

Phase Equilibria in the System Fe-Fe₂O₃-Lu₂O₃ at 1200°C

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Phase equilibria in the system Fe-Fe₂O₃-Lu₂O₃ have been established at 1200°C. The following phases were stable: lutetium sesquioxide, hematite, magnetite, wustite, metallic iron, lutetium-iron-perovskite, lutetium-iron-garnet, LuFe₂O₄, and Lu₂Fe₃O₇. The standard free energy of formation from the metallic iron, Lu₂O₃, and oxygen at 1200°C of LuFe₂O₄, Lu₂Fe₃O₇, LuFeO₃, and Lu₃Fe₅O₁₂ has been determined to be -100.3 ± 0.2 , -158.2 ± 0.2 , -57.5 ± 0.3 , and -279.1 ± 0.9 kcal/mole, respectively.

Introduction

In previous studies, Kimizuka and Katsura (1), Sugihara et al. (2), and Kimizuka and Katsura (3, 4) have established the phase equilibria in the Fe-Fe₂O₃-Ln₂O₃ systems (Ln = La, Y, Eu, and Yb) at 1200°C. They have also determined the standard free energy of formation from metallic iron, lanthanoid sesquioxide, and oxygen of ternary double oxides found in these systems. Kimizuka and Katsura (4) have proposed that the Fe-Fe₂O₃-Ln₂O₃ systems (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) could be classified into four groups with respect to the assemblage of ternary compounds which are in stable coexistence at 1200°C. According to them, the Fe-Fe₂O₃-Lu₂O₃ system may belong to the D-type having four stable ternary compounds, that is, LuFeO₃, Lu₃Fe₅O₁₂, LuFe₂O₄, and Lu₂Fe₃O₇.

The objectives of the present study are, firstly, to test the previous assumption about the classification of the Fe-Fe₂O₃-Lu₂O₃ system at 1200°C after establishing the phase equilibria in this system, and secondly, to determine the standard free energy of formation from the metallic iron, Lu₂O₃, and oxygen.

Experimental

Guaranteed reagent grade Fe₂O₃ and Lu₂O₃ (99.99%) powders were employed for all starting materials. Desired ratios of Lu₂O₃/Fe₂O₃ were obtained by mixing thoroughly in an agate mortar under ethyl alcohol. Mixtures thus obtained were treated by the same procedures as those described previously (4).

Apparatus and procedures for controlling the oxygen partial pressure, keeping constant temperature, method of thermogravimetry, the criterion for equilibrium establishment, the method of identification of solid phases after quenching, and the method of wet chemical analysis are the same as those described in previous papers (1-4). Thus, the range of experimental errors in determining the standard free energy is in the same order of magnitude as those of previous results.

Results and Discussion

1. Phase Equilibria

Figure 1 shows the phase equilibria in the Fe-Fe₂O₃-Lu₂O₃ system at 1200°C. The following phases were stable under the experimental conditions used: lutetium sesquioxide

