Concentrating of Iron, Slag and Apatite Phases from High Phosphorous Iron Ore Gaseous Reduction Product at 1 473 K by Super Gravity

Jintao GAO, Lei GUO and Zhancheng GUO*

State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing, 100083 China.

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According to the melting behavior of high phosphorous iron ore gaseous reduction product at 1 473 K, the iron grains remain in solid state, and the other minerals have formed into slag phase, as well as the phosphorus mainly exist in the form of apatite coexisting with slag phase, while it is impossible to accomplish the iron-slag separation at that temperature under the conventional conditions. Hence, concentrating experiments of iron, slag and apatite phases from high phosphorous iron ore gaseous reduction product at 1 473 K by super gravity were carried out in this study, and the results confirmed that it was a feasible and effective method. The layered structures appear significantly in the samples obtained by super gravity treatment, the iron grains and molten slag moved in opposite direction and concentrated at the bottom and upper of the sample, respectively, and the apatite crystals concentrated in the iron-slag interface. Moreover, increasing the gravity coefficient is definitely beneficial for the separating and concentrating of iron, slag and apatite phase. With the gravity coefficient of \( G = 1 \times 10^3 \), the mass fraction of \( \text{MFe} \) in the iron rich phase is up to 90.50 wt%, and that of P is decreased to 0.061 wt% after removing the slag inclusion in iron rich phase.

KEY WORDS: high phosphorous iron ore; super gravity; concentrating; iron rich phase; slag phase; apatite phase.

1. Introduction

With the gradual decrease of high grade iron ore resources, the iron ore deposits exhibit an increasing complex mineralogical composition around the world. In order to solve the crisis of iron ore resources, utilization of the refractory iron ore has been in an urgent need. High phosphorous hematite is one of the typical refractory iron ore in massive reserves, which is hard to be used not only due to the presence of high phosphorous content but also for its special oolitic structure. As the hematite and apatite as well as gangue mineral are intimately intermixed in the oolitic structure, it is difficult to grind the ore to a fine enough size to remove the phosphorus containing phase from the iron oxides by conventional physical methods, such as some reverse flotation process and magnetic separation process. Hence, some hydrometallurgy methods were proposed for the phosphorus removal of high phosphorous iron ores, including the acid leaching process, the alkaline leaching process, the bioleaching process and some combined process. M. J. Fisher-White and J. T. Yu have investigated the dephosphorization effect on the iron ores through different acid leaching, and they both found that the phosphorus can be removed with little dissolution of iron and acid consumption at optimum conditions.

As for the pyrometallurgy methods to deal with the high phosphorous iron ores, the coal-based direction reduction is one of the typical process, which is always assisted with some physical methods to separate iron and other gangue phases from the sintering reduction product, such as the fine grinding and magnetic separation process. Inevitably, increasing the reduction temperature is not only beneficial for the improvement of reduction rate, but also leading to the increase of the sintering degree of reduced phase, which will restrict the following grinding and magnetic separation. Moreover, according to thermodynamic data of the reactions among the carbon and the apatite, the ferrous oxide and the silicon dioxide phases, when the reduction temperature is up to 1 129–1 771 K, the apatite will be also reduced by carbon to \( \text{Fe}_2\text{P} \), \( \text{P}_2 \text{O}_5 \) vapor or PO vapor respectively, which can be further incorporated into metallic iron. Conversely, lower the reduction temperature is beneficial for the dephosphorization during the coal-based reduction process, while it will hinder the reduction rate of the reduced product. Therefore, E. Matinde, S. J. Bai and W. Yu have widely investigated the function of dephosphorization by adding Ca(OH)$_2$ and Na$_2$CO$_3$ on the coal-based reduction, the experiment results show that the additives is beneficial for the dephosphorization during the ore-carbon reduction process.
in a semi-molten state.

The gas-based direction reduction is another typical pyrometallurgy process, which is combined with the high temperature melt-separation process to separate molten metal and slag phases from the gaseous reduction product. According to thermodynamic data of the reactions between the H$_2$/CO and the ore phases, the iron oxide can be reduced by reducing gas at low temperature, while theapatite is hard to be reduced in the temperature range of 300 K to 1 900 K. L. Guo, Z. L. Zhao and H. Q. Tang have investigated the gas-based reduction by H$_2$/CO at the temperature of 1 073 K to 1 273 K, the results show that gaseous reduction in fluidized bed or in static state can both reach a high reduction extent of iron oxide with the phosphorus still exists in apatite. Recently, M. Omran and H. Q. Tang have studied the function of microwave heating on the structure of high phosphorous oolitic iron ores, and they both found that the oolitic unit generated cracks and fissures due to microwave, and the microwave treatment can improve the phosphorus separation and magnetic properties. H. Q. Tang further investigated the gas-based reduction of high phosphorous iron ore after microwave treatment, and the experiment results show that microwave treatment has an intensification effect on gas-based reduction, which can further reduces the gas internal resistance and increase the chemical reaction rate.

