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Cathode processes during the synthesis of the Al-Zr alloys in $KF-AlF_3-Al_2O_3-ZrO_2$ melt

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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 $KF-AlF_3$ is proposed.

Cyclic voltammetry method was used for the investigation of the cathode process kinetics in the $KF-AlF_3-Al_2O_3$ and $KF-AlF_3-Al_2O_3-ZrO_2$ melts on the glassy carbon substrate at the temperature of 750 °C. It is shown that in the $KF-AlF_3-Al_2O_3$ 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 $KF-AlF_3-Al_2O_3$ 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 ν1/2), 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 $KF-AlF_3-Al_2O_3-ZrO_2$ 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 $KF-AlF_3-Al_2O_3-ZrO_2$.

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 $KF-AlF_3-SiO_2$ melt. *Butlerov Communications*. **2015**. Vol.43. No.9. P.116-120. ROI: jbc-02/15-43-9-116
[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. ROI: jbc-02/17-49-1-43

[6] P.S. Pershin, A.V. Suzdaltsev, Yu. P. Zaikov. Synthesis of silumins in $KF-AlF_3-SiO_2$ 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 $LiF–CaF_2$: 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 Zr^{4+} 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 $LiF–KF–ZrF_4$ 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 $AlCl_3$-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)