Smelting separation behaviors and mechanisms of high-alumina rich-manganese ore obtained from metallic reduction and magnetic separation

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Abstract: The smelting separation of high-alumina rich-manganese ore prepared with selective reduction and magnetic separation was proposed to produce the high carbon ferromanganese alloy (HCFeMn) in this paper. The rational smelting separation parameters for high-alumina rich-manganese ore includes a FC/O of 1.1, a smelting temperature of 1550°C, a melting time of 60 min, and a basicity of 0.7. The smelting separation of high-alumina rich-manganese ore was achieved successfully. The content of Fe, C, Si and other impurities (P, S) are 12.13%, 6.73%, 0.17% and 0.14, 0.008, respectively. Especially, the recovery and content of Mn reach around 80.47% and 76.76%. The obtained high carbon ferromanganese alloy has met the higher standard (FeMn78C8) of ferromanganese alloy, especially, the content of Si P and S in the HCFeMn alloy is far below the standard value. Based on the SEM-EDS, XRD and thermodynamic calculation, the smelting and separation mechanisms of high-alumina rich-manganese ore was proposed to more effectively explain the effect of smelting parameters on slag/metal separation behaviors during the process of smelting HCFeMn alloys.

Keywords: Rich-manganese ore; smelting separation; high carbon ferromanganese alloy; thermodynamics.

1. Introduction

Ferruginous manganese ores are one kind of important manganese resources for manganese extraction. South Africa ranks first in manganese production, with about 4.0 Mt produced and also currently accounts for about 24.1% of the worlds identified manganese resources, whereas high-grade manganese ores as an acceptable feed (Mn/Fe mass ratio over 5) for ferromanganese alloys production are being seriously scarcity of the global market [1-4]. It has become an indisputable fact that high-quality manganese ore has been seriously scarce in the global maker. To meet the growing demand, the metallic reduction roasting process-magnetic separation followed by electric furnace process is brief and suitable way for industrial applications to address high-alumina Fe-Mn ore as a result of selective mining of high-grade manganese ore.

As reported, more than 50% of low-grade manganese ore as a result of selective mining of high grade manganese ore belongs high-iron manganese ore in South Africa. The reduction roasting of low grade manganese ore containing high iron content followed by magnetic separation to separate metallic iron and manganese was proposed to produce rich manganese concentrates in nonmagnetic product and metallic iron in magnetic product in previous work [5-8]. Therefore, the Mn and Fe were successfully separated thoroughly in high-alumina ferruginous manganese ores (Al2O3>7%, SiO2<4%) by metallic reduction at 1050°C [9]. In addition, few studies have discussed metallic reduction roasting process-magnetic separation followed by electric furnace process to smelt manganese alloy from high-alumina Fe-Mn ores. Nevertheless, it is essential to find a rational understanding for smelting manganese alloy form high-alumina ferruginous manganese ore and propose some suggestions for the smelting process to the utilization of high-alumina Fe-Mn ore.

The high-alumina ferruginous manganese ore from manganese tailing in South Africa with high Al and Fe content will also inevitably obtained high-alumina rich manganese ore (HAMO) containing high Al/Si and Mn/Fe ratio by the above mentioned pre-treatment method. Previous works have research on the rich manganese ore to smelt HCFeMn alloy, and different Al/Si ratio and Al content in slag compositions have been summarized and displayed in Figure 1. Several workers [10-18] have studied and calculated equilibrium...
phase chemistry in the Al₂O₃-MgO-SiO₂-CaO-MnO slag system. The slag basicity was optimized by flux addition to obtain the higher manganese recovery and qualified metal with slag containing Al₂O₃ content at a range of 7.5 to 16.0 wt% and an Al₂O₃/SiO₂ weight ratio of 0.2-0.5. In the work of Park et al., [19] the Al₂O₃ behaves as an amphoteric oxide with the composition of slags. The influence of alumina on the viscosity decrease can be explained on the basis of a decrease in the degree of polymerization by the increase in the relative fraction of the [AlO₆]-octahedral units. The slag transform from silicates-based to aluminates-based with an increase of Al content and Al/Si ratio [20]. Therefore, the high-alumina rich-manganese ore containing high Al₂O₃ content and Al/Si ratio was applied to smelt HCFeMn alloy to research the substitution of SiO₂ with Al₂O₃ and provide an opportunity to explain smelting and separation mechanisms.

