

Making Ferronickel from Laterite Nickel Ore by Coal-Based Self-Reduction and High Temperature Melting Process

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Abstract

Based on the process of coal-based self-reduction and melting separation at high temperature, it was investigated that the effect of process factors on the reduction of iron and nickel oxide, the metal yield and the nickel content in ferronickel about the laterite nickel ore, was from Philippines and contented low nickel, high iron and aluminum. The results showed that if the C/O mole ratio was not higher than 0.5 and the reduction temperature was kept as 1200°C and then increased up to 1500°C, the metal could not separate from molten slag for the A series of experiments, which were only added CaF₂. However, when the C/O ratio was added up to 0.6 - 0.8, the metal could separate well from the slag, and the yields of Fe and Ni increased gradually. But the nickel content in the metal declined from 1.79% to 1.34%. When the C/O ratio increased to 1.2, and the temperature of melting products obtained at 1200°C and rose to 1550°C, the separation of metal from slag could not be realized in B group of tests, which were only added hydrated lime. However, when both of CaF₂ and hydrated lime were added, the metal could separate from slag in C group. In order to increase the content of nickel in the metal, it is necessary to restrain the reduction of iron oxide. When the C/O mole ratio is 0.6, the nickel content of metal could be 1.79%, which was higher than the theoretical ratio 1.65% of Ni/(Ni + Fe) of the latcritic nickel ore, but the yield of nickle was only 71.3%.

Keywords

Low Grade Latcritic Nickel Ore, Coal-Based Self-Reduction, Ferronickel

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1. Introduction

Nickel was an important material for the production of austenitic stainless steel, heat resistant steel and nickel-based superalloy [1] [2]. For a long time, the nickel was mainly extracted from nickel sulfide ore [3] [4]. As the exhaustion of nickel sulfide ore in China, developing the resource of laterite nickel ore with low nickel grade but abundant reserves has been paid attention [5]-[8]. Laterite nickel ore is an ore by long-term weathering of ultrabasic rocks containing magnesium and iron silicate mineral. During the weathering process, Mg and Fe in the lattice of silicate were partially substituted by Ni gradually, to form the mineral deposit with different contents of nickel and gangue composition. The content of nickel less than 1.2% was called the low grade ore customarily, which had high iron content and more Al_2O_3 in the gangue. When the content of nickel was 1.2% to 1.8%, the nickel laterite ore was called middle grade ore, and the nickel laterite ore, which the content of nickel was more than 1.8%, was called the high grade nickel laterite which had low iron content and more SiO_2 in the gangue. Laterite nickel ore was mainly distributed in tropical countries, within 30 degrees in north and south of the equator in the world. China mainly imported laterite nickel ore from Indonesia and Philippines, however, the Indonesian government went through the law about mineral and coal in 2009, and the law stipulated that the export of metal ores which included laterite nickel ore was prohibited from 2014. Therefore, this article mainly aims to prepare ferronickel from low grade laterite nickel ore from Philippines by coal-based self-reduction process, which provides guidance for rational exploiting and utilizing of the low grade laterite nickel ore.

2. Experimental Research Method

2.1. Raw Material Pretreatment and Its Physicochemical Properties

The crude laterite nickel ore used in the study was from Philippines, which was crushed by jaw crusher, then grinded to -0.125 mm with a ball mill and put in the oven to reserve after dried at 110°C . The chemical composition was shown in Table 1. The Ni content was just 0.78 wt%, the Fe content as high as 46.54 wt%, and the content of Al_2O_3 in gangue reached 9.26 wt%. This laterite nickel ore used in investigation is the low-nickel, high-iron, high-alumina and low-silica ore.

The X-ray diffraction spectrum of laterite nickel ore is shown in Figure 1. The Ni mainly exists in the form of NiFe_2O_4 and the Fe mainly exists in the form of $\text{FeO}(\text{OH})$ and Fe_2O_3 .

The reductant in this study was anthracite, while the flux was calcium hydroxide and CaF_2 . The chemical composition was shown in Table 2. Both the anthracite and calcium hydroxide were sieved by -0.125 mm sieve.