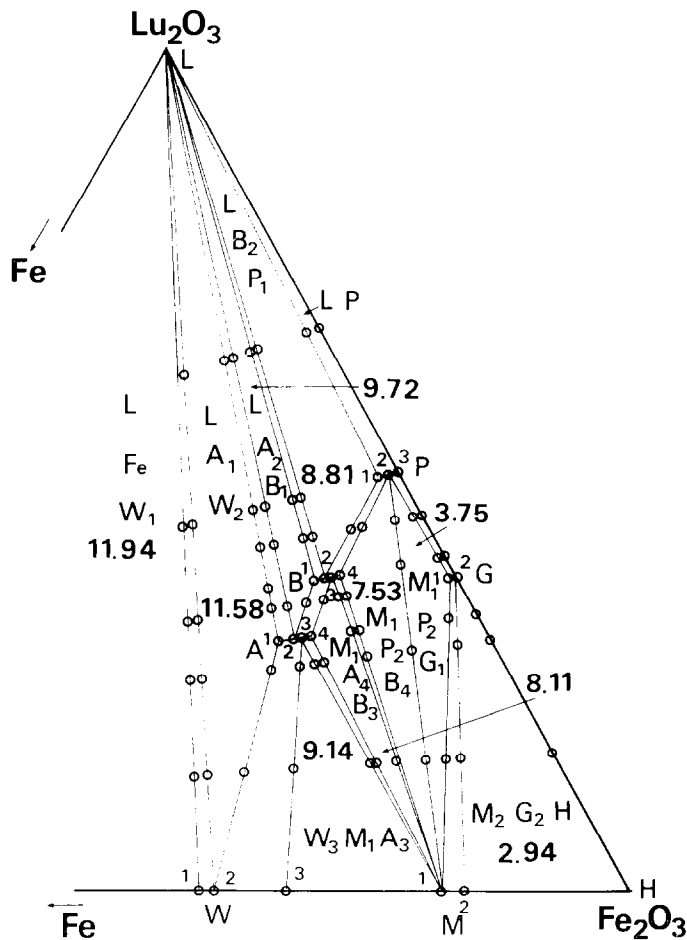


FIG. 1. The phase diagram of the Fe-Fe₂O₃-Lu₂O₃ system at 1200°C. Values in area of three solid phase equilibria mean $-\log P_{O_2}$ (atm). The composition corresponding to each letter is given in Table III. Open circles show the experimental results. A boundary line M₁-P₂ by which the area G₁ + M₁ + P₂ is separated from the area B₄ + M₁ + P₂ is, strictly drawn, composed of two boundary lines: One is M₁-P₂, and the other M₁-P₂'. The composition of P₂' is very slightly shifted to the direction of stoichiometric perovskite P. The small area for M₁ + (solid solution from P₂ to P₂') was recognized experimentally.

(Lu₂O₃), hematite (Fe₂O₃), magnetite (Fe₃O₄), lutetium-iron-perovskite (LuFeO₃), lutetium-iron-garnet (Lu₃Fe₅O₁₂), LuFe₂O₄, Lu₂Fe₃O₇, wustite (FeO), and γ -Fe.

Lutetium sesquioxide was stable at oxygen partial pressures from 1 to 10⁻¹⁶ atm and showed no significant nonstoichiometry in its composition. The volatility of Lu₂O₃ at 1200°C over the experimental range of oxygen partial pressures was almost the same order of magnitude as that of Yb₂O₃ studied by Kimizuka and Katsura (4) and was deter-

mined to be approximately 2 mg/3 g of Lu₂O₃ during heating for 3 days.

The deviation from the stoichiometric composition of lutetium-iron-perovskite ranged up to LuFeO_{2.958} on the basis of the weight change. The lattice constants of the LuFeO₃ phase are given in Table I on the basis of an orthorhombic crystal system. As seen in Table I, no significant effects on the lattice constants due to the nonstoichiometry were observed. This is the same trend observed in EuFeO₃ (2), YFeO₃ (3), and YbFeO₃ (4).