![Graph showing slag compositions of smelting HCFeMn alloy from other workers’ studies](image)

Figure 1. Slag compositions of smelting HCFeMn alloy from other workers’ studies

On the basis of the previously discussed background, the authors proposed an innovative process to smelt high quality HCFeMn alloy from high-alumina rich-manganese ore (HAMO) that obtained from the high-alumina ferruginous manganese ore by metallic reduction roasting followed by magnetic separation. The effect of smelting temperature and time, FC/O and basicity on manganese grade and recovery was proposed to produce high quality HCFeMn alloy. The influence of smelting parameters on the recovery and grade of manganese and the smelting mechanisms were discussed at the process smelting separation of HAMO.

2. Experiment

2.1. Raw Materials

The High-alumina rich-manganese ore was obtained from high-alumina ferruginous manganese ore by metallic reduction roasting and magnetic separation in the author’s previous work [9]. The metallic reduction roasting includes reduction temperature 1050°C, time 6 h, particle size 8-13 mm, FC/O 2.5 and magnetic field strength 100 mT. The FC/O is the mole ratio of fixed carbon in coal to reducible oxygen of iron and manganese in low-grade manganese ore or HAMO. The chemical composition and X-ray diffraction (XRD) analysis of HAMO are shown in Table 1 and Figure 2 respectively. It indicated that manganese mainly comprised of MnO and MnSiO₃, and the iron compounds mainly exist as metallic Fe and spinelle (FeO·Al₂O₃) in HAMO. The Al element in HAMO, which has negative influences on smelting separation of rich manganese ore, is detected in form of galaxite (MnO·Al₂O₃) and hercynite (FeO·Al₂O₃). The analytically pure CaO is applied as flux. The activated carbon is used as reduction agent and carburization.

<table>
<thead>
<tr>
<th>Table 1. Chemical compositions of HAMS /wt %</th>
</tr>
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<tbody>
<tr>
<td>TFe</td>
</tr>
<tr>
<td>6.15</td>
</tr>
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</table>
2.2. Experimental Procedure

In this paper, the smelting process of HAMO is carried out in a medium frequency induction furnace (XZ-40B) for simulating the electric furnace process. The sketch schematic of induction furnace is shown in Figure 3. The experimental apparatus consists mainly of a power control system, a furnace body, a protective gas system, a cooling system and an induction heating system. The medium frequency induction heating of HAMO with the copper coil are conducted by adjusting the output oscillatory power of control system, and the specified smelting temperature can be achieved within a short time. The copper coil is internally protected by cooling water to prevent superheated melting of copper coil. A calibrated infrared thermometer (DT-8869h) with a measure range of -50~2200°C and a accuracy of 0.1°C is used for the temperature measurements in the smelting process.

![Figure 3. Schematic diagram of induction furnace](image)

Firstly, the reduced low grade manganese ore was ground by 2-MZ centrifugal grinding machine to 100% passing 74 μm, followed by magnetic separation using a Davies Magnetic Tube (DTCXG-ZN50) to obtain HAMO in nonmagnetic product and metallic iron in magnetic product. The materials including HAMO powders, activated carbon and reagent CaO are weighted in a certain proportion. Subsequently, according to the chemical compositions of HAMO, the effect of CaO/(SiO2+Al2O3) and FC/O was investigated in the below experiments. The mixtures were loaded in a dense high pure graphite crucible (inner diameter × inner height: 30 mm×85 mm, external diameter × external height: 40 mm×100 mm). The crucible was then placed into the effective temperature section of the induction furnace and heated to the designed temperature rapidly to realize separation of HCFeMn alloy and slag. After the smelting separation experiments, the induction furnace was shut down, and the HCFeMn alloy and slag were rapidly cooled down to the room temperature in argon atmosphere.