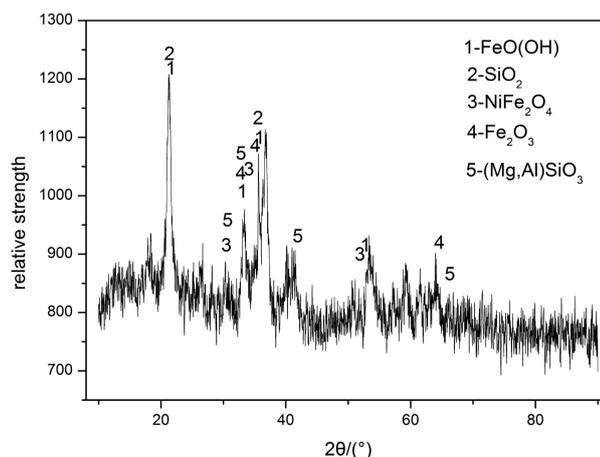


Figure 1. X-ray analysis diffraction patterns of the laterite nickel ore.

Table 1. Chemical compositions of lateritic nickel ore.

TFe	FeO	Fe_2O_3	CaO	MgO	SiO_2	Al_2O_3	Ni	P_2O_5	S	Burning Loss
46.54	1.27	65.08	0.15	1.84	4.74	9.26	0.78	0.055	0.32	7.98

Table 2. Chemical compositions of anthracite and calcium hydroxide.

Chemical Analysis	C	S	SiO ₂	Al ₂ O ₃	P ₂ O ₅	CaO	MgO	Burning Loss
Anthracite	76.56	0.54	6.09	2.68	0.23	1.28	0.35	-
Calcium Hydroxide	-	0.041	0.56	-	0.005	67.52	4.56	26.72

2.2. Preparation of the Sample

The reductant was anthracite, the mole ratio of C/O was defined as the ratio of carbon in anthracite to oxygen of iron oxide and nickel oxide contained in the laterite nickel ore. In this work the C/O was 0.5, 0.6, 0.8, 1.0 and 1.2. It was divided to A, B, C three groups according to the different additives. Only CaF₂ was added in group A. Only calcium hydroxide was added in group B; both of them were added in group C. Calcium hydroxide was used to adjust the slag phase composition and its content was determined by the ratio of CaO and Al₂O₃ in the 12CaO; 7Al₂O₃ formed in the slag phase. CaF₂ was used to reduce the melting point of the slag phase. According to preliminary studies, the adding amount of CaF₂ was 10 % of the sum quantity of CaO, MgO, SiO₂ and Al₂O₃ in slag phase.

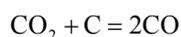
After the laterite nickel ore, anthracite, calcium hydroxide and CaF₂ were blending in proportion, then add a little of water as a wetting agent. The mixture was pressed into cylindrical specimens of $\varnothing 20 \times 30$ mm, then put it into stove and dried at 110°C.

2.3. Experimental Equipment and Methods

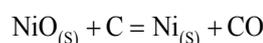
Reduction experiments were carried out in 25 kVA high temperature carbon tube furnace with rapid heating function, where the sample was heated to 1200°C in the rate of 120°C - 150°C/min and reduced for 10 minutes. It was then heated up rapidly to 1500°C or 1550°C and insulated for 20 minutes. After melting separation, it was cooled to below 600°C in the furnace. Removing the crucible to make the sample cool to room temperature in the air, the experimental sample number and the theoretical chemical composition of pressing block under the various ingredients scheme were shown in [Table 3](#) and [Table 4](#).

