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Thermodynamic modeling of LiF-NaF-KF-CrF_3 system

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ABSTRACT

The thermodynamic evaluation and optimizations of the KF-CrF_3 and NaF-CrF_3 systems were carried out within the framework of CALPHAD (CALculation of PHAse of Diagrams) approach. The liquid phase was described by the associated solution model, and the intermediate phase were treated as stoichiometric compound model. All the model parameters were optimized based on the experimental phase equilibria data from experimental measurements and theoretical predictions (First-principles calculation and empirical equation). A set of self-consistent and reliable thermodynamic parameters was obtained, which can well describe the phase equilibria and thermodynamic properties of the KF-CrF_3 and NaF-CrF_3 system. Furthermore, the database for the LiF-NaF-KF-CrF_3 quaternary system was preliminarily established using Muggianu extrapolation model. Meanwhile, the solubility of CrF_3 in FLiNaK at different temperatures was obtained. The calculated value is in good agreement with the reported measurements by ORNL, considering kinetic factor of K_3CrF_6 involved in FLiNaK.

1. Introduction

Molten salt reactor (MSR), where the fluorides of fissile and/or fertile (such as UF_4, PuF_3, ThF_4 and so on) are dissolve in a mixture of molten fluorides, is regarded as one of the six promising candidate reactors for the Generation IV Nuclear Energy System [1–3]. Unlike the conventional “solid” fuel system, MSR has incomparable advantages, such as high negative temperature coefficient of reactivity, inherent safety, very low operate pressure, refueling, processing and fission product removal online, potential unique capabilities and so on [4–6]. Due to the high temperature and very low pressure features of MSR, the reactor core tends to miniaturization and modularization. It can be widely used in nuclear electricity generation, thermochemical hydrogen production [7], oil processing and oil refineries [8], etc.

The mixture of ^7LiF and BeF_2 (mole fraction of LiF-BeF_2 : 0.66-0.34) is a good solvent for fissile and fertile material fluorides [9]. However, FLiBe is extremely poisonous (the maximum permissible concentration of beryllium in working condition is 10^{-3} mg/m^3) [10]. FLiNaK (mole fraction of LiF-NaF-KF: 0.465-0.115-0.42) which has the similar thermo-physical properties as FLiBe [11–13] shown in Table 1, is used as the model of FLiBe during the test stage. It can be learned that the element Cr of nickel-based alloys are corroded easily by fluoride salt compared with other metal elements at high temperature [14–16]. The complex ions of Cr can be formed which cannot be readily removed due to the intrinsic stability. CrF_3 is the major existing form of chromic fluoride in FLiNaK [11,17]. Although the solubility of CrF_3 in FLiNaK is very important for determining the equilibrium between FLiNaK and nickel-based alloys, there are few related experimental data. The CALPHAD method which is viable in fast obtaining phase equilibria in multicomponent system, is employed to study the solubility and multivariate distribution forms of Cr in FLiNaK melts.

In order to obtain the phase equilibrium and thermodynamic properties of LiF-NaF-KF-CrF_3, thermodynamic descriptions of each binary subsystem is essential. Thus, this work will give the thermodynamic modeling of the KF-CrF_3 and NaF-CrF_3 binary systems based upon the CALPHAD approach. Within the framework of CALPHAD method, the model parameters are usually optimized in terms of the required phase equilibria and thermochemical information. If lacks of the pertinent measurement, the data from theoretical prediction are sometimes considered for the parameter optimization, such as the first principles calculation is adopted for the prediction of the formation enthalpies of the intermediate compounds $KCrF_4$, $NaCrF_4$, $Na_5Cr_3F_{14}$ and Na_3CrF_6. Finally, the acquired thermodynamic parameters of these two binary system along with the other subsystems [18–20] are employed to extrapolate into the quaternary LiF-NaF-KF-CrF_3 system for predicting the solubility of CrF_3 and existent forms in FLiNaK melts.

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Table 1
Properties of molten FLiNaK salt and FLiBe at 700 °C [13].

