

PRODUCTION OF Al-Sc ALLOY BY ELECTROLYSIS OF CRYOLITE-SCANDIUM OXIDE MELTS

Yuriy Shtefanyuk¹, Victor Mann¹, Vitaliy Pingin², Dmitriy Vinogradov²,
Yuriy Zaikov³, Olga Tkacheva³, Andrey Nikolaev³, Andrey Suzdaltsev³

¹UC "RUSAL"; 15 Nikoloyamskaya St., Moscow, 109240, Russia

²RUSAL's Engineering and Technology Centre; 88 Lenin St., Krasnoyarsk, 660049, Russia

³Institute of High Temperature Electrochemistry UB RAS; 20 Akademicheskaya St., Yekaterinburg, 620990, Russia

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Abstract

Primary testing for producing Al-Sc alloy by electrolysis of Sc_2O_3 dissolved in a cryolite bath containing molten aluminum was performed. A lab-scale cell consisted of graphite anode and aluminum cathode located on the bottom of corundum crucible. A graphite current lead to the aluminum cathode was also served as a stirrer. Molten cryolite NaF-AlF_3 or KF-AlF_3 , or their mixture with cryolite ratio in a range of 1.3-2.3 was used as a solvent for Sc_2O_3 . Electrolysis was carried out in the sodium cryolite with composition similar to conventional electrolyte at 980 °C and in the low-melted sodium and potassium-cryolite-based-electrolytes with cryolite ratio 1.3 and 1.5 at 750, 800 and 850 °C. The cathode current density impact on the composition of producing alloys was studied. The alloy's and electrolyte's composition was analyzed with SEM EDX and ICP methods. A uniform distribution of scandium throughout the Al-Sc alloy matrix for all studied samples was observed.

Introduction

Produced by electrolysis of cryolite-alumina melts (at 950-970 °C) aluminum is basically used in electrical engineering. Recently, such industrial sections as aerospace, airplane and hi-tech increased their demands for aluminum alloys with boron, titanium, zirconium and other modifying elements due to significantly improved processing characteristics of alloys [1-3]. Particularly, already 0.2 wt% of Sc in an Al-Sc alloy leads to excellent performance in strength, weldability, resistance to re-crystallization, corrosion resistance [4, 5].

Currently, the Al-Sc alloys are produced by mixing Sc with overheated liquid Al and following melt crystallization [6, 7]. A high price of pure Sc, its losses during alloy preparation, and strict control of cooling process parameters in order to obtain a uniform distribution of Sc in an alloy are the essential disadvantages of this method. The pure Sc can be replaced with the fluoride salt flux containing scandium [8], which is costly as well; moreover, this method requires more complicated design of reactor and still the uniform alloy crystallization remains the issue.

An alternative method for the Al-Sc production is an electrolytic deposition of Sc at liquid Al during electrolysis of cryolite-alumina melt. The electrolyte can have either a conventional composition based on sodium cryolite [9-11] or a low-melted composition based on potassium cryolite [12, 13]. In both cases, a red mud enriched with Sc_2O_3 can be used as a scandium-containing raw material [14] that is an undeniable advantage of the electrolytic method. Furthermore, the uniform scandium distribution can be realized by means of electromagnet forces which are essential in conditions of operating electrolysis cell.

The purposes of present work were to study a mechanism of the Sc and Al codeposition in the cryolite-scandium oxide electrolyte by voltammetry, galvanostatic polarization and thermodynamic evaluations; to perform electrolysis in the cryolite-scandium oxide melts with different composition and to determine an effect of the electrolyte cation composition, electrolysis conditions (including cathode current density, stirring) on composition and microstructure of the Al-Sc alloys in a temperature range of 700-1000 °C.

Experimental

Electrolyte

The electrochemical measurements and electrolysis testing were carried out either in a sodium cryolite electrolyte with a composition similar to conventional bath or in a novel low-melting potassium-cryolite-based electrolyte recommended for the low-temperature alumina electrolysis [15-18].