TABLE I
 LATTICE CONSTANTS OF LuFeO₃, Lu₃Fe₅O₁₂, Lu₂Fe₃O₇ AND LuFe₂O₄

Composition	<i>a</i>	<i>b</i>	<i>c</i> (Å)	<i>V</i> (Å ³)
LuFeO₃^a				
LuFeO _{3.000}	5.2123 ± 0.0003	5.5531 ± 0.0005	7.5622 ± 0.0006	218.88 ± 0.03
LuFeP _{2.960}	5.2130 ± 0.0004	5.5555 ± 0.0006	7.5609 ± 0.0007	218.97 ± 0.03
Lu₃Fe₅O₁₂^b				
Lu ₃ Fe ₅ O _{12.00}	12.2783 ± 0.0003			1851.1 ± 0.1
Lu ₃ Fe ₅ O _{11.96}	12.2786 ± 0.0002			1851.2 ± 0.1
Lu₂Fe₃O₇				
Lu ₂ Fe ₃ O _{7.000}	3.4537 ± 0.0001		28.427 ± 0.003	293.65 ± 0.04
Lu ₂ Fe ₃ O _{6.997}	3.4493 ± 0.0001		28.434 ± 0.003	292.98 ± 0.04
Lu ₂ Fe ₃ O _{6.984}	3.4527 ± 0.0001		28.420 ± 0.002	293.40 ± 0.03
Lu ₂ Fe ₃ O _{6.927}	3.4539 ± 0.0001		28.434 ± 0.002	293.76 ± 0.04
Lu ₂ Fe ₃ O _{6.896}	3.4527 ± 0.0004		28.449 ± 0.008	294.4 ± 0.1
LuFe₂O₄				
LuFe ₂ O _{4.015}	3.4261 ± 0.0002		25.294 ± 0.004	257.13 ± 0.06
LuFe ₂ O _{4.007}	3.4305 ± 0.0001		25.278 ± 0.002	257.63 ± 0.03
LuFe ₂ O _{3.998}	3.4353 ± 0.0002		25.250 ± 0.003	258.06 ± 0.05
LuFe ₂ O _{3.982}	3.4373 ± 0.0001		25.260 ± 0.003	258.47 ± 0.03
LuFe ₂ O _{3.951}	3.4390 ± 0.0001		25.267 ± 0.002	258.80 ± 0.03
LuFe ₂ O _{3.935}	3.4417 ± 0.0002		25.266 ± 0.004	259.19 ± 0.05

^a *a* = 5.213 ± 0.003, *b* = 5.547 ± 0.003, *c* = 7.565 ± 0.003 (12).

^b *a* = 12.283 ± 0.003 (13).

As seen in Fig. 1, lutetium-iron-garnet has a significant range of nonstoichiometry up to Lu₃Fe₅O_{11.96}. However, no effect was observed on the lattice constant, and the data are given in Table I. In previous studies, it was hard to find the existence of nonstoichiometric lanthanoid-iron-garnet (Eu, Yb, and Y). Perhaps, the Lu₃Fe₅O₁₂ phase may be the only case having any significant nonstoichiometry.

The LuFe₂O₄ and Lu₂Fe₃O₇ solid solutions have wide compositional ranges at 1200°C, as shown in Fig. 1. The compositional range of the LuFe₂O₄ solid solution was from LuFe₂O_{3.935} to LuFe₂O_{4.018} and that of the Lu₂Fe₃O₇ was from Lu₂Fe₃O_{6.879} to Lu₂Fe₃O_{7.000}. Both phases are black and neither was attracted by a hand magnet at room temperature. The *hkl* indices of the X-ray powder patterns of LuFe₂O₄ were obtained on the basis of the results by Kato et al. (5), and that of Lu₂Fe₃O₇ by Kimizuka et al. (6) and Kato et al. (7). The change of lattice constants of

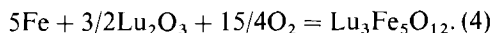
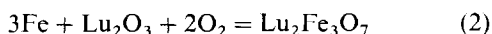
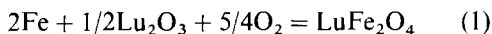
both the solid solutions with composition is given in Table I based on a hexagonal crystal system. It is interesting that the *c* value in the LuFe₂O₄ solid solution changes with composition so that it has a minimum at the stoichiometric composition.

Kimizuka and Katsura (4) have classified the Fe-Fe₂O₃-Ln₂O₃ systems (*Ln* = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) into four groups with respect to the assemblage of ternary compounds as: Type A has only one stable compound *Ln*FeO₃ (*Ln* = La and Nd); type B, *Ln*FeO₃ and *Ln*₃Fe₅O₁₂ (*Ln* = Sm, Eu, Gd, Tb, and Dy); type C, *Ln*FeO₃, *Ln*₃Fe₅O₁₂, and *Ln*Fe₂O₄ (*Ln* = Ho, Er, Tm, and Y); and type D, *Ln*FeO₃, *Ln*₃Fe₅O₁₂, *Ln*Fe₂O₄, and *Ln*₂Fe₃O₇ (*Ln* = Yb and Lu). Indeed, the Fe-Fe₂O₃-Lu₂O₃ belongs to the D type, as illustrated in Fig. 1, but it is noteworthy that there is some basic difference in phase diagrams between these two systems classified into the D type. In the case of the Fe-Fe₂O₃-Lu₂O₃

