

Products of carbothermic reduction of Fe–Cr–O and Fe–Cr–Ni–O systems

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Abstract: The reduction behaviors and characteristics of products of the Fe–Cr–O system (FeCr_2O_4 and $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$) and Fe–Cr–Ni–O system ($\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}$) under various conditions were studied. The results show that more Fe–Cr or Fe–Cr–Ni solution and less residual carbon content were obtained at higher temperatures and lower initial molar ratio of C to O ($n_{\text{C}}:n_{\text{O}}$). The degree of reduction was highly dependent on both time and temperature, and the residual carbon content greatly increased with increasing $n_{\text{C}}:n_{\text{O}}$ at each temperature. The products generated during the carbothermic reduction of the Fe–Cr–O system were examined using X-ray diffraction (XRD). A scanning electron microscope (SEM) coupled with energy dispersive spectrometer was used to observe the microstructure and the distribution of elements in the various phases of the final reduction products of the Fe–Cr–O and Fe–Cr–Ni–O.

Key words: Fe–Cr–O system; Fe–Cr–Ni–O system; reduction product; element distribution; residual carbon content

1 Introduction

The Fe–Cr–O and Fe–Cr–Ni–O systems are widespread in byproducts such as dust, slag, and pickling sludge when stainless steel is produced. Previous studies [1,2] have shown that 18–33 kg/t of steel dust is generally produced during the production of stainless steel, and the dust has been clearly classified as a hazardous material due to its high levels of leaching toxic elements such as Cd and Pb [3,4]. However, recovering such byproducts is of great value because they contain high concentrations of metals, especially giving the increasing scarcity of mineral resources. Further, investigations [3,5,6] on the characteristics of the dust generated during the production of stainless steel suggest that such metals coexist mainly as metal oxide. Therefore, it is essential to understand the reduction behaviors of such multi-metal systems and the mechanisms of the interactions of the metals with each other in order to effectively maximize the recovery of the metals.

Many studies have been conducted on the reduction of single metal oxides such as Fe_2O_3 , Cr_2O_3 , and NiO with carbon, hydrogen, or some other reductants.

However, the data available are limited on the reduction of mixtures of Fe, Cr, and Ni oxides coexisting in a single system, especially data available on the residual contents of impurities such as carbon and the mechanisms of the interactions between the oxides and the characteristics of possible end products.

KHEDR [7] and WEI et al [8] studied the H_2 reduction of Fe–Cr–O and Fe–Ni–O systems and suggested that the existence of Cr/Ni significantly affected the rate of Fe_2O_3 reduction. TAKANO et al [9] studied the carbothermic reduction of chromites (i.e. coexisting iron and chromium oxides) in self-reducing agglomerates and discussed the possible rate controlling step. CHAKRABORTY et al [10] investigated the carbothermal reduction of chromite ores and found that the iron in the ores was almost completely reduced before the chromium began to reduce. ABDEL-HALIM et al [11] studied the solid-carbon reduction of nanocrystallite compacts of pure and 26% NiO-doped iron oxides in the range of 800–1000 °C and mainly reported the effects of various factors that affected the reduction rate and the structural characteristics of the products. Experimental thermal analyses have been used to study the mechanism of reduction of the Fe_2O_3 – Cr_2O_3 –NiO–C system [12] and the results suggested

that the presence of transitional solid-state compounds such as FeCr_2O_4 and Fe_2O_3 promoted the complete reduction of Cr_2O_3 at temperatures lower than that required for pure Cr_2O_3 . Fe–Cr–Ni and Fe–Cr–C alloys have been previously detected in the final products in the carbon reduction of pickling sludge [13,14] and electric arc furnace (EAF) slag [15], generated during the production of stainless steel respectively, in addition to some metal carbides. However, fewer information about the characteristics of such alloys and carbides phase is available.

In the present work, experimental studies on the reduction behaviors of the Fe–Cr–O system (FeCr_2O_4 and $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$) and Fe–Cr–Ni–O system ($\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{NiO}$) were performed in the range of 1350–1550 °C. The effects of factors such as temperature and the initial amount of carbon, which affect the rate of reduction and the residual carbon content in the sample, were then discussed. Further, the phases and morphologies of the products that formed during reduction under various conditions were examined together with the distribution of elements among various phases.

2 Experimental

2.1 Material

Chemical reagents such as Cr_2O_3 , Fe_2O_3 , NiO (purity of higher than 99%), metallic Fe powder and graphite C (purity of higher than 98%) were employed in the experiments. The mean diameters of the above

chemical reagents were all less than 74 μm . FeCr_2O_4 was prepared by heating a mixture of Cr_2O_3 , Fe_2O_3 , and metallic Fe (molar ratio of Cr_2O_3 to Fe_2O_3 to Fe was 3:1:1) at 1000 °C for 5 h under Ar atmosphere in a resistance furnace, which was described in detail in the previous study [16]. In the experimental Fe–Cr–O samples the molar ratio of Fe to Cr was kept at 1:2, and the initial carbon amount was varied depending on the different experiments; in Fe–Cr–Ni–O sample, the molar ratio of Fe_2O_3 , Cr_2O_3 , and NiO was set as 3:2:2 and the initial molar ratio of C to O ($n_{\text{C}}:n_{\text{O}}$) was set as 1.2. The powders used in the experiments were mixed in a porcelain mortar firstly, then the cylindrical compacts (diameter of 16 mm) were formed using a cold isostatic press under a pressure of 300 MPa for 120 s. The mass of sample varied with the variation of thickness.

The experimental and sampling conditions used in this study are shown in Table 1.

