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A Study of Thermodynamics and Phase Equilibria in order to Predict the Behavior of Yttrium in Iron and Steel*

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Thermodynamics and phase equilibria for Fe–Y–O, Fe–Y–S and Fe–Y–O–S systems have been determined in a molybdenum wire resistance furnace under a high-purity argon atmosphere at 1575, 1600 and 1625 °C; Fe–C–Y and Fe–C–Y–S melts were investigated at 1300, 1400, 1500 and 1600 °C; Fe–N–Y melts were determined under pure nitrogen gas at 1570, 1600 and 1650 °C. Oxygen activities were measured with $ZrO_2(MgO)$ sensors [1]. Sulfur activities in Fe–C–Y–S melts were measured with $CaS(TiS_2)$ sensors by the authors. Carbon and sulfur contents were determined by infrared spectral analysis. The yttrium contents were analysed by spectrochemical methods. Nitrogen contents were determined by the fused impulsive thermal conduction method. The equilibrium products of yttrium were extracted from the samples by electrolysis in a non-aqueous medium at low temperature [2]; in this way the dissolved yttrium, sulfur, nitrogen and carbon were determined. The compositions of the equilibrium products were identified by X-ray diffraction.

Results and Discussion

The equilibrium products in the Fe–Y–O, Fe–Y–O–S, Fe–Y–S, Fe–N–Y, Fe–C–Y and Fe–C–Y–S metallic solutions were identified as Y_2O_3, Y_2O_2S, YS, YN, YC_2 and YS, respectively.

The deoxidation, deoxysulfurization, desulfurization, denitrogenation and decarbonization constants and the standard free energies of formation of Y_2O_3, Y_2O_2S, YS, YN and YC_2 as the equilibrium phases in iron–base solutions can be derived from the following equilibrium equations:

$$Y_2O_{3(s)} = 2[Y] + 3[O]$$

$$K'_{Y_2O_3} = a_O^3[\%Y]^2$$

$$K_{Y_2O_3} = K'_{Y_2O_3} f_Y^2$$

$$\log K'_{Y_2O_3} = \log K_{Y_2O_3} - 2e_Y^O a_O \tag{1}$$

$$Y_2O_2S_{(s)} = 2[Y] + 2[O] + [S]$$

$$\log K'_{Y_2O_2S} = \log K_{Y_2O_2S} - e_S^Y([\%Y] + 5.56[\%S]) \tag{2}$$

$$YS_{(s)} = [Y] + [S]$$

$$\log K'_{YS} = \log K_{YS} - e_S^Y([\%Y] + 2.78[\%S]) \tag{3}$$

$$YN_{(s)} = [Y] + [N]$$

$$\log K'_{YN} = \log K_{YN} - e_N^Y([\%Y] + 6.36[\%N]) \tag{4}$$

$$YC_{2(s)} = [Y] + 2[C]$$

$$\log K_{YC_2} = \log K'_{YC_2} + e_Y^C[\%C] + 2e_C^Y[\%Y] + 2e_C^C[\%C] + e_Y^Y[\%Y] \tag{5}$$

The temperature dependences of log *K* and $\Delta G°$ are listed in Table I.

Interaction coefficients between solute elements in liquid iron are as follows:

$$e_O^Y = -(5.662 \times 10^5/T) + 286,$$

$$e_S^Y = -(1.760 \times 10^5/T) + 82.56,$$

TABLE I. Themodynamic Parameters for the Deoxidation, Desulfurization, Deoxysulfurization, Denitrogenation and Decarbonization of Yttrium in Iron Base Solutions, at Iron and Steel-making Temperatures[a]

Reaction	$\Delta G° = C - DT$		$\log K = -(A/T) + B$		K
	$10^{-6}\ C$	$10^{-3}\ D$	$10^{-4}\ A$	B	(1600 °C)
$Y_2O_{3(s)} = 2[Y] + 3[O]$	1.793	0.658	9.365	34.40	2.5×10^{-16}
$Y_2O_2S_{(s)} = 2[Y] + 2[O] + [S]$	1.521	0.536	7.949	28.03	4.1×10^{-15}
$Y_2S_{3(s)} = 2[Y] + 3[S]$	1.171	0.441	6.119	23.10	2.4×10^{-10}
$YS_{(s)} = [Y] + [S]$	0.321	0.091	1.677	4.74	6.1×10^{-5}
$YN_{(s)} = [Y] + [S]$	0.391	0.150	2.044	7.86	8.9×10^{-4}
$YC_{2(s)} = [Y] + 2[C]$	1.704	0.124	0.809	6.49	5.2×10

[a] Energies in J mol^{-1}, *T* in K. The values of log $K_{Y_2S_3}$ and $\Delta G°_{Y_2S_3}$ have been calculated from thermodynamic data in refs. 3–5.

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$e_N^Y = -6640/T + 2.986$, $e_C^Y = -151/T + 0.050$

$e_N^O = -3497/T + 1.650$, $e_N^S = 264/T - 0.128$

The standard free energy of solution of 1 wt.% [Y] (in J mol^{-1}) in liquid iron is derived as $\Delta G^\circ_{(Y(1)=[Y])} = -3.397 \times 10^4 - 31.09T$.

