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MEASUREMENT OF THE THERMODYNAMIC PROPERTIES OF $Fe_2Ti_3O_9$ AND $Fe_2TiO_5$①

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ABSTRACT The thermodynamic properties of $Fe_2Ti_3O_9$ and Fe_2TiO_5 were measured by means of the following solid state electrolyte cells:

Pt, Fe+"FeO"‖$ZrO_2(CaO)$‖$FeTiO_3+Fe_2Ti_3O_9+Fe_2O_3$, Pt

Pt, Fe+"FeO"‖$ZrO_2(CaO)$‖$FeTiO_3+Fe_2TiO_5+TiO_2$, Pt

From the experimental data, the Gibbs energies of formation of $Fe_2Ti_3O_9$ and Fe_2TiO_5 were obtained:

$$\Delta G^0_{pr}\ (\mathrm{kJ\cdot mol^{-1}}) = -3\,459.7 - 0.847T,\ (1\,053\,\mathrm{K} < T < 1\,153\,\mathrm{K})$$

$$\Delta G^0_{pb}\ (\mathrm{kJ\cdot mol^{-1}}) = -1\,700.2 - 0.465T,\ (1\,173\,\mathrm{K} < T < 1\,273\,\mathrm{K})$$

Experimental results fit approximately to those of estimation.

Key words $Fe_2Ti_3O_9$ Fe_2TiO_5 thermodynamic property solid state electrolyte cell

1 INTRODUCTION

Ilmenite has found wide applications as the resource of iron and titanium. Alternatively, as the supplier of oxygen it will also play an important role in exploiting the moon in the future[1, 2].

In the course of upgrading ilmenite and extracting oxygen from this material, reduction plays a dominant role, and preoxidation is beneficial for the following reduction treatment, especially for the dense igneous minerals.

The reaction mechanism of the oxidation of ilmenite varies with temperature[3-7]. Rao and Rigaud studied the reaction mechanism of synthetic ilmenite in both pure oxyen and air by means of differential thermal analysis (DTA), and found that there were obvious endothermal and exothermal peaks around 1 043 K and 1 163 K, respectively.

With X-ray diffraction, they further clarified that the reaction mechanism of the oxidation of ilmenite changed with temperature as follows:

$T < 1\,043\,\mathrm{K}$,

$4FeTiO_3 + O_2 = 2Fe_2O_3 + 4TiO_2$;

$1\,043\,\mathrm{K} < T < 1\,163\,\mathrm{K}$,

$12FeTiO_3 + 3O_2 = 4Fe_2Ti_3O_9 + 2Fe_2O_3$;

$T > 1\,163\,\mathrm{K}$,

$4FeTiO_3 + O_2 = 2Fe_2TiO_5 + 2TiO_2$

While studying the kinetics of the oxidation of natural ilmenite, Sun found that the reaction mechanism changed similarly[8].

Although the thermodynamic properties of both pseudorutile ($Fe_2Ti_3O_9$) and pseudobrookite (Fe_2TiO_5) are very important for analyzing the reduction of preoxidized (or well weathered) ilmenite, about which few have been reported in details.

The solid state electrolyte cell of zirconia stabilized partially by calcium oxide was used to measure the Gibbs energy of formation of both pseudorutile (1 053～1 153 K) and pseudobrookite (1 173～1 273 K), and the average values of the enthalpy of formation and the entropy of formation of both of them over the corresponding temperature ranges.

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2 EXPERIMENTAL

2.1 *Material Preparation*

2.1.1 Synthetic Ilmenite ($FeTiO_3$) [4,5]

Synthetic ilmenite was prepared by calcining the mixture of iron powder, hematite and titania (rutile) at high temperature according to reaction (1).

$$Fe+3TiO_2+Fe_2O_3=3FeTiO_3 \qquad (1)$$

The used materials and their characteristics are listed in Table 1. The stoichiometric mixture of the three kinds of reactants was ground and then compressed into cylinders (d 15 mm × 30 mm) under the pressure of 0.5 GPa. The cylinders were consequently calcined at 1 273 K under argon atmosphere for more than 10 h. According to the results of X-ray diffraction, the calcined product was pure ilmenite[4,5].