The following chemicals were used for electrolyte preparation: KF and NaF (chemically pure grade, 99.9 wt%, Vekton); AlF_3 (pure grade, 99.8 wt%, Vekton); Sc_2O_3 (99.9 wt%). The electrolyte was prepared by melting reagents mixed in corresponding amounts. A pre-testing electrolysis in the prepared electrolyte at 1.2 V for 2 hours was performed in order to remove residual impurities, electropositive in relation to Al.

The cryolite ratio (CR) for the potassium-sodium-cryolite mixture was calculated as $([\text{KF}]+[\text{NaF}])/[\text{AlF}_3]$ mol/mol. The composition of electrolytes and their basic characteristics are presented in Table 1 where a liquidus temperature (T_{liq}) is given for electrolyte without alumina; an alumina solubility in electrolyte is specified for the operating temperature (T_0). The Sc_2O_3 concentration in all electrolytes was 1 wt%.

Table 1. Electrolyte's composition and characteristics

#	Wt%/Mol%			CR	T_0 , °C	Al_2O_3 wt% [25]	T_{liq} , °C [26]
	KF	NaF	AlF_3				
1	47.5/ 56.5	-	52.5/ 43.5	1.3	750	5.5	620
2	39.0/ 44.3	10.0/ 15.7	51.0/ 40.0	1.5	850	7.2	790
3	-	53.3/ 69.6	46.7/ 30.4	2.3	980	10.0	985
4	-	42.9/ 40.0	57.1/ 60.0	1.5	800	2.0	750

The element composition of electrolyte and obtained alloy was analyzed by ICP method employing optical emission spectrometer iCAP 6300 Duo "Thermo scientific". The obtained

alloy was also examined by SEM EDX using DMAX-2500 (Rigaku, Japan) and scanning electron microscope JMS-5900LV with INCA Energy 200 micro-analyzer and energy-dispersive micro-analyzer INCA Wave 250 (JEOL, UK).

Electrochemical measurements procedure

The electrochemical measurements were carried out in a three-electrode cell. The cell schematic is given in Figure 1. A container made of dense graphite served as a counter electrode (CE). It was filled with electrolyte (mass 200 g) being studied. A spectral pure graphite electrode (SPG-electrode, $h = 10$ mm, $\varnothing = 6$ mm) cased in a corundum tube was used as a working electrode (WE). A graphite rod surrounded by a CO+CO₂ gas mixture was a reference electrode (RE). A detailed description of such a type reference electrode used for electrochemical study in cryolite-alumina melts is given in [19]. Temperature was measured with K-type thermocouple with accuracy ± 2 °C.

The electrochemical measurements were performed with PGSTAT AutoLab 302N and NOVA software (version 1.10,

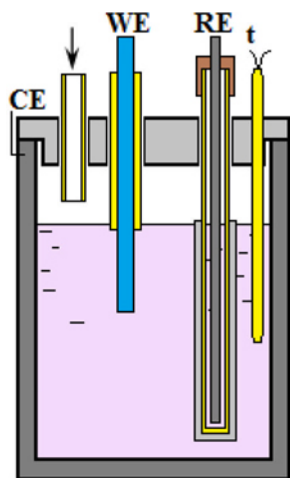


Figure 1. Cells schematics for electrochemical measurements

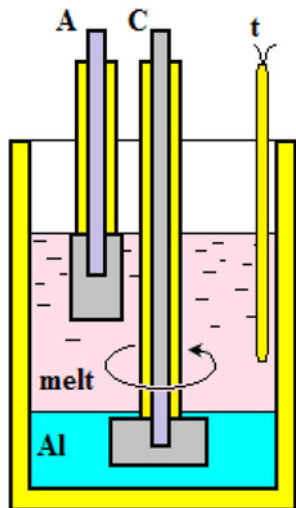


Figure 2. Cells schematics for electrolysis testing (Eco Chemie, Netherlands). The voltammograms were obtained at a potential sweep rate of $0.1 \text{ V}\cdot\text{s}^{-1}$. The galvanostatic

polarization curves were plotted point by point with the use of high speed chronopotentiometry. The ohmic potential drop was considered by measuring cell resistance using the electrochemical impedance spectroscopy and I-interrupt high speed methods.

