 \times 10^{-4} \log \frac{n-2}{4-n} \quad , \qquad (5)$$

where Me--metal; n--average valency of the metal ions = 4 - 2x; x--proportion of Me^{2+} . At low i the experimentally found average Hf ion valencies, were lower than those calculated from Eq. (5); at high current densities the experimental results were higher than the calculated ones. The cathodic polarization of Zr and Hf has the same character as that of Th and Ti but, in contrast to the latter

Card 3/5

S/826/62/000/000/005/007
Cathodic and anodic processes ...D408/D307

ASSOCIATION: Institut elektrokhimii UFAN (Institute of Electrochemistry UFAS)

Card 5/5

43056
S/826/62/000/000/007/007
D408/D307

5.4700

AUTHORS: Smirnov, M.V., Komarov, V.Ye., and Baraboshkin, A.N

TITLE: The equilibrium potentials of hafnium and zirconium in chloride and fluoride-chloride melts

SOURCE: Fizicheskaya khimiya rasplavlennykh soley i shlakov; trudy Vses. soveshch. po fiz. khimii raspl. soley i shlakov, 22 - 25 noya brya 1960 g. Moscow, Metallurgizdat, 1962, 353 - 360

TEXT: The above potentials were measured in equimolar NaCl--KCl melts containing a) 0.16 - 6.8 wt.% Zr, or 0.16 -1.51 wt.% Hf and b) 2 - 35 wt.% NaF and 0.17 - 1.05 wt.% Zr, or 0.99 - 3.4 wt.% Hf, between 700 and 950°C, to explain processes occurring during the electrolysis of chloride melts containing Zr and Hf, to calculate the thermodynamic quantities ΔZ, ΔH, and ΔS for the formation of $MeCl_2$ and $MeCl_4$ (Me--Zr of Hf) from their elements in melts of specific composition, and to

Card 1/3

The equilibrium potentials ...

n is the average valency of the Zr ions. At 770°C in electrolytes containing 2.04 - 15.82 wt.% F and 1.05 ± 0.2 wt.% Zr, the average Zr valency was $4 \geq n \geq 3.23$, when m decreased from 6 to 5. The equilibrium potential of Hf was found to be more negative than that of Zr in melts containing the same concentrations of Me and F ions, the difference in potential decreasing with increasing temperature. HfF_6^{2-} was shown to be slightly more stable than ZrF_6^{2-}. There are 3 figures.

ASSOCIATION: Institut elektrokhimii UFAN (Institute of Electrochemistry UFAS)

Card 3/3

SKIBA, O.V.; SMIRNOV, M.V.; KHAZEMOVA, T.F.

Diffusion coefficients of U^{3}, U^{4}, and UO_2 ions in fused NaCl - KCl. Trudy Inst. elektrokhim. UFAN SSSR no. 4:11-15 '63. (MIRA 17:6)

LOGINOV, N.A.; SMIRNOV, M.V.

Current efficiency in the anodic dissolution of titanium in chloride and mixed fluroide-chloride melts. Trudy Inst. elektrokhim. UFAN SSSR no. 4:29-33 '63. (MIRA 17:6)

ANFINOGENOV, A.I.; SMIRNOV, M.V.; ILYUSHCHENKO, N.G.

Electrolytic deposition of beryllium on copper in fused salts.
Trudy Inst.elektrokhim. UFAN SSSR no. 4:47-53 '63. (MIRA 17:6)

ACCESSION NR: AT4008733 S/2631/63/000/004/0055/0066

AUTHOR: Anfinogenov, A. I.; Belyayeva, G. I.; Smirnov, M. V.; Ilyushchenko, N. G.

TITLE: Structure and phase composition of beryllium coatings deposited on copper in fused salt electrolytes

SOURCE: AN SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy*, no. 4, 1963. Elektrokhimiya rasplavlenny*kh solevy*kh i tverdy*kh elektrolitov, 55-66

TOPIC TAGS: beryllium coating, beryllium plating, beryllium plated copper, coating structure, coating phase composition, fused salt electrolysis, fused salt, beryllium electrodeposition

ABSTRACT: Rates of Be deposition (i.e. cathode current density) and mutual diffusion of Be and Cu (i.e. temperature and duration of electrolysis) were studied in relation to their effects on the structure and phase composition of coatings deposited on a cathode during electrolysis in fused salts. Be was deposited on Cu cathodes in a fused electrolyte (eutectic mixture of KCl + NaCl + 16% $BeCl_2$ by weight at temperatures of 710, 750, 800 and 835C, current densities of 0.004, 0.01, 0.02 and 0.04 a/cm^2 and exposures of 1, 2, 4, 6 and 8 hours. The electrolytic cell was described in AN SSSR, Ural'skiy filial. Institut elektrokhimii. Trudy*, no. 4, 1963, 47-53. The results tabulated in the original and shown

Card 1/2

ACCESSION NR: AT4008733

in Figs. 1, 2, 3 and 4 in the Enclosure indicate that cathode deposition of Be on Cu is accompanied by the formation of deposits consisting of one or more phases. Structure of the deposits is determined by current density, temperature and duration of the electrolytic process. It was also demonstrated that such conditions of the process promote the most rapid formation and accumulation of the β-phase. Microstructure of the BeCu coating is shown on several microphotographs for the α, β and γ phases. G. V. Burov, staff member of the Institute, performed the structural x-ray analysis. G. V. Chentsovaya and L. P. Tomilovaya, other members of the Institute, performed the spectral analysis. Orig. art. has: 2 tables, 4 graphs, 7 illustrations.