Table 1 Materials and their properties

Materials	Grade	Purity/%
titania (rutile)	analytically pure	>98.0
hematite	analytically pure	>99.5
iron powder	analytically pure	>98.0

2.1.2 Pseudorutile ($Fe_2Ti_3O_9$)[4,7]

The synthetic ilmenite, particle size of which was smaller than 0.18 mm, was oxidized with pure oxygen at 1 073 K for more than 10 h. Chemical analysis confirmed that the oxidation was complete. According to the results of X-ray diffraction analyses of both the reactant and the product, the oxidation of ilmenite can be expressed as Eqn. (2) under the experimental conditions.

$$12FeTiO_3+3O_2=4Fe_2Ti_3O_9+2Fe_2O_3 \qquad (2)$$

2.1.3 Pseudobrookite (Fe_2TiO_5)[4-7]

The preparation method of pseudobrookite was similar to that of pseudorutile, and the main difference was that the oxidation of ilmenite was carried out at 1273K. The results of chemical analysis and X-ray diffraction showed that the oxidation was complete and could be expressed as Eqn. (3).

$$4FeTiO_3+O_2=Fe_2TiO_5+2TiO_2 \qquad (3)$$

2.2 *Measurement of the Thermodynamic Properties*

The thermodynamic properties of both $Fe_2Ti_3O_9$ and Fe_2TiO_5 were measured with solid state electrolyte cells of zirconia which was partially stabilized with CaO[8]. The reference electrode was Fe/"FeO". The mixture of Fe and "FeO" was prepared by the reduction of Fe_2O_3 with iron powder, the amount of which was approximately 1.85 times more than that of stoichiometry at high temperature[8].

Cells (Ⅰ) and (Ⅱ) were used to measure the thermodynamic properties of pseudorutile and pseudobrookite, respectively.

$$\text{Pt, Fe+“FeO”}\|ZrO_2(CaO)\|\ FeTiO_3+Fe_2Ti_3O_9+Fe_2O_3\text{, Pt} \qquad (\text{I})$$

$$\text{Pt, Fe+“FeO”}\|ZrO_2(CaO)\|FeTiO_3+Fe_2TiO_5+TiO_2\text{, Pt} \qquad (\text{II})$$

The experimental apparatus and the arrangement of the solid state electrolyte cells are schematically shown in Fig. 1.

The electromotive forces of cell (Ⅰ) (1 053~1 153 K) and cell (Ⅱ) (1 173~1 273 K) were measured in the course of both increasing and decreasing temperatures with a temperature interval of 20 K under pure argon atmosphere. In order to get rid of the influence of the electromagnetic field generated by the electric furnace, the cells were shielded with an earthed copper tube.

The phase composition of the substances composing cells (Ⅰ) and (Ⅱ) was examined by means of X-ray diffraction both before and after experiment, and the results showed that pseudorutile and pseudobrookite were stable during the experiment.

3 EXPERIMENTAL RESULTS AND THEORETICAL ANALYSIS

3.1 *Thermodynamic Properties of Pseudorutile*

3.1.1 Fundamentals of thermodynamics

The elctrode reactions and the overall reaction for cell (Ⅰ) can be expressed as follows.

Cathodic reaction:

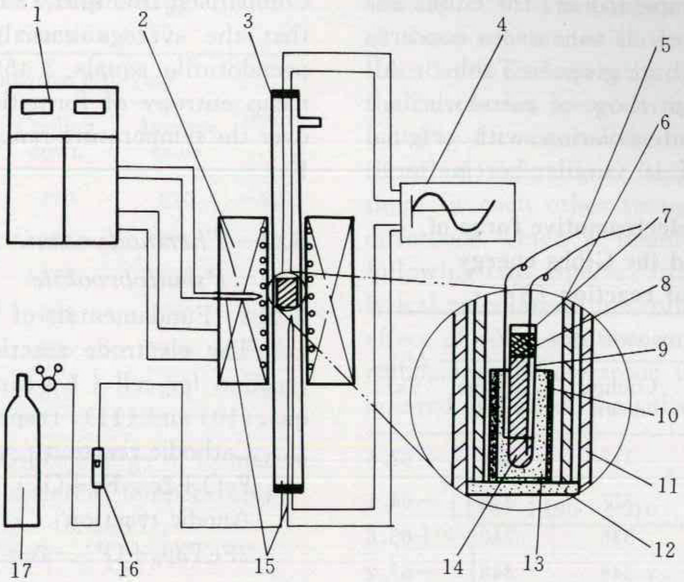

Fig. 1 Schematic diagram of the experimental apparatus

1—temperature controller; 2—electric furnace; 3—quartz reactor; 4—*X-Y* function recorder; 5—platinum wire; 6—copper tube; 7—refractory cement; 8—almina powder; 9—zirconia tube; 10—zirconia crucible; 11—quartz tube; 12—refractory brick; 13—$FeTiO_3+Fe_2Ti_3O_9+Fe_2O_3$ or $FeTiO_3+Fe_2TiO_5+TiO_2$; 14—Fe+"FeO"; 15—thermocouple; 16—rotator flow meter; 17—argon cylinder

$$FeO+2e=Fe+O^{2-} \qquad (4a)$$

Anodic reaction:

$$2FeTiO_3+O^{2-}-2e=(2/3)Fe_2Ti_3O_9+(1/3)Fe_2O_3 \qquad (4b)$$

The overall reaction for cell (Ⅰ) is:

$$FeO+2FeTiO_3=(2/3)Fe_2Ti_3O_9+(1/3)Fe_2O_3+Fe \qquad (5)$$

The Gibbs energy change of reaction (5) can be determined from the electromotive force of cell (Ⅰ).

$$\Delta G^0_{(5)} = -n_1 F\varepsilon_1 \qquad (6)$$

where n_1 is the number of electron concerned with reaction (5), $n_1 = 2$; F is the Faraday constant.

On the other hand, the Gibbs energy change of reaction (5) can also be calculated from the difference between the sum of the Gibbs energy of formation of the products and that of the reactants.

$$\Delta G^0_{(5)} = (2/3)\Delta G^0_{pr} + (1/3)\Delta G^0_{hm} + \Delta G^0_{ir} - \Delta G^0_{ws} - 2\Delta G^0_{il} \qquad (7)$$

where pr stands for pseudorutile; hm for hematite; ir for iron; ws for wustite; il for ilmenite.

The Gibbs energy of formation of pseudorutile can be derived from Eq. (7).

$$\Delta G^0_{pr} = (3/2)[\Delta G^0_{(5)} - (1/3)\Delta G^0_{hm} - \Delta G^0_{ir} + \Delta G^0_{ws} + 2\Delta G^0_{il}] \qquad (7a)$$

Consequently, the Gibbs energy of formation of pseudorutile can be determined from the Gibbs energy change of reaction (5) and the Gibbs energy of formation of all of the other substances concerning with the reaction.

Moreover, Gibbs energy can also be expressed as a linear function of temperature as given in Eqn. (8).

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \qquad (8)$$

The intercept and the negative value of the slope of Eqn. (8) are the average values of the enthalpy and entropy of formation of pseudorutile within the temperature interval respectively.

3.1.2 Experimental Results

The measured values of electromotive

force of cell (Ⅰ) are listed in Table 2.

At different temperatures, the Gibbs energies of formation of all substances concerning with reaction (5) are given in Table 3. All of the values (except those of pseudorutile) are estimated by interpolation with original data taken from Ref. 10 (similar hereinafter).