Electrolysis testing procedure

A cell schematic for electrolysis testing is shown in Figure 2. Electrolysis was performed in an open cell consisted of graphite anode (A) ($h = 20$ mm, $\varnothing = 18$ mm, $S_a = 12 \text{ cm}^2$) and aluminum cathode (C) ($\varnothing = 45$ mm, $S_{cat} = 16 \text{ cm}^2$, Al mass – 50 g) located on the bottom of alumina crucible. Current leads to the anode and cathode, cased in alumina, were a nichrome wire and graphite rod, correspondently. The latter was also served as a stirrer. Aluminum was agitated with a rate of 300-400 rpm.

Electrolysis was carried out in a galvanostatic mode at cathode current density of $0.03\text{-}0.20 \text{ A/cm}^2$ with the use of DC power supply PSW7 30-72 (GW Instek, Taiwan). The cell voltage and temperature were registered during testing. After electrolysis the melt was pour out into a graphite ingot and the liquid aluminum alloy – into a cast-iron ingot. The alloy crystallization in the cast-iron ingot goes faster that likely allows the scandium distribution to be improved [6].

Results and Discussion

Galvanostatic polarization

The galvanostatic polarization curves obtained at the SPG-cathode in the KF-AlF₃ melt without and with addition of 1.0 wt% Sc₂O₃ are presented in Figure 3. The curve slop change can be observed within the potential range from -0.8 to -1.6 V. This change is likely related to the delivering difficulties of the positive electroactive components to the electrode. The cathode current density increase in the KF-AlF₃-Sc₂O₃ melt, containing Sc₂O₃ 1 wt%, points out at the same diffusion difficulties. Apparently, the curve segment from -0.8 to -1.6 V corresponds to the Al, Sc, and K codeposition.

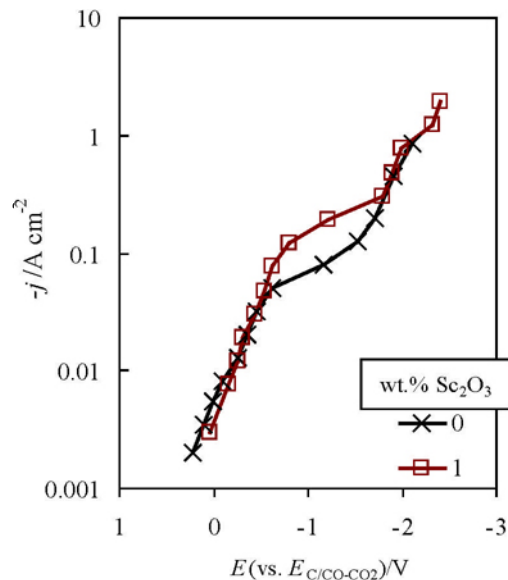


Figure 3. Galvanostatic polarization curves obtained at SPG-cathode in KF-AlF₃-Sc₂O₃ melt at 720 °C

Voltammetry

KF-AlF₃ electrolyte. The voltammograms obtained in the KF-AlF₃ melt are shown in Figure 4. The remaining current density reaches 70 mA·cm⁻² at potential sweep as low as -1.10 V (before the Al deposition begins). This is likely due to occurrence of the Al⁺ solution in the melt [22, 24], or the formation of aluminum carbide, or discharge of impurities remained in the melt as a result of incomplete electrolyte purification during pre-electrolysis. The aluminum discharges at potential about -1.25 V and current density of 0.28 A·cm⁻² (see peak marked as *Al* in Figure 4). This magnitude is close to the thermodynamically calculated value of the Al₂O₃ decomposition voltage on graphite anode and aluminum cathode, which is 1.325 V at 720 °C. The thermodynamic calculations were completed using reference data [20].

Peaks on the anode curve at -0.80, -0.55, and -0.30 V, marked as *Al'* and *Al''*, can be ascribed to the oxidation of different forms of aluminum (Al⁰, Al⁺, Al₄C₃). A peak at -1.43 V, marked as *K+Al* in the Figure 4, presumably corresponds to the beginning of the potassium deposition. This potential is slightly more positive than the thermodynamically evaluated value (1.827 V at 720 °C) that can be explained by the possible alloy formation and intercalation to the graphite cathode. A similar electrochemical behavior of graphite and platinum in the KF-AlF₃ electrolyte was reported by Liu [21]. The anode branch of the curve *F* (Figure 4) attributes to the discharge of fluoride ions with the CF₄ formation.

