

Electrolytic Reduction of Uranium and Rare Earth Oxides in LiCl-Li₂O Molten Salt

Alexei Shishkin¹⁾, Vladimir Shishkin¹⁾, Albert Mullabaev¹⁾, Vadim Kovrov¹⁾, Alexander Dedukhin¹⁾, Anna Kholkina, ¹⁾ Vladimir Tsvetov¹⁾, Sang-Eun Bae²⁾, and Yury Zaykov¹⁾*

¹⁾ Institute of High Temperature Electrochemistry, Ekaterinburg, Russia

²⁾ Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

*A.Potapov_50@mail.ru

The electrolytic reduction of tablets of uranium oxides, rare earths oxides and their mixtures has been studied in LiCl melt with additives 0-2.0 wt.% Li₂O at temperature 650 °C. Electrolysis was carried out in galvanostatic mode with a step change of current. The cathode potential was measured with a short-time current cutoff for monitoring the process. Platinum, graphite and ceramic anodes were used in the experiments. The process duration was determined by the amount of electricity passed, that was varied from 130 to 230% of the theoretically necessary one for oxides reduction.

The reference electrode was Bi-Li(~ 60 at.%) alloy behind the porous MgO diaphragm. During the experiments its potential was controlled against the potential of lithium discharged on the Mo electrode. The anode was inside the MgO tube without a bottom. The anode gases evolved were removed from the cell by a constant argon flow. The experiments made in a glove box with a controlled atmosphere, H₂O < 1 ppm, O₂(initial) < 5 ppm.

Electrolytic reduction of the UO₂ tablets was performed at cathode potential of 20-50 mV more positive than the lithium potential.

Practically complete UO₂ reduction to metallic uranium at Li₂O concentration ~ 1wt.% was achieved. The amount of electricity passed was 160-200% of the theoretical one.

In the experiments with electrolytic reduction of UO₂ tablets containing 5-17wt.% rare-earth oxides it

was found that UO₂ is also completely reduced, according to preliminary data, whereas rare-earth oxides were not reduced at all. Only CeO₂ was reduced to Ce₂O₃. The cathode potential was equal to the lithium discharge potential only during the last third of the experiment.

To confirm the results several attempts were made to metallize tablets of individual and mixed rare-earth oxides that do not contain uranium dioxide. The initial Li₂O content was varied from 0 to 1.0 wt.%. Electrolysis was carried out at cathode potentials equal to the lithium discharge potential. The amount of electricity passed was from 160 to 200% of the theoretical one. The samples after the reduction were investigated with different independent analyses. The total content of oxygen was also determined. Rare earth oxides were confirmed not to be reduced in the experiments. CeO₂ was reduced to Ce₂O₃.

Conclusion

The experimental results obtained allow making encouraging conclusions on the possibility of the fission products separation from the target product for the the pyrochemical technology of spent nuclear fuel recycle. At electrolysis the alkali or alkali - earth metals are will in the LiCl melt. Rare-earth metals will stay in the U-Pu phase as an oxide form that creates favorable conditions for further separation.