Behavior of Nickel in KF-2HF Molten Salt: An Electrochemical Study

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Fluorine gas has a wide range of industrial applications. In particular, the nuclear industry uses about 60% of worldwide production of fluorine to produce uranium hexafluoride [1]. UF_6 is a necessary intermediate product in uranium enrichment and production of fuel for nuclear reactors. Fluorine is produced by electrolysis of KF-2HF salt at about 85 °C. The molten salt is a corrosive environment due to its high concentrations of fluoride ions, and cell components submerged in it must be manufactured out of a corrosion-resistant material. Monel 400 is the most commonly used alloy for this purpose. It is a binary alloy of nickel (67%) and copper (33%). While very corrosion resistant in most environments, Monel is susceptible to corrosion in this molten salt.

Despite the industrial applications of KF-2HF, corrosion of metals in this medium has not been extensively studied. In most aqueous solutions, metals are oxidized into anions and form metal oxides and hydroxides. However, in an environment with a high fluoride content, like the KF-2HF molten salt, metal oxidation produces metal fluorides. These compounds have properties distinct from their oxide counterparts and require separate study.

The aim of this study is to explore the behavior of nickel metal in the molten KF-2HF salt at potentials close to the corrosion potential. Nickel is the majority component of Monel and it is responsible for Monel's corrosion resistance. The other component, copper, has already been studied in various fluoride salts, because it a suitable candidate for a reference electrode in these media. On the other hand, nickel, due to its good resistance to corrosion, is a suitable anode material for fluorination and electrolysis reactions in fluoride-rich media. To this end, the behavior of nickel at very high potentials has been studied. However, the behavior of nickel close to the corrosion potential has received little attention and thus it is the subject of this study.

An experimental cell and a heater have been constructed to allow for safe work with molten KF-2HF. The experimental cell used a Cu/CuF_2 reference electrode, a common approach in fluoride salt electrolytes. The electrode contaminated the molten salt with copper ions, which have been found to act as an oxidizing agent, shifting the corrosion potential of nickel towards more positive values and likely increasing the corrosion rate. At high concentrations, copper ions have been also found to electroplate on more base metals, nickel in particular. Other reduction reactions have also been investigated, with emphasis on hydrogen evolution reaction. The surface sensitive nature of this reaction has been used to characterize the electrode surface after it has been oxidized.

The experimental work consisted of cyclic-voltammetry and steady state experiments under both potential and current control. They have been used to investigate the active / passivation transition of nickel in the molten salt. Special emphasis has been placed on determining the rate limiting process. This work was further supported by SEM and XPS analytical techniques and visual observation of corroded electrodes. The experiments have confirmed the high solubility of oxidized nickel in the molten salt. Only a small fraction of oxidized nickel has been found to contribute to the growth of the passive film. The XPS technique indicated that the film was predominantly composed of $KNiF_3$. Based on analysis of all results, a model for behavior of nickel near its corrosion potential in the molten KF-2HF salt will be presented.

References:

[1] Groult, H., et al. (2007). Role of elemental fluorine in nuclear field. Journal of Fluorine Chemistry, 128, 285-295.