$RECl_3$–$CaCl_2$–$MgCl_2$ TERNARY PHASE DIAGRAMS (RE: La, Ce, Pr, Nd)①

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ABSTRACT

Nine sub-binary phase diagrams of the $RECl_3$–$CaCl_2$, $RECl_3$–$MgCl_2$ and $CaCl_2$–$MgCl_2$ systems, and thermodynamic data for these systems are critically assessed and optimized. Using Hillert model and taking $MgCl_2$ as an asymmetric component, the ternary phase diagrams of the $RECl_3$–$CaCl_2$–$MgCl_2$ systems are predicted. As well, the determination of asymmetric component in the asymmetric model is investigated.

Key words: molten salt phase diagram phase diagram calculation rare earth chloride thermodynamic analysis

1 INTRODUCTION

Rare earths (Hereafter RE) are widely used in science and advanced technology. RE phase diagrams are useful for preperation of RE metals and alloys by molten salt electrolysis. They are of great significance for better understanding the physico-chemical properties of RE. However, since RE elements are characteristic of the structure, RE chlorides present strong hydroscopicity and very easily form oxychlorides. Therefore it is rather difficult to accurately measure the multi-component RE chloride based phase diagrams.

As part of a systematic study of molten salt phase diagrams containing RE chloride, using the CALPHAD technique[1], the ternary phase diagrams of the $RECl_3$–$CaCl_2$– $MgCl_2$(RE: La, Ce, Pr, Nd) systems are thermodynamically predicted, and the determination of the asymmetric component in the asymmetric model is investigated in the present paper.

2 BINARY PHASES DIAGRAMS AND THERMODYNAMIC DATA

Assessment and optimization of sub-binary phase diagrams and thermodynamic data are the basis for predicting ternary phase diagrams. The crux of computational accuracy of ternary phase diagrams is self-consistent analysis. In the present work, all sub-binary phase diagrams are thermodynamically assessed with the methods reported in References [2, 3]. The thermodynamic properties of pure components, including melting points T, enthapies of fusion $\triangle H$ and $\triangle C_p$, are selected from Ref. [4]. Thereby, the molar Gibbs energy of fusion of the pure component is determined. All available thermodynamic properties are listed in Table 1.

2.1 $CaCl_2$–$MgCl_2$ *Systems*[5]

This binary phase diagram is a simple

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eutectic one. According to ${}^{B}G_{m}$ of the $CaCl_2$–$MgCl_2$ system measured by the EMF method and the experimental phase diagram, the binary thermodynamic properties in liquid phase are coupled as given in Table 2. The calculated results agree fairly well with the experimental results.

2.2 $RECL_3$–$CaCl_2$ *Systems*

$RECl_3$–$CaCl_2$ phase diagrams are also eutectic systems. With the aid of the experimental phase diagrams, the excess molar Gibbs energies are directly coupled as listed in Table 2. The agreement between calculated results and measured phase diagrams is good enough.

2.3 $RECl_3$–$MgCl_2$ *Systems*

Based on experimental phase diagrams and the thermodynamic data in Refs.[9–12], the related excess molar Gibbs energies are optimized and tabulated in Table 2.

3 CALCULATION OF TERNARY PHASE DIAGRAMS

When the computation model is applied to predict ternary phase diagrams with the assistance of sub–binary thermodynamic properties, at least, the following two factors should be considered. Firstly, the calculating accuracy of the model must be assured. Secondly, its analytical representation must be as simple as possiple, so that it is convenient for numerical computation. With respect to molten salt systems, because the interaction between species is very complicated, some of them present asymmetries. Therefore, an asymmetric model has to be used and the asymmetric component has to be determined. The thermodynamic criterion for determining asymmetric components is set forth in detail in Refs. [5, 16].