![Figure 2. XRD analysis of HAMO](image)
2.3 Experimental Scheme

In the experimental process, the effect of the smelting temperature and time, FC/O and ternary basicity CaO/(SiO₂+Al₂O₃) on the separation index was investigated to obtain the rational technological parameters, which these parameters ranged 1450-1550°C, 15-90 min, 0.7-1.3 and 0.4-0.8, respectively. When the CaO fluxes were not added, the smelting basicity of CaO/(SiO₂+Al₂O₃) was initially 0.06. the single-factor control variable method was used in this paper, which only a single parameter changed and other parameters were kept in the basic conditions. The basic smelting parameters included a smelting temperature of 1525°C, a smelting time of 30 min, a FC/O of 1.1 and a basicity CaO/(SiO₂+Al₂O₃) of 0.7. The detailed experimental scheme was listed in Table 2.

Table 2. Experimental scheme for the smelting separations of HAMO

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Variation Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelting temperature /°C</td>
<td>1450 1500 1525 1550</td>
</tr>
<tr>
<td>Smelting FC/O /-</td>
<td>0.7 0.9 1.1 1.3</td>
</tr>
<tr>
<td>Smelting time /min</td>
<td>15 30 45 60 90</td>
</tr>
<tr>
<td>Smelting CaO/(SiO₂+Al₂O₃) /-</td>
<td>0.4 0.5 0.6 0.70 0.80</td>
</tr>
</tbody>
</table>

After the experiments, the smelting slag and high-carbon ferromanganese alloy (HCFE&Mn) were obtained and weighed. With the smelting separations of 100 g HAMO, the diameter of obtained alloy was about 30 mm and its height was about 10 mm, as shown in Figure 4. The contents of Mn, Fe and C elements in high carbon ferromanganese alloy were analyzed by the chemical titrations and ICP-OES analysis to calculate and analyze the recovery and content of Mn, Fe and C elements in the HCFE&Mn alloy. The obtained high-alumina slags were detected by XRD to analyze the phase compositions of smelting slag. The X-ray diffraction of the samples was carried out by using a copper Kα radiation, with a scanning angle range varied from 5° to 90° using a scanning speed of 0.2°/s. The microstructure of smelting sample was observed by scanning electron microscope (SEM) equipped with an energy diffraction spectrum (EDS).

![Figure 4. Specimens appearance of HCFE&Mn and high-alumina slags (a) in CaO/(SiO₂+Al₂O₃) 0.7 and FC/O 0.9 at 1525°C for 30 min](image)

The recovery of valuable elements were calculated according to the following equation:

$$\eta_{Mn} = \frac{m_{Mn} \times \beta_{Mn}}{M_{Mn} \times \gamma_{Mn}} \times 100\%$$

where \(\eta_{Mn}\) is the recovery ratio of manganese in HCFE&Mn alloy; \(m_{Mn}\) is are the mass of HCFE&Mn alloy; \(M_{Mn}\) is the mass of HAMO; \(\beta_{Mn}\) is the content of manganese in HCFE&Mn alloy; \(\gamma_{Mn}\) is the content of manganese in HAMO. A similar expression describes how the recovery yield of iron varies with composition in HCFE&Mn alloy.
3. Results and Discussion

3.1 Thermodynamic analysis

Figure 5 displays the thermodynamic graph by FACTSAGE 7.0 of reduced manganese oxide and iron oxide in Mn-Fe ore. The mainly reduction reaction relationships is calculated by the following equations (Eq.2-34) in Table 3. Figure 5(a) indicates that MnO₂ and Mn₂O₃ should be reduced to Mn₃O₄ at lower temperature and then further reduced to MnO at above 284°C. The MnO by carbon at atmospheric pressure is reduced to Mn and Mn₃C at above 1393°C and 1397°C respectively. The reduction of Fe₂O₃ by carbon could be feasible at 324°C, and the metal Fe formed is reduced from FeO at 724°C. As is shown in Figure 5(b), the indirect reduction of manganese oxide and iron oxide mainly can be investigated by thermodynamic graph of manganese and iron oxide. The reduction reaction of MnO₂, Mn₂O₃ and Mn₃O₄ is easily converted to MnO at the low temperature. Figure 5 (c) illustrates that the initial reaction temperature of MnO reduction to Mn₇C₃ and Mn₃C is 1342°C and 1393°C, respectively. Figure 5(d) shows that MnₙCₚ is easily decomposed by CO₂, the Mn₇C₃ and Mn₃C can be converted to Mn by CO₂ at 915°C and 774°C respectively.