3. The Principle of Reduction of Nickel and Iron Oxide

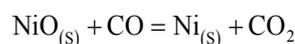
The chemical reactions are as follows when NiO and Fe₂O₃ were reduced:



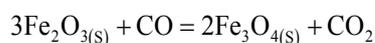
$$\Delta G^\theta = 166550 - 171T \quad (\text{J/mol}) \quad (1)$$



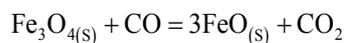
$$\Delta G^\theta = 118050 - 169.36T \quad (\text{J/mol}) \quad (2)$$



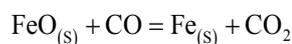
$$\Delta G^\theta = -48500 + 1.64T \quad (\text{J/mol}) \quad (3)$$



$$\Delta G^\theta = -52131 - 41.0T \quad (\text{J/mol}) \quad (4)$$



$$\Delta G^\theta = 35380 - 40.16T \quad (\text{J/mol}) \quad (5)$$



$$\Delta G^\theta = -22800 + 24.26T \quad (\text{J/mol}) \quad (6)$$

Table 3. Sample number.

Additive C/O	CaF ₂ (A)	Calcium Hydroxide (B)	CaF ₂ and Calcium Hydroxide (C)
0.5	1# (C0.5-1200-1500A)	-	-
0.6	2# (C0.6-1200-1500A)	-	-
0.8	3# (C0.8-1200-1500A)	-	-
1.0	4# (C1.0-1200-1500A)	5# (C1.0-1200-1550B)	7# (C1.0-1200-1550C)
1.2	-	6# (C1.2-1200-1550B)	8# (C1.2-1200-1550C)

Table 4. Theoretical compositions of briquettes (wt%).

Number	TFe	FeO	Fe ₂ O ₃	CaO	MgO	SiO ₂	Al ₂ O ₃	Ni	CaF ₂	S	P ₂ O ₅	C
1#	41.70	1.14	58.30	0.25	1.68	4.79	8.53	0.697	1.53	0.097	0.070	6.79
2#	41.00	1.12	57.30	0.27	1.66	4.80	8.43	0.688	1.51	0.105	0.072	8.01
3#	39.60	1.08	55.30	0.30	1.61	4.85	8.23	0.667	1.50	0.120	0.078	10.31
4#	38.30	1.04	53.50	0.33	1.57	4.89	8.05	0.642	1.49	0.133	0.083	12.47
5#	35.03	0.96	48.99	6.93	1.88	4.53	7.37	0.59	-	0.32	0.076	11.62
6#	34.00	0.93	47.54	6.81	1.84	4.57	7.23	0.57	-	0.33	0.081	13.49
7#	34.31	0.94	47.98	6.79	1.85	4.44	7.22	0.58	2.04	0.32	0.075	11.39
8#	33.32	0.91	46.59	6.66	1.81	4.48	7.09	0.56	2.00	0.32	0.079	13.23

The fixed carbon reacts with CO₂ to generate CO that participate in indirect reduction of NiO and Fe₂O₃ [8], absorbing a lot of heat. The thermodynamic equilibrium curve of nickel oxide and iron oxide reduced by carbon was shown in **Figure 2**. Region 1 ($t < 400^{\circ}\text{C}$) is a stable region for Fe₃O₄ and NiO; Region 2 ($400^{\circ}\text{C} < t < 656^{\circ}\text{C}$) is a stable region for Fe₃O₄ and Ni; Region 3 ($656^{\circ}\text{C} < t < 710^{\circ}\text{C}$) is a stable region for FeO and Ni; Region 4 ($t > 710^{\circ}\text{C}$) is a stable region for Fe and Ni.

Theoretically, when the reduction temperature was controlled between $656^{\circ}\text{C} - 710^{\circ}\text{C}$; the Ni in the ore could be reduced into metallic nickel, but iron existed in FeO, so it could use magnetic separation to enrich nickel. However, it was hard to achieve these ideal results during actual operation. The main reason was as follows: 1) the reduction temperature of $656^{\circ}\text{C} - 710^{\circ}\text{C}$ had not reached the temperature of rapid gasification reaction of carbon, so it was unable to realize the fully reduction of nickel oxide that only rely on solid-phase reduction between laterite nickel ore and coal; 2) because the nickel and iron were present as isomorphous, even if the full reduction of NiO did not change its lattice state, and it was difficult to separate the nickel and iron by physical separation [10]; 3) therefore, this study intended to improved the experimental temperature to accelerate the reduction of nickel and iron oxides, then separated the metal and gangue by high-temperature melting separation and to control the degree of reduction of iron oxide by controlling the distribution of carbon ratios.