2.2 Equipment

Figure 1 shows the schematic of the experimental apparatus. The main part is a molybdenum-wired resistive furnace equipped with a cracking furnace for NH_3 , a temperature-control instrument, a balance with a detection precision of 1 mg, a water-cooling system, and a data-collection system. The temperature in the tube was measured with Pt30%Rh–Pt6%Rh thermocouple. In the experiments, the sample pellets were placed in the high-purity aluminum crucible (diameter of 30 mm and height of 30 mm), which was then hung at the center of the reaction tube by the hook of the precision balance

Table 1 Experimental and sampling conditions

Test No.	System	Temperature/°C	Composition	Total mass/g	$n_{\text{Fe}}:n_{\text{Cr}}$ ($n_{\text{Fe}}:n_{\text{Cr}}:n_{\text{Ni}}$)	n_{C} to n_{O}	Mass fraction of initial carbon/%
1	Fe–Cr–O	1350	$\text{FeCr}_2\text{O}_4 + \text{C}$	5.43	1:2	1.17	20.0
2	Fe–Cr–O	1350	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	7.90	1:2	1.07	20.0
3	Fe–Cr–O	1450	$\text{FeCr}_2\text{O}_4 + \text{C}$	5.41	1:2	1.17	20.0
4	Fe–Cr–O	1450	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	7.61	1:2	1.07	20.0
5	Fe–Cr–O	1550	$\text{FeCr}_2\text{O}_4 + \text{C}$	5.50	1:2	1.17	20.0
6	Fe–Cr–O	1550	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	7.73	1:2	1.07	20.0
7	Fe–Cr–O	1350	$\text{FeCr}_2\text{O}_4 + \text{C}$	3.01	1:2	1.20	20.5
8	Fe–Cr–O	1350	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	2.98	1:2	1.20	21.8
9	Fe–Cr–O	1450	$\text{FeCr}_2\text{O}_4 + \text{C}$	3.02	1:2	1.20	20.5
10	Fe–Cr–O	1450	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	2.91	1:2	1.20	21.8
11	Fe–Cr–O	1550	$\text{FeCr}_2\text{O}_4 + \text{C}$	3.02	1:2	1.20	20.5
12	Fe–Cr–O	1550	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{C}$	3.04	1:2	1.20	21.8
13	Fe–Cr–Ni–O	1350	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{NiO} + \text{C}$	2.98	3:2:1	1.20	20.4
14	Fe–Cr–Ni–O	1450	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{NiO} + \text{C}$	3.02	3:2:1	1.20	20.4
15	Fe–Cr–Ni–O	1550	$\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{NiO} + \text{C}$	3.01	3:2:1	1.20	20.4

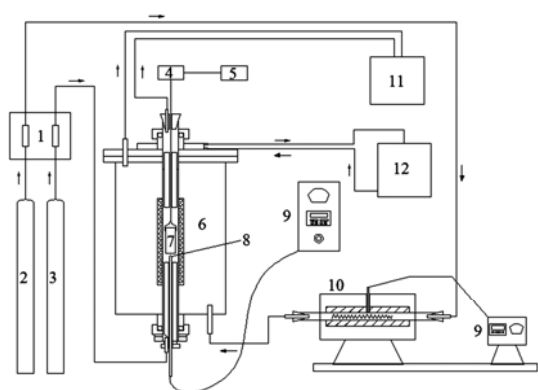


Fig. 1 Schematic diagram of experimental apparatus: 1—Flowmeter; 2—NH₃; 3—Ar; 4—Balance; 5—Computer for data collection; 6—Molybdenum wire furnace; 7—Crucible; 8—Thermocouple; 9—Temperature controller; 10—NH₃-cracking furnace; 11—Exhaust; 12—Water cooling

with a molybdenum wire. Before heating, pure Ar (purity of higher than 99%) gas was injected into the reaction tube from the bottom at a constant flow rate of 1 L/min. After the temperature reached the target value, the crucible containing the sample and hung at the hook of balance remained at the upper apart of the reaction tube for about 3 min and was then moved to the center of the reaction tube; this moment was taken as the starting time (0). During the holding time, the mass loss of the sample was continuously recorded by a data acquisition system; after completing the experiment, the sample was cooled in Ar atmosphere.

2.3 Analysis

The reduction degree of the sample (α) is given by Eq. (1):

$$\alpha = \frac{\Delta m}{m_{CO}} \quad (1)$$

where Δm and m_{CO} are the mass losses of the sample and mass of CO produced if all of the oxygen in the sample is removed, respectively. The residual carbon amount, m_{RC} , can be obtained through Eq. (2):

$$w_{RC} = \frac{m_C - \frac{\Delta m}{28} \times 12}{m_S} \times 100\% \quad (2)$$

where m_C and m_S are the initial carbon amount and the sample mass after the experiment, respectively.

The phases of the reduction products were analyzed by X-ray diffraction (M21X super power X-ray diffraction, Mac Science, Japan). The microscopic morphology and component distribution in the products were observed and analyzed by scanning electron

microscopy coupled with an energy dispersive spectrometer (JSM-6510).

3 Results and discussion

3.1 Products of carbon reduction of Fe–Cr–O system

3.1.1 Degree of reduction and residual carbon content

The degrees of reduction of the Fe–Cr–O samples, i.e. FeCr₂O₄+C and Fe₂O₃+Cr₂O₃+C, are plotted as functions of time for various temperatures and initial amounts of C in Figs. 2(a) and (b), respectively. The hollow mark represents the data for which $n_C:n_O$ is maintained at 1.2°, and the solid one shows the data for which the initial amount of carbon is 20% (in this case, the value of $n_C:n_O$ is varied for the samples.). The degrees of reduction of the two samples are highly dependent on both time and temperature. Both samples show similar tendencies: the degree of reduction linearly increases during the initial stage and then slows down and levels off. Temperature greatly affects the rate of reduction: the higher the temperature is, the shorter the time is to reach the maximum degree of reduction.

