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Behaviour of oxygen-conducting creamic materials in the melts oflithium chloride

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Abstract

The behavior of potential ceramic materials (electrolytes conducting on oxygen ions) of electrochemical control devices of technological operations in oxide-halide melts was investigated.Based on the literature data and thermodynamic estimates for long-term tests in the LiCl, LiCl-Li_2O and LiCl-Li_2O-Li melts at a temperature of 650 °C, mixtures of oxides ZrO_2-Y_2O_3 (YSZ), ZrO_2-Sc_2O_3 (ScSZ), ZrO_2-CaO (CaSZ) and CeO_2-Gd_2O_3 (CGO) were selected.These melt under the studies are the most widely used in a number of high-temperature electrochemical processes of obtaining metals and alloys, as well as in the developed schemes of pyrochemical processing of nuclear fuel.The stability of the samples was determined by changes in mass, appearance, elemental analysis of the melt, as well as via the scanning electron microscopy.

According to the results of resource tests in the LiCl-Li_2O melts, it is shown that the ZrO_2-Sc_2O_3 sample is thermally unstable (destroyed), and cerium in the CeO_2-Gd_2O_3sample partially changes the oxidation degree to III, that does not allow it to be used as a material conducting only on oxygen ions.The best stability in LiCl-Li_2O melts was shown by the samples of ZrO_2-Y_2O_3 with cubic and tetragonal structures and the samples of ZrO_2-CaO. Based on the changes in the microstructure of the samples, it was concluded that the increase in the content of Li_2O in the LiCl-Li_2O melt accelerates the destruction of the sample mainly by the mechanism of dyeing, and the presence of lithium leads to loosening of the samples.

Both factors (an increase in the content of Li_2O and the appearance of lithium in the melt) accelerate the destruction of samples, reducing the endurance of the electrochemical devices duringthe direct contact of ceramic materials ZrO_2-Y_2O_3, ZrO_2-Sc_2O_3 with the studied melts.

References

[1] 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)
[2] P.S. Pershin, A.V. Suzdaltsev and Yu.P. Zaikov. Recieving of Al-Si alloys in KF-AlF_3-SiO_2 melt. *Butlerov Communications*. **2015**. Vol.43. No.9. P.116-120. DOI: 10.37952/ROI-jbc-01/15-43-9-116
[3] 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-AlF_3-Al_2O_3-ZrO_2 melt. *Butlerov Communications*. **2017**. Vol.49. No.2. P.110-116. DOI: 10.37952/ROI-jbc-01/17-49-2-110
[4] A. Merwin, M.A. Williamson, J.L. Willit, D. Chidambaram. Review: Metallic lithium and the reduction of actinide oxides. *Journal of the Electrochemical Society*. **2017**. Vol.164(8). P.H5236-H5246.
[5] E.Y. Choi, J. Lee. Complete reduction of high-density UO_2 to metallic U in molten Li_2O-LiCl. *Journal of Nuclear Materials*. **2017**. Vol.494. P.439-447.
[6] J.L. Willit, W.E. Miller, J.E. Battles. Electrorefining of uranium and plutonium - A literature review. *JournalofNuclearMaterials*. **1992**. Vol.195(3). P.229-249.
[7] V.L. Cherginets. Chemistry of oxocompounds in ionic melts. *Kharkov: Institute of monocrystals*. **2004**. 437p.
[8] E.Y. Choi, I.K. Choi, J.M. Hur, D.S. Kang, H.S. Shin, S.M. Jeong. In situ electrochemical measurement of O^{2-} concentration in molten Li_2O/LiCl during uranium oxide reduction process. *Electrochemical and Solid-State Letters*. **2012**. Vol.15(3). P.E11-E13.