ASSOCIATION: Institut Elektrokhimii, Ural'skiy filial AN SSSR (Institute of Electrochemistry, Ural branch AN SSSR)

SUBMITTED: 00 DATE ACQ: 25Jan64 ENCL: 06

SUB CODE: ML, MA NO REF SOV: 011 OTHER: 002

Card 2/2

SMIRNOV, M.V. (Sverdlovsk); BARABOSHKIN, A.N. (Sverdlovsk); KOMAROV, V.Ye. (Sverdlovsk)

Cathodic processes in the deposition of zirconium from chloride melts. Zhur.fiz.khim. 37 no.8:1669-1676 Ag '63. (MIRA 16:9)

1. Institut elektrokhimii Ural'skogo filiala AN SSSR.
(Zirconium plating) (Fused salts)

SMIRNOV, M.V. (Sverdlovsk); BARABOSHKIN, A.N. (Sverdlovsk); KOMAROV, V.Ye. (Sverdlovsk)

Cathodic processes in the deposition of zirconium from mixed chloride-fluoride melts. Zhur.fiz.khim. 37 no.8:1677-1681 Ag '63. (MIRA 16:9)

(Zirconium plating) (Fused salts)

L 14354-63 EWP(q)/EWT(m)/BDS AFFTC JD/JW/JG

ACCESSION NR: AP3003854 S/0020/63/151/003/0591/0594

AUTHORS: Smirnov, M. V.; Usov, P. M.; Khazemova, T. F. 55

TITLE: Reaction of metallic lanthanum with a melt of its trichloride and the equilibrium constant of the reaction 27

SOURCE: AN SSSR. Doklady*, v. 151, no. 3, 1963, 591-594

TOPIC TAGS: lanthanum, melt diagram, entropy, equilibrium constant

ABSTRACT: The reaction between molten La and $LaCl_3$ was measured electrochemically. Reaction between La and $LaCl_3$ was independent of temperature, a product approximating $LaCl_{2.14}$ was obtained at 864-1063F. Oxidation-reduction potentials showed a linear increase of e.m.f. with temperature (equations are given). E.m.f. data of the systems at equilibrium, shows a mixture of $LaCl_3$ and $LaCl_2$, the latter predominating. The equilibrium-constant, heat capacity and entropy were calculated. The melt diagram for the La-$LaCl_3$ system was drawn, from pure $LaCl_3$ to equilibrium mixtures of $LaCl_2$-$LaCl_3$ and metallic La. Below 827F there was no $LaCl_2$ in the solid phase, only La finely dispersed in $LaCl_3$. Above this temperature, in the 0-9 mol.% La range, the excess $LaCl_3$ crystallized. Orig. art. has: 3 figures, 1 table, 10 equations

Card 1/2

L 17549-63

ACCESSION NR: AP3004426

elements, DELTA F = -160,000 + 38.3 T cal, DELTA H = -160.0 kcal, and DELTA S = -37.3 cal/°. Orig. art. has: 3 figures and 1 table and 13 formulas.

ASSOCIATION: none

SUBMITTED: 18Feb63 DATE ACQ: 21Aug63 ENCL: 00

SUB CODE: CH, PH NO REF SOV: 003 OTHER: 002

Card 2/2

AM4037183 BOOK EXPLOITATION S/

Kozlov, Svyatoslav Nikolayevich; Smirnov, Mikhail Vasil'yevich; Baz', Ivan Stepanovich; Sidorov, Petr Aleksandrovich

Soviet military science (O sovetskoy voyennoy nauke), 2d rev. and enl. ed. Moscow, Voyenizdat M-vo obor. SSSR, 1964. 403 p. biblio. 15,000 copies printed.

TOPIC TAGS: Soviet military science, Soviet military theory, nuclear weapons, modern warfare

PURPOSE AND COVERAGE: The book is intended for officers of the Soviet Army and Navy, and for civilian readers interested in military service. The development of military theory and the principles of modern warfare are presented and the decisive importance of rockets and nuclear weapons is explained. The effect of the decisions of the 22nd Party Congress and the Party Program on the Soviet theory of war is also discussed. No personalities are mentioned. There are no references.

TABLE OF CONTENTS:

Card 1/2

SMIRNOV, M.V.; SKIBA, O.V.

Thermodynamics of interaction of uranium tri- and tetrachloride in NaCl - KCl melts with oxygen. Trudy Inst. elektrokhim. UFAN SSSR no.5:3-6 '64. (MIRA 18:2)

SMIRNOV, M.V.; SOKOLOVSKIY, Yu.S.; KRASNOV, Yu.N.

Equilibrium between cerium a d its bi- and trivalent ions in a fused eutectic mixture of lithium and potassium chlorides. Trudy Inst. elektrokhim. UFAN SSSR no.5:7-16 '64.

(MIRA 18:2)

SOKOLOVSKIY, Yu.S.; SMIRNOV, M.V.

Polarization during the anodic dissolution of metallic cerium in a fused eutectic mixture of lithium and potassium chlorides. Trudy Inst. elektrokhim. UFAN SSSR no.5:17-31 '64.