4. The Results and Discussion

4.1. The Morphology of Sample after Melting Separation

After reduced at 1200°C , and then heated to 1500°C or 1550°C to melting separation, the patterns were shown in **Figure 3**. **Sample 1#** to **Sample 4#** were group A that the additive was CaF₂. **Sample 1#** with carbon ratio of 0.5 had melted at 1500°C , but the iron and slag were not separated (**Figure 3(a)**). After melting separation at 1500°C , the iron and slag of **Sample 2#, 3#, 4#** that carbon ratio was 0.6, 0.8, 1.0 separated well (**Figures 3(b)-(d)**). **Sample 5#** (carbon ratio 1.0) and **Sample 6#** (carbon ratio 1.2) were group B that the additive was slaked lime. In group B, when the melting separation temperature rose to 1550°C , the iron and slag were not separated, but metal particles were wrapped by slag. After reduced at 1200°C and melted at 1550°C , the iron and slag of group C that the additives were CaF₂ and slaked lime separated well, as shown in **Figure 3(g)** and **Figure 3(h)**.

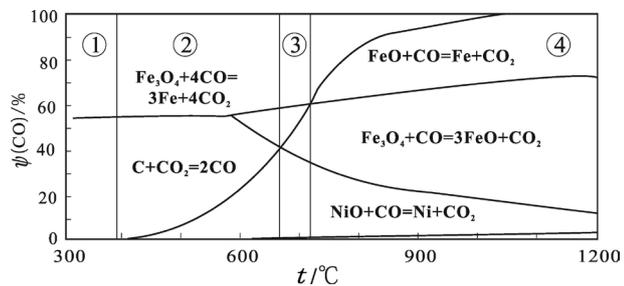


Figure 2. Thermodynamic balance diagram of iron oxide and nickel oxide reduced by carbon [9].



Figure 3. The patterns of samples reduced at 1200°C and melting separated at 1500°C and 1550°C. (a) 1# the iron and slag was not separated; (b) 2# the melted metal particles; (c) 3# the melted metal particles; (d) 4# the melted metal particles; (e) 5# metal particles was wrapped by slag; (f) 6# metal particles was wrapped by slag; (g) 7# the melted metal particles; (h) 8# the melted metal particles.

After comparing the figures, the conclusion could be obtained as follows: 1) in A group, when C/O mole ratio was 0.5, the samples had been melted after reduced at 1500°C, while the slag and iron had not been separated. The main reason may be that the C/O was too low, and the reduction of iron oxide was deficient. Moreover, the interfacial tension of slag and iron were reduced by large amounts of FeO that existed in slag which prevented the separation of slag and iron. When C/O mole ratio increased to 0.6 - 1.0, the reduction product could be separated significantly at 1500°C; 2) in B group which was added saked lime merely, when C/O mole ratio was 1.0, the separation of slag and iron cannot be realized at 1550°C. But the reduction of iron oxide was sufficient which can be certified by particles of metallic iron wrapped on the slag. When C/O mole ratio reached 1.2, the slag and iron mixed together at 1550°C and iron particles were fine, which indicated that superfluous C impede the aggregation of metallic iron. Therefore, we can conclude that when C/O mole ratio is high and saked lime is added merely, the interfacial tension of slag and iron is depressed. It is not conducive to the separation of slag and iron; 3) in C group which were added CaF₂ and saked lime simultaneously. Slag and iron can be separated adequately. Compared with A series added CaF₂ only, it can be found that the surface of separated metal phase was smoother.