[9] Yu. Kado, T. Goto, R. Hagiwara. Thermodynamic and kinetic properties of oxide ions in a LiCl-KCl-CsCl eutectic melt. *Journal of Electrochemical Society*. **2013**. Vol.160(9). E90-E93.DOI:10.1149/2.048309jes
[10] H. Zheng, H. Nian, J. Xia, G. Zhou, D. Jiang, Li Q. Bi/Bi_2O_3 sensor for quantitation of dissolved oxygen in molten salts. *Journal of Advanced Ceramics*. **2018**. Vol.7(1). P.1-4.DOI:10.1007/s40145-017-0250-4
[11] M. Shen, H. Peng, M. Ge, Y. Zuo, L. Xie. Use of square wave voltammeter for online monitoring of O^{2-} concentration in molten fluorides at 600 ºC. *Journal of Electroanalytical Chemistry*. **2015**. Vol.748. P.34-39. DOI:10.1016/j.jelechem.2015.04.023
[12] Y. Sakamura, M. Iizuka, S. Kitawaki, A. Nakayoshi, H. Kofuji. Formation and reduction behaviors of zirconium oxide compounds in LiCl-Li_2O melt at 923 K. *Journal of Nuclear Materials*. **2015**. Vol.466. P.269-279.
[13] S.H. Cho, D.Y. Kim, S. Kwon, B.H. Yoon, J.H. Lee. High-temperature corrosion characteristics of yttria-stabilized zirconia material in molten salts of LiCl-Li_2O and LiCl-Li_2O-Li. *Journal of Nuclear Science and Technology*. **2018**. Vol.55(1). P.97-103. DOI:10.1080/00223131.2017.1383214
[14] S.H. Cho, S.W. Kim, D.Y. Kim, J.H. Lee, J.M. Hur. Hot corrosion behavior of magnesia-stabilized ceramic material in a lithium molten salt. *Journal of Nuclear Materials*.**2017**. Vol.490. P.85-93. DOI:10.1016/j.jnucmat.2017.04.012
[15] S.H. Cho, S.B. Park, J.H. Lee, J.M. Hur, H.S. Lee. Hot corrosion behavior of ZrO_2-MgO coatings in LiCl-Li_2O molten salt. *Materials Chemistry and Physics*. **2012**. Vol.131. P.743-751. DOI:10.1016/j.matchemphys.2011.10.045
[16] M. Takeuchi, T. Kato, K. Hanada. Corrosion resistance of ceramic materials in pyrochemical reprocessing condition by using molten salt for spent nuclear oxide fuel. *Journal of Physical Chemistry of Solids*. **2005**. Vol.66. P.521-525.
[17] N. Otsuka. Acid-base reactions of eutectic LiCl-41m/o KCl melt equilibrated with gas atmospheres containing HCl, H_2O and O_2 at 600 ºC. *ECS Transactions*. **2012**. Vol.41(42). P.13-19. DOI: 10.1149/1.4717996.
[18] A.R. Shankar, U.K. Mudali, R. Sole. Plasma-sprayed yttria-stabilized zirconia coatings on type 316 L stainless steel for pyrochemical reprocessing plant. *Journal of Nuclear Materials*. **2008**. Vol.372. P.226-232.
[19] C.Z. Wang. Solid electrolyte and chemical sensors. *Metallurgical Industry Press. Beijing*. **2000**. 863p.
[20] H. Hu, Yu. Gao, Y. Lao, Q. Qin, G. Li, G.Z. Chen. Yttria stabilized zirconia aided electrochemical investigation on ferric ions in mixed molten calcium and sodium chlorides. *Metallurgical and Metallurgical Transactions B*. **2018**. Vol.49. P.2794-2808. DOI: 10.1007/s11663-018-1371-z
[21] S.R. Bishop, K.L. Duncan, E.D. Wachsman. Defect equilibria and chemical expansion in non-stoichiometric undoped and gadolinium-doped cerium oxide. *Electrochimica Acta*. **2009**. Vol.54. P.1436-1443.
[22] F.M.B. Marques, V.V. Kharton, E.N. Naumovich, F.M. Figueiredo, A.V. Kovalevsky, A.P. Viskup, A.L. Shaula. Oxygen transport in $Ce_{0.8}Gd_{0.2}O_{2-d}$-based composite membranes. *Solid State Ionics*. **2003**. Vol.160. No.3-4. P.247-258.
[23] M.I. Pantyukhina, O.L. Andreev, Z.S. Martemyanova, N.N. Batalov. Cation conductivity of Li_8ZrO_6-$LiYO_2$ solid solutions. *Inorganic Materials*. **2004**. Vol.40(4). P.404-406.
[24] V.P. Gorelov, V.B. Balakireva, I.Yu. Yaroslavtsev, E.G. Vaganov, and V.A. Kazantsev. Conductivity and thermal expansion of the $Ce_{0.8}Gd_{0.2}O_{1.9}$ solid electrolyte in the oxidizing and reducing atmospheres. *Russian Journal of Electrochemistry*. **2007**. Vol.43(8). P.888-893. (russian)
[25] E.T. Turkdogan. Physical Chemistry of High Temperature Technology, 1st ed. *Academic Press, New York*. **1980**. 447p.