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Thermodynamic of selective reduction of laterite ore by reducing gases

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Abstract: As the sulfide ore deposits become less economical and environmental viable as a source of nickel, increasing attention is being paid to the laterite ores. But in the pyrometallurgical process of laterite, more efforts should be paid to control the reduction of iron oxide in order to get high nickel-content nickeliferous product. For these reasons, equilibrium condition of iron oxide when laterite ore was selectively reduced by CO_2/CO , H_2O/H_2 and CO_2/H_2 was studied from the perspective of iron activity with an assumption that the activities of FeO and Fe₃O₄ equal 1 in this work, and it well accounts for the inescapability of Fe metallization. Activity coefficient of iron in Ni–Fe binary solid alloy was calculated by Miedema model based on the known thermodynamics datum filed. According to Raoult's law, the relationship among the Fe/Ni ratio, reduction temperature and reduction gas composition was discussed and also compared with the experimental result. The trend of metal iron content in the reduction product of laterite ore varying with temperature and gas composition was well predicted by the calculation result. **Key words:** selective reduction; laterite ore; activity coefficient; Miedema model

1 Introduction

Nickel, one of the most important strategic metals, is widely applied to stainless steel, electroplating, catalyst and petrochemical industry [1]. In recent years, more and more attention has been paid to the research about exploitation and utilization of nickel laterite ore rather than nickel sulfide ore, due to the factors such as resources, environment, and the cost aspects [2]. By regulating the reduction condition like reduction temperature and oxygen potential in the system, most of the nickel oxides in the ore are reduced to metallic state, while the reduction of laterite ore, as explained before, plays an important role in the treatment process of laterite ore [3–6].

Reduction temperature and gas composition are two main factors which significantly affect the efficiency of the selective reduction of laterite ore [7]. And the metal Fe in the reduction production of laterite ore tends to combine with metal Ni, which is the reduction production of NiO in laterite ore, to be Fe–Ni alloy [8].

Thus, the varying activity of Fe will greatly affect the stability of iron oxide. In OLLI et al's study [9], the predominance programs for iron and its oxides in the presence of nickel when laterite ore was reduced by CO₂/CO and H₂O/H₂ mixed gas showed that the reduction of iron oxide could be affected by the variation of the activity of Fe. However, it cannot be used directly to predict the composition of nickeliferous produced from laterite due to the lack of the activity coefficient of Fe in Fe-Ni alloy. Based on their work, equilibrium conditions of iron oxide when laterite ore was selectively reduced by CO₂/CO, H₂O/H₂ and CO₂/H₂ was studied from the perspective of iron activity with an assumption that the activities of FeO and Fe₃O₄ equal 1 in this work. Activity coefficient of Fe in Fe-Ni alloy was calculated by Miedema model [10-12], which can well calculate the enthalpies of the formation of binary solid alloy based on the known thermodynamic data. Then, the relationship between the iron content in Fe-Ni alloy produced by the reduction of laterite Fe and reduction temperature as well as gas composition can be worked out by Raoult's law, when laterite ore was reduced by CO_2/CO_1 , H_2O/H_2 , CO_2/H_2 mixed gas respectively. The

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calculation result was verified by reduction experimental result of Indonesia laterite ore with CO_2/H_2 mixed gas. A good interpretation of the inescapability of Fe metallization in the selective reduction process of laterite ore can be obtained in this work.

2 Analysis process

2.1 Calculation process of relationship of gas composition, temperature and activity of Fe in Fe–Ni alloy

Reactions as follows would take place when laterite ore was reduced by H_2O/H_2 :

NiO(s)+H₂(g)=Ni(s)+H₂O(g),

$$\Delta_r G_m^{\Theta} = -13460 - 25.60T$$
 (1)

$$3Fe_2O_3(s)+H_2(g)=2Fe_3O_4(s)+H_2O(g), \Delta_r G_m^{\Theta} = -41425 - 111.42T$$
(2)

$$Fe_{3}O_{4}(s)+H_{2}(g)=3FeO(s)+H_{2}O(g),$$

$$\Delta_{r}G_{m}^{\Theta}=66105-69.16T$$
(3)