Interaction of trivalent cerium ions with fluorine anions in a medium of a fused LiCl - KCl eutectic. Ibid.:33-40

Electrode processes in the electrolysis of cerium in chloride-fluoride melts. Ibid.:47-51

(MIRA 18:2)

SOKOLOVSKIY, Yu.S.; SMIRNOV, M.V.; SKIBA, O.V.

Coefficients of diffusion of trivalent cerium in fused salt mixtures LiCl - KCl and LiCl - KCl + LiF. Trudy Inst. elektrokhim. UFAN SSSR no.5.41-45 '64.

(MIRA 18:2)

SMIRNOV, M.V.; KRASNOV, Yu.N.; KHAZEMOV, F.F.

Reaction of lanthanum tichloride with a molten eutectic mixture of lithium and potassium chlorides. Trudy Inst. elektrokhim. RFAN SSSR no.5:53-60 '64. (MIRA 18:2)

SMIRNOV, M.V.; USOV, P.M.; KHAZEMOVA, T.F.

Melting diagram of the Ia - LaCl system. Trudy Inst. elektrokhim. UFAN SSSR no.5:119-122 '64. (MIRA 18:2)

SMIRNOV, M.V.; KHAYMENOV, A.P.

Theoretical computation of the emf of galvanic cells with molten salt electrolytes exemplified by Be solid $BeCl_2$ + fused KCl Cl_2(gas), C(graphite). Dokl. AN SSSR 158 no.5:1172-1175 O '64.

(MIRA 17:10)

1. Institut elektrokhimii Ural'skogo filiala AN SSSR. Predstavleno akademikom A.N.Frumkinym.

L 9935-66 EWT(1)/EWT(m)/ETC/EPF(n)-2/EWG(m)/T/EWP(t)/EWP(b)/ETC(m) IJP(c)
ACC NR: AT5028237 DS/JD/WW/JW/JG SOURCE CODE: UR/2631/65/000/006/0011/0017

AUTHOR: Smirnov, M. V.; Ryzhik, O. A.

ORG: Institute of Electrochemistry, Ural Branch, Academy of Sciences SSSR (Akademiya nauk SSSR, Ural'skiy Filial, Institut Elektrokhimii)

TITLE: Equilibrium between molybdenum and its ions in molten lithium chloride

SOURCE: AN SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no. 6, 1965. Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov (Electrochemistry of fused salts and solid electrolytes), 11-17

TOPIC TAGS: molybdenum, lithium chloride, electrode potential

ABSTRACT: In order to determine the dependence of electrode potentials of molybdenum in a chloride melt on the nature of the alkali metal cations, the authors used the emf method to study the equilibrium between molybdenum and molten lithium chloride containing from 0.27 to 2.49 wt.% Mo in the range of 620 — 950C. Expressions were obtained for the temperature dependence of

$$E_{Mo/Mo^{2+}},\ E^{\circ}_{Mo/Mo^{3+}},\ E^{0}_{Mo^{2+}/Mo^{3+}}$$

Card 1/2

KUDYAKOV, V.Ya.; SMIRNOV, M.V.

Potentials of Zr/Zr^{2+}, Zr/Zr^{4+} and Zr^{2+}/Zr^{4+} and equilibrium constant of the reaction $Zr + Zr^{4+} \leftrightharpoons 2Zr^{2+}$ in fused KCl. Trudy Inst. elektrokhim. UFAN SSSR no.6:19-27 '65. (MIRA 18:11)

L 10881-66 EWT(m)/ETC/EWG(m)/EWP(j)/T/EWP(t)/EWP(b) IJP(c) DS/JD/JW/JG/RM

ACC NR: AT5028238 SOURCE CODE: UR/2631/65/000/006/0029/0037

AUTHOR: Smirnov, M. V.; Krasnov, Yu. N.; Khazemov, F. F.; Komarov, V. Ye.

ORG: Institute of Electrochemistry, Ural Branch, Academy of Sciences SSSR (Akademiya nauk SSSR, Ural'skiy filial, Institut elektrokhimii)

TITLE: Instability constants of fluoride complexes of lanthanum in the molten eutectic mixture LiCl-KCl

SOURCE: An SSSR, Ural'skiy filial. Institut elektrokhimii. Trudy, no. 6, 1965. Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov (Electrochemistry of fused salts and solid electrolytes), 29-37