Table 1 The thermodynamic properties of pure chlorides

Comp.	T_{mp} / ℃	$\triangle H_{fus}$ / J · mol^{-1}	$\triangle G_f^\circ = A+BT+CT^2+DT\ln T+ET^{-1}$ / J · mol^{-1}				
			A	B	$C\times10^3$	D	$E\times10^{-5}$
$MgCl_2$	714	43 097	33 647.7	55.74	2.97	−13.39	−4.31
$CaCl_2$	772	28 424	2509	209.52	6.36	31.44	0
$LaCl_3$	855	54 395	36 091.44	155.01	10.37	28.33	0
$CeCl_3$	817	53 558	10 104.63	317.14	6.80	−47.70	−2.51
$PrCl_3$	786	50 629	26 862.02	281.61	23.85	−47.70	0
$NdCl_3$	759	48 537	10 469.03	433.05	30.55	−68.41	0

Table 2 The parameters in the analytical representation of excess molar thermodynamic properties in liquid phase

System	${}^{1}W_m^E = x_{R_pCl_q}(1-x_{R_pCl_q})(A+Bx_{R_pCl_q})$ / J · mol^{-1}			
	${}^{1}W_m^E$	$x_{R_pCl_q}$	A	B
$LaCl_3$–$CaCl_2$	G_m^E	$LaCl_3$	−9 557	12 779.6
$CeCl_3$–$CaCl_2$	G_m^E	$CeCl_3$	9 198	−29 668
$PrCl_3$–$CaCl_2$	G_m^E	$PrCl_3$	−790	−5 345
$NdCl_3$–$CaCl_2$	G_m^E	$NdCl_3$	−4 160	−2 478
$LaCl_3$–$MgCl_2$	G_m^E	$LaCl_3$	8 879	−11 476
$CeCl_3$–$MgCl_2$	G_m^E	$CeCl_3$	4 653	−1 882
$PrCl_3$–$MgCl_2$	G_m^E	$PrCl_3$	3 968	−2 964
$NdCl_3$–$MgCl_2$	G_m^E	$NdCl_3$	628	2 636
$CaCl_2$–$MgCl_2$	G_m^E	$CaCl_2$	5 273	−4 010

In this paper, according to thermodynamic criterion $MgCl_2$ is judged as an asymmetric component in the $RECl_3$–$CaCl_2$–$MgCl_2$ systems with the Hillert asymmetric model[17].

3.1 *Prediction of Ternary Thermodynamic Properties*

On the basis of the assessed and optimized thermodynamic properties of sub-binary systems, using the Hillert model and taking $MgCl_2$ as an asymmetric component, the ternary excess molar Gibbs energy ${}^{E}G^{l}_{m}$ in liquid phase is predicted.

$$
\begin{aligned}
{}^{E}G^{l}_{m} = {} & \frac{x_B}{1-x_B}\,{}^{E}G^{l}_{AB}(x_A, 1-x_A) \\
& + \frac{x_C}{1-x_A}\,{}^{B}G^{l}_{AC}(x_A, 1-x_A) \\
& + \frac{x_B x_C}{V_{BC} V_{CB}}\,{}^{E}G^{l}_{BC}(V_{BC}, V_{CB}) \qquad (1)
\end{aligned}
$$

where ${}^{E}G^{l}_{ij}$ is excess molar Gibbs energy of sub-binary i–j system; x_A, x_B and x_C stand for molar fractions of three components A, B and C, respectively. It is pointed out that

$$V_{BC} = (1+x_B-x_C)/2$$

$$V_{CB} = (1+x_C-x_B)/2$$

And in the $RECl_3$–$CaCl_2$–$MgCl_2$ systems, $A = CaCl_2$, $B = MgCl_2$ and $C = RECl_3$. By using a standard method [18], the partial molar Gibbs energy can be derived as

$$
{}^{E}G^{l}_{i} = {}^{E}G^{l}_{m} + (1-x_i)\,\frac{\partial\,{}^{E}G^{l}_{m}}{\partial x_i} - \sum_{i \neq j} \frac{\partial\,{}^{E}G^{l}_{m}}{\partial x_j} \qquad (2)
$$

where ${}^{E}G^{l}_{i}$ is the partial excess molar Gibbs energy of component i; $i = 1, 2, 3$ and $j = 1, 2, 3$. Thus, from the principles of phase equilibria, the primary crystalline surfaces, secondary crystalline lines and ternary eutectic point in the ternary system are in turn computed.