Table 3. The reduction reaction of the Mn-Fe ore based on the following equation

<table>
<thead>
<tr>
<th>Reaction equation</th>
<th>NO.</th>
<th>Reaction equation</th>
<th>NO.</th>
<th>Reaction equation</th>
<th>NO.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2MnO₂+C=Mn₂O₁₄+CO</td>
<td>2</td>
<td>3Mn₉O₁₀+C=2Mn₉O₁₄+CO</td>
<td>3</td>
<td>MnO+C=Mn₆O₁₄+CO</td>
<td>4</td>
</tr>
<tr>
<td>MnO+C=Mn+C+CO</td>
<td>5</td>
<td>3MnO+C=Mn₆O₁₄+3CO</td>
<td>6</td>
<td>3Fe₂O₃+C=2Fe₃O₄+CO</td>
<td>7</td>
</tr>
<tr>
<td>Fe₂O₃+C=3FeO+CO</td>
<td>8</td>
<td>FeO+C=Fe+CO</td>
<td>9</td>
<td>2MnO₂+CO=Mn₂O₁₄+CO₂</td>
<td>10</td>
</tr>
<tr>
<td>3Mn₂O₃+CO₂=2MnO+CO</td>
<td>11</td>
<td>MnO₂+CO=MnO+CO₂</td>
<td>12</td>
<td>MnO+CO=Mn+CO₂</td>
<td>13</td>
</tr>
<tr>
<td>C+CO₂=2CO</td>
<td>14</td>
<td>FeO+CO=Fe+CO</td>
<td>15</td>
<td>Fe₂O₃+4CO=3Fe+4CO₂</td>
<td>16</td>
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<tr>
<td>Fe₂O₄+CO=3FeO+CO₂</td>
<td>17</td>
<td>3Fe₂O₃+CO=2FeO₄+CO₂</td>
<td>18</td>
<td>7Mn+3C=Mn₇C₃</td>
<td>19</td>
</tr>
<tr>
<td>3Mn₉C=C=Mn₇C₃</td>
<td>20</td>
<td>Mn₉+2Mn₇C₃=3MnC₂</td>
<td>21</td>
<td>5Mn+2Mn₇C₃=Mn₁₅C₄</td>
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</tr>
<tr>
<td>8Mn+3Mn₂C₂=Mn₇C₃</td>
<td>23</td>
<td>7MnO₁₀+10C=Mn₇C₃+7CO</td>
<td>24</td>
<td>3MnO₄+4C=Mn₇C₃+3CO</td>
<td>25</td>
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<tr>
<td>3Mn₃C₃+3C₇O₂=7MnO₁₀+46CO</td>
<td>26</td>
<td>Mn₃C₃+4CO₂=3MnO+5CO</td>
<td>27</td>
<td>Mn₇C₃+3CO₂=7Mn+6CO</td>
<td>28</td>
</tr>
<tr>
<td>Mn₇C₃+CO₃=3Mn+2CO</td>
<td>29</td>
<td>MnO+CO=Mn+CO</td>
<td>30</td>
<td>Mn₇C₃+3MnO=10Mn+3CO</td>
<td>31</td>
</tr>
<tr>
<td>4Mn₇C₃+3MnO₁₄=37Mn+12CO</td>
<td>32</td>
<td>Mn₇C₃+MnO=4Mn+CO</td>
<td>33</td>
<td>4Mn₇C₃+MnO₁₄=15Mn+4CO</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure 5. Thermodynamics graph of direct reduction (a) and indirect reduction (b) in Mn-Fe ore, the formation of Mn₉C₃ (c) and the decompose of Mn₉C₃ (d)