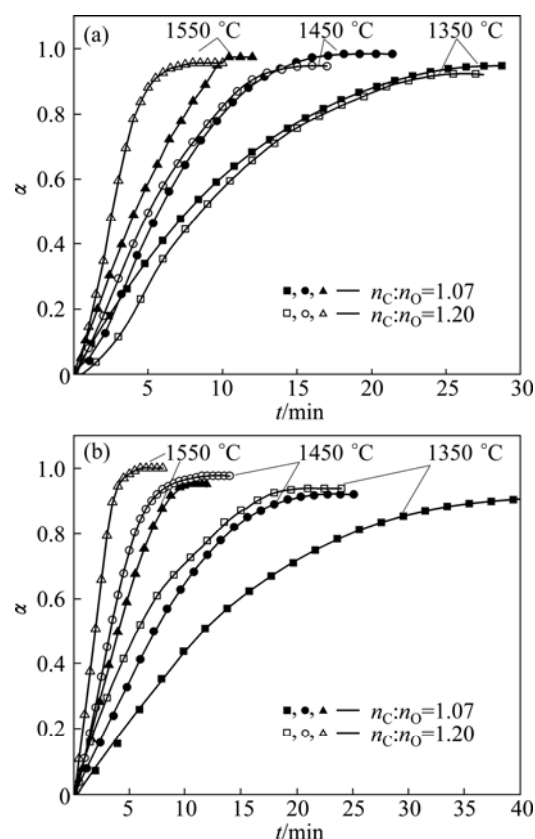


Fig. 2 Reduction curves for Fe–Cr–O samples: (a) FeCr₂O₄+C; (b) Fe₂O₃+Cr₂O₃+C

Figure 3 shows the effects of $n_C:n_O$ on the residual carbon content for all the Fe–Cr–O samples listed in Table 1. The residual carbon content strongly depends on $n_C:n_O$ and linearly increases with increasing $n_C:n_O$ at each

temperature regardless of the amounts or types (i.e. $\text{FeCr}_2\text{O}_4+\text{C}$ or $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$) of samples used. This means that the effects of other factors such as the amount and composition of the sample on the residual carbon content in the sample are negligible compared to the effect of $n_{\text{C}}:n_{\text{O}}$. Temperature is another important factor that affects the residual carbon content in the sample, which tends to decrease with increasing temperature. Hence, the lowest residual carbon content is obtained at the highest temperature and the lowest $n_{\text{C}}:n_{\text{O}}$, and the highest residual carbon content is obtained under the opposite experimental conditions. Thermodynamic predictions in our previous study [16] have shown that for carbon reduction of Fe–Cr–O systems, two kinds of phases mainly form in the end products: Fe–Cr–C solution and metal carbides such as Cr_7C_3 and $(\text{Fe,Cr})_7\text{C}_3$, and the former is more favored under higher temperature and lower $n_{\text{C}}:n_{\text{O}}$ while the latter is more stable in the opposite situation. Compared with the mass fraction of carbon in metal carbides, the saturated solubility of C in Fe–Cr–C solution is much lower. Therefore, in the situations which promote the formation of Fe–Cr–C solution (higher temperature and lower $n_{\text{C}}:n_{\text{O}}$), the residual carbon content tends to be decreased. And these are consistent with the experimental results.

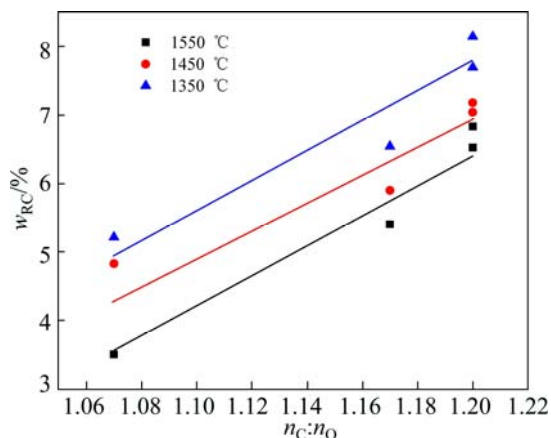


Fig. 3 Relationship between $n_{\text{C}}:n_{\text{O}}$ and residual carbon content w_{RC}

3.1.2 Phases analysis on products appearing over time

In order to examine the possible phases appearing in the products during the reaction process of the Fe–Cr–O system, experiments with these two samples ($\text{FeCr}_2\text{O}_4+20\%\text{C}$ and $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$) were carried out after holding the target time, the sample was cooled down in Ar atmosphere and analyzed by XRD.

Figures 4(a) and (b) show the XRD spectra of the FeCr_2O_4 and $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$ samples reduced by C over time at 1350 °C, respectively. As shown in Fig. 4(a), for the sample of $\text{FeCr}_2\text{O}_4+\text{C}$, FeCr_2O_4 disappears at 6 min ($\alpha=33\%$) to release a large amount of Cr_2O_3 . At the same

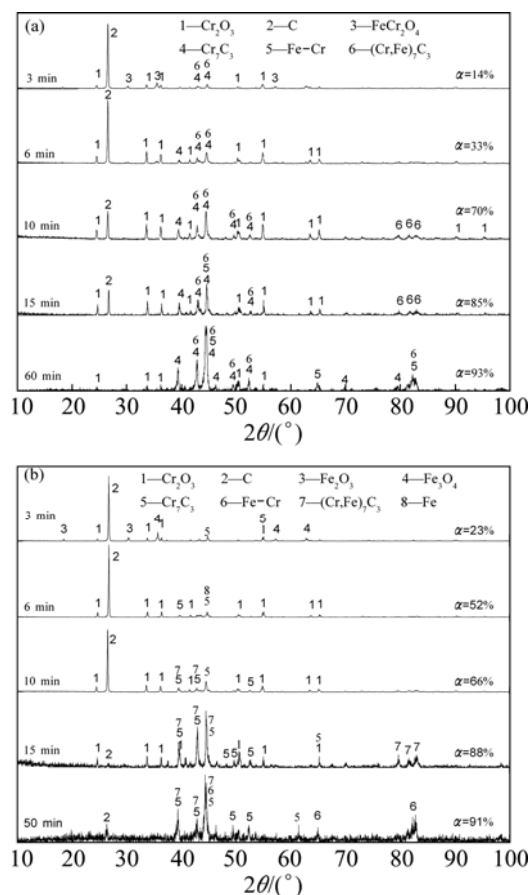


Fig. 4 XRD patterns for products of $\text{FeCr}_2\text{O}_4+\text{C}$ (a) and $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$ (b) over time at 1350 °C

