

Study of thermodynamic properties of Np-Al alloys in molten LiCl-KCl eutectic

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Abstract – The reprocessing of nuclear fuels today aims primarily to recycle the major actinides (An: U, Pu). Major objectives for future reactor systems are an effective fuel utilization and waste minimization through recycling of all actinides. This is why reprocessing systems that include also the recovery of heavier actinides, the so-called minor actinides (MA: Np, Am, Cm) are being developed. Pyrochemical techniques are investigated worldwide in molten chlorides and fluorides salts within the framework of partitioning and transmutation concepts. Electroseparation techniques in the molten LiCl-KCl using solid aluminium cathodes are developed in ITU to group-selectively separate actinides (An) from the mixture with fission products. Actinides are electrochemically reduced during the process on the cathode, forming solid actinide-aluminium (An-Al) alloys.

This work is focused on chemical characterisation and determination of thermodynamic properties of An-Al alloys. The studied An are U, Np and Pu (first results). The alloys are formed on a solid Al electrode during An electrodeposition in molten LiCl-KCl Eutectic.

Two processes were used to prepare LiCl-KCl melts containing AnCl₃ (2 to 3,4wt% An): chemical oxidation of An metal, using BiCl₃, or carbo-chlorination of AnO₂. After additional chemical purification of the formed bath, it was proven, by electrochemical measurements, that the salt contains pure AnCl₃ without impurities. An-Al alloy properties were studied in the temperature range of 400 – 550 °C by electrochemical techniques. Cyclic voltammetry were carried out using both inert (W) and reactive (Al) working electrodes. For all the studied An, reduction of An³⁺ to An⁰ occurs at more positive potential on Al electrode than on W, due to an alloy formation. Open circuit potential measurements, after small depositions of An metal onto the Al electrode were used to determine thermodynamic properties of the An-Al alloys formed (ΔG , ΔH , ΔS) by an e.m.f. method. Galvanostatic electrolyses were carried out on an Al plates. Stable An-Al deposit were obtained and identified, by XRD analysis, as a mixture AnAl₃ and AnAl₄ alloys.

Keywords – An-Al alloys, molten LiCl-KCl salt, transient electrochemistry, thermodynamic properties