3.2 $LaCl_3$–$CaCl_2$–$MgCl_2$ *System*

Substituting the thermodynamic properties of the sub-binary systems listed in Table 2 into Eq. (1), it is found that

$$
\begin{aligned}
{}^{E}G^{l}_{m} = {} & 3\,268x_Ax_B + 3\,141x_Bx_C - 3\,167x_Cx_A \\
& + 2\,005x_A^2x_B - 2\,005x_Ax_B^2 \\
& + 5\,738x_B^2x_C - 5\,738x_Bx_C^2 + 6\,390x_C^2x_A \\
& - 6\,390x_Cx_A^2 + 7\,743x_Ax_Bx_C \qquad (3)
\end{aligned}
$$

The calculated result shows that it is a simple eutectic system. The composition and temperature of ternary eutectic point are 35.0 mol% $MgCl_2$, 19.2 mol% $LaCl_3$ and 582 ℃ (Fig.1.)

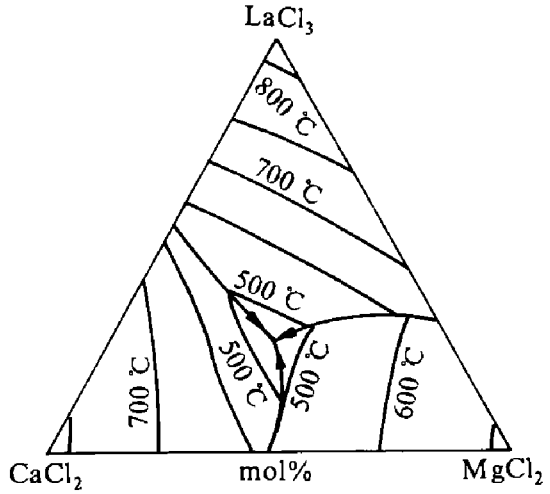

Fig.1 $LaCl_3$–$CaCl_2$–$MgCl_2$ system

3.3 $CeCl_3$–$CaCl_2$–$MgCl_2$ *System*

According to eq.(1) and relevent thermodynamic properties given in Table 2, the thermodynamic repersentation of this system is expressed as

$$
\begin{aligned}
{}^{E}G^{l}_{m} = {} & 3\,268x_Ax_B + 3\,712x_Bx_C - 5\,636x_Cx_A \\
& + 2\,005x_A^2x_B - 2\,005x_Ax_B^2 + 941x_B^2x_C \\
& - 941x_Bx_C^2 + 1483\,4x_Cx_A^2 \\
& - 14\,834x_C^2x_A + 2\,946x_Ax_Bx_C \qquad (4)
\end{aligned}
$$

It is a ternary eutectic system, the composition and temperature of eutectic point are 35.5 mol% $MgCl_2$, 26.5 mol% $CeCl_3$ and 577 ℃ (Fig.2.)

3.4 $PrCl_3$–$CaCl_2$–$MgCl_2$ *System*

Substituting the related thermodynamic properties of the sub-binary into Eq. (1), it is derived that

$$^{E}G^{l}_{m} = 3\,268x_Ax_B+3\,712x_Bx_C-5\,636x_Cx_A$$
$$+2\,005x_A^2x_B-2\,005x_Ax_B^2+941x_B^2x_C$$
$$-941x_Bx_C^2+14\,834x_Cx_A^2$$
$$-14\,834x_Ax_C^2+2\,946x_Ax_Bx_C \quad (5)$$