Sc₂O₃-containing electrolyte. The voltammograms obtained at the SPG-electrode in the KF-AlF₃-Sc₂O₃ melt with Sc₂O₃ 1 wt% and in the KF-AlF₃ melt without Sc₂O₃ are presented in Figure 5. The Sc₂O₃ addition in the cryolite melt results in occurrence of the cathode peaks *Al+Sc* and *K+Al+Sc* at -1.55 and -1.82 V, respectively. The first peak can be ascribed to the Sc deposition or to the Al and Sc codeposition. The second one can be attributed to the codeposition of all presented in the melt metals (Al, Sc, and K) or to the secondary reduction of the Sc₂O₃ by the K metal which is deposited at the cathode.

The appearance of the peak marked as *K'*, the increase in width and current density of the anode peaks (*Al'*, *Al''*) on the reverse curve of the voltammogram are associated with a large amount of electric charge passed through the cell during potential sweep to the cathode side. Generally, the occurrence of these peaks can be explained by the oxidation of different forms of aluminum and scandium presented in the electrolyte.

It was supposed that the electrochemical behavior of Sc in other melts being studied is similar to the one discussed above. The overall trend involves an increase in the current densities of voltammetric and polarization dependencies at temperature rise.

Based on the obtained voltammetric data it was assumed that the Al-Sc alloy formation occurs due to codeposition of either Al and Sc (at current density less than its limiting value) or Al, Sc, and alkali metal (at current density increasing). The latter process is accommodating by the secondary chemical reduction of the Sc₂O₃, dissolved in the melt, by the alkali metal. Moreover, according to the literature data [12, 22], the Sc metal can be formed in the melt as a result of the chemical reduction of the Sc₂O₃ dissolved as the oxide-fluoride (Sc-O-F) complexes by the aluminum metal or dissolved aluminum (as Al⁺). It was reported [22] that 0.14 wt% of Sc in Al was obtained as a result of the chemical interaction between the

Sc₂O₃, dissolved in the sodium cryolite, and Al (or Al⁺) at 970 °C.

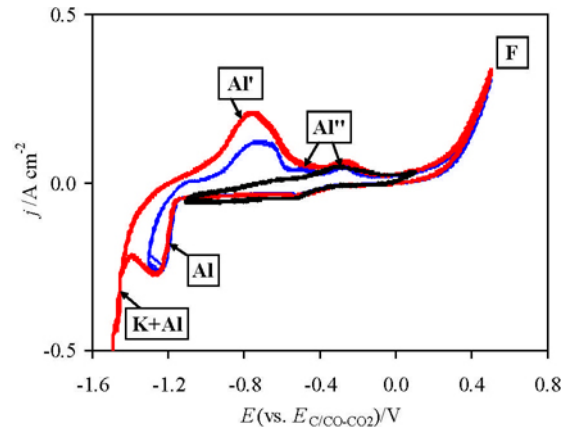


Figure 4. Voltammograms obtained at SPG-electrode in the KF-AlF₃ melt at the sweep rate of 0.1 V/s at 720 °C.

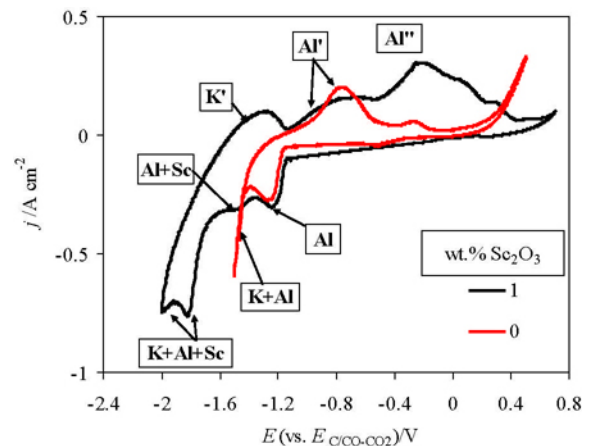


Figure 5. Voltammograms obtained at SPG-electrode in the KF-AlF₃-Sc₂O₃ melt at the sweep rate of 0.1 V/s at 720 °C.

