Effect of Sodium Carbonate on Phase Transformation of High-Magnesium Laterite Ore

Shiwei Zhou1,2,*1, Jingcheng Dong1,2,*1, Chao Lu1,2,*1, Bo Li1,2, Fan Li2,*1, Bing Zhang2,*1, Hua Wang1,2 and Yonggang Wei1,2,*2

1State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China
2Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

The phase transformation of high-magnesium laterite ore were investigated during the reduction roasting process. In the absence of sodium carbonate [Na2CO3], the x-ray diffraction results indicate that the [Fe Ni] alloy existed in ore in the form of taenite. The taenite particles are fine and the size is approximately 30–40 nm, which indicate that the nickel and iron are not migrated and aggregated during the non-smelting reduction roasting process. In the presence of sodium carbonate, the intensity of [Fe Ni] alloy phase increases; the taenite diffraction peaks disappears, corresponding to the appearance of kamacite. The results of SEM images show that the [Fe Ni] alloy particle size has a significant increase with the addition of Na2CO3. Based on the theoretical analysis, the pivotal role of Na2CO3 may be mainly attributed to the Na+, which could infiltrate into the crystal lattice of FeO, leading to the lattice distortion. Furthermore, the sodium carbonate would be decomposed at high temperature, and the generated CO2 could promote the Boudouard reaction which produced the CO to enhance the reduction of metallic oxides within ore.

Keywords: laterite ore, phase transformation, reduction roasting, sodium carbonate

1. Introduction

Since reform and opening up, China’s economic development has made achievements that have attracted worldwide attentions. Nickel as national strategy for one of the significant metals occupies extremely important position in the national economic construction. The special physicochemical properties of nickel determine its extensive applications, at present, it mainly used in the production of stainless steel.

With the gradual depletion of high grade nickel sulphide resource, laterite has been applied in nickel industry as the main raw materials. Laterite ore deposits are formed by nickleiferous olivines via prolonged wathering and leaching processes.1,2 Based on the structure of ore deposit, it can be divided into three types: limonitic, saprolitic, and garnieritic deposits.3 For most limonitic deposits (40–60% Fe, 1–1.7% Ni), the pressure acid leach and Caron process are suitable for processing; whereas the saprolitic and garnieritic deposits (1.5–3% Ni) are more suitable for pyrometallurgical process due to the high content of magnesium.1,4 As a matter of fact, the low nickel laterite ores (< 1.5%) widely exists in nature and cannot be exploited easily due to the low grade and complex mineralogy. Nevertheless, low nickel laterite ore has been studied extensively for its effective utilization. Thermo-dynamic and experimental analyses of phase transformations occurring during the reduction and roasting process at high temperature have suggested that nickel recovery from the iron rich matrix is limited by equilibrium.5,6 In addition, sulfate, chlorine salt, and calcium oxide have been used as accelerants to promote the reduction of low nickel (< 1.5%) laterite ore, and they all achieved fruitful results.7–13

The Yunnan nickel laterite deposit, located in the southwest of China, contains an estimated ore resource of 0.43 Mt of nickel ore. It belongs to a high magnesium (> 30.0 mass% MgO), low iron (< 10.0 mass% total Fe) and low nickel (< 1.0 mass% Ni) laterite ore. Because of the extremely low grade nickel and complex compositions, the processing of this type of nickel silicate minerals is very complex and cost high, so far it has not been reasonable exploited. In order to extract valuable metals from this ore, the phase transformation of the laterite ore has been investigated in detail during the coal based reduction process in current study. Furthermore, in the presence of sodium carbonate, the change law and correlative mechanism of ferronickel size and morphology have also been studied on the process reduction. Where possible, the results can provide a theoretical reference for the comprehensive utilization of high magnesium and low nickel laterite ore.

2. Experimental

2.1 Materials

The chemical compositions of laterite ore were listed in Table 1, which shows it belongs to a typical saprolitic laterite with a small amount of nickel (0.82%). The raw ore was analyzed using X-ray diffraction (XRD) (Fig. 1). It is mainly composed of lizardite, quartz and maghemite. Anthracite was used as a reductant, the content of fixed carbon within anthracite is 76.43%. The Na2CO3 used in this study was of chemical grade.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fe (total)</th>
<th>Ni</th>
<th>Co</th>
<th>MgO</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content mass%</td>
<td>9.67</td>
<td>0.82</td>
<td>0.033</td>
<td>31.49</td>
<td>37.37</td>
<td>1.89</td>
<td>0.033</td>
<td>0.083</td>
</tr>
</tbody>
</table>

2.2 Apparatus and procedure

A series of reduction roasting tests were performed in a
horizontal tube furnace using corundum crucibles. All tests were conducted based on the conditions provided in Table 2. First, the laterite ore was crushed and ground to 98 mass% passing 74 μm using an XZM-100 laboratory mill; and then the ground laterite sample with a certain amount of Na₂CO₃ and 8 mass% anthracite (the amount of Na₂CO₃ addition varied from 0 to 20 mass% on the basis of laterite sample weight) was homogeneously mixed in a laboratory rotary mixing drum and transferred into the corundum crucible; the corundum crucible was then placed in a horizontal tube furnace and heated to the required temperature at a constant rate of 10°C/min. After reduction roasting, the roasted ore was then cooled under nitrogen atmosphere to prevent re-oxidation. To investigate the phase transformation and microstructure after reduction roasting, the cooled ores were subjected to X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analyses.