system, the extremely oxidized $\text{Lu}_2\text{Fe}_3\text{O}_7$ phase is in equilibrium with both the LuFeO_3 and Fe_3O_4 phases at an oxygen partial pressure of $10^{-7.53}$ atm. On the contrary, in the $\text{Fe}-\text{Fe}_2\text{O}_3-\text{Yb}_2\text{O}_3$ system, the extremely oxidized $\text{Yb}_2\text{Fe}_3\text{O}_7$ phase can never be in equilibrium with the Fe_3O_4 phase, but is in equilibrium with both the YbFeO_3 and the extremely oxidized YbFe_2O_4 phases. Thus, the D-type is rather complicated in comparison with the other three types.

2. Calculations of the Standard Free Energy of Formation of Ternary Compounds from Metallic iron, Lu_2O_3 , and Oxygen

On the basis of the present phase equilibria, we will determine the standard free energy of formation of the compounds LuFe_2O_4 , $\text{Lu}_2\text{Fe}_3\text{O}_7$, LuFeO_3 , and $\text{Lu}_3\text{Fe}_5\text{O}_{12}$, referred to the following equations:



Now, Fig. 1 makes it possible to calculate the standard free energy of reactions (5) to (12) tabulated in Table II. Once we could

determine the standard free energy of these reactions, (5)–(12), then the standard free energy of formation referred to each equation, (1)–(4), is readily calculated as

$$\Delta G^\circ(1) = 2\Delta G^\circ(5) + \Delta G^\circ(6) \quad (1')$$

$$\Delta G^\circ(2) = 3/2\Delta G^\circ(1) + \Delta G^\circ(7) \quad (2')$$

$$= \Delta G^\circ(10) - 1/3\Delta G^\circ(9) + 2\Delta G^\circ(1) \quad (2'')$$

$$\Delta G^\circ(3) = 1/3\Delta G^\circ(2) + \Delta G^\circ(8) \quad (3')$$

$$= 1/2\Delta G^\circ(11) - 1/6\Delta G^\circ(9) \quad (3'')$$

$$+ 1/2\Delta G^\circ(2) \quad (3''')$$

$$\Delta G^\circ(4) = 2\Delta G^\circ(5) + 3\Delta G^\circ(3) \quad (4')$$

$$+ 2/3\Delta G^\circ(9) + \Delta G^\circ(12). \quad (4'')$$

To determine the standard free energy of the reactions referred to each equation, (5)–(12), it is necessary to calculate the activity of each component, FeO , Fe_3O_4 , LuFe_2O_4 , $\text{Lu}_2\text{Fe}_3\text{O}_7$, and LuFeO_3 . Here, the reference activity of each component in each solid solution was set equal to one where the composition of the solid solution reached the most reduced composition, that is, $a_{\text{FeO}} = 1$ where its composition is $\text{FeO}_{1.049}$ (W_1 in Fig. 1), $a_{\text{Fe}_3\text{O}_4} = 1$ at $\text{Fe}_3\text{O}_{4.000}$ (M_1 in Fig. 1), $a_{\text{LuFe}_2\text{O}_4} = 1$ at $\text{LuFe}_2\text{O}_{3.935}$ (A_1 in Fig. 1), $a_{\text{Lu}_2\text{Fe}_3\text{O}_7} = 1$ at $\text{Lu}_2\text{Fe}_3\text{O}_{6.879}$ (B_1 in Fig. 1),