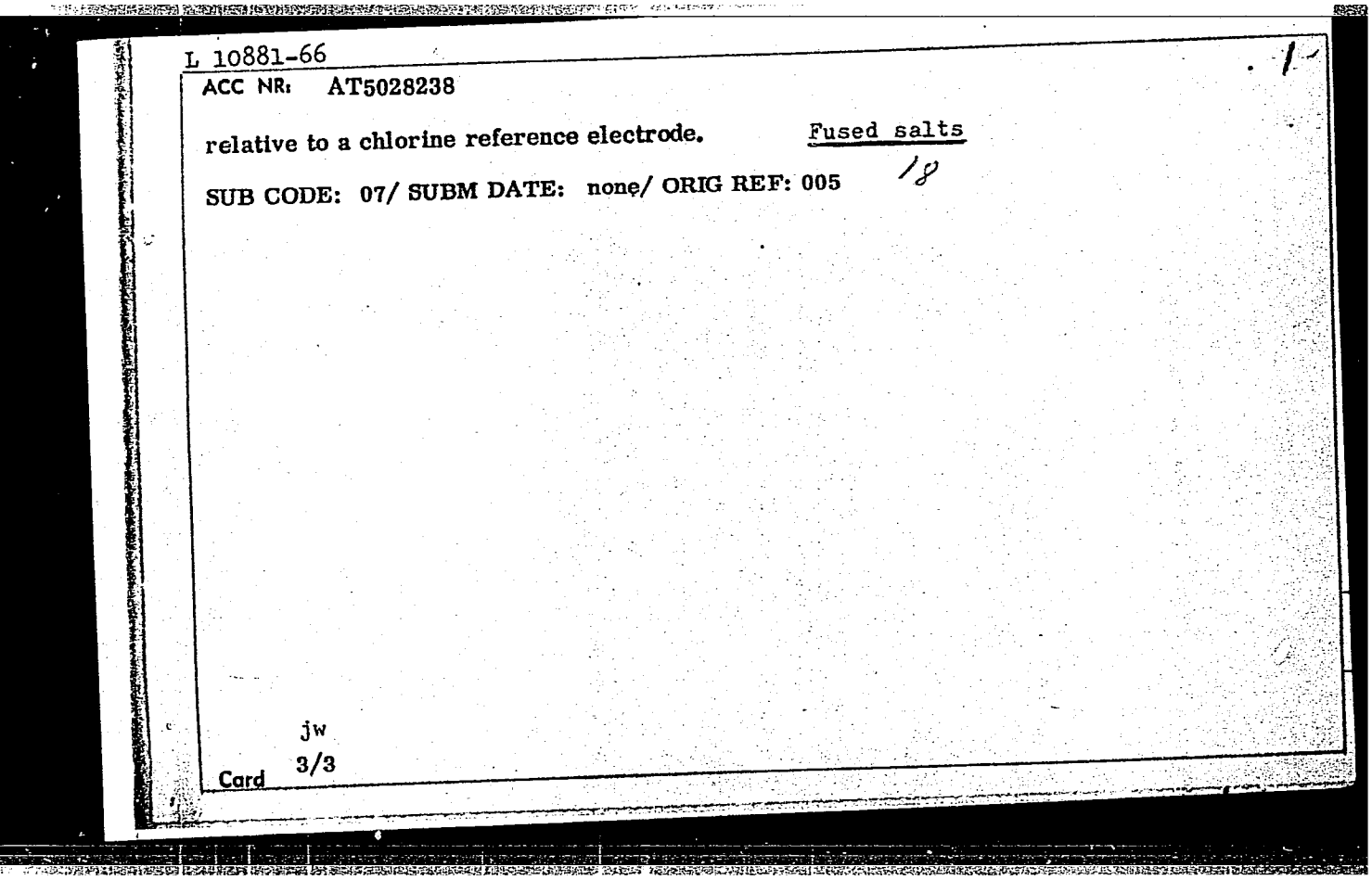
TOPIC TAGS: lanthanum compound, complex molecule, lithium fluoride, emf

ABSTRACT: The emf's of the galvanic cells

$$La \mid KCl - LiCl + LaCl_3 + x\,LiF \parallel KCl - LiCl \mid Cl_2, C$$

were measured at 600—800C, LiF being present in the electrolyte in amounts of 2.5, 5.0, 10, and 20 wt. %. The experimental data showed the existence of the following lanthanum complexes in the melt: LaF^{2+}, LaF_2^+, and LaF_3. Expression for the temperature dependence of the instability constants of these complexes were obtained:

Card 1/3



L 10881-66

ACC NR: AT5028238

relative to a chlorine reference electrode. Fused salts

SUB CODE: 07/ SUBM DATE: none/ ORIG REF: 005 18

jw

Card 3/3

L 62938-65 EPF(c)/EPF(n)-2/EPA(s)-2/EWT(1)/EWT(m)/EWP(b)/EWP(t) IJP(c) WW/JD/JG
ACCESSION NR: AR5019133 UR/0137/65/000/007/A010/A010

SOURCE: Ref. zh. Metallurgiya, Abs. 7A61

AUTHOR: Smirnov, M. V.; Usov, P. M.; Lbov, V. S.; Shabanov, O. M.

TITLE: Electrical conductivity and transfer numbers in the melt system $LaCl_3$ + La

CITED SOURCE: Tr. In-ta elektrokhimii. Ural'skiy fil. AN SSSR, vyp. 6, 1965, 57-64

TOPIC TAGS: liquid metal, lanthanum, lanthanum chloride, inorganic anion, electric conductivity

TRANSLATION: The specific electrical conductivity of a melt of $LaCl_3$ + La, from pure $LaCl_3$ to $LaCl_{2.14}$ was measured in the interval 900-1015C. The specific ionic conductivity increases from approximately 1.5 $ohm^{-1} \cdot cm^{-1}$ for $LaCl_3$ to approximately 2.5 $ohm^{-1} \cdot cm^{-1}$ for $LaCl_{2.14}$. Determinations were made of the transfer numbers of cationic and anionic chlorine in melts of $LaCl_3$ and $LaCl_2$, with respect to a solid porous diaphragm, at 900C. In a melt of $LaCl_3$, the current through the diaphragm is basically carried by chlorine anions (n_a = 0.9),

Card 1/2

L 62941-65 EPF(c)/EPF(n)-2/EPA(s)-2/ENT(m)/ENP(b)/ENP(t) IJP(c) WW/JD/JG

ACCESSION NR: AR5019134 UR/0137/65/000/007/A013/A013

SOURCE: Ref. zh. Metallurgiya, Abs. 7A78

AUTHOR: Usov, P. M.; Smirnov, M. V.