time, many metal carbides such as Cr_7C_3 and $(\text{Cr,Fe})_7\text{C}_3$ are formed. During the first 10 min ($\alpha=70\%$), the density of C greatly decreases, while the densities of Cr_2O_3 and carbides such as Cr_7C_3 and $(\text{Cr,Fe})_7\text{C}_3$ increase; this reveals that the release of Cr_2O_3 from FeCr_2O_4 and carburization of Cr/Fe happen almost simultaneously, but the rate of the former is larger than that of the latter. After 10 min, the densities of Cr_2O_3 /carbides Cr_7C_3 and $(\text{Cr,Fe})_7\text{C}_3$ tend to decrease, and a weak peak suggests that a small amount of Fe–Cr solid solution appears at 15 min ($\alpha=85\%$). The final products for $\text{FeCr}_2\text{O}_4+\text{C}$ are mainly constituted by two kinds of phases or materials: Fe–Cr solid solution and metal carbides. For the sample of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$, as shown in Fig. 4(b), metal carbides like Cr_7C_3 and $(\text{Cr,Fe})_7\text{C}_3$ appear after 10 min ($\alpha=66\%$). At 15 min, the peak of C almost completely disappears, and the density of metal carbides becomes much stronger. Within 15 min ($\alpha=88\%$), Fe–Cr solution is not observed. At 50 min ($\alpha=91\%$), there is clear evidence for the existence of Fe–Cr solution. Similar with that of FeCr_2O_4 , the final product of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$ also consists of Fe–Cr solution and metal carbides.

From these results, it tends to reveal that the common tendency for the reduction of the Fe–Cr–O

system is metal carbides forming in the initial stage and the Fe–Cr solution generates when the reduction degree is sufficiently high. The Fe–Cr solution appears earlier in FeCr_2O_4 , and the corresponding reduction degree is 85%. It is not observed when the reduction degree is 88% in $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$ sample. The generation of the Fe–Cr solution seems to be mainly led by the reaction between metal carbides (iron and chromium carbides) and Cr_2O_3 due to an identical phenomenon shown in Figs. 4(a) and (b). Both of the intensities of Cr_2O_3 and metal carbides (Cr_7C_3 and $(\text{Fe,Cr})_7\text{C}_3$) almost simultaneously decrease with the appearance of Fe–Cr solution at the later stage. MORI et al [17] reported a detailed mechanism for carbothermic reduction of Cr_2O_3 , which suggests that several kinds of chromium carbides such as Cr_3C_2 , Cr_7C_3 , and Cr_{23}C_6 form initially, and then metal Cr is generated from the interaction of chromium carbides and Cr_2O_3 . This looks to be consistent with the present results.

3.1.3 Microscopic observation and analysis

SEM coupled with EDS was used to further investigate the microscopic morphologies and the distribution of the elements among the various phases in the final products of the C-reduced Fe–Cr–O system. Figures 5 (a)–(c) show the backscattered electron (BSE) images of the final products for the samples of $\text{FeCr}_2\text{O}_4+20\%\text{C}$ reduced at 1350, 1450, and 1550 °C, corresponding to Nos. 1, 3, and 5 listed in Table 1, respectively, and the corresponding contents of the elements found in the areas highlighted in Fig. 5 are listed in Table 2.

As shown in Fig. 5, the final product of the C reduction of FeCr_2O_4 mainly consists of two kinds of phases or materials: a light-colored base matrix and irregularly shaped dark particles. From the perspective of appearance, the light-colored base matrix seems to be a liquid and some of the irregularly shaped dark particles (such as the particles shown in areas 1, 3, and 5) remain solid under the experimental temperatures. On the basis of the dendrite structures, the other particles such as those shown in areas 6 and 7 seem to have precipitated from the liquid phase when the sample is cooled.

The data listed in Table 2 show that much more Fe and fewer Cr are distributed in the liquid phase (as shown in area 2) for the reduction products of $\text{FeCr}_2\text{O}_4+20\%\text{C}$ and that the dark particles (as shown in areas 1 and 3–7) have higher Cr contents and much lower Fe contents: the content of Cr varies from 68% to 80% while that of Fe is in the range of 9.0%–19.0%. Similar tendencies can be observed from the line analysis and from the distribution of elements in the SEM images of the final products for the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample reduced at 1350 °C, as shown in Fig. 6. This result also indicates that the distribution of Cr is more extensive in dark particles and that the distribution of Fe is more

