Solubility of Rare Earth Xxides in the NaCl-2CsCl Melt

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Pyrochemical separation process in molten salts media has been proposed as a promising option in the nuclear fuel cycle. Among the molten salts that can be considered as solvent for these processes, alkali molten chlorides are particularly attractive [1-3]. Hence obtaining basic chemistry data of actinides and lanthanides in molten halogenide salts is a major concern. The LiCl-KCl eutectic [2,3], the equimolar mixture CaCl₂-KCl [2] and the eutectic LiF-KF-NaF (FLINAK) [4] are the most frequently used for this kind of study, and some differences have been found in the stability and the electrochemical properties of rare earth ions in these media.

In this study, a NaCl-2CsCl (mole ratio) molten system was considered as the best candidate of the solvent. We present a study on the chemical and electrochemical properties of rare earth chloride (MCl₃, M = La, Ce, Nd) in the molten chloride mixture NaCl-2CsCl. The identification of the M-O compounds that are stable in the melt as well as the determination of their solubility, can be carried out by potentiometric titration using an oxide ion sensor.

A magnesia stabilized zirconia tube with an inner reference of Cr/Cr_2O_3 was used for the oxide sensor, and a Ag/AgCl electrode was used as the reference electrode. Solid NaOH was used as the source of O^{2^-} ions. Figure 1 shows the typical result of potentiometric titration. It is clear that MClO and M_2O_3 are two solid stable compounds in melt studied. The solubility parameters can be obtained through the fitting and calculating of experimental data.

The $E-pO^{2-}$ (potential-oxide ion) diagram for M-O compounds stable has been constructed by combining both theoretical and experimental data. The best chlorinating conditions could be extracted from the comparison of the $E-pO^{2-}$ diagram corresponding to the M-O compounds and that of some chlorinating mixture.



Figure 1: A representative result of potentiometric titration of rare earth chloride.

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