3.2 Effects of CaO / (SiO₂+Al₂O₃)
The effect of smelting basicity CaO/(SiO$_2$+Al$_2$O$_3$) on the recovery of Mn and quality of HCFeMn is given in Figure 6. The smelting basicity CaO/(SiO$_2$+Al$_2$O$_3$) was referred to the molar ratio of CaO to SiO$_2$ and Al$_2$O$_3$ in the experimental process. It is obvious that the recovery rate of Mn in HCFeMn increases from 40.80% to 75.92% with an increase of CaO/(SiO$_2$+Al$_2$O$_3$) from 0.4 to 0.7. When the ternary basicity CaO/(SiO$_2$+Al$_2$O$_3$) exceeds 0.7, the recovery of Mn instantly decreases to 70.78%. All the indexes reach the highest at a basicity of 0.7. The recovery of Mn reach 75.92%, and the content of Mn, Fe, and C is 77.04%, 12.50% and 6.97% in HCFeMn alloy, respectively. When smelting basicity CaO/(SiO$_2$+Al$_2$O$_3$) in raw ore is 0.06, this slag/metal was not separated successfully. This is mainly due to the sum and polymerization degree of complex viscous units [SiO$_4$]$^4$ tetrahedral and [AlO$_3$]$^3$ tetrahedral in slag are in a high level [21, 22]. High Al$_2$O$_3$ content in the CaO-SiO$_2$-MnO-Al$_2$O$_3$ slag system result in lower absolute amounts of SiO$_2$, which infer that complex silicate structures decrease and the relative amount of Al-O structures become increasingly dominant. The higher Al$_2$O$_3$ content increased the slag viscosity due to the polymerization of the aluminate structure. The increasing slag viscosity results in the large viscosity of slag and the poor dynamic conditions for the smelting separation of HAMO which not only impedes the enrichment of Mn in HCFeMn, but also hinders the carbothermic reductions of iron oxides and manganese oxides in the smelting separation process. This is the root cause of the experiment using ternary alkalinity. An increase of CaO/(SiO$_2$+Al$_2$O$_3$) is able to simplify the complex viscous units which lead to the decreased viscosity and improved fluidity in HAMO, mainly because the O$^2-$ in CaO (alkaline oxide) can easily escape from the constraint of Ca$^{2+}$ at the high temperature, and it will destroy the network structure of silicate and make the complex Si$_x$O$_y$ [23].

![Figure 6. Effect of CaO/(SiO$_2$+Al$_2$O$_3$) on the smelting index](image)

![Figure 7. Effect of basicity on the liquid slag region of CaO-SiO$_2$-Al$_2$O$_3$-MgO-MnO](image)

In addition, the Phase Diagram Module in FACTSAGE 7.0 is applied to calculate the phase diagram of the liquid phase region of CaO-SiO$_2$-MgO-Al$_2$O$_3$-MnO with different CaO/(SiO$_2$+Al$_2$O$_3$) at 1525°C. The effects of CaO/(SiO$_2$+Al$_2$O$_3$) on the meltability of slag are analyzed to explain the effect of basicity on the efficiency of above various indicators in smelting process of HAMO. The calculated results are shown in Figure 7. As increased basicity, the entire area proportion of the full liquid slag enlarged, and the solubility of MnO in slag increased simultaneously. When the CaO/(SiO$_2$+Al$_2$O$_3$) reaches to 0.8, the area proportion of the liquid slag is decreased dramatically. More liquid slag at a certain temperature can promote the complete
separation of slag and iron in the smelting separation, which improves the meltability and fluidity of HAMO [24]. Therefore, the effective separation of HAMO is enhanced with increasing basicity, and the recovery and grade of Mn in pig iron is significantly improved.

To further verify the effects of the CaO/(SiO₂+Al₂O₃) on smelting separation of HAMO, the phase composition of separation slag under different Basicity is analyzed by XRD in Figure 8. The gehlenite (2CaO Al₂O₃ SiO₂), unreduced MnO are detected by XRD in slag, and little metal Fe, 3MgO Al₂O₃ 3SiO₂ and MnO Al₂O₃ are also simultaneously found. The diffraction peak intensity of MnO is extended with the basicity increasing from 0.4 to 0.7. The effect of slag basicity on efficiency of smelting separation can be attributed to the activity of MnO in slag. Increased basicity can promote an increase of free MnO which in turn accelerates the reduction of manganese oxide. The basicity of CaO/(SiO₂+Al₂O₃) exceeds 0.8, the indexes of smelting have various degree decreases. In addition, the diffraction peak intensity of gehlenite and MnO at a basicity of 0.8 reaches a higher level and the area proportion of the liquid slag reach the lowest value which will lead to increasing liquid temperature of slag. It results that the deteriorated superheat and homogeneity of slag and bringing about the increasing viscosity of slag which leads to decrease the efficiency of smelting separation [24, 25]. The lower manganese recovery at high basicity can be explained by XRD and thermodynamic calculation in these slags. Therefore, comprehensively considering the experimental results, phase transition, and thermodynamic equilibrium analyses. The rational smelting ternary basicity of CaO/(SiO₂+Al₂O₃) in HAMO is approximately 0.7.