FeO(s)+H₂(g)=Fe(s)+H₂O(g), $\Delta_r G_m^{\Theta} = 17580 - 11.60T$ (4)

$$\frac{1}{4}Fe_{3}O_{4}(s)+H_{2}(g)=3/4Fe(s)+H_{2}O(g),$$

$$\Delta_{r}G_{m}^{\Theta}=29700-25.94T$$
(5)

The reduction of iron complies with stepwise reaction mechanism. If the temperature is below 570 °C, reactions were carried out by two steps: $Fe_2O_3 \rightarrow$ $Fe_3O_4 \rightarrow Fe$; otherwise, reactions were carried out by three steps: $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.

Gibbs free energies of Fe_2O_3 , Fe_3O_4 , FeO, NiO and H_2O as a function of temperature are shown in Fig. 1. In the reduction system, the difficulty of Eq. (2), Eq. (1), Eq. (3), Eq. (4), and Eq. (5) increases successively. Therefore, virtually, selective reduction of the laterite ore is to inhibit the occurrences of Eq. (3), Eq. (4) and Eq. (5).



Fig. 1 Gibbs free energy of Fe_2O_3 , Fe_3O_4 , FeO, NiO and H_2O as function of temperature

For reactions from Eq. (2) to Eq. (5), the equilibrium constant expression can be stated as follows with an assumption that the activities of FeO, Fe_3O_4 and Fe_2O_3 equal 1.

$$K_2 = \frac{p_{\rm H_2O} \cdot (a_{\rm Fe_3O_4})^2}{p_{\rm H_2} \cdot (a_{\rm Fe_2O_3})^3}$$
(6)

$$K_{3} = \frac{p_{\rm H_{2}O} \cdot (a_{\rm FeO})^{3}}{p_{\rm H_{2}} \cdot a_{\rm Fe_{3}O_{4}}}$$
(7)

$$K_{4} = \frac{p_{\rm H_{2}O} \cdot a_{\rm Fe}}{p_{\rm H_{2}} \cdot a_{\rm FeO}} = \frac{p_{\rm H_{2}O} \cdot a_{\rm Fe}}{p_{\rm H_{2}}}$$
(8)

$$K_{5} = \frac{p_{\rm H_{2}O} \cdot (a_{\rm Fe})^{3/4}}{p_{\rm H_{2}} \cdot (a_{\rm Fe_{3}O_{4}})^{1/4}} = \frac{p_{\rm H_{2}O} \cdot (a_{\rm Fe})^{3/4}}{p_{\rm H_{2}}}$$
(9)

For Eq. (8) and Eq. (9), the activity of Fe depends on the corresponding equilibrium constant and the $p_{\rm H_2O}/p_{\rm H_2}$ ratio. According to Eq. (10), the relations between the partial pressure of hydrogen, the reduction temperature and the activity of Fe can be worked out based on the value of $\Delta_{\rm r} G_{\rm m}^{\Theta}$ at different temperatures.

$$\Delta_{\rm r} G_{\rm m}^{\Theta} = -RT \ln K \tag{10}$$

There is something different in the analysis process when laterite ore was reduced by CO_2/H_2 mixed gas compared with H_2O/H_2 mixed gas and CO_2/CO mixed gas.

Reaction as Eq. (11) may take place when $\rm CO_2/H_2$ mixed gas is used to reduce the laterite ore.

$$CO_2+H_2=CO+H_2O, \ \Delta_r G_m^{\Theta}=30459-28.14T$$
 (11)

The mole fraction of H₂ in initial mixed gas was supposed to be $x(H_2)^{\Theta}$. Thus, the mole fraction of CO₂ in initial mixed gas was $[1-x(H_2)^{\Theta}]$. When the reactions were balanced, conversion amount of H₂ was supposed to be x. Then equilibrium constants can be stated as follows.

$$K = \frac{p_{\rm CO} \cdot p_{\rm H_2O}}{p_{\rm CO_2} \cdot p_{\rm H_2}} = \frac{x^2}{[1 - x({\rm H_2})^{\Theta} - x][x({\rm H_2})^{\Theta} - x]}$$
(12)