Electrolysis testing

Primary electrolysis tests were carried out in electrolytes with composition indicated in Table 1. Parameters of electrolysis are given in Table 2. The cathode current density was chosen in accordance with the limiting current density determined from the polarization curves obtained in the electrolyte with 1 wt% of Sc₂O₃. The limiting current density corresponding to supposed codeposition of Al and Sc is 0.125 A·cm⁻² at temperatures 750-850 °C and 0.25 A·cm⁻² at 980 °C.

Table 2. Parameters of electrolysis

Melt #	T, °C	I, A	U, V	i _{cat} , A·cm ⁻²	Q, A·h	CE _{Sc} , %
1	750	0.5	2.00	0.032	1.1	40.3
2	850	0.5	1.85	0.032	3.8	7.4
3	980	3.2	3.00	0.200	6.4	1.6
4	800	2.0	2.00	0.125	6.8	1.5

The scandium current efficiency ($CE_{Sc}/\%$) was estimated based on the content of Sc ($\varphi_{Sc}/\%$) in the Al metal with mass (m_{Al}/g) and quantity of charge passed through the cell:

$$CE_{Sc} = \varphi_{Sc} \cdot m_{Al} \cdot z \cdot F / (M_{Sc} \cdot Q_{Sc} \cdot 3600),$$

where $z = 3$ – number of electrons; $F = 96487$ – $C1 \cdot mol^{-1}$ – Faraday's constant; $M_{Sc} = 45 g \cdot mol^{-1}$ – molar mass of scandium.

Content of Sc in electrolyte and cathode product determined by two methods (ICP and SEM) is given in Table 3.

Table 3. Content of Sc in electrolyte and cathode product

Melt	Sc in Al (ICP), wt%	Sc in Al (SEM), wt%	Na+K in Al (ICP), wt%	Sc in melt (ICP), wt%
1	0.50	0.52	0.003	0.40
2	0.32	0.35	0.007	0.43
3	0.16	0.17	0.036	0.40
4	0.11	0.10	0.020	0.41

According to the obtained results, if the cation composition of the cryolite melts changes from $KF-AlF_3$ to $NaF-AlF_3$ and the cathode current density increases then the fraction of current consumed on Sc deposition decreases but the content of alkali metal in Al rises. The highest scandium current efficiency was reached during electrolysis in the $KF-AlF_3$ melt (Table 2).

The effect of the cation composition can be explained by the following:

- according to the thermodynamic analysis, the cathode reduction of potassium metal occurs at potential 0.25 V more negative than the reduction of sodium metal;
- based on the ionic potentials values of the potassium and sodium cations ($\mu(K^+) = 0.72$ and $\mu(Na^+) = 1.01$ [23]) it was assumed that the bond energy of the sodium cation with the Sc-O-F complexes is stronger than that of the potassium cation.

It should be noted that the discussed results obtained in the lab-scale cell are initial. To confirm this data it is necessary to perform electrolysis in a cell with a higher current capacity.

Distribution of Sc in Al

Micrographs (SEM) of a cut of the Al-Sc alloy obtained by electrolysis in the $KF-AlF_3-Sc_2O_3$ melt (Table 1 and 2, #1) and a distribution of Sc in Al (according to the EDX analysis) are presented in Figure 6. The average size of the Sc-containing grains is less than $1 \mu m$. The similar Sc distribution was obtained also in other electrolysis tests whereas the average grain size was within the range of 1-10 μm .