![XRD patterns of smelting slag with different ternary basicity of CaO/(SiO₂+Al₂O₃)](image)

Figure 8. XRD patterns of smelting slag with different ternary basicity of CaO/(SiO₂+Al₂O₃)

### 3.3 Effect of Smelting FC/O

The various indexes in the smelting separation process of HAMO with different smelting FC/O values are described in Figure 9. With an increase of FC/O from 0.7 to 1.3, the recovery rate and content of Mn in HCFeMn increased accordingly from 52.26 to 75.92% and 73.14 to 77.04%, respectively. At a smelting FC/O of 1.1, the recovery and content of Mn reach up to the optimum smelting indexes. Further increasing smelting FC/O to 1.3, the recovery rate and content of Mn decrease to 67.60% and 76.77%, respectively, and the content of carbon in HCFeMn alloy remains around 7.0%. For the distribution of Fe, its content reaches initially 13.02% at a FC/O of 0.7, and subsequently slowly increase from 12.50% to 13.96% with an increasing of FC/O from 1.1 to 1.3. Therefore, the rational smelting FC/O should be maintained at 1.1 for smelting separation process of HCFeMn alloy.
To further investigate the effect of smelting FC/O on the smelting separation of HAMO, the Equilib Module in Factsage 7.0 package is applied to assess the thermodynamic equilibrium. 100 g of the mixed samples were analyzed at the temperature range of 1350°C-1700°C. The relative amount variation of the main products is shown in Figure 10. With increasing the smelting FC/O from 0.7 to 1.1, the generation mass of liquid Mn(l) is significantly improved, meanwhile the mass of nonmetal C in metal also declines. In addition, the mass of MnO phases in slag gradually decrease which proves that carbothermal reductions of MnO are significantly improved. Further, the smelting FC/O increasing from 1.1 to 1.3, the generating amount of Mn, Fe and C in metal slowly grow below the smelting temperature of 1600°C. For the mass of Fe in metal, the generated amount of Fe(l) in metal does not result significant fluctuations. It is mainly due to the reduction of FeO in the main iron reduction stage can occur by dissolved carbon as the dominant reaction in the product metal at the initial stage. And FeO does not easily polymerize with the flux and is easily reduced by carbon in the initial stage. Therefore, comprehensively considering the experimental results and thermodynamic equilibrium analyses, the rational smelting FC/O of HAMO is approximately 1.1.

3.4 Effect of Smelting Time

The variation of smelting separation index at different smelting time of HAMO is shown in Figure 11, it indicates that the recovery rate and content of Mn in HCFeMn alloy at initial stage increases from 39.42% to 75.92 and from 72.40% to 77.04% with an increase of smelting time from 15 min to 60 min, However, the content of carbon and iron in HCFeMn alloy decreases from 8.27% to 6.97% and from 16.75% to 12.70% respectively. At the smelting time of 60 min, the recovery rate and content of manganese reach 75.92% and
77.04%, respectively. Further, an increase of smelting time declines tardily the recovery rate and content of manganese in HCFeMn alloy.

![Figure 11. Effect of smelting time on the smelting index](image)

The XRD analysis of reduced HAMO at different smelting time is shown in Figure 12. When smelting time is under 60 min, the diffraction peaks of MnO get weaker gradually, which demonstrates that MnO in HAMO is reduced by carbon with an increase of smelting time. The diffraction peaks of gehlenite as the basic phases maintain stabilization. However, when smelting time reaches to 90 min, the diffraction peaks of MnO remarkably decrease, while the peaks value of gehlenite clearly increases due to the complete reduction of manganese oxidation in HAMO. It can explain that the content of iron and carbon in the alloy gradually declines with an increase of smelting time. When the time is longer than 60 min, both recovery rate and content of Mn decrease. This is primarily due to manganese vaporization losses on the smelting process. At initial smelting reduction stage, the Fe metal serves as a reservoir for Mn formed from MnO reduction and so limits manganese vaporization losses, the formation of this Fe-Mn alloy results in lowered activity of manganese, as compared to pure manganese formation resulting in favorable thermodynamics to drive the MnO reduction reaction [26]. At the later stage, little or no metallic iron and FeO in the slag, the produced Mn by carbothermic reduction is rapidly evaporated due to high vapor pressure of Mn at high temperature [27].