So,

$$\Delta_{\rm r} G_{\rm m}^{\Theta} = -RT \ln K = -RT \ln \frac{x^2}{[1 - x({\rm H}_2)^{\Theta} - x][x({\rm H}_2)^{\Theta} - x]}$$
(13)

$$\ln \frac{x^2}{[1-x(H_2)^{\Theta}-x][x(H_2)^{\Theta}-x]} = \frac{30459-28.14T}{-RT}$$
(14)

At the same time,

$$\frac{x(H_2O)^{e}}{x(H_2)^{e}} = \frac{x}{x(H_2)^{\Theta} - x}$$
(15)

where $x(H_2O)^e$ and $x(H_2)^e$ are the mole fractions of H_2O and H_2 when Eq. (11) is balanced, respectively. And they can be calculated by the corresponding equilibrium constant based on the known corresponding equilibrium constant value of $\Delta_r G_m^{\Theta}$ at different temperatures. The relations between $x(H_2)^{\Theta}$, reduction temperature and activity of Fe can be worked out by Eq. (14) and Eq. (15).

Actually, when laterite ore was reduced by CO_2/H_2 mixed gas, the reduction potential of this system was equivalent to the equilibrium component (including CO_2 , CO, H₂O, H₂) as the reaction of CO₂ with H₂ is balanced at a certain temperature. That is to say, the calculation method also applies to $CO_2/H_2/CO/CO_2$ mixed gas.

2.2 Calculation process of activity coefficient of iron in Ni-Fe binary solid alloy

Due to its convenience and the high consistence of calculation result, Miedema model was widely used for thermodynamic calculation of binary alloy. Based on the known parameter of Miedema model, activity coefficient of iron in Ni–Fe binary solid alloy was calculated in this work.

The calculation expression of heat of formation of A–B binary alloy by Miedema model is [10–12]

$$\Delta H_{AB} = f_{AB} \{ x_A [1 + \mu_A x_B (\phi_A - \phi_B)] x_B [1 + \mu_B x_A \cdot (\phi_B - \phi_A)] \} / \{ x_A V_A^{2/3} [1 + \mu_A x_A (\phi_A - \phi_B)] x_B V_B^{2/3} \cdot [1 + \mu_B x_B (\phi_B - \phi_A)] \}$$
(16)

$$f_{\rm AB} = \frac{2pV_{\rm A}^{2/3}V_{\rm B}^{2/3}[p(\Delta n_{\rm WS}^{1/3})^2/q - (\Delta\phi)^2 - \alpha(r/p)]}{(n_{\rm WSA}^{1/3})^{-1} + (n_{\rm WSB}^{1/3})^{-1}}$$
(17)

where the x_A and x_B are the molar fractions of A and B; V_A and V_B are the molar volumes of A and B; n_{WSA} and n_{WSB} are the electron densities of A and B in electrons per (0.529 Å)³; $\Delta \phi (\phi_A - \phi_B)$ is the electro-negativity difference of A and B; p, q, r, μ , α are empirical constants.

For Ni–Fe binary solid alloy, p/q=9.4, $\alpha=1$, r/p=1, p=10.6. And the relations among the partial molar excess free energy (G_{AB}^{E}), the excess entropy (S_{AB}^{E}), the enthalpy change (ΔH_{AB}) and the activity coefficient (γ) can be described by equations as follows [13]:

$$\overline{G}_{\rm A}^{\rm E} = RT \ln \gamma_{\rm A} \tag{18}$$

$$\overline{G}_{A}^{E} = G_{AB}^{E} + (1 - x_{A}) \frac{\partial G_{AB}^{E}}{\partial x_{A}}$$
(19)

$$G_{AB}^{E} = [1 - 0.1 \times (1/T_{m(A)} + 1/T_{m(B)})] \times \Delta H_{AB}$$
(20)

where $T_{m(A)}$ and $T_{m(B)}$ are melting points in Kelvin of pure elements A and B, respectively. From Eq. (16) to Eq. (20), activity coefficient of iron in Ni–Fe binary

solid alloy can be calculated by expression as follows [14]:

$$\ln \gamma_{\rm Fe} = \frac{\left[1 - 0.1T(1/T_{\rm m(Fe)} + 1/T_{\rm m(Ni)})\right]\Delta H_{\rm AB}}{RT} \{1 + (1 - x_{\rm Fe}) \cdot \frac{1}{x_{\rm Fe}} - \frac{1}{1 - x_{\rm Fe}} - \frac{\mu_{\rm Fe}(\phi_{\rm Fe} - \phi_{\rm Ni})}{1 + \mu_{\rm Fe}(1 - x_{\rm Fe})(\phi_{\rm Fe} - \phi_{\rm Ni})} + \frac{\mu_{\rm Ni}(\phi_{\rm Ni} - \phi_{\rm Fe})}{1 + \mu_{\rm Ni}x_{\rm Fe}(\phi_{\rm Ni} - \phi_{\rm Fe})} \{V_{\rm Fe}^{2/3}[1 + \mu_{\rm Fe}(1 - 2x_{\rm Fe}) \cdot (\phi_{\rm Fe} - \phi_{\rm Ni})] + V_{\rm Ni}^{2/3}[-1 + \mu_{\rm Ni}(1 - 2x_{\rm Fe})(\phi_{\rm Ni} - \phi_{\rm Fe})]\}\}/ \{x_{\rm Fe}V_{\rm Fe}^{2/3}[1 + x_{\rm Fe}(1 - x_{\rm Fe})(\phi_{\rm Fe} - \phi_{\rm Ni})] + (1 - x_{\rm Ni})V_{\rm Ni}^{2/3}[1 + \mu_{\rm Ni}x_{\rm Fe}(\phi_{\rm Ni} - \phi_{\rm Fe})]\}\}$$
(21)

The relevant parameters are shown in Table 1.

 Table 1 Relevant physical parameters used in calculation

 process of activity coefficient of Ni–Fe binary solid alloy [15]

Element	V	ϕ	$(n_{\rm WSi})^{1/3}$	T _m /K	μ
Fe	7.1	1.64	3.69	1808.15	0.04
Ni	6.6	1.75	4.25	1726.15	0.10

Activity coefficient of iron in Ni–Fe binary solid alloy at different temperatures and different contents of metal Fe can be worked out by combining Eq. (16), Eq. (17), and Eq. (21) together. By setting pure substance as standard state, and combining the activity coefficient expression of iron and the relationship among reduction temperature, reducing gas partial pressure and activity of iron together, relations among reduction temperature, reducing gas partial pressure and metal iron content in reduction product of laterite ore can be worked out.

3 Calculation result and discussion

The partial calculation results of iron activity coefficient by Miedema model are shown in Table 2. And they are consistent with the characteristics of Fe–Ni system, which can be considered to be the approximate ideal solution [16].

The relations among reduction temperature, initial reducing gas partial pressure and metal iron content in reduction product of laterite ore are shown in Figs. 2–4 when the initial mixed gas was CO_2/CO , H_2O/H_2 , CO_2/H_2 , respectively.

In the equilibrium diagram of iron oxide in reduction condition, the activity of Fe is 1, and the whole area is divided to Fe zone, Fe_3O_4 zone, FeO zone by curves *ab*, *bc*, and *bd*, which are the critical lines of transformation from Fe_3O_4 to Fe, Fe_3O_4 to FeO, and FeO to Fe, respectively. As the formation of Fe–Ni alloy when laterite is reduced by CO_2/CO , H_2O/H_2 and CO_2/H_2 , the activity of Fe will vary with the alloy composition and temperature. At the same time, three zones become