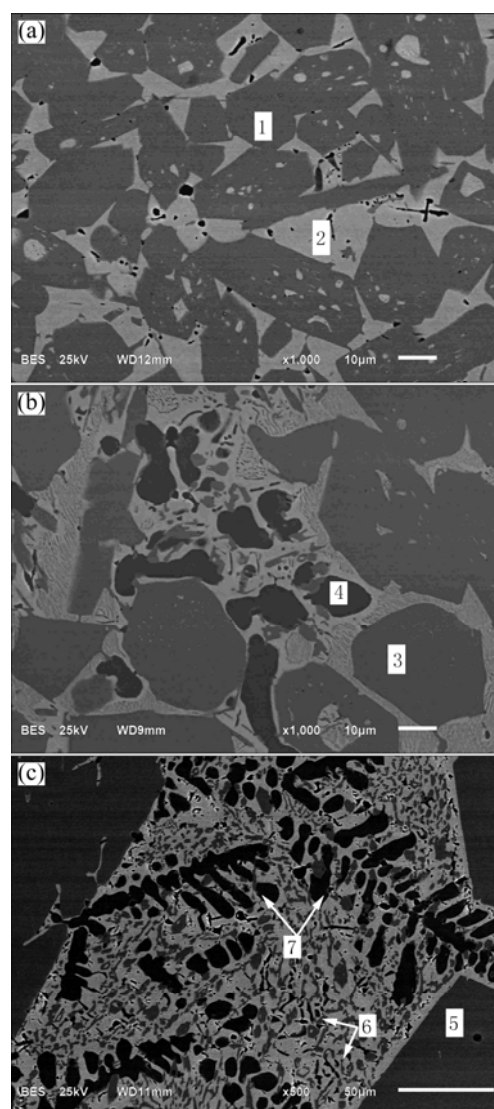


Fig. 5 SEM images of final products of FeCr_2O_4 reduced at 1350 °C (a), 1450 °C (b), and 1550 °C (c)

Table 2 EDS analysis of element contents of areas 1–7 identified in Fig. 5

Area	Mass fraction/%		
	C	Cr	Fe
1	12.37	68.60	19.03
2	9.08	30.25	60.67
3	12.51	72.47	15.03
4	11.34	76.71	11.95
5	10.03	79.79	10.78
6	11.19	70.40	18.41
7	10.39	80.21	9.40

extensive in the light-colored phase.

Combining these results and those of the XRD analysis shown in Fig. 4, it suggests that two kinds of phases are formed during the C reduction of Fe–Cr–O

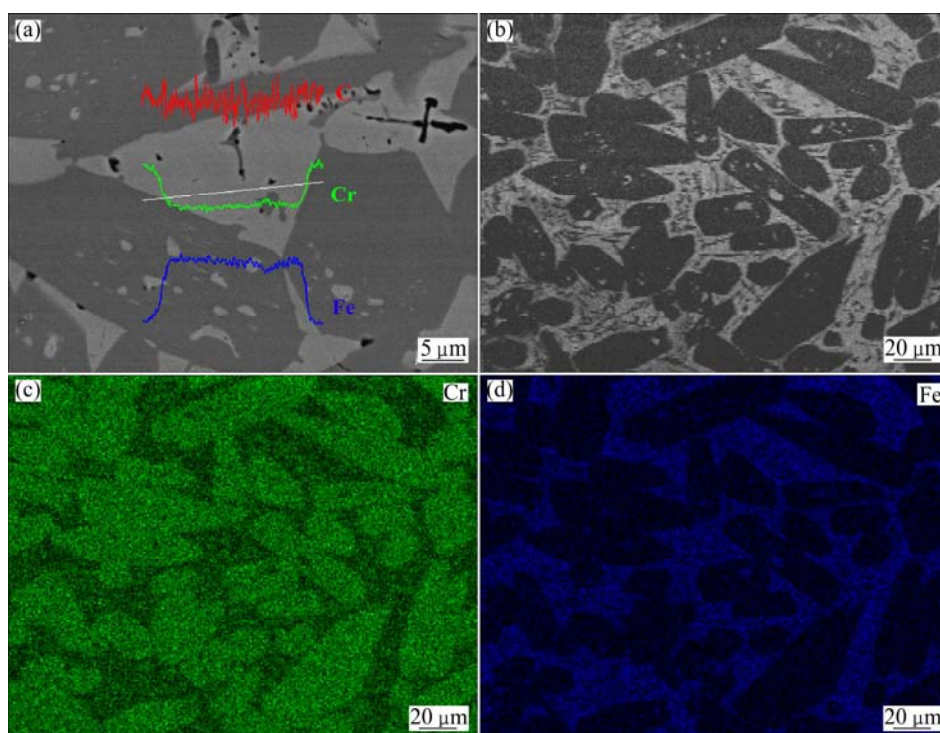


Fig. 6 SEM images of line analysis and distribution of elements in final products of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$ reduced at 1350 °C: (a) Line analysis of elements; (b) SEM image of final product; (c) Surface distribution of Cr; (d) Surface distribution of Fe

systems at high temperatures: a light-colored Fe–Cr–C liquid phase and metal carbides appearing as dark particles, as shown in Fig. 5. More Cr exists as metal carbides and more Fe is distributed in the Fe–Cr–C solutions together with higher C content in the metal carbides during the C reduction of the Fe–Cr–O systems at high temperatures. The metal carbides should be composed of Cr_7C_3 and a small amount of $(\text{Cr,Fe})_7\text{C}_3$ because the mass fraction of Cr in Cr_7C_3 is about 91% while the mass fraction of Cr varies from 68% to 80% when the Cr combines with 9%–19% of Fe in metal carbide particles, as shown in Table 2. The primary metal carbides formed during reduction tend to remain solid, especially under a relatively low reduction temperature such as 1350 °C, because of their high melting point. When the sample is cooled, some of the metal carbides precipitate out of the Fe–Cr–C solution and produce dendrite crystals because the solubility of Cr in the solution decreases with decreasing temperature.