Table 2 The electromotive force of cell (Ⅰ) and the Gibbs energy change of reaction (5)

T /K	Electromotive force/mV			$\Delta G^0_{(5)}$ /kJ
	Heating up	Cooling down	Average value	
1 053	331	317	324	−62.5
1 073	337	327	332	−64.1
1 093	344	336	340	−65.6
1 113	350	346	348	−67.2
1 133	356	355	355	−68.5
1 153	360	360	360	−69.5

Table 3 Standard Gibbs energies of formation of all substances concerning with reaction (5)

T /K	Standard Gibbs energies of formation /kJ·mol^{-1}				
	Fe	FeO	Fe_2O_3	$FeTiO_3$	$Fe_2Ti_3O_9$
1053	−45.80	−366.68	−991.59	−1424.05	−4351.4
1073	−47.26	−369.28	−996.86	−1429.18	−4368.2
1093	−48.73	−371.86	−1002.14	−1434.29	−4384.9
1113	−50.22	−374.52	−1007.54	−1439.56	−4402.2
1133	−51.74	−377.22	−1013.00	−1444.93	−4419.3
1153	−53.25	−379.92	−1018.46	−1450.30	−4435.9

The Gibbs energy of formation of pseudorutile is determined according to Eqn. (7a) with the standard Gibbs energies of formation of all the other substances concerned with reaction (5) and the result is also given in Table 3. From the values listed in Table 3, the relationship between the Gibbs energy of formation of pseudorutile and temperature can be determined as Eqn. (9).

$$\Delta G^0 = -3\,459.7 - 0.847T, \quad (1\,053\,\mathrm{K} < T < 1\,153\,\mathrm{K}), \quad r = 0.999\,9 \tag{9}$$

where r is the linear correlation coefficient. Comparison of Eqns. (8) and (9) results in that the average enthalpy of formation of pseudorutile equals 3 459.7 kJ/mol and its mean entropy of formation is 847 J/mol·K over the temperature range from 1 053 to 1 153 K.

3.2 *Thermodynamic Properties of Pseudobrookite*

3.2.1 Fundamentals of Thermodynamics

The electrode reactions and the overall reaction for cell (Ⅱ) can be expressed as Eqns. (10) and (11), respectively.

Cathodic reaction:

$$FeO + 2e = Fe + O^{2-} \tag{10a}$$

Anodic reaction:

$$2FeTiO_3 + O^{2-} - 2e = Fe_2TiO_5 + TiO_2 \tag{10b}$$

From the aforementioned electrode reactions (10a) and (10b), the overall reaction for cell (Ⅱ) is obtained as Eqn. (11):

$$FeO + 2FeTiO_3 = Fe_2TiO_5 + TiO_2 + Fe \tag{11}$$

Similar to that of pseudorutile, the Gibbs energy of formation of pseudobrookite can be derived from Eqn. (12) and expressed as a linear function of temperature similar to Eqn. (8) as well.

$$\Delta G^0_{\mathrm{pb}} = \Delta G^0_{(11)} - \Delta G^0_{\mathrm{rt}} - \Delta G^0_{\mathrm{ir}} + \Delta G^0_{\mathrm{ws}} + 2\Delta G^0_{\mathrm{il}} \tag{12}$$

where pb stands for pseudobrookite; rt for rutile.

3.2.2 Experimental Results

The electromotive force of cell (Ⅱ) and the Gibbs energy change of reaction (11) are listed in Table 4.

Similarly, the standard Gibbs energies of formation of all the substances concerned with reaction (11) are listed in Table 5. The Gibbs energy of formation of pseudobrookite is determined according to Eqn. (12) with the data of the Gibbs energy change of reaction (11) and the standard Gibbs energy of formation of all substances (except pseudobrookite) concerned with reaction (11).

Regression equation (13) can be obtained

Table 4 Electromotive force of cell (Ⅱ) and the Gibbs energy change of reaction (11)

T /K	Electromotive force/mV			$\Delta G^0_{(11)}$
	Heating up	Cooling down	Average value	
1 173	270	270	270	−52.1
1 193	280	271	275	−53.3
1 213	288	278	283	−54.6
1 233	294	286	290	−56.0
1 253	298	295	296	−57.1
1 273	308	315	311	−59.0

from the data of the Gibbs energy of formation of pseudobrookite at different temperatures:

$$\Delta G^0 = -1\,700.2 - 0.465T, \quad (1\,173\,\mathrm{K} < T < 1\,273\,\mathrm{K}), \quad r = 0.982\,3 \qquad (13)$$

The average values of the enthalpy of formation and the entropy of formation of pseudobrookite within the temperature rang 1 173 ~1 273K can be determined as $\Delta H^0 = -1700.2$ kJ/mol and $\Delta S^0 = 465.0$ J/mol·K respectively, by comparing Eqns. (8) and (13).