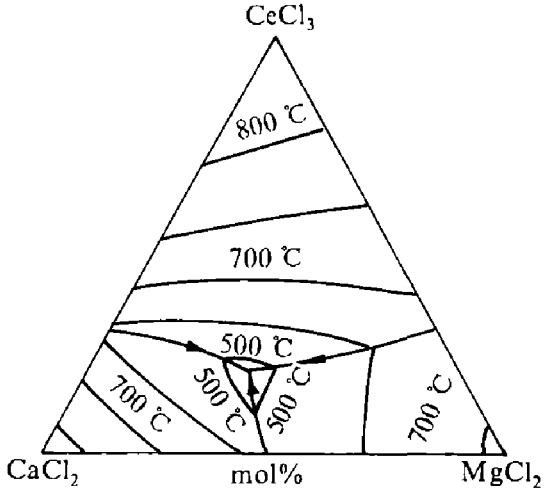

Fig. 2 $CeCl_3$–$CaCl_2$–$MgCl_2$ system

This ternary phase diagram is also an eutectic type. The composition and temperature of the eutectic point are 32.5 mol% $MgCl_2$, 26.0 mol% $PrCl_3$ and 560 ℃, respectively (Fig.3).

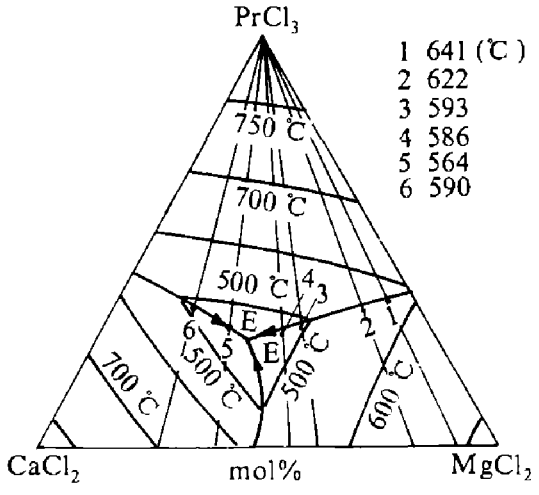

Fig.3 $PrCl_3$–$CaCl_2$–$MgCl_2$ system

3.5 $NdCl_3$–$CaCl_2$–$MgCl_2$ System

Substituting the assessed thermodynamic properties of the sub-binary systems into Eq. (1), the excess molar Gibbs energy in the liquid phase can be represented as

$$^{E}G^{l}_{m} = 3\,268x_Ax_B+1\,946x_Bx_C-5\,399x_Cx_A$$
$$+2\,005x_A^2x_B-2\,005x_Ax_B^2-1\,318x_B^2x_C$$
$$+1\,318x_Bx_C^2-1\,239x_C^2x_A$$
$$+1\,239x_Cx_A^2+687x_Ax_Bx_C \quad (6)$$

The composition and temperature of the eutectic point are 26.0 mol% $MgCl_2$, 30.0 mol% $NdCl_3$ and 548℃, respectively(Fig.4).

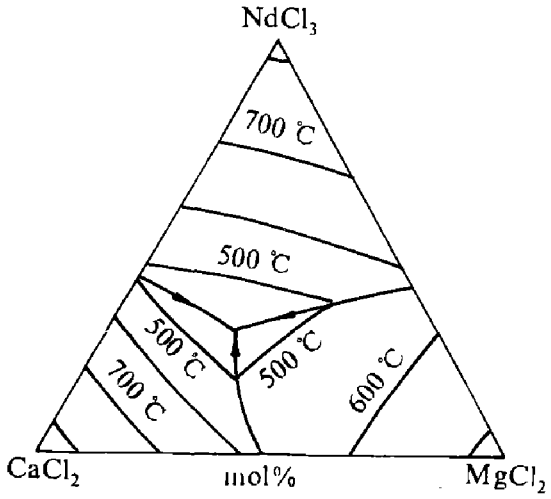

Fig.4 $NdCl_3$–$CaCl_2$–$MgCl_2$ system

4 CONCLUSION

In this paper, sub-binary phase diagrams and thermodynamic data were assessed and optimized while the $RECl_3$–$CaCl_2$–$MgCl_2$ phase diagrams are successfully calculated. This is of importance to practical application and theoretical study of molten salt systems.

The calculated results indicate that the $RECl_3$–$CaCl_2$–$MgCl_2$ (RE: La, Ce, Pr, Nd) phase diagrams are ternary eutectic ones. Due to the lanthanide contraction, with the increase of atomic number of rare earth elements the radii of RE^{3+} gradually decrease and polarization is reinforced. Thus, the degree of co-valence is reinforced. Therefore, the temperature of eutectic point in $RECl_3$–$CaCl_2$–$MgCl_2$ is decreased from La→Nd. In fact, the calculated results agree well with theoretical predictions.