The final products of the $\text{FeCr}_2\text{O}_4+20\%\text{C}$ sample reduce at 1350 °C, the final products of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample reduce at 1350 °C, the final products of $\text{FeCr}_2\text{O}_4+20\%\text{C}$ sample reduce at 1550 °C, and the final products of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample reduce at 1550 °C are shown in Figs. 7(a)–(d), respectively, and correspond to Nos. 1, 2, 5, and 6, respectively, as listed in Table 1. The two systems exhibit similar tendencies: more Fe–Cr–C solution and fewer metal carbide

particles are formed with increasing temperature which agrees well with the thermodynamic predictions [16], the size of the metal carbide particles primarily formed is more uniform and smaller at lower temperatures, and the mass of the dendrite metal carbide particles precipitates when the samples reduced at temperature of 1550 °C are cooled. However, when the two samples are compared, more Fe–Cr–C solution tends to be obtained in the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample than in the $\text{FeCr}_2\text{O}_4+20\%\text{C}$ sample at each reduction temperature, which may be because of the lower $n_{\text{C}}:n_{\text{O}}$ in the former (i.e., $n_{\text{C}}:n_{\text{O}}$ is 1.07 for the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample when the amount of C is maintained at 20%, and $n_{\text{C}}:n_{\text{O}}$ is 1.17 for the $\text{FeCr}_2\text{O}_4+20\%\text{C}$ sample). This finding is also consistent with the thermodynamic predictions [16] introduced above, that is, lower $n_{\text{C}}:n_{\text{O}}$ enables the formation of the Fe–Cr–C solution. The residual carbon content in the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+20\%\text{C}$ sample should be correspondingly lower than that in the $\text{FeCr}_2\text{O}_4+20\%\text{C}$ sample since fewer C is distributed throughout the Fe–Cr–C solution than C in the metal carbides (as shown in Fig. 7 and listed in Table 2), which is also consistent with the experimental results, as shown in Fig. 3.

3.2 Products of carbon-reduced Fe–Cr–Ni–O system

3.2.1 Degree of reduction and residual carbon content

Figures 8(a) and (b) show the reduction degree over time and the residual carbon content, respectively, in the

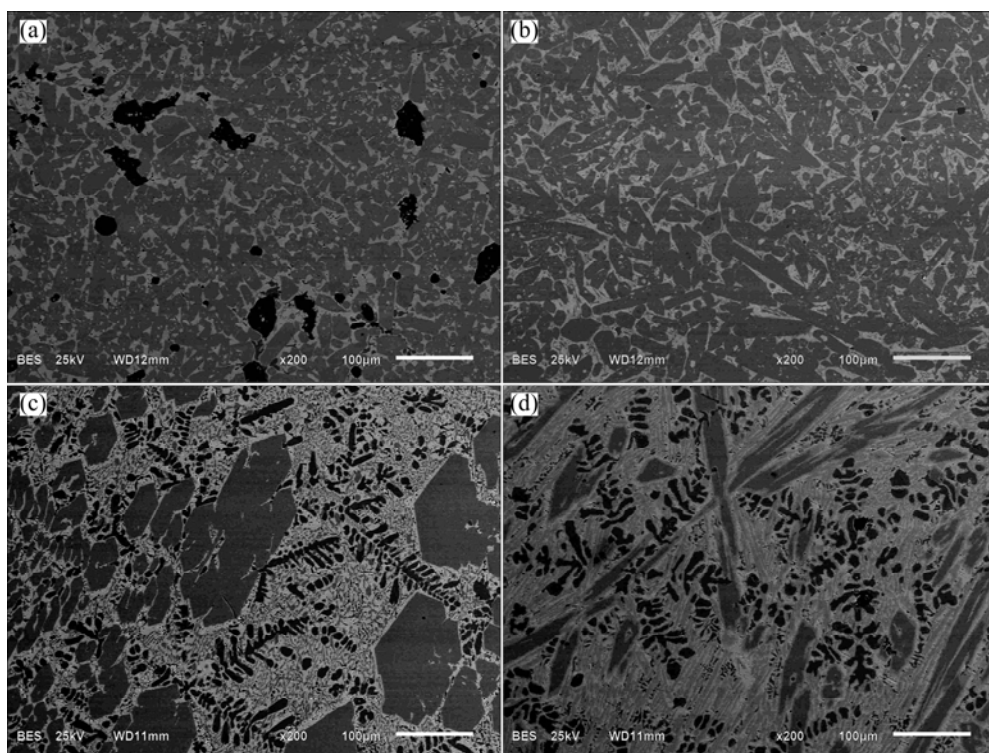


Fig. 7 SEM images of final products of carbon-reduced Fe–Cr–O system: (a) FeCr_2O_4 reduced at 1350 °C; (b) $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$ reduced at 1350 °C; (c) FeCr_2O_4 reduced at 1550 °C; (d) $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$ reduced at 1550 °C

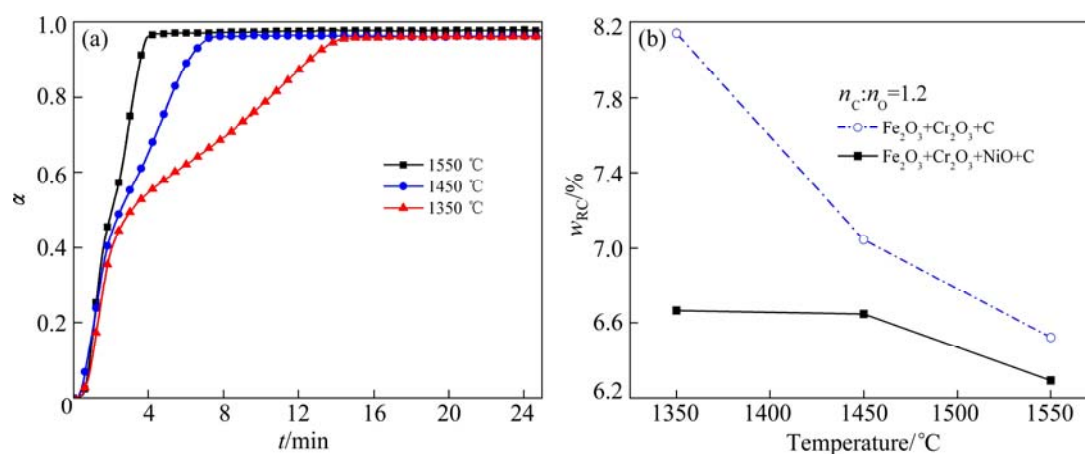


Fig. 8 Degree of reduction (a) and residual carbon content (b) in $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ sample reduced over time at various temperatures

