Thermodynamic Modeling of MCl - $CrCl_3$ (M = Na, K) Systems and Prediction of Chromium Dissolution in Chloride Molten Salts

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1. Introduction

Molten Salt Reactor (MSR) is one of the emerging field of interest in steelmaking and nuclear industry, and have recently triggered research on the thermodynamic properties for chloride salt systems. The nuclear fuel is mixed with base salt that acts as both fuel carrier and coolant in MSR operation, then fission products are produced. The structure material suggested for MSR is typically stainless steel contains Cr as a major alloy element. Chromium tends to be the most reactive component in molten salt environment producing $CrCl_2$ and $CrCl_3$. Despite the importance of chromium chlorides in MSR process, there is lack of phase diagram calculations for $CrCl_3$ system, especially. In addition, the U(IV)/U(III) ratio controls the redox potential of the molten salt, and chromium dissolution strongly depends on this redox state. [1] However, there are few corrosion experiment data in chloride MSRs in contrast to fluoride MSRs. The present study aims to perform thermodynamic modeling of NaCl-$CrCl_3$, KCl-$CrCl_3$ system and to predict the dissolution behavior of Cr in actual chloride molten salt environment with the ternary eutectic composition of NaCl-KCl-UCl_3 system. CALculation of PHAse Diagram (CALPHAD) method is widely accepted for phase diagram modeling and predicting thermodynamic properties of salt systems. All the thermodynamic calculations and predictions in this study were performed using the FactSage thermodynamic software. [2, 3]

2. Thermodynamic Optimization

2.1 Thermodynamic Models

For liquid salt solution, Modified Quasichemical Model (MQM) [4] which takes into account the short-range ordering of the second-nearest neighbors of cations in liquid chloride solution was used. In the NaCl-$CrCl_3$ salt solution, for example, the following pair exchange reaction can be considered: (same as KCl-$CrCl_3$ system)

$$(Na^+ - Na^+) + (Cr^{3+} - Cr^{3+}) = 2(Na^+ - Cr^{3+})$$

where (i-j) represents the pair of i and j cations which shares chlorine anion in between. $\Delta G_{Na-Cr(III)}$ is the pair exchange reaction energy which is main model parameter of MQM being expressed as function of temperature and pair fraction. Then, the Gibbs energy of solution can be expressed by:

$$G^{soln} = \left(n_{NaCl} g^{\circ}_{NaCl(l)} + n_{CrCl_3} g^{\circ}_{CrCl_3(l)}\right) - TS^{conf} + \frac{n_{Na-Cr(III)}}{2} \Delta g_{Na-Cr(III)}$$

where n_i and g_i° are each the number of mole and Gibbs energy of i species (i = NaCl, $CrCl_3$), respectively. S^{conf} refers the configuration entropy of mixing depends on $\Delta G_{Na-Cr(III)}$, which is optimized to reproduce all of the phase diagram and thermodynamic data of liquid solution.

2.2 NaCl-$CrCl_3$ system

The phase diagram experiments of the NaCl-$CrCl_3$ system were conducted by Korshunov and Raskin [5], Cook [6] and Vasil'kova et al. [7] mostly using thermal analysis. The calculated phase diagram is presented in Fig. 1., there is only one intermediate compound, Na_3CrCl_6 at 0.25 $CrCl_3$ mol fraction. There have been arguments regarding the presence of phase transition of Na_3CrCl_6 (s1 $\rightarrow$ s2) all of three papers, nevertheless, the possible solid phase transition of Na_3CrCl_6 is not considered in the present study because of the relatively quite large 150 °C difference among the data.

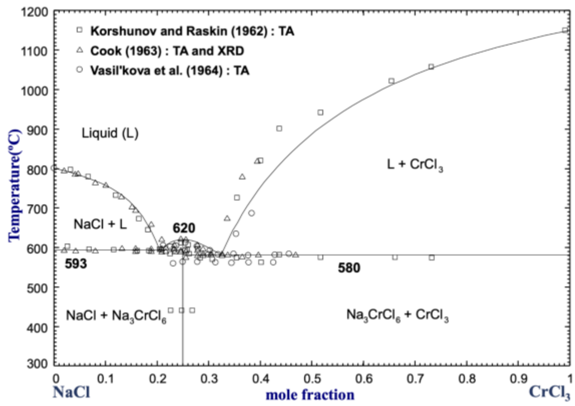

Fig. 1. Calculated phase diagram of the NaCl-$CrCl_3$ using the optimized parameters in this study.

