

## Experimental Study and Thermodynamic Optimization of the FeO-V<sub>2</sub>O<sub>3</sub> System

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**Abstract:** Optimization of the phase diagram of FeO-V<sub>2</sub>O<sub>3</sub> system is a part of an on-going research project to develop a self-consistent multi-component thermodynamic database for vanadium slag from hot metal. Due to the lack of experimental data for optimization, a novel experimental investigation has been carried out by thermal analysis (DSC) with a series of slags on different V<sub>2</sub>O<sub>3</sub> contents (i. e. 3mass%–12mass%). All available thermodynamic and phase diagram data for the binary systems have been simultaneously optimized with CALPHAD (Calculation of Phase Diagrams) methods to give one set of model equations for the Gibbs free energy of the liquid slag as functions of composition and temperature. The modified quasi-chemical model was used to describe the binary slag system. It was demonstrated that the calculated phase diagram with the optimized parameters was in good agreement with the experimental data.

**Key words:** calculated phase diagram; thermal analysis; modified quasi-chemical model; vanadium slag

Vanadium is a very important metallic element that has been widely used in many kinds of materials due to its excellent physical and chemical characteristics. For example, vanadium, as an alloying element, could strengthen the intensity, hardness, malleability toughness, wearability and fatigue performance of the steel<sup>[1,2]</sup>.

Vanadium slag, which is often produced by pre-oxidizing the vanadium-containing hot metal with oxygen before decarburization process, is a main raw material for producing the previously mentioned vanadium products. Currently, four methods are dominant for extracting vanadium from vanadium-containing hot metal<sup>[3–5]</sup>. Although these methods are distinguished, they share the common basic principle that vanadium is oxidized by oxygen into vanadium slag. Furthermore, it is characterized as concentrating vanadium to vanadium-iron spinel in the vanadium slag. Then, the vanadium slag was roasted and oxidized in the presence of salts and leached to obtain vanadium-containing liquid<sup>[6]</sup>. As an intermediate product, phase composition and physicochemical properties of the vanadium slag have significant effects on not only the formation

process of vanadium slag in the converter but also the subsequent roasting process. However, phase diagram of vanadium-containing multi-component slag, which is very important to understand and predict these previously mentioned properties of vanadium slag, is very limited in published literatures<sup>[1–6]</sup>. In order to have a better understanding on the evolution of phase composition and physico-chemical properties of vanadium slag during vanadium extraction process in converter, the phase diagram of vanadium slag is thus required to be studied.

The present study uses the research program that naturally combines experimental investigation and thermodynamic modeling of FeO-V<sub>2</sub>O<sub>3</sub> system. Although iron and vanadium are multivalent oxidation states, yet the typical compositions of vanadium slag of Pan-Steel are based on the matrix composed of FeO, SiO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>. The ultimate goal of present research is to develop a self-consistent multi-component thermodynamic database for optimizing the metallurgy process of extracting vanadium from hot metal.

For the development of the thermodynamic database of the vanadium slag for reliable predictions

and descriptions of liquidus, phase transition, equilibrium and activity in the multi-component system, the thermodynamic modeling and the experimental study of phase equilibrium have been combined by means of the CALPHAD method<sup>[7,8]</sup>. To be more specific, parameters of thermodynamic models are optimized to fit the experimental data collected from literature. When there are not enough data to constrain the thermodynamic optimization, experimental measurements are required.

In the thermodynamic optimization of a chemical system, all available thermodynamic and phase equilibrium data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition<sup>[9–11]</sup>. In the present study, all calculations were carried out using the FactSage thermochemical software and databases.

## 1 Evaluation of Experimental Data

A critical assessment of the previously published thermodynamic and phase equilibrium data for the FeO-V<sub>2</sub>O<sub>3</sub> system revealed that the binary phase diagram has not been critically investigated<sup>[1,3,12]</sup>. A comprehensive thermodynamic assessment of the FeO-V<sub>2</sub>O<sub>3</sub> system is necessary to perform thermodynamic extrapolations of the related higher order systems. The investigation of the FeO-V<sub>2</sub>O<sub>3</sub> system has been carried out only by Koerber and Oelsen in 1940<sup>[12]</sup>, who detected only one compound of FeV<sub>2</sub>O<sub>4</sub>. This compound was reported to melt incongruently at 1750 °C. In their work, the phase relation of FeO-V<sub>2</sub>O<sub>3</sub> system containing less than 4mass% V<sub>2</sub>O<sub>3</sub> was investigated comprehensively while the system containing more than 4mass% V<sub>2</sub>O<sub>3</sub> has not been studied. The study has revealed that the oxide solid solution character does not exist at all temperatures and compositions of the binary system. Since this binary system was seldom investigated, data of activities and heats of mixing was quite deficient. Therefore, an experimental investigation of the FeO-V<sub>2</sub>O<sub>3</sub> system was undertaken in the present study to supply the fundamental data for optimizing the binary phase diagram. Then obtained experimental data as well as the previously published experimental results were employed during the thermodynamic optimization of the binary system.

