REDUCTION OF Fe AND Ni IN Fe-Ni-O SYSTEMS

Y. Zhanga, W. Weia,*, X. Yanga, F. Wei

*State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

(Received 08 February 2012; accepted 22 October 2012)

Abstract

The reduction behaviors of Fe-Ni-O compounds/systems (NiO, Fe₂O₃, NiFe₂O₄, Fe₂O₃+ NiO and Fe₂O₃+ Ni) were studied using H₂ and activated carbon C as reducing agents, and the mechanism of NiFe₂O₄ reduction was analyzed. With H₂ as reductant, these systems showed lower starting reaction temperatures and lower reaction rates. The differences of reaction rates among the different samples were small compared to those using C as reductant. With C as reductant, the reduction of the Fe₂O₃+ NiO system was much more facile compared to NiFe₂O₄, Fe₂O₃+ Ni, and pure Fe₂O₃. The heat released from the initial reduction of NiO by CO led to a higher temperature, which was more favorable for the further reduction of the Fe₂O₃+ NiO system. In both cases, NiFe₂O₄ appeared to be more difficult to reduce, as it required a higher starting temperature and exhibited a lower reaction rate and lower final reduction degree. Additionally, the data suggested that with increasing temperature, the products for the reduction of NiFe₂O₄ appeared in the order NiFe₂O₄ → Fe₃O₄+ NiO → Fe₃O₄+ Ni → FeO + FexNiy → FexNiy + Fe (Fe₇C₃). Based on this data, kinetic information about the H₂ reduction for the five compounds/systems, such as apparent activation energy and reaction mechanism, was obtained.

Keywords: Fe-Ni-O system; H₂; Activated carbon; Reduction behavior; Kinetics.

1. Introduction

In recent years, the stainless steel industry has developed rapidly in China, and as a consequence, a large amount of stainless steel dust has been generated. Generally, 18–30 kg·t⁻¹ (steel) dust is produced during the stainless steel-making process, in which the contents of Fe, Cr and Ni are 40–60%, 8–15% and 3–9%, respectively [1–3]. High-grade Ni/Cr-bearing resources are very expensive. Based on the current conditions for stainless steel production in China, a rough estimate showed that raw material costs constituted nearly half of the total cost. Therefore, the effective recovery of Ni/Cr from the dust is of great importance. On the other hand, generally in Ni-bearing ores such as laterite, Ni is also coexisted with Fe (the total Fe (%) in laterite is about 30% [4]). In order to effectively utilize such kinds of resources, a better understanding of the reduction behaviors of Ni-Fe-O systems and their interactive influence is necessary.

The non-isothermal hydrogen reduction of nickel oxide, synthesized by the sol-gel procedure, was investigated by Jankovic [5]. The apparent activation energy E_a was 90.8 kJ·mol⁻¹, the logarithm of the frequency factor was 19.5 min⁻¹, and the kinetic equation was f(α) = αⁿ⁺¹(1−α)ⁿ, in which α was the reduction degree. Sharma et al. [6–7] investigated the interaction of micron-sized nickel oxide particles with pieces of stress-recrystallized pyrolytic graphite between 950 and 1000°C. Microscopic results suggested that reaction took place only at activated sites, and the nickel produced in the reduction reaction coated the NiO with a sintered layer.

With both H₂ and activated carbon (C) as reductants, previous investigations [8–11] have shown that the reaction path for Fe₂O₃ was as follows: Fe₂O₃ → Fe₃O₄ → FeO → Fe, according to the theory of Gradual Deoxidizing. Morphological study confirmed the formation of a compact iron layer during the reduction of Fe₂O₃ by H₂ at temperatures higher than 420°C [8]. A study in which NiFe₂O₄ was prepared at 1000–1200°C and reduced by hydrogen at 900–1100°C [12] reported an incomplete reduction (about 80%), which was attributed to the formation of a dense metallic layer (Fe₇Ni₃) surrounding the wustite layer which prevented the further diffusion of the reduction gas. The data suggested that at temperatures between 1000 and 1100°C, the initial NiFe₂O₄ reduction rate was mix-controlled by gaseous diffusion and interfacial chemical reaction, while in the final stage, the interfacial chemical reaction was

* Corresponding author: weiwjenie_99@163.com
DOI:10.2298/JMMB120208038Z

Journal of Mining and Metallurgy, Section B: Metallurgy
the rate-controlling step. At 1200°C, the initial rate-controlling step was the interfacial chemical reaction, while solid-state diffusion was the rate-controlling step in the final stages.