![Figure 12. XRD patterns of smelting slag with different smelting time](image)

To further confirm the effects of smelting time of the smelting separation of HAMO, the various compositions of slag after smelting separation were analyzed by SEM and EDS. The results are presented in Figure 13. There are three main phases in samples. The white is Mn-Fe particles; the light gray (Point C) is the slag containing mainly MnO, and the dark gray (Point B) is the slag containing much gehlenite and little spinel not only by EDS analysis but also by XRD analysis. Furthermore, it is obvious that the Fe-Mn alloy
and unreduced phase MnO are closely connected and not effectively separated with each other at a smelting time of 15 min (Figure 13(A)). The Fe-Mn particles are carburized after its initial formation [26]. With increasing smelting time, the phase of MnO in the slag gradually decreases. Figure 13 (A) shows that the slag droplet forms and moves during reduction of the smelting separation. Numerous pores formation is caused by CO gas bubble formation or aggregation and growth of metal particle in the slag. A comparison of the SEM analysis, only a small amount of MnO phase in the Mn-Fe slag are found in Figure 13(E). This explains that the carbothermic process of MnO in the slag is basically completed. Therefore, if the smelting time is short (<45 min) or too long (>60 min), the short smelting time is not enough for deep reduction and carburization. But the long smelting time will cause the increasing manganese vaporization losses on the smelting process [27, 28]. Therefore, comprehensively considering the experimental results, XRD and SEM-EDS analyses, rational smelting time of HAMO is approximately 60 min.

Figure 13. SEM-EDS analyses of the smelting slag with different smelting time: (A) 15 min, (B) 30 min, (C) 45 min, (D) 60 min and (E) 90 min

3.5 Effects of Smelting Temperature

The effect of smelting temperature on the Mn recovery and content is shown in Figure 14. The recovery and content of Mn increase from 27.18% to 80.47% and from 67.87 to 76.76% with the smelting temperature raising from 1475 to 1550°C respectively. The content of Fe and C slightly decreases from 16.55 to 12.13% and from 7.04 to 6.73% at an increase of smelting temperature. Especially, at the smelting temperature of 1550°C, the recovery and content of Mn reach 80.47% and 76.76%.

Figure 14. Effect of smelting temperature on the smelting index

The XRD patterns of smelting separation slag are described as Figure 16. The key precipitated phases of slag are gehlenite and MnO. Besides, the minor manganese spinel and metal iron can also be found. With the temperature increasing from 1475 to 1550°C, the gehlenite and MnO phase in the precipitated phase obviously
changes. And diffraction peaks of complex gehlenite gradually increase, while the diffraction peaks of MnO decrease. It proves that the effect of smelting temperature on the carbothermic reaction of the free MnO. Especially, at 1550 ℃, the diffraction peaks of gehlenite are clearly higher than other temperatures, only a small amount of MnO phase is detected by XRD. According to the thermodynamic phase diagram analysis (Figure 10), the content of Mn Fe and C in HCFeMn alloy maintains basically constant which prove that the smelting temperature has less influence on the content of element in HCFeMn alloy when the temperature exceeds 1550 ℃. Morphology of the separation between alloy and slag with different smelting temperature is shown in Figure 15. The morphology of HCFeMn alloy has obvious changes with different smelting temperature. Obviously, a large number of Fe-Mn particles retained in the slag at smelting temperature 1475 ℃, and the aggregation and growth of Fe-Mn particle in the slag is appeared, but the smelting separation isn’t achieved successfully due to the big viscosity and bad fluidity of slag at lower temperature. Accordingly, it is necessary to further study the separation mechanism of HAMO, which can be seen in the following work. In Figures 17 (A), one can find Fe-Mn enriched phase droplets dispersed in the slag phase at low smelting temperature, which proves that low temperature has a significant impact on the separation of slag and Fe-Mn alloy. The higher the smelting temperature, the better the smelting separation of slag in Figure 14 and Figure 17 (C and D).

