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Pavel Soucek, Laurent Cassayre, Rikard Malmbeck, Eric Mendes, Jean-Paul Glatz. Electrorefining of U-Pu-Zr alloy on solid Al electrodes in LiCl-KCl eutectic melt initially containing Zr ions. European Nuclear Conference, Sep 2007, Bruxelles, Belgium. pp.0. hal-04106040

HAL Id: hal-04106040

<https://hal.science/hal-04106040>

Submitted on 25 May 2023

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ELECTROREFINING OF U-PU-ZR ALLOY ON SOLID AL ELECTRODES IN LiCl-KCl EUTECTIC MELT INITIALLY CONTAINING Zr IONS

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ABSTRACT

Electrorefining process in molten chloride salts using solid aluminium cathodes to recover actinides (An) is developed in ITU. Complete recovery of actinides in electrorefining of An-Zr alloy fuels can not be achieved without co-dissolution of Zr. It has been shown in previous experiments that the presence of Zr ions resulted in a significant deterioration in quality of the deposit. The present work has been focussed on a better understanding of the electrochemical behaviour of Zr ions in LiCl-KCl melt. In addition, electrorefining of U-Pu-Zr alloy in a melt containing dissolved Zr at the beginning of the process has been carried out. At first, Zr⁴⁺ content was chemically reduced by addition of U-Pu-Zr alloy forming a dispersion of Zr-containing particles in the melt. Electrorefining process in this modified melt yielded compact deposits consisting of UAl₃, UAl₄, PuAl₃ and PuAl₄ alloys.

1. Introduction

Partitioning and transmutation technologies are developed worldwide in order to minimize the long term radiotoxicity of the spent nuclear fuel produced during operation of the conventional nuclear reactors. Management of partitioning processes is also a key point in a development of future reactor systems, where application of an advanced nuclear fuel cycle is considered [1-3]. Pyrochemical techniques represent a promising alternative to aqueous reprocessing processes. Electrorefining and liquid – liquid metal reductive extraction are the most developed pyrochemical techniques designed for a group selective separation of actinides (An) from a mixture with lanthanides (Ln) in a molten salt media [4].

Electrorefining process in the molten chloride salts using solid aluminium cathodes is being developed in ITU. In this process, actinides are recovered from a metallic An-Zr alloy fuel in a form of An-Al alloys. In previous experiments, excellent grouped separation of actinides from lanthanides has been demonstrated [5, 6]. A very high capacity of aluminium to load actinides has been also experimentally proven [6, 7]. However, a complete recovery of actinides during electrorefining of An-Zr alloy fuels can not be achieved without co-dissolution of Zr [8]. It has been observed in previous experiments that the presence of Zr ions resulted in a deterioration in quality of the deposit [7].

The presented work was focussed on a better understanding of the electrochemical behaviour of Zr ions in LiCl-KCl melt and a determination of Zr distribution during the electrorefining process has been estimated. On basis of the obtained results, electrorefining of U-Pu-Zr alloy (71-19-10 wt. %) in a melt containing Zr ions at the beginning of the process has been demonstrated.

2. Experimental

All experiments, storage and handling of chemicals were carried out in a glovebox under purified Ar atmosphere (<5 ppm of water and oxygen). The detailed description of the technical background is described elsewhere [7]. Cyclic voltammetry measurements were carried out using a three-electrode setup and a PAR 273 potentiostat with EG&G M270 electrochemical software. The working electrode was prepared using a metallic wire (d = 1 mm) and inserted approximately 5 mm into the bath, while a Mo wire bent into the shape of a spiral served as the auxiliary electrode. The active part of the cathode surface area could be determined after each experiment by measuring the immersion depth of the wire.

The reference electrode used was an Ag/LiCl-KCl-AgCl (1 wt %) prepared in a Pyrex glass tube and all potentials stated in this work are related to the corresponding reference potential. During electrorefining experiments, working electrode was replaced by an aluminium plate and a tantalum basket containing oxidised material was inserted instead of the auxiliary electrode. Both anodic and cathodic potentials were monitored during the electrorefining experiments using a specially prepared combination of two multimeters with a laboratory power supply.

The initial bath was prepared by oxidation of Zr metal (ITU stock material) in 40.259 g of LiCl-KCl eutectic melt (Aldrich 99.99%) by reaction with BiCl₃. Reduced Bi metal was collected in a Bi pool at the bottom of an Al₂O₃ crucible. The initial concentration of Zr⁴⁺ ions in the melt was 0.55 wt.%. The chemical composition of the salt was monitored by ICP-MS analysis [9] of regularly taken salt samples dissolved in 1 M nitric acid.