TITLE: Cathode polarization in electrolysis of a lanthanum trichloride melt

CITED SOURCE: Tr. In-ta elektrokhimii. Ural'skiy fil. AN SSSR. vyp. 6, 1965, 65-68

TOPIC TAGS: liquid metal, lanthanum, lanthanum chloride, cathode polarization, electrolytic deposition, molybdenum

TRANSLATION: A study was made of the polarization of a molybdenum cathode during the electrolysis of a $LaCl_3$ melt at 860 and 960C. The vertical sections (on the polarization curves), observed at $D > 1$ a/cm^2, correspond to the separating out of metallic lanthanum. Its equilibrium potential in a melt of $LaCl_{2.14}$ is equal to 2.524 volts at 860C and to 2.439 volts at 960C. The diffusion coefficients for La^{3+} and La^{2+} in a melt of $LaCl_3$ are equal respectively to $(0.9\text{-}1.1)\cdot 10^{-6}$ and $(2.9\text{-}3.2)\cdot 10^{-4}$ cm^2/sec. Metallic lanthanum starts to separate out on

Card 1/2

L 9940-66 EWT(m)/ETC/EWG(m)/T/EWP(t)/EWP(z)/EWP(b) IJP(c) JD/HW

ACC NR: AT5028242 SOURCE CODE: UR/2631/65/000/006/0069/0073

AUTHOR: Smirnov, M. V.; Tsiovkina, L. A.; Oleynikova, V. A.

ORG: Institute of Electrochemistry, Ural Branch, Academy of Sciences SSSR (Adademiya nauk SSSR, Ural'skiy filial, Institut elektrokhimii)

TITLE: Processes occurring at a platinum and nickel cathode during electrolysis of carbonate melts

SOURCE: AN SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy. no. 6, 1965. Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov (Electrochemistry of fused salts and solid electrolytes), 69-73

TOPIC TAGS: carbonate, electrolysis, cathode polarization, platinum, nickel, carbon, carbon monoxide

ABSTRACT: The cathodic polarization of platinum (at 640C) and nickel (at 600 and 700C) was studied during the electrolysis of the ternary mixture Li_2CO_3-Na_2CO_3-K_2CO_3 (4:3:3) in the range of current densities of 10^{-4} to 1-2 A/cm^2. The products formed at the cathode were investigated. It is shown that depending upon the current density, various electrode reactions take place: at current densities below

Card 1/2

L 9940-66

ACC NR: AT5028242

10^{-3} A/cm^2, the cathode surface remains lustrous without any trace of deposition of any products; at 10^{-3} - 10^{-2} A/cm^2, a spongy deposit of finely divided carbon is formed; above 10^{-2} A/cm^2, carbon monoxide is evolved, and its volume increases with the current. Polarization has a concentration character and is associated with the migration of carbonate ions from the volume of the electrolyte to its surface. Orig. art. has: 3 figures and 2 formulas.

SUB CODE: 07 / SUBM DATE: None / OTH REF: 003

Card 2/2

L 48969-65 EPA(s)-2/EWT(m)/EPF(c)/EWA(d)/EWP(t)/EWP(z)/EWP(b)/EPF(n)-2
IJP(c) JD/WW/JG

ACCESSION NR: AP5007749 S/0364/65/001/001/0059/0062

42
38
B

AUTHOR: Smirnov, M. V.; Ryzhik, O. A.; Kazantsev, G. N.

TITLE: Diffusion of trivalent molybdenum in a medium of fused chlorides of alkali metals

SOURCE: Elektrokhimiya, v. 1, no. 1, 1965, 59-62

TOPIC TAGS: molybdenum, chloride, alkali metal, diffusion coefficient

ABSTRACT: The diffusion of molybdenum in dilute solutions of its trichloride in fused chlorides of alkali metals was studied. The concentration of molybdenum in these melts did not exceed $5 \cdot 10^{-4}$ g-equiv/cm^3. Therefore the interaction of its ions was significant only with a salt solvent. The chronopotentiometric method with polarization of the electrode by a current with a constant density higher than the maximum diffusion density was used to measure the diffusion coefficient of the dilute component of the melt. The tests were conducted in hermetically sealed cells in which the gas chamber was filled with thoroughly purified helium (see fig. 1 of the Enclosure). The solvent electrolytes were previously recrystallized chlorides

Card 1/3

L 48969-65
ACCESSION NR: AP5007749

of lithium,[27] potassium,[27] and cesium[27] and also eutectic LiCl-KCl. The diffusion coefficient of trivalent molybdenum was calculated according to the equation

$$D = 1.37 \cdot 10^{-6} \left(\frac{MI}{3a\rho S}\right)^2 \tau \ \text{cm}^2/\text{sec}$$

where a is the concentration of molybdenum in weight %; M is the molecular weight; I is the strength of current in amperes; S is the area of the cathode in cm^2; ρ is the density of the electrolyte in g/cm^3. As the cation radius of the alkali metal increases, the rate of diffusion of the trivalent molybdenum decreases. The values of the activation energy are linearly related to the inverse magnitudes of the cation radii of the salt solvents. It is suggested that the diffusion process occurs through "jumping" of the molybdenum cations from one point of the quasi-lattice of the fusion to another. Orig. art. has: 3 figures.