As for the following melt-separation process after the gas-based reduction, a high temperature of 1 823–1 873 K is needed to achieve the effectively separation of molten metal and slag. However, almost all of the phosphorus in the gaseous reduction product were smelted into the metal phase during the high temperature melt-separation process. L. Guo adopted the melt-separation of raw ore after gaseous reduction at the temperature of 1 823 K, which realizes the separation of metal and slag, while the phosphorous content in the metal phase is up to 1.22 wt%; further by adding CaO into the ore with basicity of 1.5 before melt-separation, the phosphorous content in the metal can be decreased to 0.82 wt%. Simultaneously, H. Q. Tang adopted the melt-separation of the ore after microwave treatment by adding CaO and Na$_2$CO$_3$ powders as dephosphorizing agent at 1 823 K, and the phosphorous content in the metal is still 0.31 wt%. As for the transform and transmission mechanism of phosphorus from slag phase to metal phase during the melt-separation process when there is no carbon in the gaseous reduction product, Z. L. Zhao and H. Q. Tang considered that phosphorus mainly exists in the metal as apatite inclusions, L. Guo inferred that phosphorus was smelted into metal due to the reactions between the Fe and P$_2$O$_5$, which is evidenced by the thermodynamic calculations.

Consequently, the contradiction of the metal/slag separation and the phosphorus removal of metal phase become the major difficult problem during the high temperature melt-separation process. If the temperature of iron-slag separation can be reduced to 1 473–1 573 K, which is below the melting point of iron and the iron grains remain in solid state at that temperature, it will be beneficial for keeping the phosphorus out of iron phase, which is proven in this study. Simultaneously, S. Fukagai has studied the reaction mechanism of the 2CaO-SiO$_2$ and the FeO$_x$–CaO–SiO$_2$–P$_2$O$_5$ slag, and reported that the CaO–SiO$_2$–P$_2$O$_5$ solid phases with high P$_2$O$_5$ content and the FeO–CaO–SiO$_2$ system were coexisted at 1 573 K, so lower the temperature of iron-slag separation will be also beneficial for the concentrating of phosphorus in slag phase. However, it is impossible to accomplish the separation of slag and iron phases at 1 473–1 573 K under the conventional conditions. Inspired by the successful application of super gravity technology in the preparation of functionally gradient materials and removing impurities from alloy melt, the super gravity field was applied to the iron-slag separation process at low temperature in this study. In this paper, the experiments on concentrating of iron, slag and apatite phases from high phosphorous iron ore gaseous reduction product at 1 473 K by super gravity were carried out, and the feasibility of this process was verified. Simultaneously, the effect of super gravity on the concentrating behaviors and respective components of iron rich phase, slag phase and apatite phase were further investigated.

### Table 1. Chemical compositions (wt%) of the high phosphorous iron ore before and after gaseous reduction.

<table>
<thead>
<tr>
<th>Composition</th>
<th>TFe</th>
<th>FeO</th>
<th>MFe</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw ore</td>
<td>50.15</td>
<td>1.56</td>
<td>13.15</td>
<td>4.80</td>
<td>4.52</td>
<td>0.48</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>Original reduction product (Basicity=0.37)</td>
<td>64.44</td>
<td>16.58</td>
<td>51.55</td>
<td>16.89</td>
<td>6.17</td>
<td>5.81</td>
<td>0.62</td>
<td>1.04</td>
</tr>
<tr>
<td>Adjusted reduction product (Basicity=1.0)</td>
<td>58.20</td>
<td>14.97</td>
<td>46.55</td>
<td>15.25</td>
<td>15.25</td>
<td>6.17</td>
<td>1.04</td>
<td>0.94</td>
</tr>
</tbody>
</table>

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the quartz phase building the concentric shell of oolites in size of 0.2–0.5 mm, while the phosphorus and calcium exist in the form of fine fluorapatite phase and mainly distribute in the oolitic layers. Nevertheless, the hematite phase was reduced into metallic iron after the gaseous reduction, while the phosphorus maintained in the form of apatite and distributed in the original position, which is the basis for the removing phosphorus out of iron rich phase in the following iron-slag concentrating process.

\[ M_R = \frac{M_{Fe}}{T_{Fe}} \times 100\% \] ........................ (1)

Where, \( M_R \) is the average metallization ratio (%), \( M_{Fe} \) is the mass fraction of metallic iron (wt%), \( T_{Fe} \) is the mass fraction of total iron (wt%).

2.2. Apparatus
2.2.1. Fluidized Bed Reactor
The schematic diagram of the fluidized bed reactor used for the gaseous reduction of high phosphorous iron ore powders is shown in Fig. 3(a).

