Thermodynamics of Lanthanide Elements in the Presence of Sulfur in Iron–Base Metallic Solutions*

DU TING†, WANG LONGMEI and WU YIEMIN

Central Iron and Steel Research Institute, Beijing, China

Equilibria of Fe–Ln–S and Fe–C–Ln–S melts (where Ln = lanthanide) have been investigated in a molybdenum wire resistance furnace under a high-purity argon atmosphere at 1300, 1400, 1500 and 1600 °C. Oxygen activities were measured with ZrO_2 (MgO) sensors; sulfur activities in Fe–C–Y–S melts were measured with $CaS(TiS_2)$ sensors prepared in our institute [1]. The Ln elements were analysed by a spectrochemical method. Sulfur contents were determined by infrared spectral analysis. The equilibrium phases for each Ln element were extracted from the samples by electrolysis in a non-aqueous medium at low temperature, thus allowing the determination of the dissolved Ln elements and sulfur. The equilibrium products were identified by metallographic examination, scanning electron miscroscopy and X-ray measurements.

Results and Discussion

The Equilibrium Products for the Systems Under Investigation

The equilibrium products of the Fe–Ln–S and Fe–C–Ln–S melts depend upon the relative activities of sulfur and Ln elements. LnS are formed under our experimental concentrations of sulfur and Ln elements.

Determination of the Equilibrium Constants for the Reactions $LnS_{(s)}$ = [Ln] + [S] and the Standard Free Energies for LnS Formed in Iron–Base Solutions in the Temperature Range 1300–1600 °C

For the Fe–Ln–S systems:

$$LnS_{(s)} = [Ln] + [S] \tag{1}$$

$$K_{LnS} = a_{Ln}a_s = K'_{YS}f_Y f_S; \log K'_{LnS} =$$

$$\log K_{LnS} - e_S^{Ln}\left\{[\%Ln] + \frac{M_{Ln}}{M_{Fe}}[\%S]\right\} \tag{2}$$

where $K'_{LnS} = [\%Ln][\%S]$ (% = wt.%).

On the basis of reactions (1) we used our experimental data to derive the equations for the equilibrium constants $\log K = -(A/T)+B$ of the Ln elements in iron--base solutions, as well as for the standard free energies, $\Delta G° = -C + DT$, for the sulfides formed. The results for these equations, which are valid in the temperature range 1300–1600 °C, are shown in Table I and in Figs. 1 and 2.

TABLE I. Equations for the Equilibrium Constants of Reactions $LnS_{(s)}$ = [Ln] + [S], Log $K = -(A/T) + B$ and Equations for the Standard Free Energies $\Delta G° = -C + DT$ (in J mol^{-1}, T in kelvin) for LnS Formed in Iron–Base Solutions, as a Function of Temperatures in the Range 1300–1600 °C

	$\log K = -(A/T) + B$		$\Delta G° = -C + DT$	
	$10^{-4} A$	B	$10^{-5} C$	D
LaS	3.333	11.86	6.3793	227.0
CeS	3.767	15.36	7.2113	294.0
NdS	4.744	20.99	9.0810	401.8
SmS	2.758	9.01	5.2798	172.5
YS	2.266	7.90	4.3381	151.2

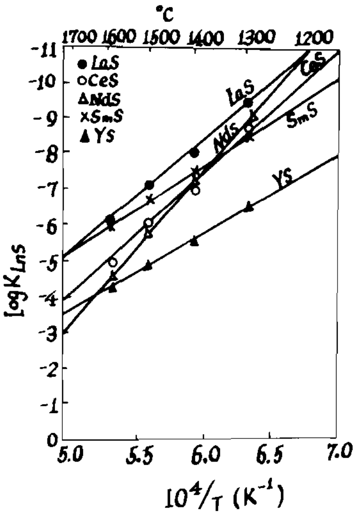

Fig. 1. Comparison of the equilibrium constants for the reactions $LnS_{(s)}$ = Ln + S as a function of temperatures in iron–base solutions.

Determination of the Interaction Coefficients Between Sulfur and Ln Elements

The interaction coefficients between sulfur and Ln elements may be obtained from formula (3):

$$e_S^{Ln} = \frac{\log K_{LnS} - \log K'_{LnS}}{[\%Ln] + \dfrac{M_{LnS}}{M_{Fe}}[\%S]} \tag{3}$$

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†Author to whom correspondence should be addressed.

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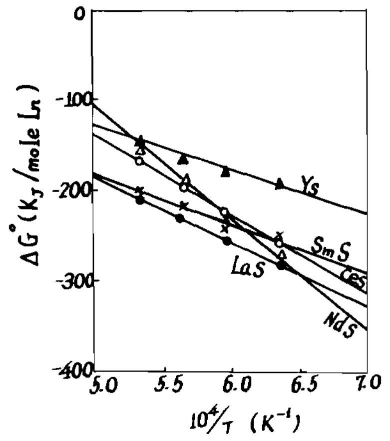

Fig. 2. Comparison of the standard free energies of formation of LnS as a function of temperatures in iron–base solutions.

Using our experimental data, the relationships of e_S^{Ln} in iron–base solutions with temperature in the range 1300–1600 °C are shown in Table II and are plotted in Fig. 3.

The thermodynamics of lanthanide elements in the presence of sulfur in iron–base metallic solutions are fundamental for the development and application of Ln elements in iron and steel. Most thermodynamic data are unknown [2]. Some relative research work in iron–base solutions has been published in recent papers by the authors [3–6]. This paper is a continuation of this work, with the same purpose.

TABLE II. The Temperature Dependence of e_S^{Ln} in Iron–Base Solutions in the Temperature Range 1300–1600 °C

Ln	$e_S^{Ln} = -(E/T) + F$	
	$10^{-4} E$	F
La	2.462	10.35
Ce	2.333	11.60
Nd	2.126	10.59
Sm	2.682	11.93
Y	2.749	14.12

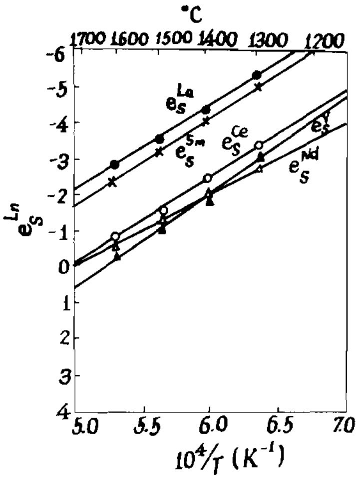

Fig. 3. Comparison of the interaction coefficients e_S^{Ln} as a function of temperatures in iron–base solutions.

Figures 1, 2 and 3 show that the data are regular. Most data are new. These are of theoretical and practical interest for application of lanthanide elements in iron–base metallic solutions.

References

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