TABLE II

SUMMARY OF THE STANDARD FREE ENERGY VALUES

Reactions	$-\Delta G^\circ$ (kcal)
(1) $2\text{Fe} + 1/2\text{Lu}_2\text{O}_3 + 5/4\text{O}_2 = \text{LuFe}_2\text{O}_4$	100.3 ± 0.2
(2) $3\text{Fe} + \text{Lu}_2\text{O}_3 + 2\text{O}_2 = \text{Lu}_2\text{Fe}_3\text{O}_7$	158.2 ± 0.2 (mean value) ^a
(3) $3\text{Fe} + 1/2\text{Lu}_2\text{O}_3 + 3/4\text{O}_2 = \text{LuFeO}_3$	57.5 ± 0.3 (mean value) ^b
(4) $5\text{Fe} + 3/2\text{Lu}_2\text{O}_3 + 15/4\text{O}_2 = \text{Lu}_3\text{Fe}_5\text{O}_{12}$	279.1 ± 0.9
(5) $\text{Fe} + 1/2\text{O}_2 = \text{FeO}$	40.2 ± 0.2
(6) $2\text{FeO} + 1/2\text{Lu}_2\text{O}_3 + 1/4\text{O}_2 = \text{LuFe}_2\text{O}_4$	19.7 ± 0.1
(7) $3/2\text{LuFe}_2\text{O}_4 + 1/4\text{Lu}_2\text{O}_3 + 1/8\text{O}_2 = \text{Lu}_2\text{Fe}_3\text{O}_7$	7.79 ± 0.1
(8) $1/3\text{Lu}_2\text{Fe}_3\text{O}_7 + 1/6\text{Lu}_2\text{O}_3 + 1/12\text{O}_2 = \text{LuFeO}_3$	4.85 ± 0.1
(9) $3\text{FeO} + 1/2\text{O}_2 = \text{Fe}_3\text{O}_4$	33.8 ± 0.3
(10) $2\text{LuFe}_2\text{O}_4 + 1/6\text{O}_2 = \text{Lu}_2\text{Fe}_3\text{O}_7 + 1/3\text{Fe}_3\text{O}_4$	8.84 ± 0.1
(11) $1/2\text{Lu}_2\text{Fe}_3\text{O}_7 + 1/12\text{O}_2 = \text{LuFeO}_3 + 1/6\text{Fe}_3\text{O}_4$	4.18 ± 0.1
(12) $3\text{LuFeO}_3 + 2/3\text{Fe}_3\text{O}_4 + 1/6\text{O}_2 = \text{Lu}_3\text{Fe}_5\text{O}_{12}$	3.55 ± 0.2

^a 158.3 from (2'), 158.0 from (2'').

^b 57.6 from (3'), 57.4 from (3'').

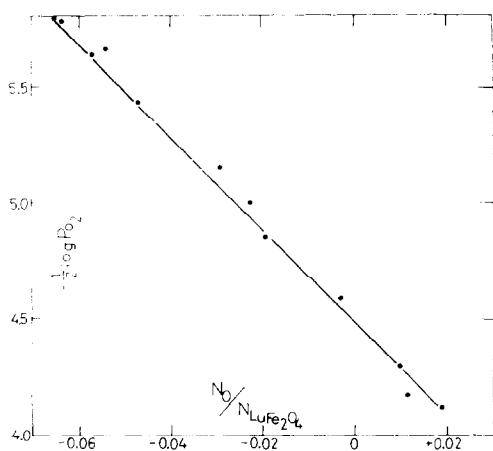


FIG. 2a. The relationship between $-\frac{1}{2} \log P_{O_2}$ and $N_O/N_{LuFe_2O_4}$.

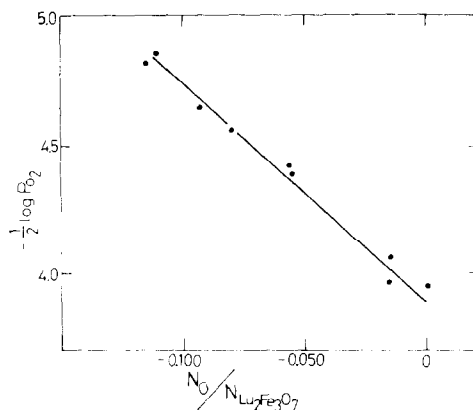


FIG. 2b. The relationship between $-\frac{1}{2} \log P_{O_2}$ and $N_O/N_{Lu_2Fe_3O_7}$.