From the view of the asymmetric distribution of the energy in molten salt systems, a thermodynamic criterion for determination of

the asymmetric component is suggested. In the ternary systems under study, the $MgCl_2$ is chosen as an asymmetric component due to its peculiar feature. In pure melting $MgCl_2$ there exists a bridge bond Mg–Cl–Mg[20], while pure $MgCl_2$ is mixed with $CaCl_2$ or $RECl_3$ and forms a binary molten solution, the original bridge bond is broken. The additional energy is absorbed and the whole energy of the mixed system rises. This kind of contribution ordinarily exceeds the interactions through coulomb forces and diffusions of particles. It is macroscopically embodied in the thermodynamic properties of the system. In fact, the deviations of $MgCl_2$–$CaCl_2$ and $MgCl_2$–$RECl_3$ from ideal solutions are positive, nevetherless, that of $RECl_3$–$CaCl_2$ is negaive in most compostion ranges. It is reasonable to choose $MgCl_2$ as an asymmetric component.

REFERENCES

1 CALPHAD, The International Research Journal for Calculation of Phase Diagrams, Editor: Kaufman L, Cambridge, Massachusetts, USA, 1997–1992.

2 Qiao, Z Y; Xing, X R; Zheng, C G; Duan, S Z. Jouranl of the Rare Earth Society (English Edition), 1990, 8(2): 92.

3 Qiao, Zhyu; Zhuang, Weidong; Su, Mianzeng. Science in China(Series A), 1992, 35(8): 957.

4 Barin, I; Knacke, O; Kubaschewski, O. Thermochemical Properties of Inorganic Substance (and Supplement), N. Y Springer–Verlag: 1973, 1977.

5 Qiao, Z Y; Xing, X R; Zheng, C G; Duan, S. In: Proceedings of the Third China –Japan Bilateral Conference on Molten Salt Chemistry and Technology, Beijing, Sept. 20–25, 1990, 110.

6 Морозов, И С. Ж. Н. Х.. 1957, 2(7): 1639–1642.

7 Корщунов, Б Г;. Морозов, И С. Высщих Учебных Завсдени СССР Фимичсск Технология, 1960, 3, 402–404.

8 Трифонов. И И. Известия Высщх Учебных Заведени, Цветная Метацргия, 1983, 2, 61.

9 Vogal, G ; Schneider A. Inorg Nucl Chem Letters, 1972, 8: 513.

10 Суицнъчжу, Ц С. Морозов. Ц С. Ж. Н.Ф, 1956, 3; 1914, 8.

11 Щецова; З Н. Известия Высщих Учебных Завсдени, Цветна Метацургия, 1960, 3: 109–111.

12 Austin, S R; Matsushima T; Schneider, A. Zeitschrift fur Allgemeine Chemie Band, 1970, 373: 133–147.

13 Lin, P–L; Pelton, A D; Bale, C. W.. J Am Ceram Soc, 1978, 62(7–8): 415.

14 Qiao, Z Y; Sangster, J; Pelton, A D. CALPHAD, 1987, 11(4): 277.

15 Qiao, Z Y; Mo, W J; Wu, S M; Zhu, Y K; Hillert M. CALPHAD, 1985, 9(2): 143.

16 Xing, X R. Qiao, Z Y; Zheng, C G, Duan, S Z. J of Univ of Science and Technology Beijing, 1992: 14(6).

17 Hillert, M. CALPHAD, 1980, 4(4): 1.

18 Hillert M. Diffusion and Thermodynamics of Alloys. Beijing: Metallurgical Industrial Press, 1984.

19 Zheng, Chaogui; Liu, Hongping; Qiao, Zhiyu; Ye, Yupu. Acta Metallurgica Sinica, 1990, 26(1): B68.

20 Papatheodorou, G N *et al.* J Chem Phys, 1967, 47(6): 2014.