

Electroreduction of aluminium and scandium from the fluoride and oxide-fluoride melts

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Abstract

A growing demand for alloys and composite materials based on aluminum and other light metals is widely observed. Thus the new energy-efficient ways of their production are relevant. In this work we studied the main kinetic features of the aluminium and scandium electro reduction during electrolysis of fluoride and oxide-fluoride melts by means of electrochemical methods. Particularly, features under study would be helpful at the choosing parameters of stable electrolysis of low-melting KF-AlF₃-based melts, which are selected as the main perspective melts due to their high capture with oxides. To clarify the potentials of aluminium and scandium electro reduction, measurements were also performed in KF-AlF₃-ScF₃, LiF-NaF-AlF₃-ScF₃, and LiF-CaF₂-ScF₃ melts.

It was shown that aluminium is electrically reduced into tungsten electrode in the potential range from -0.1 to -1.3 V in KF-AlF₃-Al₂O₃ melt. At the same time, the discharge precedes from different electroactive species. This accompanied with the diffusion peak formation at a potential around -0.4 to -0.5 V and further maintenance of the cathode current when the potential is shifted to the negative region. Despite the maintaining general kinetic features and parameters of the process under study replacing Al₂O₃ by Sc₂O₃ in KF-AlF₃ melts leads to a co-electroreduction of aluminium and scandium. Depending on the potential sweep rate, a noticeable difference in the cathode process in KF-AlF₃-Sc₂O₃ melts is the potassium electroreduction with depolarization caused by the probable formation of K-Sc compounds. Under stationary conditions, the appearance and increase in the Sc₂O₃ content in KF-AlF₃ melt up to 5.7 wt. % leads to an increase in the limiting cathode current of co-electroreduction of aluminium and scandium from 0.45 to 0.81 A/cm² at a temperature of 800 °C. The character of voltammograms obtained in KF-AlF₃-ScF₃ melts is complicated with using ScF₃ fluoride as a source of scandium. This is due to electroreduction of Al-Sc intermetallic compounds of different composition. Individual scandium electroreduction without visible aluminium and alkali metal reducing was observed in the LiF-CaF₂ fluoride melt at a potential of -0.40 to -0.45 V relative to the potential of the aluminum reference electrode. Obtained value is close to the thermodynamic one.

The obtained data are necessary at the development of the scientific foundations of new energy-efficient technology of producing Al-Sc master alloys production from their oxides during the electrolysis of oxide-fluoride melts.

References

- [1] V.I. Napalkov, S.V. Makhov, Alloying and modifying of aluminium and magnesium. *MISiS: Moscow*. **2002**. 376p (russian)
- [2] E.M. Zhilina, S.N. Agafonov, A.S. Russkih, S.V. Zhidovinova, V.P. Chentsov, and S.A. Krasikov. Aluminium interaction with multicomponent oxide system consisting of zirconium, titanium, silicon, iron. *Butlerov Communications*. **2017**. Vol.51. No.7. P.55-60. DOI: 10.37952/ROI-jbc-01/17-51-7-55
- [3] E.M. Zhilina, S.A. Krasikov, S.N. Agafonov, L.B. Vedmid, and S.V. Zhidovinova. Thermodynamic and kinetic peculiarities of joint aluminothermic reduction of titanium and zirconium from oxides. *Butlerov Communications*. **2016**. Vol.45. No.1. P.130-135. DOI: 10.37952/ROI-jbc-01/16-45-1-130