## 2 Experimental Technique and Procedure

The reagent grade V<sub>2</sub>O<sub>3</sub> (analytical reagent, 99.0mass%) and FeC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O (analytical reagent,

99.5mass%) powder, supplied by KeLong chemical reagent corporation, were used as raw materials for the experimental sample preparation. As the FeO reagent is easy to be oxidized in air at room temperature, the iron oxalate dehydrate is used to replace the FeO powder to mix with V<sub>2</sub>O<sub>3</sub> powder in order to prepare samples. Seven slag samples of which chemical compositions are shown in Table 1 were well mixed by using magnetic stirrer and dried in a drying oven for 12 h. The powder mixture was put into a pure iron crucible and heated employing the electric furnace which was completely sealed at 550 K and held for 90 min to make the iron oxalate dehydrate in mixing sample decompose into FeO<sup>[13]</sup>. In the process, heating rate was controlled at a very low value so as to avoid rapid decomposition of the iron oxalate dehydrate, which might lead to blowing out of the mixing sample from the crucible. After that, the sample was cooled to the room temperature.

**Table 1 Measured transformation temperatures of FeO-V<sub>2</sub>O<sub>3</sub> mixtures with different compositions**

Sample No.	FeO/mass%	V <sub>2</sub> O <sub>3</sub> /mass%	Liquidus temperature (T <sub>L</sub> )/°C	Eutectic temperature (T <sub>E</sub> )/°C
1	97	3	1412	1360
2	95	5	1543	1364
3	94	6	1468	1361
4	92	8	1502	1360
5	90	10	1535	1363
6	89	11	1548	1364
7	88	12	1560	1362

Then, the cooled samples were compressed in a platinum crucible ( $\phi$ 5 mm × 5 mm) and heated employing the electric furnace completely sealed at 1773 K for 20 h to establish equilibrium followed by quenching of all the heated samples in argon gas. Finally, prepared sample was load in another platinum crucible and measured with a NETZSCH DSC STA 449C differential scanning calorimeter (DSC). The DSC measurements were performed between room temperature and 1873 K with a heating rate of 20 K/min, and a cooling rate of 10 K/min down to 1273 K. It was notable that all the experiments above mentioned have been done under a flow of argon gas atmosphere ( $P_{O_2} < 10^{-3}$  Pa).

## 3 Experimental Results

The experimental procedure involves approximate equilibrium and ultra-rapid quenching followed by measurements of liquidus temperature using DSC.

The thermal analysis is made in non-equilibrium, but if the cooling rate is appropriate, the changes in temperature during non-equilibrium do not affect the accuracy of the results much. Therefore, the liquidus can be measured directly by using DSC, providing essential data for subsequent thermodynamic modeling.

In terms of DSC thermal analysis, the freezing temperature was chosen as the starting point temperature of exothermic peak considering the effect of degree of supercooling and superheating. Since phase

transition temperature is the focus in present experiment and there was no phase transition from room temperature to 1000 °C, the temperature range of the cooling curves of DSC was chosen as 1000–1600 °C.

Fig. 1 shows the DSC cooling curves of the FeO-V<sub>2</sub>O<sub>3</sub> mixtures with different mass percents of V<sub>2</sub>O<sub>3</sub> ( $x=0.06$  and  $0.12$ ), obtained at a cooling rate of 10 K/min. A summary on the phase identification is listed in Table 1.