In order to determine the stirring impact on the Sc distribution a single electrolysis in the $KF-AlF_3-Sc_2O_3$ melt (Table 1, #1) was performed without stirring. The Al-Sc alloy containing Sc in

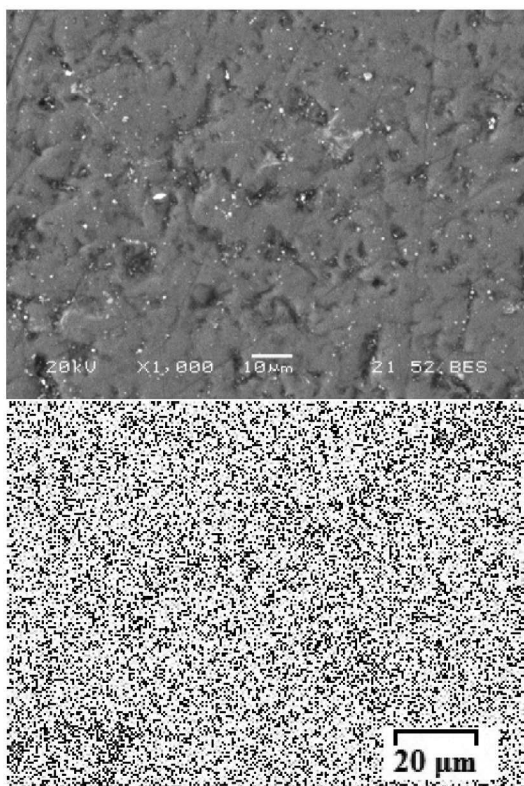


Figure 6. Micrographs (SEM) of the Al-Sc alloy (a cut) obtained by electrolysis in $KF-AlF_3-Sc_2O_3$ melt (Table 1 and 2, #1) and Sc distribution in Al (EDX)

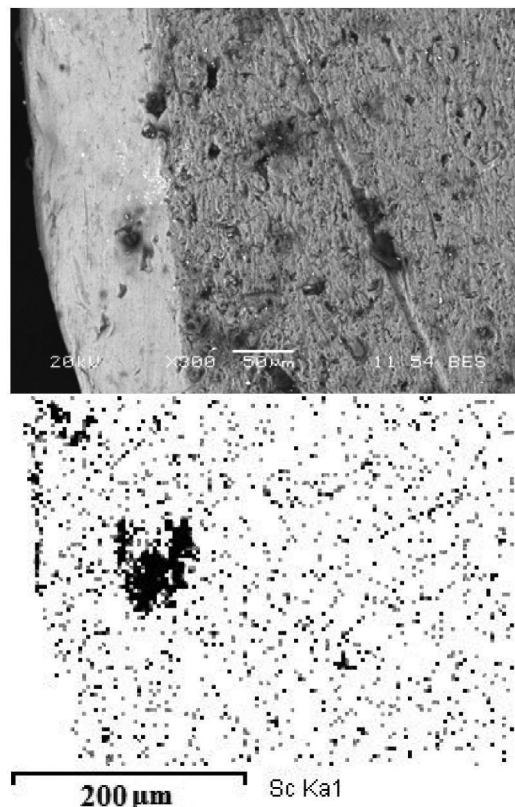


Figure 7. Micrographs (SEM) of the Al-Sc alloy (a cut) obtained by electrolysis in $KF-AlF_3-Sc_2O_3$ melt (Table 1 and 2, #1) and Sc distribution in Al (EDX). Stirring was not applied.

amount of 0.51 wt% on the alloy cake surface and of 0.33 wt% in its bulk was obtained. The micrograph of the alloy cut and the Sc distribution in Al for this test are shown in Figure 7. Moreover, the Sc-containing intermetallic compound with a composition similar to the Al₃Sc (wt%, 18-25 Sc, 75-82 Al) was found in the surface layer of obtained alloy. This designates that the uniform distribution of Sc in Al for the specific conditions (electrolyte composition and temperature) can be reached primarily by means of the mechanical agitation of electrolyte and liquid aluminum.

Nevertheless, an increase of operating temperature, i.e. performing electrolysis in a cryolite-alumina-scandium oxide melt at about 980 °C, can neutralize the agitation impact because the liquid Al will be highly overheated in this case and the Sc moving from the surface of the reaction zone into the alloy bulk will be less difficult.

Conclusions

Some kinetics peculiarities for the Al and Sc codeposition during electrolysis of the oxide-fluoride melts (KF-AlF₃-Sc₂O₃) were established.