4.2. The Chemical Compositions of Slag and Iron and Ni, Fe Yield of the Laterite Ore after Reduction and Melting

The chemical compositions of slag and iron after reduction at 1200°C and melting at 1500°C (or 1550°C) were shown in **Table 5** and **Table 6** respectively. The yield of Ni and Fe could be calculated by Equation (7) and Equation (8) respectively. And the results were shown in **Table 5**.

$$\text{The yield of Ni: } \eta_{\text{Ni}} = \frac{M_{\text{Ni}}^1}{M_{\text{Ni}}^0} \times 100\% \quad (7)$$

$$\text{The yield of Fe: } \eta_{\text{Fe}} = \frac{M_{\text{Fe}}^1}{M_{\text{Fe}}^0} \times 100\% \quad (8)$$

where M_{Ni}^1 and M_{Fe}^1 represent the quality of Ni and Fe in metallic particles after melted; M_{Ni}^0 and M_{Fe}^0 represent the quality of Ni and Fe in lateritic ore with carbon compacts before reduction.

From the two tables, the following result can be concluded: 1) in A group, with the C/O mole ratio changing from 0.6 to 1.0, the rate of iron reduction increased gradually, while the content of FeO and Ni in slag decreased from 39.11%, 0.55% to 9.14%, 0.084% respectively (**Table 6**); 2) as for C group, with the C/O mole ratio increasing from 1.0 to 1.2, the content of Ni in metallic particles improved from 1.37% to 1.42% and the yield of Ni enhances from 88.74% to 92.12%, while the yield of Fe changed little; 3) the desulfurization of slag can be improved when adding saked lime in compacts, the content of sulfur in metallic particles decreased observably.

Table 5. Chemical compositions of metal particles and the yield of nickel and iron (wt%).

Number	MFe	Ni	P	S	C	η_{Ni}	η_{Fe}
2#	89.65	1.79	0.042	0.627	4.967	71.3	59.96
3#	89.42	1.39	0.011	0.641	5.167	71.4	77.61
4#	87.33	1.34	0.011	0.651	6.045	88.2	95.91
7#	88.73	1.37	0.013	0.23	2.78	88.74	96.29
8#	89.91	1.42	0.013	0.22	2.82	92.12	97.69

Table 6. Chemical compositions of the slags (wt%).

Number	SiO ₂ %	Al ₂ O ₃ %	CaO%	MgO%	Ni%	FeO%
2#	12.86	28.92	4.76	5.76	0.55	39.11
3#	12.00	24.34	3.70	5.04	0.47	30.91
4#	17.12	35.34	5.59	6.97	0.084	9.14

Consequently, when increasing the content of Ni in the metal, the Inhibition of iron oxide reduction was needed. When the C/O mole ratio was 0.6, the nickel grade can be 1.79%, which was higher than the theoretical ratio 1.65% of Ni/(Ni + Fe) of the lateritic nickel ore, but the yield of nickel was only 71.3%.

5. Conclusions

1) The laterite nickel ore used in this investigation is the low-nickel, high-iron, high-alumina and low-silica ore. The theoretical ratio 1.65% of Ni/(Ni + Fe) of lateritic nickel ore is merely 1.65%. To enhance the content of Ni in metal after reduction, the reduction of iron must be suppressed.

2) The self-reduction investigation of coal mixed briquettes indicates that when C/O mole ratio is 0.5, large amount of iron oxide have not been reduced to metallic iron, even with the method of high temperature melting after reduction, the metal phase and slag cannot be separated. In group A, the added CaF₂ is merely a flux, when C/O mole ratio changes from 0.6, 0.8 to 1.0; the yield of metallic iron enhances from 59.96%, 77.61% to 95.91%; the content of Ni in metallic particles decreases from 1.79%, 1.39% to 1.34%; the yield of Ni increases gradually.

3) In group C, the CaF₂ and saked lime were added simultaneously. With the C/O mole ratio improving from 1.0 to 1.2, the content of Ni in metallic particles increases from 1.37% to 1.42% and the yield of Ni enhances from 88.74% to 92.12%. But the yield of Fe has little changed. When saked lime added in the briquettes, the content of sulphur reduced significantly.

4) Low C/O mole ratio restrains the reduction of ferric oxide and increases the content of Ni in metal, while the yield of Ni decreases.

Acknowledgements

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