Thermograms present the DSC freezing curves of

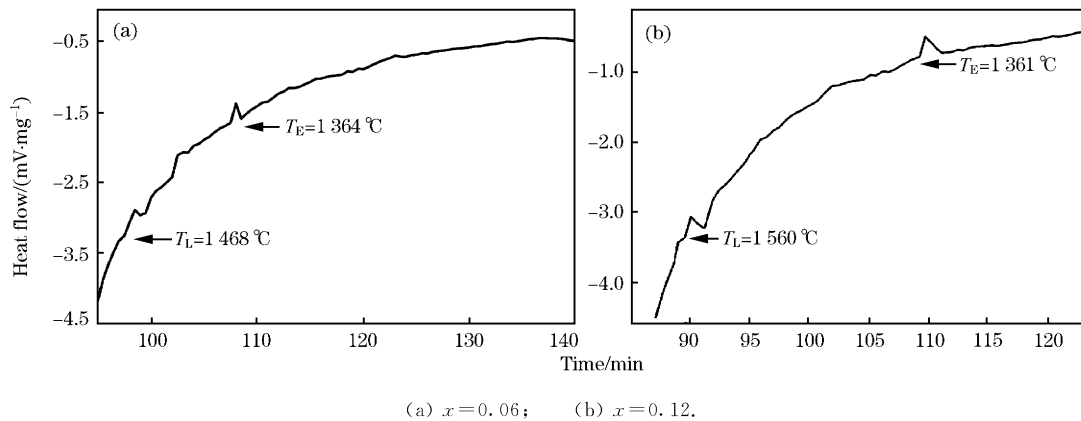


Fig. 1 DSC cooling thermograms for FeO-V<sub>2</sub>O<sub>3</sub> mixtures with different V<sub>2</sub>O<sub>3</sub> mass percents

seven samples, in which the phase transition (eutectic and liquidus) temperatures are marked. Clearly, all the freezing thermographs of these samples in the composition range in present research are characterized by only two exothermic peaks. The second exothermic peak, not only occurs at the lowest temperature, but also occurs at almost the same temperature in all DSC cooling curves. And considering the experimental uncertainty, this temperature was believed to be consistent with each other within experimental error limits. So it can undoubtedly be ascribed to the eutectic temperature of the binary system. Combining the present DSC data with the results in Refs. [3,12,14,15], the temperature of the invariant reaction, the transformation of L (liquid)→FeV<sub>2</sub>O<sub>4</sub>+FeO, was deduced to be located near 1364 °C, in which liquid contains 1mass% V<sub>2</sub>O<sub>3</sub>. The first exothermic peak in cooling thermograms occurring at the highest temperature should be attributed to the precipitation of iron divanadium tetraxide phase (FeV<sub>2</sub>O<sub>4</sub>, activity of 1, zero mass) in the liquid solution and the temperature was defined as liquidus temperature. It was also indicated that liquidus temperatures were decreased with V<sub>2</sub>O<sub>3</sub> contents in FeO-V<sub>2</sub>O<sub>3</sub> system. All the experimental data obtained by DSC investigations were used in the subsequent optimization.

## 4 Thermodynamic Modeling

It is well known that spinel and FeO form solid solutions in the form of Fe<sub>1+y</sub>V<sub>2-y</sub>O<sub>4</sub> and FeO<sub>y</sub>, respectively. However, the accurate solubility data of solid solute of Fe<sub>1+y</sub>V<sub>2-y</sub>O<sub>4</sub> has not been reported. In this paper, FeO<sub>y</sub> and Fe<sub>1+y</sub>V<sub>2-y</sub>O<sub>4</sub> are considered as FeO and FeV<sub>2</sub>O<sub>4</sub>. Gibbs free energy of phases in FeO-V<sub>2</sub>O<sub>3</sub> system was summarized as follows.

### 4.1 Unary phase

The Gibbs energy for the component  $i$  (FeO or V<sub>2</sub>O<sub>3</sub>) in a certain phase  $\phi$  is described as a function of temperature by the following equation<sup>[14]</sup>:

$${}^{\theta}G_i^{\phi}(T) = a_1 + b_1 T + c_1 T \ln T + d_1 T^2 + e_1 T^3 + f_1 T^{-1} + g_1 T^7 + h_1 T^{-9} \quad (1)$$

where,  ${}^{\theta}G_i^{\phi}(T)$  is the Gibbs energy at standard state and  $T$  is the absolute temperature. The values of the coefficients  $a_1$  to  $h_1$  are taken from the SGTE (Scientific Group Thermo data Europe).

### 4.2 Intermetallic compound

The iron divanadium tetraxide compound in the system is only intermetallic compound and considered as stoichiometric compound. The Gibbs energy for stoichiometric compound is described by the following thermodynamic equation:

$$\begin{cases} G = H - TS \\ H^\theta(T) = H_{298}^\theta + \int_{298}^T C_P dT \\ S^\theta(T) = S_{298}^\theta + \int_{298}^T C_P / T dT \\ C_P = a_2 + b_2 T + c_2 T^{-2} + d_2 T^{-1/2} + e_2 T^{-3} + \\ \quad f_2 T^2 + g_2 T^3 \end{cases} \quad (2)$$

$$(3)$$

where, the values of the coefficients  $a_2$  to  $g_2$  are taken by the above equation from fitting relevant thermodynamic data<sup>[15]</sup> (in Table 2). The fitted results are presented in Table 3.