3. Results and discussion

3.1 Cyclic voltammetry

Cyclic voltammetry (CV) measurements were performed on inert W and reactive Al working electrodes. A comparison of voltammograms measured on W electrode at temperatures 450 and 500°C is shown in Figure 1a. Two electrochemical systems were detected: (i) a pair of peaks II_c and II_a ($E_{p,c} = -1.20$ V at both temperatures, $E_{p,a} = -0.85$ V / -0.67 V at 450 / 500°C, respectively) and (ii) two low intensity waves I_c and I_a at more positive potentials. The waves I indicate a soluble-soluble transition most likely associated with Zr⁴⁺/Zr²⁺ reduction. The peaks II have a characteristic shape corresponding to a formation of an insoluble product, which is probably Zr metal, while an over-potential is required to facilitate the deposition of the metal. This feature became slightly more significant at 500°C, as the observed difference between potentials of the cathodic and anodic peaks was greater. The electrochemical reduction of Zr⁴⁺ in molten LiCl-KCl can therefore be interpreted as a two-step reaction mechanism on an inert working electrode, which is in a good agreement with the available published data [10].

A comparison of CVs measured on both electrodes at 450°C is shown in Figure 1b. On the reactive aluminium electrode (bold curve), one intensive cathodic peak was detected at $E_{p,c} = -1.26$ V, followed only by a negative current slope. As the Zr-Al phase diagram [11] contains several different alloys, this peak was expected to be associated with ZrAl₃ alloy formation. However, the reduction peaks starts at the same potential as the one measured on W electrode, which could indicate a metal deposition. A sharp current increase was detected on the anodic side, which disabled distinguishing between re-oxidation of reduced Zr species and dissolution of Al.

3.2 Drawdown of Zr dissolved in LiCl-KCl

In order to avoid complications associated with the presence of Zr dissolved in the bath used for the

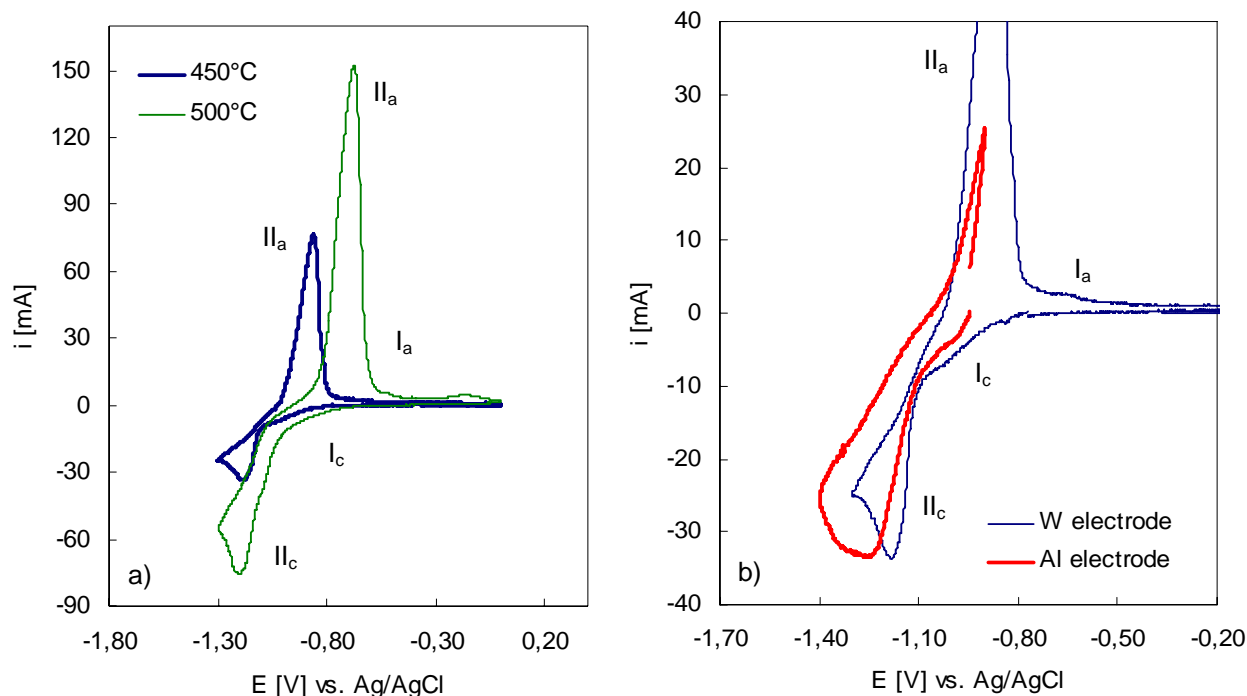


Fig. 1 a) Comparison of CV measured on W electrode at 450 and 500°C
b) Details of CV measured on W and Al electrodes at 450°C

