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ABSTRACT

Zirconium is a strategic metal used in various activity sectors and particularly for nuclear applications because of its physicochemical properties: a low cross-section of neutron capture, excellent mechanical and corrosion resistance under extreme conditions (high temperature, aggressive media), . Thus 90% of the production of zirconium metal is used in the nuclear field, as zirconium alloy claddings, U–Zr fuel, and dissolvers used for spent fuel reprocessing. Zirconium metal is commonly obtained in the form of zirconium sponges produced by Kroll process that consists in a chemical reduction of zirconium chlorides into zirconium metal. On the other hand, spent zircaloy claddings represent a consequent amount of zirconium considered nowadays as a waste. There could be an economic interest to recycle the irradiated zircaloy claddings in order to valorize Zr for further reuse within nuclear applications.

One promising zircaloy recycling process consists in electrorefining in molten salt media. The use of chloride salts to operate such a process might be difficult mainly because of the several stable oxidation states of Zr coexisting in these media, whereas the use of fluoride systems should stabilize Zr oxidation state as Zr^{4+}.

A first step consists in investigating the feasibility of the electrochemical recovery of Zr metal in fluoride media. Thus, the present work focused on the electrochemical behavior study of zirconium in molten fluoride using transient electroanalytical techniques, e.g. cyclic voltammetry, square wave voltammetry, and chronopotentiometry. These different technics allowed to understand the zirconium reduction mechanism by determining the number of exchanged electrons and assessed the thermochemical properties of Zr in the salt (diffusion coefficient, etc.). Zirconium electrocrystallisation process was also investigated by chronoamperometry and cyclic voltammetry. This set of data is of first importance in order to estimate the further feasibility of the process.

KEYWORDS

Pyroprocessing, Recycling, Zirconium, molten fluorides