

Cathode processes during the synthesis of the Al-Zr alloys in KF-AlF₃-Al₂O₃-ZrO₂ melt

© Pavel S. Pershin,¹⁺ Alexander A. Filatov,^{1,2} Andrey Yu. Nikolaev,^{1,2}
Andrey V. Suzdaltsev,^{1*} and Yury P. Zaikov^{1,2}

¹Laboratory of Electrode Processes. Institute of High Temperature Electrochemistry of Ural Branch of Russian Academy of Sciences. S. Akademicheskaya St., 20. Yekaterinburg, 620137. Russia.

Phone: +7 (343) 374-50-89. E-mail: paffka19@yandex.ru

²Department of Technologies of Electrochemical Productions. Chemical-Technological Institute of Ural Federal University. Mira St., 19. Yekaterinburg, 620002. Russia.

Phone: +7 800-100-50-44. E-mail: rector@urfu.ru

*Supervising author; ⁺Corresponding author

Keywords: zirconium, zirconia, aluminium, alloy, melt, voltammetry.

Abstract

An overview of the methods of electrochemical synthesis of aluminium with zirconium alloys, indicating the relevance of the search and development of new resource-saving methods for its preparation. The data on the kinetics of electro-reduction of zirconium and joint electrodeposition of zirconium with aluminium from halide melts and ionic liquids is provided. New energy efficient method, which concluded in the preparation of such alloys by the electrolytic decomposition of aluminium and zirconium oxides in a low-melting melts on the basis of the system KF-AlF₃ is proposed.

Cyclic voltammetry method was used for the investigation of the cathode process kinetics in the KF-AlF₃-Al₂O₃ and KF-AlF₃-Al₂O₃-ZrO₂ melts on the glassy carbon substrate at the temperature of 750 °C. It is shown that in the KF-AlF₃-Al₂O₃ melt the only one peak on the voltammograms in the potential range -0.1...-0.2 V corresponding to the discharge of aluminium at the cathode is observed. Introduction of zirconium dioxide into the KF-AlF₃-Al₂O₃ melt leads a peak on the voltammograms at the potential range of 0.13-0.17 V corresponding to zirconium discharge to appear. The discharge current of both aluminium and zirconium increase with the rate, meanwhile potentials of current peaks shifted slightly. The obtained data was analyzed from the voltammetry diagnostic criteria point of view. In particular, the dependence of the current density peak from the square root of scan rate of potential (iP from v^{1/2}), which is linear in the range of studied sweep rates of the potential and crosses the beginning of the ordinates, was performed. This indicates that under the experimental conditions the recovery process of zirconium-containing ions from the KF-AlF₃-Al₂O₃-ZrO₂ melt is quasi-reversible and mainly controlled by the diffusion.

The number of electrons involved in the cathode recovery process of zirconium was calculated by the equation for the reversible process and equals to 4.

The results will be used for the determination and optimization of parameters for obtaining aluminium alloys with zirconium via the electrolysis of melts on the basis of the system KF-AlF₃-Al₂O₃-ZrO₂.

References

- [1] M.I. Hasik, N.P. Lyakishev, B.I. Emlin. Theory and technology of ferroalloys producing. *Moscow: Metallurgy*. **1988**. 784p. (russian)
- [2] D.V. Ogorodov, D.A. Popov, A.V. Trapeznikov. The ways of obtaining of Al-Zr master alloys (review). *VIAM works*. **2015**. No.11. P.2-9. DOI: 10.18577/2307-6046-2015-0-11-2-2
- [3] V.I. Napalkov, S.V. Makhov. Alloying and modification of aluminium and magnesium. *Moscow: Moscow Institution of Steels and Alloys*. **2002**. 375p. (russian)
- [4] P.S. Pershin, A.V. Suzdaltsev, Yu.P. Zaikov. Receiving of Al-Si alloys in KF-AlF₃-SiO₂ melt. *Butlerov Communications*. **2015**. Vol.43. No.9. P.116-120. DOI: 10.37952/ROI-jbc-01/15-43-9-116
- [5] A.V. Larionov, V.M. Chumarev, L.Yu. Udoeva, D.V. Taranov, S.A. Vokhmentsev. Thermodynamic modeling of the process of aluminium-thermic smelting of Al-V-Ti-C ligature. *Butlerov Communications*. **2017**. Vol.49. No.1. P.43-49. DOI: 10.37952/ROI-jbc-01/17-49-1-43
- [6] P.S. Pershin, A.V. Suzdaltsev, Yu. P. Zaikov. Synthesis of silumins in KF-AlF₃-SiO₂ melt. *Journal of Electrochemical Society*. **2016**. Vol.163. No.5. D167-D170. DOI: 10.1149/2.0521605jes