Molten Salt	FLiNaK	FLiBe
Melting point (°C)	454	460
900 °C vapor pressure (mmHg)	0.7	1.2
Density (g/cm^3)	2.02	1.94
Volumetric heat capacity(cal/cm^3 °C)	0.91	1.12
Thermal conductivity(W/m K)	0.92	1.0

2. Data evaluation and prediction

Thermodynamic description of a certain system based on the CALPHAD approach requires the systematical analysis, evaluation and selection of the experimental data from the literature. When experimental measurements are scarce, theoretical predictions are sometimes needed prior to the thermodynamic optimization.

2.1. Review of literature information

There are many thermodynamic assessments related to the three systems (LiF-NaF, LiF-KF and NaF-KF) and a very exhaustive review has been processed by Wang [18] in 2013, hence it is not repeated in this work. The results reported by Wang for the LiF-NaF, LiF-KF and NaF-KF binary systems are mainly adopted in our work.

The experimental information concerning phase equilibria and thermochemical data of MF-CrF$_3$ (M = Li, Na and K) are very limited. Only Kozak et al measured their phase equilibria information in 1969 and 1975, respectively. Recently, thermodynamic assessment of LiF-CrF$_3$ and KF-CrF$_3$ have been done in our previous work [19,20] using the associated solution model in liquid phase. Thermodynamic parameters of LiF-CrF$_3$ from our previous work are adopted in the present work. Here, KF-CrF$_3$ was reevaluated using a different stoichiometric compounds in liquid phase, compared with our previous work [20]. The literature evaluation of LiF-CrF$_3$ and KF-CrF$_3$ has been summarized in refs. [19,20]. Until now, the NaF-CrF$_3$ system has not been described thermodynamically. The detailed literature evaluation of NaF-CrF$_3$ system is shown in the following part.

There are two groups of researchers who have measured the experimental phase equilibria of NaF-CrF$_3$ binary system. In 1969, Kozak et al. [21] firstly determined the phase relations of this system through differential thermal analysis. Again, this binary system was measured by Kozak and Samouel in 1975 [22] aiming at establishing the phase equilibria of the ternary NaF-ZnF$_2$-CrF$_3$ system. However, some disagreements existed in the two reported phase relations of this binary system, where Na$_5$Cr$_3$F$_{14}$ is congruent melting in Ref. [22] and incongruently melting in Ref. [21]. The later measured results are regarded to be more reliable, which are thus adopted for optimization. This system includes three intermediate compounds, namely Na$_5$Cr$_3$F$_{14}$, Na$_3$CrF$_6$ and NaCrF$_4$, which were identified by means of X-ray diffraction (XRD). The whole phase diagram is thus divided into various phase regions featured by one peritectic reaction ($CrF_3 + liquid \xleftrightarrow[T=1240.15K]{Per} NaCrF_4$) and three eutectic reactions ($liquid \xleftrightarrow[T=1133.53K]{Eut} NaCrF_4 + Na_5Cr_3F_{14}$, $liquid \xleftrightarrow[T=1143.71K]{Eut} Na_3CrF_6 + Na_5Cr_3F_{14}$ and $liquid \xleftrightarrow[T=1162.81K]{Eut} Na_3CrF_6 + NaF$).

2.2. First-principles methodologies

First-principles calculation, based on density functional theory (DFT) can reduce the uncertainties in model parameters of thermodynamic databases, can complement thermodynamic parameter optimization by providing some needed thermochemical data of individual phases with the dearth of relative experimental data [23].

Table 2
Single point energy of intermediate compounds in the MF-CrF$_3$ (M = Li, Na and K) system from First-principles calculation.