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Mole fraction of Fe in	Iron activity coefficient								
Fe-Ni alloy/%	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C		
1	0.6757	0.7078	0.7336	0.7546	0.7721	0.7869	0.7995		
11	0.9721	0.9754	0.9779	0.9799	0.9815	0.9828	0.9840		
21	0.9886	0.9899	0.9910	0.9918	0.9924	0.9930	0.9935		
31	0.9942	0.9949	0.9954	0.9958	0.9961	0.9964	0.9966		
41	0.9968	0.9972	0.9975	0.9977	0.9979	0.9980	0.9982		
51	0.9982	0.9984	0.9986	0.9987	0.9988	0.9989	0.9990		
61	0.9991	0.9992	0.9992	0.9993	0.9994	0.9994	0.9994		
71	0.9995	0.9996	0.9996	0.9997	0.9997	0.9997	0.9997		
81	0.9998	0.9998	0.9998	0.9998	0.9998	0.9999	0.9999		
91	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999		
99	1	1	1	1	1	1	1		

Table 2 Partial calculation results of iron activity coefficient



Fig. 2 Relations of reduction temperature, initial reducing gas partial pressure and metal iron content in product of laterite ore reduced by CO_2/CO mixed gas



Fig. 3 Relations of reduction temperature, initial reducing gas partial pressure and metal iron content in product of laterite ore reduced by H_2O/H_2 mixed gas

the stable zones of $[Fe,Ni]_{ss}$ (zone *A*), $Fe_3O_4+[Fe,Ni]_{ss}$ (zone *B*), and $FeO+[Fe,Ni]_{ss}$ (zone *C*). As shown in Fig.

2 to Fig. 4, when the activity of Fe is reduced from 1 to 0.2, the positions of curves ab and bc will be down to be curve $a_{0.2}b_{0.2}$ and $b_{0.2}c_{0.2}$, and the area of zone A increases while the areas of zone B and zone C decrease accordingly. That also means the iron oxide will be unstable because of the reduction of Fe activity.



Fig. 4 Relations of reduction temperature, initial reducing gas partial pressure and metal iron content in product of laterite ore reduced by CO_2/H_2 mixed gas

When Figs. 2–4 are compared with each other, some visible differences could be found when laterite is selectively reduced by CO₂/CO, H₂O/H₂, CO₂/H₂. The area of zone *A* in Fig. 3 is smaller than the others, and the position of curve a_xb_x (0 < x <1) in Fig. 3 is the highest in the three figures at temperature below 810 °C. That means H₂O/H₂ mixed gas has the best selective ability to reduce the laterite ore at temperature below 810 °C, but the worst selective ability at temperature above 810 °C. Besides, in Fig. 2, the content of Fe in Fe–Ni alloy (*x*(Fe_{[Ni,Fe]ss})) increases with the rising of the reduction temperature, especially in zone *C*. But in Fig. 3, the $x(Fe_{[Ni,Fe]ss})$ decreases obviously with the rising of the reduction temperature. For the case of that laterite is reduced by CO₂/H₂, the $x(Fe_{[Ni,Fe]ss})$ is not sharply affected by the reduction temperature, especially in zone *C*. A resemblance is that the $x(Fe_{[Ni,Fe]ss})$ increases obviously with the increase of the partial pressure of reduction gas.

In general, as the formation of Fe–Ni alloy, the activity of Fe varies with the $x(Fe_{[Ni,Fe]ss})$, and it is feasible in thermodynamic for iron oxide to be reduced to metal Fe, which will be combined with metal Ni to be Fe–Ni alloy. Thus, the activity of Fe increases, and the reduction of iron oxide becomes more difficult, while the activity of Ni decreases, and it is easier for the reduction of nickel oxide. Therefore, the reduction of iron oxide and nickel oxide is a mutually reinforcing process. In order to obtain a low-Fe Fe–Ni alloy product at low temperature, in contrast, H_2O/H_2 mixed gas would be the best reduction gas in this thermodynamic analysis.

Laterite ore from Indonesia was selectively reduced by CO_2/H_2 mixed gas with different CO_2/H_2 ratios at different temperatures for 1 h. The raw ore was broken, ground to 180 µm, thoroughly incorporated, and then calcined at 700 °C for 2 h before reduction. The reduction was carried out in a tube furnace shown in Fig. 5. About 1 g samples in a corundum crucible were roasted at 500, 600, 700, 800 and 900 °C respectively for 1 h with a fixed CO_2/H_2 ratio. Ni metallization ratios were detected by inductively coupled plasma atomic emission spectrometry after bromine-methanol extraction, and Fe metallization ratios were determined through titrating by potassium dichromate solution after ferric trichloride solution extraction. And the experimental result is shown in Fig. 6.