In this paper, the reduction behaviors of five oxide systems (NiO, Fe₂O₃, Fe₃O₄, Fe₂O₃ + NiO and Fe₂O₃ + Ni) were studied using H₂ and C as reducing agents. The mechanism of NiFe₂O₄ reduction (the primary form of Ni in stainless steel dust [13]) and the products obtained at different temperatures were analyzed with the aid of X-ray diffractometry (XRD). Based on the experimental data, kinetic information, such as activation energy and reaction mechanism, was obtained.

2. Experimental

2.1 Materials

NiO, Fe₂O₃, Ni and activated carbon powder were employed in the experiments. The purities of these materials are AR. H₂ (99%) and activated carbon powder (C) were used as reductants. Ceramic crucibles, which were outfitted with the thermal analyzers, were used in non-isothermal experiments, and alumina crucibles were used in isothermal experiments. NiFe₂O₄ was prepared by heating a mixture of NiO and Fe₂O₃ (molar ratio 1:1) at 900°C for 8 h in a resistance furnace. XRD patterns of the product agreed well with the referred one, and are shown in Fig. 1. The results strongly suggested that high purity NiFe₂O₄ was obtained, which was used in the subsequent experiments.

2.2 Apparatus

For reductions using C, non-isothermal tests were carried out in a different integrated thermal analyzer (STA409C, NETZSCH Scientific Instruments, Germany). And for reductions with H₂, non-isothermal reduction tests were carried out in an integrated thermal analyzer (HTC-2, Beijing Hengjiu Instrument Ltd., China).

In order to obtain detailed information about the reaction mechanism of NiFe₂O₄ reduction, isothermal experiments were performed at five operating temperatures (450, 500, 550, 600 and 700°C) in a resistance furnace (shown as Fig.2, made by Baotou Agile Furnace, China).

2.3 Experiment program

Experiment program are shown in Table 1 and 2. The molar ratio of elements of Fe and Ni in these complex sample is always 2:1. In experiments for reduction with C, C content is 30% and the protective atmosphere is Ar with flow of 30ml/min. In TG experiments for reduction with H₂, the flow of H₂ is 40ml/min. For isothermal experiments, the reduction atmosphere are H₂ (1L/min) and N₂ (2L/min).

The values of heating rates in experiments are in the range of normal heating rate of the instruments. Therefore, there is no influence of the heating rate on reduction temperatures.

2.4 Analysis

2.4.1 Reduction degree

The reduction degree (α) of the sample reduced by H₂ and C can be expressed as Eq.(1) and (2), respectively. And, in the case of using C the formation of CO₂ was ignored.

\[
\alpha = \frac{m_i - m_t}{m_i - m_{CO_2}} \quad (1)
\]

\[
\alpha = \frac{16(m_i - m_t)}{28m_{CO_2}} \quad (2)
\]

where, \(\alpha\) is the reduction degree (%); \(m_i\) is the initial mass of the sample (mg); \(m_t\) is an actual mass...
at time $t$ (mg); and $m_o$ is the total content of oxygen in the initial sample (mg).

### 2.4.2 Activation energy and reaction mechanism

The apparent activation energy of the reduction process under non-isothermal conditions can be calculated by the Kissinger-Akahira-Sunose (KAS) method [4], which follows from the logarithmic form of Eq. (3):  

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{RT}$$  \hspace{1cm} (3)

where, $\beta$, $T$, and $A$ represent the heating rate (K min$^{-1}$), temperature (K), and frequency factor (s$^{-1}$), respectively; $R$, $E_a$, and $g(\alpha)$ are the gas constant (8.314 J (mol·K$^{-1}$)), activation energy (J mol$^{-1}$), and the integral form of the reaction model, respectively. $E_a$ could be calculated by iso-conversational method.

If the integral form of the mechanism shows a linear relationship with time based on the experimental data, then the corresponding function would be the rate-controlling mechanism.