Compound	Space group	Single point energy	Resource
LiF	$Fm\bar{3}m$	− 9.7108 eV	[19]
CrF$_3$	$R\bar{3}cr$	–25.6115 eV	[20]
CrF$_3$	$R\bar{3}ch$	− 25.6019 eV	[20]
Li$_3$CrF$_6$	C12/C1	− 55.1735 eV	[19]
KF	$Fm\bar{3}m$	− 8.4342 eV	[20]
KF	$Pm\bar{3}m$	− 8.2271 eV	[20]
KCrF$_4$	$Pnma$	− 34.6875 eV	[20]
NaF	$Fm\bar{3}m$	− 8.7538 eV	This work
NaCrF$_4$	P21/C	− 34.7474 eV	This work
Na$_5$Cr$_3$F$_{14}$	P21/N	− 122.0770 eV	This work
Na$_3$CrF$_6$	P21/C	− 52.7634 eV	This work

Up to now, the thermochemical information is unavailable on the intermediate compounds of the MF-CrF$_3$ (M = Na and K) binary system. First-principles calculation is used to predict their formation enthalpies. The following Eq. (1) will show how to obtain the formation enthalpies of the compounds.

$$\Delta_f H_{(MF)_x(CrF_3)_y} = E_{tot}((MF)_x(CrF_3)_y) - xE_{tot}(MF) - yE_{tot}(CrF_3) \tag{1}$$

For the above equations, E_{tot} is the single point energy of MF, CrF_3 and $(MF)_x(CrF_3)_y$ at 0 K listed in Table 2. In fact, CrF$_3$ has two allotropic forms cited from the Inorganic Crystal Structure Database (ICSD). Here, the more stable form $R\bar{3}cr$for CrF$_3$ is selected to predict the formation enthalpy. The formation enthalpies of intermediate compounds (NaCrF$_4$, Na$_5$Cr$_3$F$_{14}$ and Na$_3$CrF$_6$) in the NaF-CrF$_3$ binary system are obtained by the following equations. However, only KCrF$_4$ of the KF-CrF$_3$ binary system could be calculated by First-principles methodologies (Due to the lack of relative crystal structure information and lattice parameters of K$_2$Cr$_5$F$_{17}$ and K$_2$CrF$_5$, First-principles calculation failed to be performed on K$_2$Cr$_5$F$_{17}$ and K$_2$CrF$_5$. What's more, although the crystal structure of K$_3$CrF$_6$ can be known, single point energy of K$_3$CrF$_6$ is not be determined, where the site of F atom is not kept fixed at their static lattice positions [24]).

$$\Delta_f H_{NaCrF_4} = E_{tot}(NaCrF_4) - E_{tot}(NaF) - E_{tot}(CrF_3) \tag{2}$$

$$\Delta_f H_{Na_5Cr_3F_{14}} = E_{tot}(Na_5Cr_3F_{14}) - 5E_{tot}(NaF) - 3E_{tot}(CrF_3) \tag{3}$$

$$\Delta_f H_{Na_3CrF_6} = E_{tot}(Na_3CrF_6) - 3E_{tot}(NaF) - E_{tot}(CrF_3) \tag{4}$$

The total energies of the compounds in the MF-CrF$_3$ system were calculated using Vienna ab ignition Simulation Package (VASP) [25] based on spin-polarized density function theory (DFT) and generalized gradient approximation (GGA) [26] employed. We used Projector Augmented Wave pseudopotentials (PAW) [27] with the constant energy cutoff of 450 eV for all the calculations to ensure the more accurate results. Extensive tests of k-point calculation indicated that all the energy differences were converged to within 1 meV/atom. Eventually, homologous k-point space mesh can be obtained by means of Monkhorst-Pack scheme with self-consistent iteration convergence threshold of 10^{-4} eV, and geometry optimization convergence criteria for all the atomic positions optimized around each atom force was less than 0.02 eV/Å. To validate the rationalization of calculated parameters, the comparisons between before and after structure optimization of cell parameters are shown in Table 3. As seen in Table 3, the relative deviations of all the unit cell lattice constants in NaF-CrF$_3$ before and after the lattice relaxation are less than 2.1%, and the deviation of the largest volumes are less than 3.1%. Although the first principles calculation is at 0 K, the calculated parameters are reasonable in terms of experimental errors introduced in this paper and the enthalpy of formation independent of temperature.