The Al-Sc alloys with the Sc concentration from 0.1 to 0.5 wt% were obtained by electrolysis in the KF-AlF₃, KF-NaF-AlF₃, and NaF-AlF₃ melts containing 1 wt% Sc₂O₃ in the temperature range of 750-980 °C at different cathode current densities. The scandium current efficiency changed from 1.5 to 40.3 % in dependence of the cathode current density, temperature and cation composition of melt.

The uniform distribution of scandium throughout the Al-Sc alloy matrix was reached due to the mechanical agitation of the liquid aluminum.

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References

1. Harata M., Yasuda K., Yakushiji H., and Okabe T.H. *J. Alloys and Compounds*, 2009, 474, p.124.
2. Castrillejo Y., Vega A., Vega M., Hernandez P., Rodriguez J.A., and Barrado E. *Electrochim. Acta*, 2014, 118, p.58.
3. Okamoto H. *J. Phase Equilibria*, 1991, 12, p. 612.
4. Zakharov V.V. *Metal Science and Heat Treatment*, 2003, 45, p.246.
5. Costa S., Puga H., Barbosa J., and Pinto A.M.P. *Materials and Design*, 2012, 42, p.347.

6. Royset J., and Ryum N. *International Materials Reviews*, 2005, 50, p.19.
7. Korshunov B.G., Reznik A.M., Semenov S.A. Scandium, 1987, Moscow, Metallurgiya.
8. Jatsenko S.P., Jatsenko A.S, Ovsjannikov B.V., Varchenja P.A. Patent RU 2421537 C2, priority date 02.02.2009.
9. Schwellinger P. Patent WO 2006/079353 A1, priority date 25.01.2005.
10. Makhov S.V., Moskvitin V.I. *Russian Journal Non-Ferrous Metals (Tsvetnye Metally)*, 2010, 5, p. 95.
11. Qian Y., Xue J., Liu Q., Zhu J. *Light Metals*, 2013, p.1311.
12. Guan Ch., Zhu J., Xue J., Liu Q. *Light metals. 3rd International Symposium on High-Temperature Metallurgical Processing*, 2012, p. 243.
13. Liu Q., Xue J., Zhu J., Guan Ch. *Light metals*, 2012, p.685.
14. Pyagai I.N., Yatsenko S.P., Pasechnik L.A., Sabirzyanov N.A. *Proc. of the 4th International Congress "Non-Ferrous Metals-2012"*, Sept. 5-7, 2012, Krasnoyarsk, Russia, p.176.
15. Yang J., Hryn J.N, Davis B.R., Roy A., Krumdick G.K., J.A. Pomykala, Jr. *Light Metals* 2004, p. 321.
16. Tkacheva O., Hryn J., Spangenberg J., Davis B., Alcorn T. *Light metals* 2012, p. 675.
17. Hryn J., Tkacheva O., Spangenberg J. *Light metals* 2013, p. 1289.
18. Galan L.L., Barreiro G.J., Apisarov A.P., Dedyukhin A.E., Redkin A.A., Tkacheva O.Yu., Zaykov Yu.P. Patent ES 2379434A1, priority date 10.10.2010.
19. Suzdaltsev A.V., Khramov A.P., Zaikov Yu.P. *Russian Journal of Electrochemistry* 2012, 48, p. 1141.
20. Thermodynamic Constants of Individual Substances: Reference Book, Ed. by Glushko V.P., Moscow: Nauka, 1978–1982, Vols. 1–4.
21. Liu D., Yang Zh., Li W. *J. Electrochem. Soc.* 2010, 157(7), p. D417.
22. Baraboshkin A.N. Electrocrystallization of metals in molten salts (Elektrokristallizatsiya metallov iz rasplavlennykh soley), Moscow: Nauka, 1976.
23. Shannon R.D. *Acta Cryst.* 1976, A-32, N5, p.751.
24. Bredig M.A. In: Molten salts chemistry, Ed. M. Blender. NY, Interscience Publishers, 1964, p. 367.
25. Dedyukhin A., Apisarov A., Redkin A., Tkacheva O., Zaikov Yu., Nikolaeva E., Tinghaev P. *Light Metals*, 2009, p. 401.
26. Apisarov A., Dedyukhin A., Nikolaeva E., Tinghaev P., Tkacheva O., Redkin A., Zaikov Yu. *Light Metals*, 2010, p.395.