### 3. Results and Discussion

#### 3.1 Differences with $H_2$ and $C$ as reductants

The curves obtained from thermogravimetry (TG) tests for the three systems (NiFe$_2$O$_4$, Fe$_2$O$_3$ + NiO and Fe$_2$O$_3$ + Ni), including reduction degrees and instantaneous rates with temperature increases, are shown in Figs. 3–5. $T_i$ and $T_f$ represent the extrapolated initial and final temperatures, respectively. Several peaks appear in instantaneous

![Figure 3. Evolution of reduction degree and instantaneous rate vs. temperature for NiFe$_2$O$_4$](image3.png)

![Figure 4. Evolution of reduction degree and instantaneous rate vs. temperature for Fe$_2$O$_3$ + NiO](image4.png)
rate curve.

The data in Figs. 3-5 suggested that reduction in these three systems could be enhanced by H₂, as compared to C. The H₂ reduction temperatures were much lower. For example, the Tₚ for NiO, Fe₂O₃ and NiFe₂O₄ reduced by H₂ were 602, 520 and 513°C, respectively, while Tₚ for those reductions using C were 783, 1017 and 1000°C, respectively. Moreover, higher reduction degrees were obtained when using H₂. The reduction degrees of all three oxide systems reduced by H₂ reached 100%, while those of NiFe₂O₄ and Fe₂O₃ + NiO reduced by C were 92.1 and 99.2%, respectively. A possible explanation for this lower relative reduction degree could be that the solid-solid reaction took place only at activated sites, while the metal produced in the reduction reaction covered the unreacted oxide with a sintered layer, resulting in less favorable conditions for kinetic control of the reaction [5–6, 9]. Furthermore, the differences in the reaction rates among the three systems were much smaller in the case of H₂ compared with that of C. The maximum reaction rates for Fe₂O₃ + NiO and Fe₂O₃ + Ni with C were 57.9 and 30.0%·min⁻¹, which were much higher than the rates of 9.7 and 13.6%·min⁻¹ obtained with H₂, respectively. This could be due to the higher temperature at which the reduction by C was performed.

3.2 Differences among the five systems

The reduction curves (heating rate: 10°C·min⁻¹) for the five systems reduced by C and H₂ are shown in Fig.6 and Fig.7, respectively. The reduction degrees and reaction rates for the five systems showed variable dependence on temperature.

With C as reductant (Fig.6), the release of Ni from NiFe₂O₄ was more difficult than from NiO, while the reduction of Fe from NiFe₂O₄ was easier than from Fe₂O₃. For the three mixed Fe and Ni systems (Fe₂O₃ + NiO, Fe₂O₃ + Ni and NiFe₂O₄), Fe₂O₃ + NiO was obviously the most easily reduced, with the lowest

![Figure 5. Evolution of reduction degree and instantaneous rate vs. temperature for Fe₂O₃ + Ni](image)

![Figure 6. Reduction degree (a) and rate curves (b) for the five systems by C.](image)

![Figure 7. Reduction degree (a) and rate curves (b) for the five systems by H₂.](image)
The degree of Fe₂O₃ + Cr₂O₃ was much higher than that of the same conditions (1550°C, 1 h), the total reduction C as reductant by Wei [13], it was observed that under revealing that this effect does not predominate.

NiFe₂O₄ samples may be attributed to the formation of for lower final reduction degree in both of NiO and difficult to be reduced. Another possible explanation temperature increases, a rough reduction process of for promoting the reduction of Cr in the later stage. Additionally, Fig.6 suggested that compared with FeO, + NiO and Fe₂O₃ + Ni, both of the final reduction degree and reaction rate of NiFe₂O₄ is much lower, suggesting that NiFe₂O₄ is the most difficult to be reduced. Another possible explanation for lower final reduction degree in both of NiO and NiFe₂O₄ samples may be attributed to the formation of a dense metallic layer (Ni/FeNi₃) coating the unreacted layer which kinetically limited the further reaction, as previously reported by literature [6, 7, 10].

On the other hand, in the case of H₂ as reductant (Fig.7), both of the final reduction degree and the temperature corresponding to the maximum reduction rate showed extremely small difference among the three Fe-Ni-O system: FeO + Ni, Fe₂O₃ + NiO and NiFe₂O₄. And the temperature corresponding to the maximum reaction rate of the three Fe-Ni-O system (Fig.7b) slightly decreased in the order: NiFe₂O₄ > Fe₂O₃ + NiO > Fe₂O₃ + Ni. It tends to suggested that Fe in the Fe₂O₃ + Ni system appeared to be more easily reduced than from NiO + Fe₂O₃ system, which may be explained by the reaction of NiO + H₂ is endothermic. Anyway, compared with the case of using C as reductant, the difference among different samples is much smaller.