For the activity coefficients and self-interaction coefficients of yttrium in liquid iron, the following equations were derived from $\Delta G^\circ_{(Y(1)=[Y]} = RT$ ln-(γ_Y^O $0.5585/M_Y$) and $\epsilon_Y^Y = -2$ ln γ_Y^O, log $\gamma_Y^O = 1776/T + 0.578$, $\epsilon_Y^Y = 8178/T - 2.693$, $e_Y^Y = 22/T - 0.006$.

The equilibrium phase diagram of log a_Y – log a_S for the Fe–Y–S–O system at 1600 °C is plotted in Fig. 1. This diagram provides the basis for predicting the sequence and the type of equilibrium phase formed.

The equilibrium phase diagram of log a_Y – log a_C for the Fe–N–Y system is plotted in Fig. 2. This diagram provides a basis for predicting the formation of YN and the relative activities or solubilities of nitrogen and yttrium at different temperatures in liquid iron and steel.

The equilibrium phase diagram of log a_Y – log a_C for the Fe–C–Y system is shown in Fig. 3, from which we can predict the formation of YC_2 in iron-base solutions, at iron and steel-making temperatures.

Comparison of the standard free energies of formation of some yttrium compounds as a function of temperature in steel-making is shown in Fig. 4. This Figure provides a basis for predicting the behavior of the yttrium interacted with oxygen, sulfur, nitrogen and carbon in iron–base solutions, at iron and steel-making temperatures.

The interaction coefficients between yttrium and oxygen, and yttrium and sulfur in liquid iron at 1600 °C only have been published in ref. 6. Because of the use of ZrO_2 (MgO) sensors for the determina-

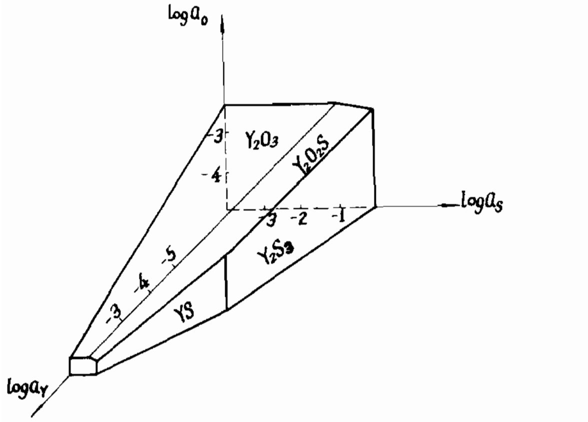

Fig. 1. The phase equilibria for the Fe–Y–O–S system at 1600 °C.

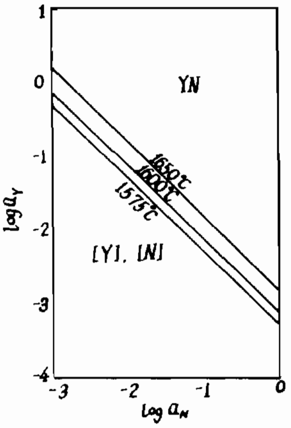

Fig. 2. The phase equilibria for the Fe–N–Y system at 1575, 1600 and 1650 °C.

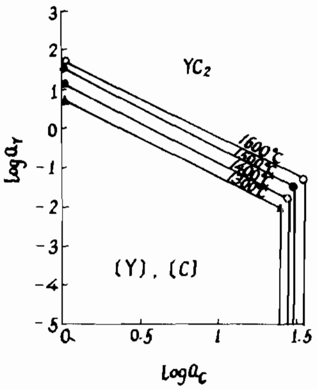

Fig. 3. The phase equilibria for the Fe–C–Y system at 1300, 1400, 1500 and 1600 °C.

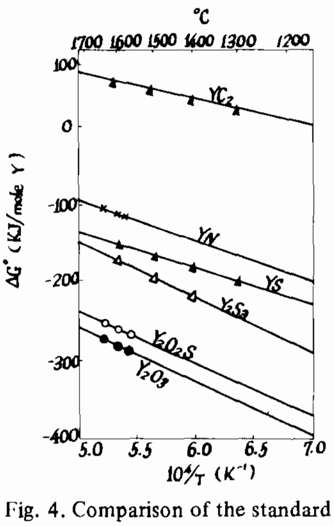

Fig. 4. Comparison of the standard free energies of formation of some yttrium compounds in iron–base solutions at iron and steel-making temperatures.

tion of the oxygen activities and the electrolysis of the equilibrium products in a non-aqueous medium at low temperature for the determination of the dissolved yttrium and sulfur in our work, the data in the present paper are more reliable and, moreover, our data also provide the temperature dependence of these interaction coefficients.

The thermodynamic properties of yttrium in liquid iron and the equilibria diagrams for the Fe–Y–S–O, Fe–N–Y, Fe–C–Y systems have not been published before. The inclusion precipitation diagram, and the phase equilibria for the Fe–Ce–O–S system at 1627 °C, have been published in refs. 7 and 8, respectively. Our equilibrium diagram of the Fe–Y–S–O system is somewhat analogous to that of the Fe–Ce–O–S system.

Yttrium is of growing importance in iron–base alloys. The thermodynamic properties of yttrium and some of its compounds, and the phase equilibria determined in this work, are useful to predict the behavior of yttrium in iron–base solutions.

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