2.3 KCl-$CrCl_3$ system

Fig. 2. shows the experimental data which were also performed by Korshunov and Raskin [5], Cook [6] and Vasil'kova et al. [7] and calculated phase diagram of the KCl-$CrCl_3$ system. There are two intermediate compounds K_3CrCl_6 and $K_3Cr_2Cl_9$, and overall liquidus lines have good agreement with literatures. However, it was difficult to reproduce the second eutectic temperature, so it should be re-examined in future.

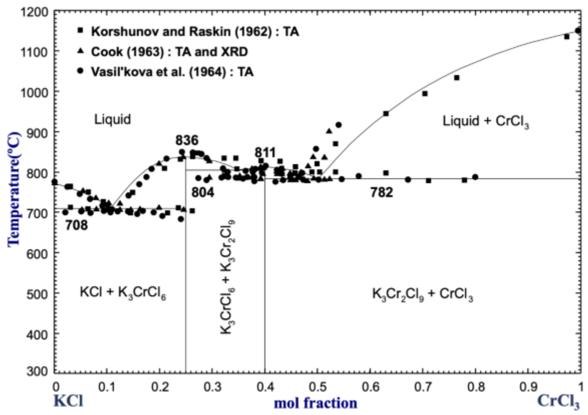

Fig. 2. Calculated phase diagram of the KCl-$CrCl_3$ using the optimized parameters in this study.

2.4 Dissolution of Chromium Chlorides

Cr can be oxidized to Cr^{2+} and Cr^{3+} in molten salt environment during chloride MSR operation. The possible reaction pathways are as follows:

$$Cr + UCl_4 = 2UCl_3 + CrCl_2$$
$$UCl_3 + CrCl_3 = UCl_4 + CrCl_2$$

FactSage calculations using Equilib function were performed to determine the amount of Cr dissolution based on the thermodynamic database for chloride salt systems. The result is shown in Fig. 3. for a composition of 0.433NaCl-0.217KCl-0.35UCl_3 at 500 °C. Focusing on chromium chlorides, the amount of both $CrCl_2$ and $CrCl_3$ dissolved in the molten salt increase with increasing the U(IV)/U(III) ratio. As the UCl_4 concentration increases during operation, more $CrCl_2$ is dissolved in the molten salt than $CrCl_3$.

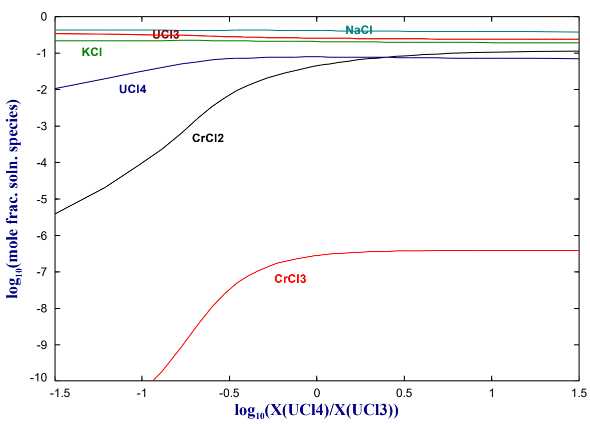

Fig. 3. Mole fraction for several chloride solutions including $CrCl_2$ and $CrCl_3$ referred to the ratio of Uranium redox state at 500 °C in this study.

3. Conclusions

Corrosion between the fuel salt and structure material is crucial issue in MSR operation, and corrosion research is essential for ensuring safety. Then, it is needed to know dissolution information between fused salt and structure materials. While Cr–U redox coupling is well understood in fluoride melts, it remains poorly characterized in chloride systems. Therefore, in the present study, thermodynamic modeling of chromium chlorides using FactSage was first performed, followed by calculations of chromium dissolution. This study provides a necessary foundation for understanding redox-driven corrosion behavior and offers insight for the future MSR applications.

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