### 4.3 Solution phase

The liquid oxide phase is an ionic melt where metal cations are always surrounded by oxygen ani-

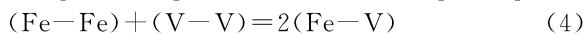
**Table 2** Measured thermal capacity of FeV<sub>2</sub>O<sub>4</sub> compound

Temperature/ K	Thermal capacity/ (J · mol <sup>-1</sup> · K <sup>-1</sup> )	Temperature/ K	Thermal capacity/ (J · mol <sup>-1</sup> · K <sup>-1</sup> )
298.15	152.962	1200	206.076
300	153.373	1300	209.196
400	168.837	1400	212.261
500	177.527	1500	215.285
600	183.551	1600	218.278
700	188.316	1700	221.248
800	192.411	1800	224.198
900	196.115	1900	227.134
1000	199.577	2000	230.057
1100	202.881		

**Table 3** Summary of thermodynamic parameters describing the FeO-V<sub>2</sub>O<sub>3</sub> system under stable element reference state ( $T=298.15$  K,  $P=100$  kPa)

$G_{\text{FeO}}^\ominus$	298.15 < $T$ < 1644.15	$-322147.542 - 330.687T + 18.024T \ln T - 0.0153T^2 + 1266649.997T^{-1} + 6003.6T^{0.5}$
	1644.15 < $T$ < 2000	$-299283.753 + 417.258T - 68.199T \ln T$
$G_{\text{V}_2\text{O}_3}^\ominus$	298.15 < $T$ < 1644.15	$-290958.454 - 349.657T + 18.024T \ln T - 0.0153T^2 + 1266649.997T^{-1} + 6003.6T^{0.5}$
	1644.15 < $T$ < 2000	$-268094.665 + 398.289T - 68.199T \ln T$
$G_{\text{V}_2\text{O}_3}^{\text{S}}$	298.15 < $T$ < 1200	$-1057405.514 - 1221.008T + 81.629T \ln T - 0.032T^2 - 629928.526T^{-1} + 30067.725T^{0.5} - 84148.684 \ln T$
	1200 < $T$ < 2800	$-1240076.517 + 559.786T - 98.086T \ln T - 0.0175T^2 - 2615668.126T^{-1}$
$G_{\text{V}_2\text{O}_3}^{\text{L}}$	298.15 < $T$ < 900	$-1067899.004 + 1136.761T - 186.689T \ln T + 0.0386T^2 - 7.705 \times 10^{-6}T^3 + 277126.369T^{-1} - 16880.845 \ln T$
	900 < $T$ < 1600	$-393710140.469 + 1580922.315T - 157135.093 \ln T + 14.841T^2 - 0.00063T^3 + 5856308977.849T^{-1} - 30512001.445T^{0.5} + 121853856.227 \ln T$
	1600 < $T$ < 4000	$-1166474.624 + 943.124T - 156.9T \ln T$
$H_{\text{FeV}_2\text{O}_4}^\ominus$	298.15	$-1505989 \text{ J} \cdot \text{mol}^{-1}$
$S_{\text{FeV}_2\text{O}_4}^\ominus$	298.15	$156.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$C_{P(\text{FeV}_2\text{O}_4)}$	298.15 < $T$ < 1200	$87.734 + 0.2996T - 0.000296T^2 + 1.08 \times 10^{-7}T^3$
	1200 < $T$ < 2000	$165.558 + 0.0359T - 1.879 \times 10^{-6}T^2$
$\Delta g_{\text{FeO-V}_2\text{O}_3}$		$378366.47 - 211.53T + (72275.45 + 5.27T)Y_{\text{V}_2\text{O}_3}$

ons<sup>[16–18]</sup>. Furthermore, there is a strong tendency of short-range ordering (SRO) of second-nearest neighbor cations in ionic melts. So the liquid phase in this work is modeled using the modified quasichemical model<sup>[9,16,19,20]</sup> where the pair approximation is utilized to describe the short-range ordering existing in the liquid phase. It is observed that the oxide system which shows a strong compound forming tendency in the solid state displays a pronounced minimum in the enthalpy of mixing of the liquid phase and this is caused due to the existence of short-range ordering. In the binary FeO-V<sub>2</sub>O<sub>3</sub> liquid solution, the short-range ordering is taken into account by considering the following second-nearest-neighbor pair exchange reaction with the Gibbs energy change of  $\Delta G_{mn}$  and  $(m-n)$  representing a second-nearest-neighbor pair:



The number of moles and the coordination number of component  $m$  are marked as  $n_m$  and  $Z_m$  re-

spectively. The “coordination-equivalent” fractions ( $Y_m$ ) are then defined as:

$$Y_m = Z_m n_m / \sum_i Z_i n_i \quad (5)$$

Thus  $\Delta G_{mn}$  can be expressed as

$$\Delta G_{mn} = \Delta G_{mn}^0 + \sum_{(i+j) \geq 1} q_{mn}^{ij} Y_m^i Y_n^j \quad (6)$$

where,  $\Delta G_{mn}^0$  and  $q_{mn}^{ij}$  are empirical binary coefficients which may be functions of temperature and pressure. These binary coefficients are optimized to reproduce all available experimental data.