3.3 Discuss on the reduction process of NiFe₂O₄

Further studies were carried out to understand the process of NiFe₂O₄ reduction. Fig. 8(a) and (b) show the XRD (M21X super power X-ray diffraction made by Mac Science of Japan) patterns of the products obtained at different temperatures by using of C and H₂ as reductants, respectively.

As shown in Fig.8(a), in the reduction of NiFe₂O₄ by C, FeO and a single Ni substance were the first products at 895°C, and the corresponding reduction degree was 18.6%; At 938°C, Fe₂O₃ and Ni had disappeared, and FeO and Fe-Ni alloy (mainly in the form of FeNi₅) were present; At 1100°C, the oxides were completely reduced, and the main products were Fe-Ni alloy and iron carbide.

In the case of H₂ as reductant (Fig.8(b)), FeO was the first reduction product. Then, Ni was gradually released with increasing temperature, and combined with the produced Fe to form different Fe-Ni alloys.

There were two differences between the reduction processes of NiFe₂O₄ by H₂ and C. First, FeO was absent during reduction process by H₂, which is attributable to the low reduction temperature. Second, the form of Fe-Ni alloy was also different (for example, using C as reductant FeNi₃ was observed, while in the case of H₂ Fe₅₆Ni₃₄ was present). One reason was the change in reduction temperature, and the other was the different Fe/Ni mass ratio due to the formation of iron carbide.

Both of these data suggested that in the reduction process of NiFe₂O₄, FeO is the first reduction product, followed by the reduction of Ni. With the temperature increases, a rough reduction process of NiFe₂O₄ by H₂ and C is NiFe₂O₄ → FeO + NiO → FeO + Ni → FeO + FeNi₅ → FeNi₅ + Fe (or Fe₃C). Under the given experimental conditions, this tends to suggest that when using carbon as reductant, metallic Ni could be obtained below 895°C.

3.4 Activation energy for H₂ reduction

Based on the experimental data by using H₂ as reductant, the relationships between ln(β / T²) and 1/T, as well as reaction mechanism diagrams for the four systems (NiO, Fe₂O₃, NiFe₂O₄ and Fe₂O₃ + NiO), are showed in Figs. 9-12, respectively.

The kinetic information for these compounds / systems is summarized in Table 3. The Eₐ of 87.8 kJ mol⁻¹ of NiO(Fig 9a) was calculated. This value was close to that obtained by Jankovic [5]. And the powder particles used in this experiment had good permeability, and the integral form of the mechanism of NiO was F(α) = −(1−α)¹¹ [4] (Fig. 9b). Therefore, the rate-controlling step was a phase-boundary-controlled reaction.

At the first Fe₂O₃ reduction stage, the Eₐ of 185.1 kJ mol⁻¹ was obtained (Fig. 10a), which is larger than the value published by Wang et al. [16]. Both the heating rate and reductive degree values used to
Figure 8. XRD results: (a: C; b: H2) (1: NiFe2O4; 2: C; 3: Fe2O3; 4: NiO; 5: Fe3O4; 6: Ni; 7: (Fe, Ni); 8: Fe0.64Ni0.36; 9: FeNi3; 10: FeO; 11: Fe; 12: Fe5C2)