$\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ sample at various temperatures. As shown in Fig. 8(a), the reduction degree linearly increases during the initial stage and then slows down and becomes constant. This behavior is similar to that observed for the Fe–Cr–O samples. It needs to be noted that the initial rate of reduction for this sample is highly independent of temperature and maintains nearly a constant when the degree of reduction of the sample is below 50%. Thermodynamic predictions [16] on the products of carbon reduction of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}$ system showed that almost all the NiO was reduced and combined with the Fe reduced from Fe_2O_3 to form an

Fe–Ni–C liquid phase below 1000 °C while chromium-bearing oxides (pure Cr_2O_3 or complex oxides like FeCr_2O_4) did not start to lose oxygen until temperature reached 1100 °C. Similar results can be found in Ref. [18]. Consequently, it can be inferred that during the initial stage when the reduction degree is below 50%, Ni mainly reduces and Fe partially reduces from their respective oxides and the liquid Fe–Ni solution also forms since both of these reactions are thermodynamically favored even at temperature as low as 1000 °C. The experimental data on the C reduction of the $\text{Fe}_2\text{O}_3\text{--NiO}$ sample [11] also show no temperature

dependency of the initial reduction rate, even in the range of 800–1100 °C. When the degree of reduction of the sample is above 50%, the data in Fig. 8(a) show that the rate of reduction is highly temperature dependent; that is, the higher the temperatures are, the shorter the time is required to reach the maximum degree of reduction. This finding suggests that Cr mainly reduces from its simple oxide or from the complex oxides containing Fe (such as FeCr_2O_4) during this period. Previous experimental studies on the carbothermic reduction of Cr_2O_3 [17] have shown that even the very initial rate of reduction is strongly dependent on temperature in the range of 1100–1400 °C, which is further indirect evidence that this finding could be reasonable.

Figure 8(b) shows the residual carbon content, w_{RC} , in the final products of the reduced $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ samples plotted as functions of temperature. w_{RC} decreases with increasing temperature. This is also consistent with thermodynamic predictions [16] on possible products of C reduction of $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}$ samples: more Fe–Ni–Cr–C solution and fewer metal carbides are obtained with increasing temperature and decreasing $n_{\text{C}}:n_{\text{O}}$, which is similar to the behavior exhibited in the Fe–Cr–O system, and higher temperature and lower $n_{\text{C}}:n_{\text{O}}$ lead to the decrease of the residual carbon content in the system. Another important point needed to be note is that the residual carbon content is higher in the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$ sample than that in the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ sample when $n_{\text{C}}:n_{\text{O}}$ is 1.2. The reasons behind this could be explained as follows. On one hand, in the end products compared with Fe–Cr–C liquid phase, the addition of Ni (Fe–Cr–Ni–C solution) tends to decrease the saturated solubility of C, since the interaction between Ni and C has the opposite effect of the affinity between Cr and C in iron alloys. Previous study [19] has shown that the values of the interaction parameters e_{C}^{Ni} and e_{C}^{Cr} are 0.01 and -0.023 , respectively, suggesting that the existence of Ni can decrease the solubility of C in iron alloys while the existence of Cr tends to increase the solubility of C at the same carbon potential. On the other hand, when $n_{\text{C}}:n_{\text{O}}$ is maintained at a constant level, the mass fractions of initial C content in the two systems are different: 21.8% and in $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$ and 20.4% $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$. This means that even when the two systems are reduced to the same degree, the residual carbon content in $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{C}$ tends to be larger than that in $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$.

3.2.2 Final products

Figures 9 (a) and (b) show the SEM images of the final products of the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ samples reduced at 1350 and 1550 °C, corresponding to Nos. 13–15, respectively, as listed in Table 1, and the

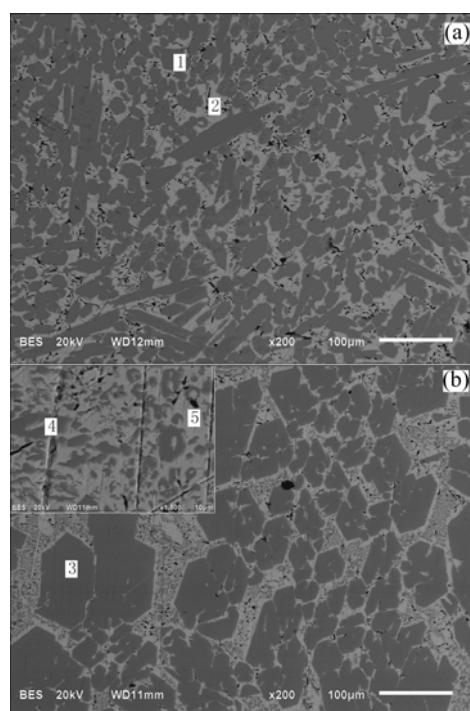


Fig. 9 SEM images of final products of $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{NiO} + \text{C}$ samples reduced at 1350 °C (a) and (b) 1550 °C

corresponding contents of the elements found in the areas identified in Fig. 9 are listed in Table 3.