The possibility of electrodeposition of Zr on solid Al electrode was investigated using electrorefining of Zr metal in the melt resulting from the chemical drawdown experiment, i.e. LiCl-KCl-AlCl₃ (0.18 wt.%). Two connected runs were carried out using Al plates with the active area app. 5 cm² and a charge of 4070 C was passed during the experiment. If the charge consumed for reduction of the aluminium present in the salt at the beginning of the experiment (0.075 g) is removed, then the remaining charge of 3265 C for Zr electrodeposition corresponds to 0.772 g of reduced Zr. The deposits from both runs were scraped from the electrodes, dissolved and analysed by ICP-MS. The total Zr and Al masses in both deposits were determined to be only 0.008 g and 0.011 g, respectively. However, Zr concentration in the salt remained less than 0.11 wt %, i.e. max. 0.045 g of Zr was dissolved (see Table1 below). Reduced Zr thus most likely fell down from the electrode and remained in the salt in a form of fine metallic particles.

Run	Total charge [C]	Zr dissolved analysed [wt. %]	Zr non-dissolved		Al dissolved analysed[wt. %]
			calculated [wt. %]	analysed[wt. %]	
E-1	0	0.00	0.13	< dl	0.18
	252	0.00	0.28	< dl	0.28
	932	0.11	0.56	< dl	0.15
	1981	0.03	1.25	1.60	0.03
	2860	0.01	1.78	< dl	0.05
E-2	4070	0.08	2.43	2.00	0.05

Table 1 Concentration profile during the Zr electrorefining experiments

During the Zr electrorefining, 6 salt samples was taken and dissolved in water instead of HNO₃. However, only 2 samples proved the existence of non dissolved particles in the melt. It can be explained by a high heterogeneity of its distribution in the melt resulting in significant difficulties in sampling. The calculation was made in order to estimate the expected mass of Zr particles in the salt $m(Zr_{particles})$ according to the following equation (2):

$$m(Zr_{particles}) = m(Zr_0) + \frac{M(Zr) \cdot Q}{z \cdot F} - m(Zr_{dissolved}), \quad (2)$$

where $m(Zr_0)$ is the initial expected mass of Zr particles generated during the previous experimental steps (estimated accordingly) and $m(Zr_{dissolved})$ is the mass of Zr analysed by ICP-MS in the salt at the corresponding phase of electrolysis. As shown in Table 1, both analysed values fit within a reasonable range with the expected values calculated according to equation (2).

3.3 Zr distribution during electrorefining process

The melt was left equilibrated after the electrorefining runs and the additional treatment was realized to determine the final Zr distribution in the system and to prepare a bath for the UPuZr electrorefining experiment. The following steps were performed:

1. Crucible was broken and the Bi pool with Zr particles absorbed during equilibrating was removed
2. Melt was re-melted in a new crucible and a fresh Bi pool was introduced
3. BiCl₃ was stepwise introduced to oxidise Zr particles remaining in the melt
4. U-Pu-Zr alloy was introduced to reduce Zr ions oxidised in step 3 by reaction with Pu and U
(more detailed description of the step 4 see in the following chapter 3.4 due to a thematic overlap)

The mass of the metallic Zr particles presented in the melt was evaluated both from the known mass of added BiCl₃ (0.339g Zr, step 3) and from the mass of oxidised U and Pu obtained from ICP-MS analyses of the salt samples (0.277 g Zr, step 4). The average value, 0.308 g, was taken for the mass balance evaluation. It can be seen that majority of the Zr particles fell down to the Bi pool during the equilibration of the salt, because 0.808 g of Zr particles was analysed to be presented in the melt at the

end of the electrorefining step (2.00 wt.%, see Table 1, the last row). Samples from the removed Bi pool were analysed by the ICP-MS to complete the mass balance and an average value of 0.806 g of Zr was detected. The summary of the Zr distribution is shown in Table 2. However the sum of input and output mass is in a reasonable agreement, the evaluated distribution is only approximate due to a high heterogeneity of the sampled material and uncertainties of the mass determination during the applied chemical processes.

Input		Output		Distribution ratio [%]
mass	where	mass	where	
221 mg	initial Zr mass in the salt	32 mg	Zr dissolved in the melt	2.8
962 mg	Zr oxidised during electrorefining	308 mg	Zr metallic particles in the melt	26.7
		806 mg	Zr in Bi pool	69.8
		8 mg	Zr deposit on the electrodes	0.7
1183 mg	sum input	1154 mg	sum output	100.0

Table 2 Mass balance of the Zr distribution

The process was followed by the CV measurements and the results correspond well to the expected composition of the bath. An Al system was detected after the step 2, only peaks associated to a Zr system were observed after the step 3 and finally, a clear spectrum with peaks corresponding only to U and Pu systems was measured after the step 4.