4 DISCUSSION

4.1 *Comparison of the Measured Values With Those of Estimation*

The values of ΔH^0_{298} and ΔS^0_{298} of pseudorutile and pseudobrookite were estimated according to Zhang's method[11, 12], and Berman-Brown's correlation was adopted for expressing the specific heat of the two substances[13, 14]. The Gibbs energies of formation of these substances at experimental temperatures were consequently calculated. Details of the calculation are given in the Appendix.

Fig. 2 compares the measured values with those of estimation, showing that both of them fit each other though there is a slight difference which is mainly attributed to the following two aspects: first of all, in the analytical calculation presented in Section 2, the effect of solid solution among the substances composing the electrode to be measured was ignored and all of the substances were treated

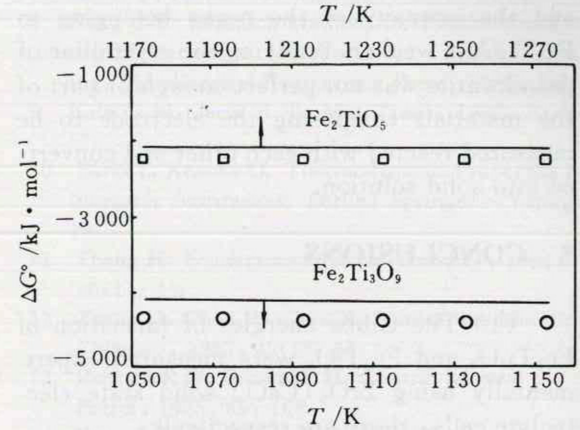

Fig. 2 Comparison of the Gibbs energies of formation of $Fe_2Ti_3O_9$ and Fe_2TiO_5 (ΔG^0) with those of estimation

(Solid lines are estimated values, points are measured data)

Table 5 Standard Gibbs energies of formation of the substances concerned with reaction (11)

T /K	Standard Gibbs energies of formation/kJ·mol^{-1}				
	TiO_2	Fe	FeO	$FeTiO_3$	Fe_2TiO_5
1 173	−1 040.45	−54.76	−382.61	−14 455.66	−2 250.8
1 193	−1 053.31	−56.30	−385.30	−1 461.02	−2 251.0
1 213	−1 056.21	−57.88	−388.08	−1 466.54	−2 261.7
1 233	−1 059.13	−59.47	−390.89	−1 472.13	−2 272.5
1 253	−1 062.05	−61.06	−393.69	−1 477.72	−2 283.1
1 273	−1 064.97	−62.65	−396.49	−1 483.31	−2 294.5

as in their standard state; second, thermodynamic data from different references were used in estimating the thermodynamic properties of these substances.

4.2 *Stability of* $Fe_2Ti_3O_9$ *and* Fe_2TiO_5

In order to determine the stability of the main ingredients of the cells, $Fe_2Ti_3O_9$ and Fe_2TiO_5, the phase composition of the materials composing the electrodes to be measured was examined by means of X-ray diffraction after the high temperature experiments. The results are shown in Fig. 3, which indicates that both $Fe_2Ti_3O_9$ and Fe_2TiO_5 are stable within the experimental temperature range, and the intensity of the peaks belonging to $Fe_2Ti_3O_9$ is weaker, implying the crystalline of pseudorutile was not perfect enough or part of the materials composing the electrode to be measured reacted with each other and converted into solid solution.