After heat treating at the required temperatures, each of the sample was subjected to XRD analysis. XRD analysis for phase transformation was performed with a Japan Science D/max-R diffractometer (Cu Kα radiation generated at 40 kV and 40 mA). The diffractograms were measured in the 10–80° 2θ range using a step size of 0.01°.

The microstructures and modes of occurrence of the main elements in roasted ore were analyzed by SEM (HITACHI-S3400N) coupled with energy dispersive X-ray spectroscopy EDS. In addition, the roasted ore was mounted with epoxy resin for SEM observation.

3. Results and Discuss

3.1 X-ray diffraction analysis of laterite mineral phase

3.1.1 Effect of temperature on phase transformation

The results of phase transformation of laterite ore roasted with 8% anthracite for 45 min as a function of roasting temperature are depicted in Fig. 2. The serpentine has been transformed into olivine group (Mg₃Si₂O₇ → Mg₂SiO₄ + MgSiO₃) after roasting temperature above 900°C. At 900°C and 1000°C, the XRD patterns of the roasted ore show forsterite [Mg₂SiO₄] as the major phase, with quartz [SiO₂] and enstatite [MgSiO₃] as minor phases. The forsterite diffraction peaks increase with increasing roasting temperature, and the taenite [Fe Ni] diffraction peaks could not be observed when the temperature below 1000°C. As the temperature increased to 1100°C, the forsterite diffraction peaks reaches maximum, in addition, the taenite diffraction peaks begin to appear. Thereafter, the forsterite diffraction peaks intensity decreased significantly due to the recrystallization of forsterite (Mg₂SiO₄ + SiO₂ → 2MgSiO₃) leading to the increase of enstatite diffraction peaks. Furthermore, the diffraction peaks of taenite become dominant as temperature increased to 1200°C. These findings indicate that elevated reduction temperature could promote the formation of ferronickel alloy. The reasons could be summarized as follows: (a) the grades of nickel and iron are low in the raw ore and mainly existed uniformly in the form of isomorphism, which hindered the reduction of the metallic oxides at low temperature; (b) the recrystallization of forsterite could promote the formation of enstatite, and NiO embedded in MgSiO₃ is easier to reduce at higher temperature, which showed stronger peak intensity of FeNi at higher temperature.
3.1.2 Effect of roasting duration on phase transformation

Figure 3 shows the phase transformation of laterite ore roasted with 8% anthracite at 1200°C as a function of roasting duration (5 to 60 min). The results indicate that the forsterite diffraction peaks decreased gradually with prolonging roasting duration from 5 to 45 min. Whereas the diffraction peaks of enstatite and taenite have opposite variation trend. These phenomena are in accordance with the aforementioned results. Prolonging the reaction time is conducive to the reduction of metallic oxides, so that the ferronickel particles can be aggregated better. Furthermore, as the roasting duration is further increased to 60 min, the diffraction peaks intensity of taenite decreased significantly. This finding reveals that it is not conducive to the formation of ferronickel alloy with excessive extension of roasting duration. Thus, 45 min is deemed to the optimal reduction duration to this type of ore.

3.1.3 Effect of Na2CO3 dosage on phase transformation

Figure 4 presents the results of reduction roasted ore with 8% anthracite and various dosages of Na2CO3 at 1200°C for 45 min. In the presence of Na2CO3, the intensity of peaks have a significant increase. Forsterite as the major phase, with kamacite and taenite as minor phases. When the Na2CO3 dosage increases from 5 to 10%, the kamacite peak intensity reach maximum values, and the taenite peak disappeared completely. With the increase of dosage, the reduction process is enhanced and a large number of iron is obtained as a results, the ratio of iron in [Fe Ni] increased, therefore the taenite is gradually transformed into kamacite. Further increasing the Na2CO3 dosage, the kamacite peak intensity gradually decreases. This finding indicates that the appropriate Na2CO3 could promote the generation of kamacite phase. When the dosage exceed 15%, the Na2MgSiO4 phases are observed. In addition, the enstatite [MgSiO3] phases cannot be observed in the presence of Na2CO3. This phenomenon may be due to the reaction [Na2CO3 + MgSiO3 → Na2MgSiO4 + CO2], leading to the disappearance of MgSiO3.