Figure 15. Morphologies of the separation iron and slag with different smelting temperature

Figure 16. XRD patterns of smelting slag with different smelting temperature
Figure 17. SEM-EDS analysis of the smelting slag with different smelting temperature: (A) 1475°C; (B) 1500°C; (C) 1525°C; (D) 1550°C

3.6 Microstructure of ferromanganese and smelting slag

Based on the effect of smelting parameters on the recovery and grade of valuable elements of HAMO in the smelting separation process, the rational smelting parameters of HAMO includes a CaO/(SiO₂+Al₂O₃) of 0.7, a FC/O of 1.1, a smelting temperature of 1550°C and a smelting time of above 60 min. The test under the related optimal smelting separations of HAMO (time: 60 min) is carried out. The content of Fe, C, Si and other impurities (P, S) is 12.13%, 6.73%, 0.17% and 0.14, 0.008, respectively. The recovery and content of Mn reach around 80.47% and 76.76%, respectively. In addition, the volatilization of Mn is about 8.75% in process of smelting ferromanganese alloy. It was listed in Table 4. During the steelmaking process, the HCFeMn alloy is added as a desulfurizer, a deoxidizer, or an alloy additive. The HCFeMn alloy is classified by their Mn, Si, C contents and other impurities. Comparing with the national standard of HCFeMn alloy in china, the HCFeMn alloy has met the higher Chinese Standard (GB/T3795-2014) of ferromanganese alloy (FeMn78C8).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mn</th>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMn78C8.0</td>
<td>75.0~82.0</td>
<td>8.0</td>
<td>1.5</td>
<td>2.5</td>
<td>0.20</td>
</tr>
<tr>
<td>FeMn74C7.5</td>
<td>70.0~77.0</td>
<td>7.5</td>
<td>2.0</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>FeMn68C7.0</td>
<td>65.0~72.0</td>
<td>7.0</td>
<td>2.5</td>
<td>4.5</td>
<td>0.25</td>
</tr>
<tr>
<td>HCFeMn alloy</td>
<td>76.76</td>
<td>6.73</td>
<td>0.17</td>
<td>0.14</td>
<td>0.008</td>
</tr>
</tbody>
</table>

The SEM-EDS analyses of metal and slag after the optimal smelting separation of HAMO are shown in Figure 18 and 19. It can be seen that the metal and slag are achieved successfully, and the Mn-rich with Fe and C is extensively distributed in the metal. In addition, the gehlenite phase and MnO phase in the slag are clearly separated from each other. The Fe-Mn particles are not detected in the slag. The distribution of elements in the metal is clearly shown in Figure 19. It is revealed that most element of Mn Fe and C is evenly distributed in the HCFeMn alloy. It is difficult to find the aggregation of sulphur and phosphorus impurity in the metal, but the distribution of impurity P element occurs aggregation phenomenon in a certain area of slag.
4. Conclusion

The smelting and separation mechanisms of high-alumina rich-manganese ore were proposed to produce the excellent high carbon ferromanganese alloy (HCFeMn) in this paper. Main conclusions can be summarized as follows:

The optimized smelting separation parameters for high-alumina rich-manganese ore includes a smelting temperature of 1550°C, a smelting time of 60 min, a CaO/(SiO₂+Al₂O₃) of 0.7 and a FC/O of 1.1. The smelting separation of high-alumina rich-manganese ore was achieved successfully. The content of Fe, C, Si and other impurities (P, S) is 12.13%, 6.73%, 0.17% and 0.14, 0.008, respectively. Especially, based on the abovementioned parameters, the recovery and content of Mn reach around 80.47% and 76.76%. The obtained high carbon ferromanganese alloy has met the higher standard (FeMn75C7.5) of ferromanganese alloy.

Based on the SEM-EDS, XRD and thermodynamic calculation, the smelting and separation mechanisms of high-alumina rich-manganese ore were proposed to more effectively explain the effect of smelting
parameters on slag/metal separation behaviors during the process of smelting HCFeMn alloys. It can be seen that the metal and slag are achieved successfully. The Mn-rich with Fe and C is extensively distributed in the metal. The main gehlenite phase and MnO phase in the slag are clearly separated from each other. It is difficult to find the aggregation of sulphur and phosphorus impurity in the metal, and the distribution of impurity P partly occurs aggregation phenomenon in a certain area of slag.

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