The experimental result shows that the Fe content in Fe–Ni alloy increases with the rising of the partial pressure of H_2 , and it is consistent with the calculation result described before. For low temperature such as 500–600 °C, the content of Fe in Fe–Ni alloy is not

affected by the partial pressure of H₂, it is perhaps because 1 h is not enough for CO_2/H_2 mixed gas to bring out all its reduction potential at relative low temperature. For reduction temperature of 800 °C, the content of Fe in Fe–Ni alloy increases with the rising CO_2/H_2 ratio, the experimental result value of content of Fe in Fe–Ni alloy is higher with a CO_2/H_2 ratio no less than 1, but lower with a CO_2/H_2 ratio less than 1, when it is compared with the calculation result. Three reasons could be used to account for this phenomenon.

1) The metal products of this reduction reaction are not only Fe and Ni, but also Co. And metal Co is easy to combine with metal Fe and metal Ni to be alloy. But in this calculation work, the effect of Co was not taken into account.

2) The reactions of laterite's selective reduction complies with the rule of gas-solid reaction, the diffusion of metallic element is a critical factor for the formation of the alloy, and it also has a great influence on the alloy composition.

3) The reduction time of 1 h may be not enough for the mixed gas to bring out all its reduction potential, thus lead to this deviation.

It is worth mentioning that at the beginning of the calculation, the activities of FeO, Fe₃O₄ and Fe₂O₃ were assumed to be 1. But in fact, the activities of FeO, Fe₃O₄ and Fe₂O₃ may change with the varying reduction potential. When laterite ore is reduced at temperature above 570 °C, the reduction of FeO, actually, is the reduction of wusitite (Fe_xO). Fe_xO could be considered as solid solution, which is the production of Fe₃O₄ dissolved into FeO. Thus, the activity of FeO would change with the varying of wusitite composition. When laterite ore is selectively reduced by reducing agent with a certain reduction potential, the smaller the FeO activity is, the more difficult the reduction of wusitite to Fe would be. This variation reflected in Fig. 2 to Fig. 4 is that the position of curve $a_x b_x c_x$ (0 < x <1) would rise in some degrees.





Fig. 6 Experimental result of laterite ore reduced by $\rm CO_2/H_2$ mixed gas

4 Conclusions

1) The reduction of iron oxide and nickel oxide is mutually reinforcing process.

2) The trend of the content of Fe in Fe–Ni alloy varying with the partial pressure of H_2 in experiment is well predicted by the calculation result.

3) In order to better predict the relations of reduction temperature, initial reducing gas partial pressure and metal iron content in reduction product of laterite, more factors such as the variation of FeO activity, the effect of Co and the diffusion of metal element, should be taken into consideration.

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气体选择性还原红土镍矿的热力学

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摘 要:由于硫化镍矿生产镍铁在经济和环境上不断出现的问题,采用红土镍矿生产镍铁越来越受到重视。但是 红土镍矿制备镍铁的火法工艺中,在提高铁镍产品中的镍含量方面的理论研究仍存在许多不足。出于这方面的考 虑,假设 Fe₂O₃、FeO 和 Fe₃O₄的活度为 1,计算了 CO₂/CO、H₂O/H₂和 CO₂/H₂三种气氛下选择性还原红土镍矿 时,不同铁活度下铁--铁氧化物的平衡条件。从已有的热力学数据出发,利用 Miedema 二元合金生成热模型,计 算了 Ni-Fe 固态二元合金中铁的活度系数。并以活度系数为纽带,最终计算出这三种还原气氛下,镍铁合金产物 中的铁含量与还原气体分压、还原温度的关系。并用 CO₂/H₂ 还原红土镍矿,得到的实验数据与理论值进行了对 比分析与讨论,热力学计算结果很好地解释了选择性还原红土镍矿时铁金属化无法避免的原因,并较好地预测了 红土镍矿还原产物中铁含量随温度和气体组分的变化趋势。

关键词:选择性还原;红土镍矿;活度系数;Miedema 模型