- [7] Z. Chen, M. Zhang, W. Han, Z. Hou. Electrochemical reduction of Zr (IV) in the LiCl-KCl molten salt. *Rare Metal Materials and Engineering*. **2009**. Vol.38. No.3. P.456-459.
- [8] Z. Chen, Y.J. Li, S.J. Li. Electrochemical behavior of zirconium in the LiCl-KCl molten salt at Mo electrode. *Journal of Alloys and Compounds*. **2011**. Vol.509. No.20. P.5958-5961. DOI: 10.1016/j.jallcom.2010.10.048
- [9] Y. Wu, Z. Xu, S. Chen, G. Li. Electrochemical behavior of zirconium in molten NaCl-KCl- K_2ZrF_6 system. *Rare Metals*. **2011**. Vol.30. No.1. P.8-13. DOI: 10.1007/s12598-011-0187-7
- [10] L.P. Polyakova, P.T. Stangrit. Cathodic processes at electrolysis of chloride and chloride-fluoride melts of zirconium. *Electrochimica Acta*. **1982**. Vol.27. No.11. P.1641-1645. DOI: 10.1016/0013-4686(82)80092-3
- [11] C. Guang-Sen, M. Okido, T. Oki. Electrochemical studies of zirconium and hafnium in alkali chloride and alkali fluoride-chloride molten salts. *Journal of Applied Electrochemistry*. **1990**. Vol.20. P.77-84.
- [12] S. Ghosh, S. Vandarkuzhali, P. Venkatesh, G. Seenivasan, T. Subramanian, B. Prabhakara Reddy, K. Nagarajan. Electrochemical studies on the redox behaviour of zirconium in molten LiCl-KCl eutectic. *Journal of Electroanalytical Chemistry*. **2009**. Vol.627. No.1-2. P.15-27. DOI: 10.1016/j.jelechem.2008.12.011
- [13] Y. Sakamura. Zirconium behavior in molten LiCl-KCl eutectic. *Journal of the Electrochemical Society*. **2004**. Vol.151. No.3. P.C187-C193. DOI: 10.1149/1.1644605
- [14] R. Baboian, D.L. Hill, R.A. Bailey. Electrochemical studies on zirconium and hafnium in molten LiCl-KCl eutectic. *Journal of the Electrochemical Society*. **1965**. Vol.112. No.12. P.1221-1224. DOI: 10.1149/1.2423405
- [15] M. Gibilaro, L. Massot, P. Chamelot, L. Cassayre, P. Taxil. Investigation of Zr(IV) in LiF-CaF₂: Stability with oxide ions and electroreduction pathway on inert and reactive electrodes. *Electrochimica Acta*. **2013**. Vol.95. P.185-191. DOI: 10.1016/j.electacta.2013.02.022
- [16] H. Groult, A. Barhoun, H. El Ghallali, S. Borensztjan, F. Lantelme. Study of the electrochemical reduction of Zr⁴⁺ ions in molten alkali fluorides. *Journal of the Electrochemical Society*. **2008**. Vol.155. No.2. P.E19-E25. DOI: 10.1149/1.2811848
- [17] H. Groult, A. Barhoun, E. Briot, F. Lantelme, C.M. Julien. Electrodeposition of Zr on graphite in molten fluorides. *Journal of Fluorine Chemistry*. **2011**. Vol.132. P.1122-1126. DOI:10.1016/j.jfluchem.2011.06.040
- [18] L. Xu, Y. Xiao, Q. Xu, A. v. Sandwijk, J. Li, Z. Zhao, Q. Song, Y. Yang. Electrochemical behavior of zirconium in molten LiF-KF-ZrF₄ at 600 °C. *RSC Advances*. **2016**. Vol.6. P.84472-84479. DOI: 10.1039/c6ra17102h
- [19] B. Gilbert, G. Mamantov, K.W. Fung. Electrochemistry of Zirconium(IV) in Chloroaluminate Melts. *Inorganic Chemistry*. **1975**. Vol.14. No.8. P.1802-1806.
- [20] M. Ueda, T. Teshima, H. Matsushima, T. Ohtsuka. Electroplating of Al-Zr alloys in AlCl₃-NaCl-KCl molten salts to improve corrosion resistance of Al. *J Solid State Electrochem*. **2015**. Vol.19. P.3485-3489. DOI 10.1007/s10008-015-2861-4
- [21] M. Kawase, Y. Ito. The electroformation of Zr metal, Zr-Al alloy and carbon films on ceramic. *Journal of Applied Electrochemistry*. **2003**. Vol.33. P.785-793.
- [22] T. Tsuda, C.L. Hussey, G.R. Stafford, O. Kongstein. Electrodeposition of Al-Zr Alloys from Lewis Acidic Aluminum Chloride-1-Ethyl-3-methylimidazolium Chloride Melt. *Journal of the Electrochemical Society*. **2004**. Vol.151. No.7. C447-C454. DOI: 10.1149/1.1753231
- [23] Yu.M. Shtefanyuk, V.Kh. Mann, V.V. Pingin, D.A. Vinogradov, Yu.P. Zaikov, O.Yu. Tkacheva, A.Yu. Nikolaev, A.V. Suzdaltsev. Production of Al-Sc alloy by electrolysis of cryolite-scandium oxide melts. *Light Metals*. **2015**. P.589-593.
- [24] A.V. Suzdaltsev, A.P. Khramov, Yu.P. Zaikov. Aluminum electrode for electrochemical studies in cryolite-alumina melts at 700-960 °C. *Rus. Journal of Electrochem*. **2012**. Vol.48. No.12. P.1153-1159. DOI:10.1134/S1023193512120129
- [25] Z. Galus. Theoretical basis of electrochemical analysis. *Moscow: World*. **1974**. 552p. (russian)