As with the final products of the $\text{FeCr}_2\text{O}_4+\text{C}$ samples reduced at each temperature, those of the $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}+\text{C}$ samples reduced at each temperature also mainly consist of two kinds of phases or materials: a light-colored base matrix and irregularly shaped dark particles. The former seems to be a liquid, and some of the latter (such as the particles shown in areas 1 and 3) tend to be primarily formed remaining solid at the experimental temperature. The other small particles, such as those shown in area 4, seem to have precipitated from the liquid phase when the sample was cooled. Combining the data listed in Table 3 and the line analysis results shown in Fig. 10, it suggests that much more Ni and fewer Cr are distributed throughout the light-colored liquid base (areas 2 and 5 shown in Fig. 9 and listed in Table 3), and much more Cr and fewer Ni are present in the dark particles. The distribution of Fe is slightly higher in liquid phase than that in the dark particles, and the content of C in the liquid phase is much lower than that in the dark particles. Therefore, it can be induced that the liquid phase, in which Fe and Ni are predominant and the content of C is relatively low, is an Fe–Ni–Cr–C solution and that the dark particles containing high contents of Fe, Cr, and C tend to be mainly chromium and iron carbides such as Cr_7C_3 and $(\text{Cr,Fe})_7\text{C}_3$. Similar phases have been previously detected in the final products of the solid-state reduction of the

$\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--NiO--C}$ system [12] and in the carbon reduction of pickling sludge [13,14] and slag [15] generated during the production of stainless steel.

Table 3 EDS analysis of areas 1–5 identified in Fig. 5.

Area	Mass fraction/%			
	C	Cr	Fe	Ni
1	10.01	45.62	39.52	4.85
2	3.83	4.90	54.47	36.80
3	10.38	44.71	40.20	4.72
4	9.28	32.79	51.71	6.21
5	5.61	3.79	53.97	36.63

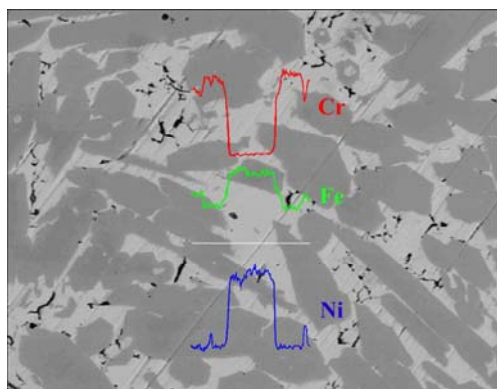


Fig. 10 Line analysis of final products of Fe–Cr–Ni–O system reduced at 1350 °C

Further, Fig. 9 suggests that more Fe–Ni–Cr–C solution and fewer iron and chromium carbide particles form with increasing temperature, and the size of the metal carbide particles primarily formed is more uniform and smaller at lower temperatures while the metal carbide particles tend to aggregate and become larger with increasing temperature.

4 Conclusions

1) Experimental data show that for the Fe–Cr–O system, the degree of reduction is highly dependent on both time and temperature and linearly increases during the initial stage and then slows down and levels off. Further, the residual carbon content strongly depends on $n_{\text{C}}:n_{\text{O}}$ and linearly increases with increasing $n_{\text{C}}:n_{\text{O}}$ at each temperature.

2) As the Fe–Cr–O system is reduced, metal carbides form during the initial stage, and the Fe–Cr solution is generated when the degree of reduction is sufficiently high. The SEM images observation of the microstructure and the EDS analysis of the distribution of the elements show that more Cr exists in metal carbides while more Fe is distributed throughout the Fe–Cr–C solution and the content of C in the former is

higher than that in the latter.

3) Experimental data on the reduction of the Fe–Cr–Ni–O system suggest that the initial rate of reduction tends to maintain nearly constant and be very independent of temperature. It is inferred that under this experimental condition when the degree of reduction of the sample is below 50%, Ni mainly reduces and Fe partially reduces from their respective metal oxides, and when the degree of reduction of the sample is above 50%, Cr mainly reduces from the oxides.

4) The SEM images observation of the microstructure and the EDS analysis of the distribution of the elements show that the final products of the C reduction of the $\text{Fe}_2\text{O}_3\text{+Cr}_2\text{O}_3\text{+NiO}$ sample mainly consist of two phases: Fe–Ni–Cr–C solution and metal carbide particles. Much more Ni and fewer Cr are distributed throughout the former, while much more Cr and fewer Ni are present in the latter. The content of Fe is slightly higher in the Fe–Ni–Cr–C solution than that in the metal carbide particles, and the content of C in the Fe–Ni–Cr–C solution is much lower than that in the metal carbide particles.

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Fe–Cr–O 和 Fe–Cr–Ni–O 体系中 C 还原产物

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摘 要: 研究不同条件下 C 还原 Fe–Cr–O 体系 (FeCr_2O_4 和 $\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3$) 及 Fe–Cr–Ni–O 体系 ($\text{Fe}_2\text{O}_3+\text{Cr}_2\text{O}_3+\text{NiO}$) 的还原行为及产物特性。结果表明: 温度与碳氧比对 C 还原 Fe–Cr–O 和 Fe–Cr–Ni–O 体系所得产物的组成有很大的影响, 在较高温度和较低碳氧比的条件下, 产物中残余碳含量更少且 Fe–Cr 和 Fe–Cr–Ni 合金含量更多; 样品的还原率在很大程度上取决于还原时间和温度, 在不同温度条件下, 产物中的残余碳含量均随着碳氧比的增加而升高。此外, 对不同时间条件下 C 还原 Fe–Cr–O 体系所得产物进行 XRD 分析, 利用 SEM 和 EDS 研究 C 还原 Fe–Cr–O 和 Fe–Cr–Ni–O 体系所得最终产物中不同相的微观形貌和元素分布。

关键词: Fe–Cr–O 体系; Fe–Cr–Ni–O 体系; 还原产物; 元素分布; 残余碳含量

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