TABLE III

COMPOSITION AND ACTIVITY IN FIVE SOLID SOLUTIONS

Component (<i>i</i>)	Composition	Symbol	$-\log P_{O_2}$	$\log a_i$
FeO	FeO _{1.049}	W ₁	11.94	0
	FeO _{1.064}	W ₂	11.58	-0.0107
	FeO _{1.165}	W ₃	9.14	-0.1435
LuFe ₂ O ₄	LuFe ₂ O _{3.935}	A ₁	11.58	0
	LuFe ₂ O _{3.982}	A ₂	9.72	0.0397
	LuFe ₂ O _{4.000}	A ₃	9.14	0.0437
	LuFe ₂ O _{4.018}	A ₄	8.11	0.0414
Lu ₂ Fe ₃ O ₇	Lu ₂ Fe ₃ O _{6.879}	B ₁	9.72	0
	Lu ₂ Fe ₃ O _{6.944}	B ₂	8.81	0.0436
	Lu ₂ Fe ₃ O _{6.984}	B ₃	8.11	0.0540
	Lu ₂ Fe ₃ O _{7.000}	B ₄	7.53	0.0527
LuFeO ₃	LuFeO _{2.958}	P ₁	8.81	0
	LuFeO _{2.985}	P ₂	7.53	0.0184
	LuFeO _{2.999}	P ₃	3.75	0.0649
	LuFeO _{3.000}	P ₄	0.00	0.0650
Lu ₃ Fe ₅ O ₁₂	Lu ₃ Fe ₅ O _{11.96}	G ₁	3.75	0
	Lu ₃ Fe ₅ O _{12.000}	G ₂	0.00	

and $a_{LuFeO_3} = 1$ at LuFeO_{2.958} (P₁ in Fig. 1). Desired activities to determine the standard free energy were calculated by applying the Gibbs-Duhem equation as described in previous papers (3, 4). The relationship between the equilibrium oxygen partial pressure and the composition in each solid solution,

which is necessary to calculate the activity, was substantially linear in all series of solid solutions as illustrated, for example, in Figs. 2a and 2b. The calculated activity data are summarized in Table III, and the standard free energy data thus obtained are given in Table II.

3. The Relationship between the Standard Free Energy of Formation of Lanthanoid-Iron-Perovskite and Lanthanoid Sesquioxide, Metallic Iron, and Oxygen and the Tolerance Factor

In previous papers, Kimizuka and Katsura (4) and Katsura et al. (8) pointed out that the standard free energy of lanthanoid-iron-perovskite (La, Nd, Sm, Eu, Gd, Tb, Dy, and Yb) changes in proportional to the tolerance factor defined by Goldschmidt (9) [tolerance factor $t = (r_a + r_o)/\sqrt{2}(r_b + r_o)$, where r_a , r_b , and r_o mean ionic radii of lanthanoid, ferric, and oxygen ions in the perovskite structure, respectively. We took the values of ionic radii reported by Espinosa (13) for lanthanoid ions with 12 coordination number in the perovskite structure, and the values of 0.645 and 1.40 Å for Fe^{3+} and O^{2-} ions, respectively, given by Shannon and Prewitt (14)]. This proportionality is also applicable to LuFeO_3 , HoFeO_3 (10), and ErFeO_3 (11) with an exception of GdFeO_3 , as seen in Fig. 3. More detailed

discussion on the relationship between the thermochemical properties of lanthanoid-iron-perovskite and their structural stability will be published in the near future after completing the study of the whole series of lanthanoid-iron-perovskite.

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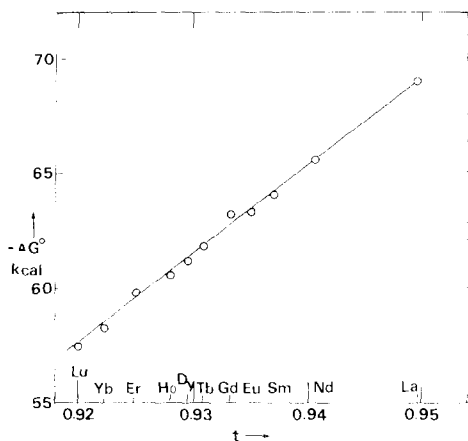


FIG. 3. The relationship between ΔG° and the tolerance factor t .