ASSOCIATION: Ural'skiy politekhnicheskiy institut imeni S. M. Kirova (Ural Polytechnical Institute)

SUBMITTED: 15Sep64 ENCL: 01 SUB CODE: MM, GC

NO REF SOV: 013 OTHER: 003

Card 2/3

L 48969-65

ACCESSION NR: AP5007749

ENCLOSURE: 01

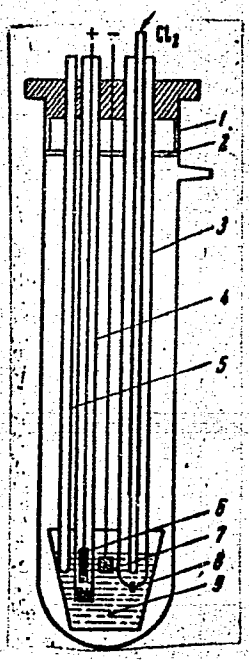


Fig. 1. Cell for measurements: 1--quartz glass test tube; 2--fluoroplastic screen; 3--quartz capsule with chlorine comparison electrode; 4--quartz jacket with diaphragm; 5--chromel-alumel thermocouple; 6--carbon anode on a molybdenum current feeder; 7--platinum cathode; 8--alundum crucible; 9--test electrolyte

Card 3/3

L 49454-65 EPF(c)/EPP(n)-2/EPA(s)-2/EWT(m)/EWP(b)/EWP(t) Pr-4/Pt-7/Pu-4 IJP(c)
WW/JD/JG
ACCESSION NR: AP5009941 UR/0364/65/001/002/0143/0148

45
43
B

AUTHOR: Kudyakov, V. Ya.; Smirnov, M. V. 71

TITLE: Equilibrium potentials of zirconium in fused cesium chloride

SOURCE: Elektrokhimiya, v. 1, no. 2, 1965, 143-148

TOPIC TAGS: zirconium, cesium 71 chloride 71, electrochemistry, galvanic cell

ABSTRACT: This is a continuation of the study of equilibrium potentials of zirconium in fused alkali metal halides. The equilibrium potentials of zirconium in a CsCl melt were measured in the 650-900°C range. The cell for measurement of the emf of zirconium was a wide hermetically sealed quartz test tube, shown in fig. 1 of the Enclosure. Doubly recrystallized CsCl was used. From the experimental data standard electrode potentials of Zr/Zr^{+2}, Zr/Zr^{+4} couples were calculated and also the oxidation-reduction potential of the Zr^{+2}/Zr^{+4} system. By measuring the current efficiency of anodic dissolution of metallic zirconium it was shown that the primary ions which are in equilibrium with the metal in CsCl melt are Zr^{+2} and Zr^{+4} rather than Zr^{+3}. For Zr^{+2}/Zr^{+4} couples the oxidation-reduction potential in

Card 1/2

L 3781-66 EWT(m)/EWP(t)/EWP(b) IJP(c) JD/JG

ACCESSION NR: AP5014138 UR/0365/65/001/003/0335/0337
669.28 : 620.193.43

57
54
03

AUTHOR: Smirnov, M. V.; Ryzhik, O. A.; Savochkin, Yu. P.

TITLE: Electrochemical corrosion of molybdenum in a chloride melt

SOURCE: Zashchita metallov, v. 1, no. 3, 1965, 335-337

TOPIC TAGS: molybdenum, corrosion, potassium chloride

ABSTRACT: The stationary potentials of molybdenum are measured with respect to a chlorine comparison electrode in thoroughly purified molten potassium chloride. The experiments were done at 790-920° in a helium-filled hermetically sealed capsule. The empirical equation for the temperature relationship of the stationary potential of molybdenum in a KCl solution with regard to the thermoelectromotive force between the molybdenum and carbon electrodes is

$$E_{st} = -2.082 + 2.47 \cdot 10^{-4} \cdot T \pm 0.004 \text{ v.}$$

Calculations show that corrosion rates in the 800-950° temperature range are of the order of 10^{-7} a/cm^2 in pure KCl. However, when easily reduced impurities are

Card 1/2

SMIRNOV, M.V.; MAKSIMOV, V.S.

Solubility and decomposition potential of titanium tetrachloride in fused potassium chloride. Elektrokhimiia 1 no.6:727-730 Je '65. (MIRA 18:7)

1. Institut elektrokhimii Ural'skogo filiala AN SSSR.

L 7969-66 EWT(m)/ETC/EWG(m)/T/EWP(t)/EWP(b) IJP(c) DS/JD/JG

ACC NR: AP5025080 SOURCE CODE: UR/0364/65/001/010/1218/1224

AUTHOR: Tsiovkina, L. A.; Smirnov, M. V.; Oleynikova, V. A.