5 CONCLUSIONS

(1) The Gibbs energies of formation of $Fe_2Ti_3O_9$ and Fe_2TiO_5 were measured experimentally using ZrO_2 (CaO) solid state electrolyte cells, those are respectively:

$$\Delta G^0_{pr}(\mathrm{kJ \cdot mol^{-1}}) = -3459.7 - 0.847T, \quad 1053\,\mathrm{K} < T < 1153\,\mathrm{K}$$

$$\Delta G^0_{pb}(\mathrm{kJ \cdot mol^{-1}}) = -1700.2 - 0.465T, \quad 1173\,\mathrm{K} < T < 1273\,\mathrm{K}$$

(2) The measured Gibbs energies of formation of $Fe_2Ti_3O_9$ and Fe_2TiO_5 generally fit with those of estimation, and one of the main reasons causing the slight difference may be attributed to the influence of solid solution among the materials composing the electrode to be measured.

(3) Both $Fe_2Ti_3O_9$ and Fe_2TiO_5 are stable within the experimental temperature range.

APPENDIX

Estimation of Thermodynamic Properties of Complex Oxides

According to Refs. [11] and [12], ΔH^0_{298} and ΔS^0_{298} of a binary complex oxide can be expressed as Eqns. (14) and (15), respectively.

$$\Delta H^0_{298} = a\Delta H^0_1 + b\Delta H^0_2 + aA_1 + bA_2 + ab(A_1' + A_2')/(a + b) \tag{14}$$

$$\Delta S^0_{298} = aB_1 + bB_2 \tag{15}$$

As confirmed by Ref. [13], the specific heat of a binary complex oxide can be estimated in the light of Eqn. (16).

$$C_p = aC_1^* + bC_2^* \tag{16}$$

The thermodynamic properties of the complex oxides can be further calculated with Eqns. (17)～(19).

$$\Delta H^0 = \Delta H^0_{298} + \int_{298}^{T} C_p \mathrm{d}T \tag{17}$$

$$\Delta S^0 = \Delta S^0_{298} + \int_{298}^{T} (C_p/T) \mathrm{d}T \tag{18}$$

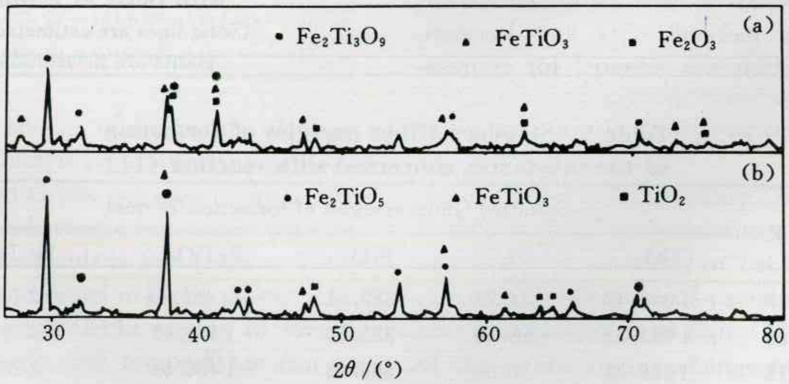

Fig. 3 X-ray diffraction patterns of the materials composing the electrodes to be measured of cell (Ⅰ) (a) and cell (Ⅱ) (b)

Table 6 Original data needed for estimation of the thermodynamic properties

Subscript i	ΔH_i^0 /kJ · mol^{-1}	A_i /kJ · mol^{-1}	A_i' /kJ · mol^{-1}	B_i /J · mol^{-1} · K^{-1}	C_i^* /J · mol^{-1} · K^{-1}
Fe_2O_3	−825.50	−14.23	54.60	92.471	$168.211-975.72T^{-0.5}-1.73034\times10^{8}T^{-3}$
TiO_2	−944.75	18.85	−102.01	46.719	$85.059-220.72T^{-1.5}-2.25138\times10^{6}T^{-2}+2.24979\times10^{8}T^{-3}$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \qquad (19)$$

Pseudorutile and pseudobrookite can be formally expressed by the following formula:

$Fe_2Ti_3O_9 = Fe_2O_3 \cdot 3TiO_2 (a = 1, b = 3)$

$Fe_2TiO_5 = Fe_2O_3 \cdot TiO_2 (a = 1, b = 1)$

The original data needed for the calculation are summarized in Table 6[10−14].

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