3.4 UPuZr electrorefining

Electrorefining of the UPuZr alloy (ITU stock material, 71-19-10 wt.%) was carried out after the above described treatment to evaluate the feasibility of the process starting in a melt initially containing Zr ions (melt after step 3, i. e. LiCl-KCl-ZrCl₄). The Zr content was calculated to be 0.75 wt.%, but the exact analysis of the bath is not available at this step. A piece of UPuZr alloy ($m_0 = 1.746$ g) was introduced to the melt in a tantalum basket to reduce the Zr content by reaction with Pu and U. After the reduction was completed, the basket was connected as an anode and used for the electrorefining experiment. The mass and composition of the starting anodic material was calculated to be $m_i = 0.835$ g and U:Pu:Zr = 68.5:10.5:21.0 according to the composition of the bath before start of the electrorefining, which was analysed as LiCl-KCl-UCl₃ (1.39 wt.%) - PuCl₃ (0.74 wt.%). An aluminium plate used as the cathode had the dimensions of 18×14×0.5 mm.

Galvanostatic electrolysis was carried out and the maximum applied current was controlled with respect to the cathodic potential, which was limited by a value of -1.3 V to follow the conditions enabling An/Ln separation. Currents in a range between 20 – 50 mA were applied and 845 C passed during the experiment. The average value of the cathodic potential was -1.15 V, which corresponded to the actinide-aluminium alloy formation, and it had a slowly decreasing tendency. Up to the passed charge of 600 C, anodic potential remained constant at -1.0 V, which corresponded to U and Pu oxidation only. Then it increased up to -0.8 V, which indicated the start of Zr co-oxidation due to the actinides content decrease.

After termination of the run, a solid, compact and metallic-shiny deposit was found on the electrode surface. The electrode containing the adhered salt was analysed by γ -spectroscopy to determine the total mass of deposited actinides and the mass ratio between uranium and plutonium. After that, the vacuum distillation of the electrode was performed at a temperature of 450°C, but only 0.096 g (22.6 % of the expected value) of the salt was removed. After the distillation, the deposit was scraped out and analysed by XRD. The evaluated results are summarized in Table 3. The aluminium/actinides mass ratio (Al:An) was calculated using data from γ -spectroscopy. XRD analysis proved the presence of UAl₃, UAl₄, PuAl₃ and PuAl₄ alloys, but it was not possible to quantify the mass ratio among the presented species. XRD patterns for U- and Pu-Al alloys are at the same positions and in addition, an unidentifiable specie was detected, which is most likely a Zr-Al alloy. However, the Zr content was not positively proved by XRD in this case.

Table 3 Mass balance of the UPuZr electrorefining

Passed charge	Deposit – mass of An [g]		Deposit – analysis [g]			Current efficiency [%]	Al:An ratio
	Theoretic	Analysed	U	Pu	U:Pu		
845 C	0.591	0.600 ± 0.024	0.583	0.017	34:1	101.5 ± 4.2	1:1.76

4. Conclusions

Studies of Zr electrochemical behaviour were carried out in eutectic LiCl-KCl-ZrCl₄ (0.55 wt.%) melt at 450 and 500°C on inert W and reactive Al electrodes. On inert electrode, a two step reduction mechanism was observed. Zr starts to be reduced at a potential of -1.1 V vs. Ag/LiCl-KCl-AgCl (1 wt.%) reference electrode, which is preceded by reduction of Zr⁴⁺ to Zr²⁺. On reactive Al electrode, one reduction step was observed most probably yielding Al-Zr alloys. However, the reduction starts at the same potential as detected on the inert electrode. Aluminium dissolution occurs practically at the same potential as Zr metal re-oxidation detected on W electrode. This potential overlap indicates that a molten chloride salt containing dissolved Zr and solid Al creates a very complicated system, enabling spontaneous chemical reactions between Al and Zr ions.

It has been shown that Zr ions presented in the melt can be completely chemically reduced both by solid Al and by actinides from a fresh UPuZr alloy. Formed product, most likely ZrAl₃ alloy, does not stick on the Al surface during chemical reduction and also during the electrorefining of Zr metal, almost no Zr content was detected in the deposit. Reduction of Zr ions yields a fine dispersion of Zr-containing solid particles in the bath.

The electrorefining of UPuZr alloy on solid Al electrode was successfully carried out in LiCl-KCl melt, which contained app. 0.75 wt. % of Zr⁴⁺ at the beginning of the process. Initially, Zr ions were completely reduced by the fresh fuel. Electrorefining process was carried out in the formed bath and compact metallic deposit consisting from UAl₃, UAl₄, PuAl₃ and PuAl₄ alloys was obtained on Al electrode with a very high current efficiency. Although Zr was co-oxidised during the last third of the process, it did not significantly influence the quality of the deposit.

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