ORG: Institute of Electrochemistry of the Ural Branch of the Academy of Sciences SSSR (Institut elektrokhimii Ural'skogo filiala Akademii nauk SSSR)

TITLE: Anode processes on platinum in the electrolysis of carbonate melts

SOURCE: Elektrokhimiya, v. 1, no. 10, 1965, 1218-1224

TOPIC TAGS: electrolytic cell, electrode, platinum, gas adsorption, oxygen, carbonate, lithium, potassium, sodium

ABSTRACT: The article is an attempt to fully explain the effect of adsorbed oxygen on the polarization of a platinum electrode. The experiments were carried out in hermetically sealed cells which made it possible to eliminate the dissolved oxygen from the carbonate melts. A melted mixture of the carbonates Li_2CO_3, K_2CO_3, and Na_2CO_3 in the ratio 3:4:3 was placed in a platinum crucible. The electrode investigated was a platinum sheet about 1 cm^2 in area. Its potential was

Card 1/2

UDC:541.135.3

SMIRNOV, M.V.; RYZHIK, O.A.

Inertness of metal electrodes in fused salt electrolytes. Izv. vys. ucheb. zav.; tsvet. met. 8 no.1:86-89 '65.
(MIRA 18:6)

1. Ural'skiy politekhnicheskiy institut.

[redacted], M.V., [redacted], V.A.

Thermodynamics of the reaction of zirconium di- and tetrachlorides with alkali metal chlorides in melts. Zhur. neorg. khim. 10 no.5:1211-1214 My '65. (MIRA 18:6)

L 38373-66 EWT(m)/T/EWP(t)/ETI IJP(c) DS/JD

ACC NR: AT6021370 (A) SOURCE CODE: UR/2631/65/000/007/0091/0095

AUTHOR: Ozeryanaya, I. N.; Krasil'nikova, N. A.; Smirnov, M. V.; Danilin, V. N.

ORG: none

TITLE: Use of the oxygen reference electrode in molten carbonates

SOURCE: AN SSSR. Ural'skiy filial. Institut elektrokhimii. Trudy, no. 7, 1965, Elektrokhimiya rasplavlennykh solevykh i tverdykh elektrolitov; termodinamika i kinetika elektrodnykh protsessov (Electrochemistry of fused salts and solid electrolytes; thermodynamics and kinetics of electrode processes), 91-95

TOPIC TAGS: platinum, oxygen, electrode potential, carbonate, chloride

ABSTRACT: In order to elucidate the stability of the potential of the platinum oxygen reference electrode in molten carbonates under various conditions, the emf of the galvanic cell

$$-Pt,\ CO_2+O_2 \mid Na_2CO_3+K_2CO_3 \mid NaCl+KCl \mid (Cl_2),\ C+$$

was studied at 770-1000°C as a function of temperature and composition of the gas mixture bathing the platinum. One of the half-cells was platinum bathed with a CO_2+O_2 mixture in a molten eutectic mixture of potassium and sodium carbonates, and

Card 1/2

L 42157-66 EWT(m)/T/EWP(t)/ETI IJP(c) DS/WW/JD/JG/GD

ACC NR: AT6022482 (A) SOURCE CODE: UR/0000/65/000/000/0254/0257

AUTHOR: Smirnov, M. V.; Usov, P. M.; Krasnov, Yu. N.; Khazemova, T. F.

ORG: Institute of Electrochemistry, UFAN SSSR (Institut elektrokhimii UFAN SSSR)

TITLE: Reaction of metallic lanthanum with its trichloride

SOURCE: Vsesoyuznoye soveshchaniye po fizicheskoy khimii rasplavlennykh soley. 2d, Kiev, 1963. Fizicheskaya khimiya rasplavlennykh soley (Physical chemistry of fused salts); trudy soveshchaniya. Moscow, Izd-vo Metallurgiya, 1965, 254-257.

TOPIC TAGS: lanthanum, ~~chloride~~, electrolysis, TRICHLORIDE, CHEMICAL REACTION, EMF

ABSTRACT: The emf method was used to study the reaction of La with $LaCl_3$ and solutions of $LaCl_3$ in the fused eutectic mixture LiCl-KCl in order to determine whether compounds of lanthanum of lower oxidation states exist, and if so, what part they play in the electrolysis of La in fused salt media. The phase diagram of the $LaCl_3$-La system was determined experimentally in the range from the pure trichloride to the product of its saturation with metallic La. The emf of galvanic concentration cells composed of two cells (liquid La in molten $LaCl_3$ saturated with La, and Mo immersed in molten $LaCl_3$ containing 0.35-23/4 mole % dissolved La) at 850-1000°C showed that the dissolution of La in the trichloride involves its reduction to the di- or monochloride. Emf isotherms plotted from experimental points were similar to those which should be expected for electrolytes made up of a mixture of $LaCl_3$ and $LaCl_2$. It is concluded that metallic La

Card 1/2

L 09193-67 EWT(m)/EWP(t)/ETI IJP(c) JD/JG
ACC NR: AP7002758 SOURCE CODE: UR/0364/66/002/008/0953/0957

31

SMIRNOV, M. V. and SHABANOV, O. M., Institute of Electrochemistry of the Ural'sk Branch, Academy of Sciences SSSR, Sverdlovsk (Institut elektrokhimii Ural'skogo filiala AN SSSR)

"Diffusion of Ions of Uranium and Molybdenum in Molten Chlorides of Alkali Metals"

Moscow, Elektrokhimiya, Vol 2, No 8, 1966, pp 953-957

ABSTRACT: According to the Stokes-Einstein equation, the diffusion coefficient for ions of tetravalent uranium must be greater than for trivalent, and the rate of diffusion of ions of trivalent molybdenum in a medium of molten chlorides of alkali metals must rise in the order: LiCl - KCl - CsCl with decrease in viscosity. Measurements have show the reverse order to apply. This gives evidence to the fact that the Strokes-Einstein equation does not account for all factors that can affect diffusion rate.