Figure 9. Arrhenius diagrams (a) and reaction mechanism (b) for NiO

Table 3. Reaction parameters and mechanisms of oxide reduction with H2

<table>
<thead>
<tr>
<th>Process</th>
<th>Activation energy (kJ·min⁻¹)</th>
<th>Published activation energy (kJ·min⁻¹)</th>
<th>The integral form of reaction mechanism</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO → Ni</td>
<td>87.8</td>
<td>90.8 [4]</td>
<td>1−(1−α)³/₃</td>
<td>phase-boundary reaction.</td>
</tr>
<tr>
<td>Fe2O3 → Fe3O4</td>
<td>185.1</td>
<td>107 [13]</td>
<td>1−(1−α)³/₃</td>
<td>phase-boundary reaction</td>
</tr>
<tr>
<td>Fe3O4 → Fe</td>
<td>53.8</td>
<td>54 [14]</td>
<td>−ln[(1−α)]⁴</td>
<td>4D formation and growth of nuclei</td>
</tr>
<tr>
<td>NiFe2O4 → FeNi</td>
<td>69.4</td>
<td>62.6 [11]</td>
<td>ln[α / (1−α)]</td>
<td>autocatalytic reaction</td>
</tr>
<tr>
<td>Fe2O3 + NiO → FeNi</td>
<td>71.3</td>
<td></td>
<td>1−(1−α)³/₃</td>
<td>phase-boundary reaction and autocatalytic reaction</td>
</tr>
</tbody>
</table>
calculate $E_a$ in this paper were small. Therefore, the temperature corresponding to $\alpha$ was relatively low, and the activation energy would be high. Fig. 10b shows the average activation energy was 53.8 kJ mol$^{-1}$ in the later stage, which was nearly same as the values obtained by Tiernan (54 kJ mol$^{-1}$) [14]. As shown in Fig. 10c, the integral form of the mechanism was $F(\alpha) = 1 - (1-\alpha)^{1/3}$, and the rate-controlling step was a phase-boundary reaction at the first reduction stage of Fe$_2$O$_3$. For the second stage, the integral form of the mechanism was $F(\alpha) = [\ln(1-\alpha)]^{1/4}$ [14], and the rate-controlling step was the 4D formation and growth of nuclei. The phase-boundary reaction and the formation and growth of nuclei controlled the reduction reaction of Fe$_2$O$_3$.

The same two kinetic parameters of NiFe$_2$O$_4$ could be obtained from Fig. 11. The $E_a$ was 69.4 kJ mol$^{-1}$, which was similar to the value reported in literature [12] (62.6 kJ mol$^{-1}$). Good reactivity of powder particles indicates that there is not an obvious boundary between the two stages [12]. The results of tests performed using the resistance furnace and TG prove that the formation of the Fe-Ni alloy was favorable in the reduction reaction. And the integral form of the mechanism was $F(\alpha) = \ln(\frac{\alpha}{1-\alpha})$ [11], so the reaction of NiFe$_2$O$_4$ with H$_2$ was an autocatalytic process.

From Fig. 12, the integral form of the mechanism was $F(\alpha) = 1 - (1-\alpha)/3$ at the initial stage. This illustrated that the phase-boundary reaction was the rate-controlling step for the reduction of Fe$_2$O$_3$ + NiO.

At the later stage, the form was $F(\alpha) = \ln(\frac{\alpha}{1-\alpha})$ and the reaction was autocatalytic.
4. Conclusions

According to the results in this paper, the following conclusions were obtained:

Compared the case of using H$_2$ as reductant, all of the five Fe-Ni-O systems showed higher starting reaction temperatures and larger reaction rates during their reductions by C. And, the differences on reduction behaviors by C among these five Fe-Ni-O systems are much larger than using H$_2$ as reductant.

In the case of C as reductant, the reduction of Fe$_2$O$_3$ + NiO system was much easier compared to NiFe$_2$O$_4$, Fe$_2$O$_3$ + Ni, and pure Fe$_2$O$_3$. A possible reason is that the heat released from the initial reduction of NiO by CO leads to a higher temperature and better kinetic conditions. In both cases, NiFe$_2$O$_4$ appeared more difficult to be reduced because it required a higher starting temperature, exhibited a lower reaction rate and lower final reduction degree.

The experimental data suggested that, with increasing temperature, the products for the reduction of NiFe$_2$O$_4$ appeared in the order NiFe$_2$O$_4$ → Fe$_3$O$_4$ + Ni → FeO + Fe$_2$Ni$_3$ → Fe$_3$Ni$_2$ + Fe (or Fe$_{m-n}$).

From the results of the TG experiments, the activation energies of NiO and NiFe$_2$O$_4$ were 87.8 kJ mol$^{-1}$ and 69.4 kJ mol$^{-1}$, and the phase-boundary reaction and autocatalytic reaction were the rate-controlling mechanisms, respectively. The reduction path for Fe$_3$O$_4$ can be expressed as: Fe$_3$O$_4$ → Fe$_2$O$_3$ → Fe. The activation energies were 185.1 kJ mol$^{-1}$ and 53.8 kJ mol$^{-1}$, and the initial rate-controlling step was the phase-boundary reaction, while the 4D formation and growth of nuclei was rate-controlling at the final stage; The activation energy of Fe$_3$O$_4$ + NiO was 71.3 kJ mol$^{-1}$, and the rate-controlling mechanisms were the phase-boundary reaction and the autocatalytic reaction.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No.51074025) and the Fundamental Research Funds for the Central Universities (FRF-SD-12-009A).

References