- [4] J. Royset, N. Ryum. Scandium in aluminium alloys overview: physical metallurgy, properties and applications. *International Materials Reviews*. **2005**. Vol.50. P.19-46.
- [5] A.V. Suzdaltsev, A.Yu. Nikolaev, and Yu.P. Zaikov. Modern ways for obtaining Al-Sc master alloys: A review. *Tsvetnye Metally*. **2018**. No.1. P.69-73. DOI: 10.17580/tsm.2018.01.09 (russian)
- [6] V.M. Skachkov, and S.P. Yatsenko. Obtaining of Sc, Zr, Hf and Y base metals on the basis of aluminum by method of high-temperature exchange reactions in salt melts. *Tsvetnye Metally*. **2014**. No.3. P.22-26. (russian)
- [7] V.I. Moskvitin, S.V. Makhov. On possibility of fabrication of aluminum-scandium alloying composition in aluminum electrolyzer. *Tsvetnye Metally*. **1998**. No.7. P.43-46, (russian)
- [8] Yu. Zaikov, O. Tkacheva, A. Suzdaltsev, A. Kataev, Yu. Shtefanyuk, V. Pingin, and D. Vinogradov. Lab scale synthesis of Al-Sc alloys in NaF-AlF₃-Al₂O₃-Sc₂O₃ melt. *Advanced Materials Research*. **2015**. Vol.1088. P.213-216. DOI: 10.4028/www.scientific.net/AMR.1088.213.
- [9] Sh. Yang, B. Gao, Zh. Wang, Zh. Shi, Y. Ban, H. Kan, X. Cao, and Zh. Qiu. Preparation of Al-Sc alloys by molten salts electrolysis. *Light Metals*. **2007**. P.54-57.
- [10] Q. Liu, J. Xue, J. Zhu, Y. Qian and L. Feng. Processing Al-Sc alloys at liquid aluminum cathode in KF-AlF₃ molten salt. *ECS Transactions*. **2012**. Vol.50(11). P.483-489. DOI: 10.1149/05011.0483ecst.
- [11] Q. Liu, J. Xue, J. Zhu, and Ch. Guan. Preparing aluminium-scandium inter-alloys during reduction process in KF-AlF₃-Sc₂O₃ melts. *Light metals*. **2012**. P.685-689.
- [12] M. Harata, K. Yasuda, H. Yakushiji, and T.H. Okabe. Electrochemical production of Al-Sc alloy in CaCl₂-Sc₂O₃ molten salt. *Journal of Alloys and Compounds*. **2009**. Vol.474. P.124-130. DOI: 10.1016/j.jallcom.2008.06.110.
- [13] Y. Castrillejo, A. Vega, M. Vega, P. Hernandez, J.A. Rodriguez, and E. Barrado. Electrochemical formation of Sc-Al intermetallic compounds in the eutectic LiCl-KCl. Determination of thermodynamic properties. *ElectrochimicaActa*. **2014**. Vol.118. P. 58-66. DOI: 10.1016/j.electacta.2013.11.163.
- [14] S.P. Yatsenko, V.M. Skachkov, and A.S. Yatsenko. Receipt of ligature on basis of aluminium by method of high-temperature exchange reaction in molten salts. V. Injection of technological powders in liquid aluminium. *Raspilavy*. **2011**. No.4. P.41-46. (russian)
- [15] P.S. Pershin, A.V. Suzdaltsev, and Yu.P. Zaikov. Receiving of Al-Si alloys in KF-AlF₃-SiO₂ melt. *Butlerov Communications*. **2015**. Vol.43. No.9. P.116-120. ROI: jbc-02/15-43-9-116
- [16] P.S. Pershin, A.A. Filatov, A.Yu. Nikolaev, A.V. Suzdaltsev, and Yu.P. Zaikov. Cathode processes during the synthesis of the Al-Zr alloys in KF-AlF₃-Al₂O₃-ZrO₂ melt. *Butlerov Communications*. **2017**. Vol.49. No.2. P.110-116. DOI: 10.37952/ROI-jbc-01/17-49-2-110
- [17] A.A. Filatov, P.S. Pershin, A.V. Suzdaltsev, A.Yu. Nikolaev, Yu.P. Zaikov. Synthesis of Al-Zr master alloys via the electrolysis of KF-NaF-AlF₃-ZrO₂ melts. *Journal of the Electrochemical Society*. **2018**. Vol.165(2). P. E28-E34. DOI: 10.1149/2.0571802jes.
- [18] A.V. Suzdaltsev, A.P. Khramov, and Yu.P. Zaikov. Aluminum electrode for electrochemical studies in cryolite-alumina melts at 700-960 °C. *Russian Journal of Electrochemistry*. **2012**. Vol.48. P.1153-1159. DOI: 10.1134/S1023193512120129
- [19] E.T. Turkdogan. *Physical Chemistry of High Temperature Technology, 1st ed.* **1980**. Academic Press, New York. 447p.
- [20] G. Cacciamani, P. Riani, G. Borzone, N. Parodi, A. Saccone, R. Ferro, A. Pisch, and R. Schmid-Fetzer. Thermodynamic measurements and assessment of the Al-Sc system. *Intermetallics*. **1999**. Vol.7. P.101-108. DOI: 10.1016/S0966-9795(98)00022-3.
- [21] *State diagrams of double metallic systems: a Handbook*. Ed. N.P. Lyakishev in 3 Vols: V.1. Moscow: Mashinostroenie. **1996**. (russian)
- [22] A.Yu. Nikolaev, A.V. Suzdaltsev, P.V. Polyakov, and Yu.P. Zaikov. Cathode process at the electrolysis of KF-AlF₃-Al₂O₃ melts and suspensions. *Journal of the Electrochemical Society*. **2017**. P.164(8). P.H5315-H5321. DOI: 10.1149/2.0571802jes.