An examination was made of the mechanism of diffusion of multicharged cations in molten chlorides of alkali metals, where they form complex anionic groupings. Displacement of the cation exchange resins occurs chiefly in the composition of complexes, the size and charge of which determine the relaxation retardation on the part of the atmosphere of cations of the salt-solvent. The diffusion coefficents of the above indicated ions calculated on the basis of this mechanism quite satisfactorily agree with experimental data.

It is shown why the ion of trivalent uranium diffuses more rapidly than

Card 1/2

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ACC NR: AP6036115 SOURCE CODE: UR/0365/66/002/006/0700/0704

AUTHOR: Ozeryanaya, I. N.; Manukhina, T. I.; Belyayeva, G. I.; Burakova, E. A.; Smirnov, M. V.

ORG: Academy of Sciences SSSR, Ural Branch, Institute for Electrochemistry (Akademiya nauk SSSR, Ural'skiy filial, Institut elektrokhimii)

TITLE: Behavior of chromium nickel alloys in carbonate melts

SOURCE: Zashchita metallov, v. 2, no. 6, 1966, 700-704

TOPIC TAGS: chromium containing alloy, nickel containing alloy, corrosion rate, lithium compound, sodium compound

ABSTRACT: The experiments were carried out in a low melting binary eutectic mixture of lithium and sodium carbonates (melting point 497°). To suppress thermal decomposition and possible hydrolysis of the carbonates, the salts were melted in an atmosphere of carbon dioxide gas. The alloys investigated, EI-559A and EI-437B, are solid solutions in nickel of the following elements: EI-559A--18% Cr; 23% Fe; 3.5% Al; other elements about 1%: EI-437B--22% Cr; 4% Fe; 2.5% Ti; about 1% Al. Samples of the alloys, in the form of plates with a polished surface area of 8 cm^2, were placed in an alundum crucible with the melt. After the experiment, the samples were washed of traces of salts in distilled water, and dried to constant weight. The weight increase

UDC: 620.193.43

Card 1/2

ACC NR: AP7002165 (A,N) SOURCE CODE: UR/0089/66/021/006/0476/0478

AUTHOR: Smirnov, M. V.; Koryushin, A. P.; Komarov, V. Ye.

ORG: none

TITLE: Interaction of tetravalent uranium with chloride-fluoride NaCl-KCl-NaF melt

SOURCE: Atomnaya energiya, v. 21, no. 6, 1966, 476-478

TOPIC TAGS: uranium metal, fluoride, chloride, electrolysis, oxidation reduction reaction

ABSTRACT: The purpose of the study was to obtain information on the thermodynamics of interaction between tetravalent uranium and molten fluoride-chloride mixtures, the electrolysis of which is frequently used to produce metallic uranium and crystalline uranium dioxide. This is a continuation of earlier work (Tr. In-ta elektrokhimii Ural. fil. AN SSSR, No. 8, Sverdlovsk, 1966, p. 47) where the equilibrium between metallic uranium and a NaCl-KCl-NaF melt containing uranium ions was studied. Using these data, and measuring the oxidation-reduction potential U(III)/U(IV), the authors studied the interaction between the tetravalent uranium and the chloride-fluoride melt. The measurements were made in a molten equimolar mixture of sodium and potassium chloride containing 3% uranium and 8.0 - 18.5% NaF by weight, in the temperature interval 973-1123K. Experimentally the work consisted of measuring the emf of a cell containing molybdenum as an indicator electrode and the molten mixture. The measurement procedure is briefly described. The results show that the U^{++++}

Card 1/2 UDC: 541.138: 661.879

ACC NR: AP7002165

produces in the investigated melt a fluoride complex UF_8^{--}. An expression is obtained for the temperature dependence of the instability constant of this complex in the melt. Orig. art. has: 8 formulas and 2 tables.

SUB CODE: 18/ SUBM DATE: 04Jul66/ ORIG REF: 005/ OTH REF: 001

Card 2/2

SMIRNOV, M V

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SMIRNOV, M V

Avtomobil' samosval MAZ-205; Rukovodstvo po ukhodu (Automobile dump truck MAZ-205; maintenance manual) Moskva, Mashgiz, 1952.
110 p. illus., diagrs., tables.
At head of title: russia. Glavnoye Upravleniye Avtomobil'nykh Zavodov.

SMIRNOV, Mikhail Vasil'yevich; BAZ', I.S.; ZUBKOV, I.I., nauchnyy red.

[On Soviet military science] O sovetskoi voennoi nauke. Moskva, Voen.izd-vo, 1960. 333 p. (MIRA 13:11)
(Military art and science)

SMIRNOV, M.V.

Designing, manufacturing, and operating hydraulic transmissions for ships. [Izd.] LONITOMASH 52:101-107 '59. (MIRA 12:12)

(Oil hydraulic machinery) (Marine engineering)