The average crystallite size of [Fe Ni] alloy within roasted ore, which roasting reduction without Na2CO3 is calculated from XRD peaks using the following Scherer’s formula,

\[ D = \frac{0.89 \lambda}{B \cdot \cos \theta} \]

Where \( D \) is the crystalline size, \( \lambda \) is the X-ray wave length (\( \lambda = 1.5406 \text{ Å} \)), \( B \) and \( \theta \) are the half-width of X-ray diffraction and diffraction angle, respectively. The result of crystalline size is depicted in Fig. 5. Figure 5(a) indicated that the crystalline size of [Fe Ni] alloy decreased from 39.91 to 31.93 nm with increasing the roasting temperature. This result is accordance with the findings of other scholars, reflecting the decreasing in crystalline size with faster reduction rate and higher reduction extent. Furthermore, in the absence of additives, the crystalline size is very fine and is approximately 30–40 nm. The tiny [Fe Ni] particles cannot be efficiently enriched in the subsequent process. In addition, in the presence of Na2CO3, the microstructure of roasted ore is investigated by SEM analysis method and reported in following part.

3.2 SEM analysis of roasted ore

To compare the occurrence state of each component within ore roasted with varying content of Na2CO3, the microstructures were investigated using the SEM analysis method, shown in Fig. 6. Without addition of sodium carbonate (Fig. 6(a)), the ferronickel within roasted ore presents fine particle size and well distributed. Whereas the particle size...
Effect of Sodium Carbonate on Phase Transformation of High-Magnesium Laterite Ore

3.3 Mechanism of Na2CO3 during reduction roasting

Based on the above discussions, in the presence of Na2CO3, the ferronickel particle size and crystallinity have a significant increase during reduction and roasting process, indicating that Na2CO3 could promote the reduction of laterite ore to form ferronickel. Therefore, there should be some mechanisms for ferronickel formation during reduction roasting.

The reduction of iron oxide can be divided into three steps: 

\[
\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe} \]  

18 The step of FeO → Fe, which is the limiting step of the whole process, is difficult to carry out under the low temperature condition. The fracture of Fe-O bond is accompanied by the change of energy in the reduction process of FeO → Fe. Guo et al. reported19 that the catalysis of Na2CO3 is mainly occurred at the stage of FeO → Fe. In addition, the Mossbauer spectrum and XRD analyses were performed,19 and the results shown that the alkali metal ions could infiltrate into FeO lattice after the addition of alkali metal salt, resulting in lattice distortion. Therefore, the Na2CO3 could promote the reduction of FeO. Furthermore, from the thermodynamics viewpoint, the Na2CO3 would be decomposed at high temperature, in particular, in the case of the presence of quartz [Na2CO3 + SiO2 = Na2SiO3 + CO2(g) \(\Delta G^\circ = 74643.14 - 123.18T, J/mol\)]. The generated CO2 could promote the Boudouard reaction \[C + CO_2(g) = 2CO(g) \Delta G^\circ = 170707 - 174.47T, J/mol\], which produced the CO to enhance the reduction of metallic oxides within ore.

In addition, the reaction product (Na2SiO3) is a low melting point compound (1089°C) and it provides favorable conditions for the mass transfer, namely, the migration and aggregation of Ni and Fe would be occurred easily during reduction at high temperature (> 1100°C).

4. Conclusion

(1) The laterite ore investigated in this study belongs to a high-magnesium (31.49% MgO) low-nickel (0.82% Ni) oxide ore, the nickel cannot be detected by X-ray diffraction due to the low content within ore.

(2) In the absence of Na2CO3, the metallic oxides within ore are mainly reduced by in-situ in the non-smelting reduction process; the [Fe Ni] alloy is mainly existed in the form of taenite, the particle is fine and crystalline size is approximately 30–40 nm.

(3) The result of the SEM analysis indicates that the Na2CO3 existed in ore system could promote the growth of [Fe Ni] alloy particles; the nickel and iron have been migrated, the phase of [Fe Ni] alloy transforms into kamacite and the particle size has a significant increase. When the Na2CO3 dosage increased to 20%, the decomposition of sodium carbonate within laterite ore would generated a lot of carbon dioxide at high temperature, resulting in the increase in volume. The forsterite structure is subjected to stress which produced by the volume expansion, and then destroyed.

Acknowledgments

Financial support for this study was supplied from the National Natural Science Foundation of China (Project Nos. U1302274 and 51304091), the Candidate Talents Training Fund of Yunnan Province (2012HB009) and the Analysis and Testing Foundation of Kunming University of Science and Technology.
REFERENCES