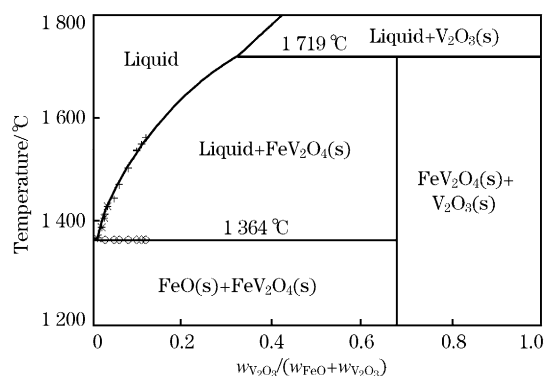
## 5 Thermodynamic Optimization and Results

The thermodynamic properties ( $H$ ,  $S$ ,  $C_P$ ) of pure solid and liquid FeO and V<sub>2</sub>O<sub>3</sub> were taken from the FactSage database. These data are reproduced and given in Table 3. The heat capacities of FeV<sub>2</sub>O<sub>4</sub> was measured in the temperature range of 298–2000 K. The measured data are reproduced in Table 2. The fitted heat capacity of FeV<sub>2</sub>O<sub>4</sub> compound is repro-

duced in Table 3 by Eq. (3). These values of all the above mentioned data and phase diagram from the literature and this experiment determination were optimized simultaneously by a least-squares technique<sup>[21]</sup>, to obtain the parameters of the modified quasi-chemical model. The resulting optimized quasi-chemical parameters of Eq. (6) are

$$\Delta G_{\text{FeO-V}_2\text{O}_3} = 378366.47 - 211.53T + (72275.45 + 5.27T)Y_{\text{V}_2\text{O}_3} \quad \text{J/mol} \quad (7)$$

The optimized thermodynamic parameters are simultaneously listed in Table 3. These parameters together with the Gibbs energies of pure substances allow the calculation of phase diagram of the FeO-V<sub>2</sub>O<sub>3</sub> system. Comparison of the calculated phase diagram with the experimental data is shown in Fig. 2. It can be seen that the difference between the calculated invariant peritectic temperature and the corresponding experimental data is less than 30 °C. Moreover, the present calculated data, 1719 °C, is acceptable in the error range, since the temperature of vanadium extraction by oxygen from hot metal is about 1370 °C. Meanwhile, Fig. 2 has revealed the eutectic temperature of the invariant reaction, namely the reaction of Liquid (1mass% V<sub>2</sub>O<sub>3</sub>) → FeO + FeV<sub>2</sub>O<sub>4</sub>, occurring at 1364 °C. The calculated value is in good accordance with the corresponding experiment. Also, the DSC experimental data is reproduced by the calculated phase diagram. If the phase diagram of FeO-V<sub>2</sub>O<sub>3</sub> system requires better accuracy in the whole range, more experimental data points need to be measured by appropriate experiments of the binary system (such as electron probe X-ray microanalysis).



\* —Data in Ref. [12]; +, ◇—Data in this work.

Fig. 2 Optimized FeO-V<sub>2</sub>O<sub>3</sub> phase diagram at 100 kPa

## 6 Conclusions

The liquidus and phase relationships of FeO-V<sub>2</sub>O<sub>3</sub> system with less than 12mass% of V<sub>2</sub>O<sub>3</sub> were determined experimentally by DSC. Based on the technique of least-squares optimization, all data from lit-

erature and this work were evaluated simultaneously to obtain one set of self-consistent model coefficients for the Gibbs energies of all phases as functions of temperature and composition. The calculated phase diagram of FeO-V<sub>2</sub>O<sub>3</sub> system are considered to be most reliable currently among all the available estimates. The evaluations are valid from room temperature to temperatures even higher than the liquidus temperature. For all compounds and the liquid solutions, the present evaluations are considered to give the most reliable currently available estimates of the true values of the thermodynamic properties. The modified quasi-chemical model with small numbers of parameters was used to describe the thermodynamic properties of the binary liquid slags. The calculated phase diagram with the optimized parameters was in good agreement with the experimental data.

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