![Fig. 3(a)](image)

Fig. 3. Sketch of the experimental apparatus: (a) fluidized bed reactor, (b) centrifugal apparatus.

![Fig. 1](image)

Fig. 1. XRD patterns of the high phosphorous iron ore before and after gaseous reduction.

![Fig. 2](image)

Fig. 2. SEM-EDS photographs of the high phosphorous iron ore before and after gaseous reduction: (a) SEM of raw ore, (b) EDS of hematite in raw ore, (c) EDS of apatite in raw ore, (d) SEM of gaseous reduction product, (e) EDS of metallic iron in product, (f) EDS of apatite in product.
2.2.2. Centrifugal Apparatus

The super gravity field used in the concentrating experiments of high phosphorous iron ore gaseous reduction product was generated by the centrifugal apparatus. The sketch of the apparatus is illustrated in Fig. 3(b), the furnace on the right is heated by resistance wire, and the temperature is controlled by a program controller with an R type thermocouple. The heating furnace (right) and the counterweight (left) are fixed symmetrically onto the centrifugal rotor, they keep verticality in the stationary state, and start and maintain level in the state of centrifugal rotor running.

2.3. Experimental Procedure

2.3.1. Iron-slag Melting Experiments at 1 473–1 573 K in Normal Gravity Filed

The melting experiments of the gaseous reduction product obtained by high phosphorous iron ore powders with size of 0.11–0.90 mm reducing in the fluidized bed were first carried out at 1 473–1 573 K aiming to investigate the melting behavior of iron and slag phases at low temperature, especially for that of one oolith. An amount of 10 grams of the original reduction product was put into an alumina crucible with the inner diameter of 12 mm, which was further put into a graphite crucible with the inner diameter of 19 mm and covered with lid and then heated to 1 473 K or 1 573 K, after melting at the constant temperature for 10 minutes the graphite crucible was took out and water quenched.

2.3.2. Iron-slag Concentrating Experiments at 1 473 K in Super Gravity Filed

In order to gain the lower melting temperature and the better fluidity of the slag phase, the basicity defined as CaO/SiO2 has been adjusted from 0.37 to 1.0 by adding CaO into the reduction product with size of 0.11–0.15 mm and well mixed based on the experiment results of L. Guo20 and H. Q. Tang.26 The adjusted reduction product of the same quality was put into the same alumina crucible and graphite crucible and heated to 1 473 K in the heating furnace of centrifugal apparatus, and then the centrifugal apparatus was started and adjusted to the specified angular velocity of 1 036 RPM, 1 465 RPM, 1 794 RPM or 2 072 RPM, namely G=300, G=600, G=900 or G=1 200 at the constant 1 473 K for 10 minutes respectively, and the gravity coefficient was calculated as the ratio of super-gravitational acceleration to normal-gravitational acceleration via Eq. (2). After that, the centrifugal apparatus was shut off, and the graphite crucible was taken out and water quenched. Simultaneously, the parallel experiment was carried out at 1 473 K for 10 minutes in normal gravity (G=1).

\[
G = \sqrt{\frac{g^2 + (\omega^2 R)^2}{g}} = \sqrt{\frac{g^2 + \left(\frac{N^2 \pi^2 R}{900}\right)^2}{g}} \quad (2)
\]

Where, \(G\) is the gravity coefficient, \(g\) is the normal-gravitational acceleration \((g=9.80 \text{ m/s}^2)\), \(\omega\) is the angular velocity \((\text{rad} \cdot \text{s}^{-1})\), \(N\) is the rotating speed of the centrifugal \((\text{RPM})\); \(R\) is the distance from the centrifugal axis to the centre of sample \((R=0.25 \text{ m})\).

2.4. Analytical Procedure

As for the samples obtained by melting at 1 473 K and 1 573 K in normal gravity, which were sectioned longitudinally along the center axis, and then measured on the scanning electron micrograph and energy disperse spectrum in order to obtain the morphology evolution and the phosphorous migration after melting at low temperature.

As for the samples obtained by super gravity concentrating at 1 473 K, which were also sectioned longitudinally along the center axis into two parts, that is along the direction of super gravity. One part was first measured on the metallographic microscope (Laitz DMRX) and image analyzer (LEICA Qwin500) by the line intercept method (average of 20 fields) in order to gain the variations of volume fraction and equivalent diameter of the iron grains in different areas of the sample, and further measured on the scanning electron micrograph and energy disperse spectrum for analyzing the distribution and mineral composition of the phosphorous phase in the sample. Simultaneously, another part was crossly divided along the interface between the iron rich phase and slag phase into two parts, and the mass fraction of MFe (metallic iron) and P (phosphorus) in the iron rich phase were measured by the chemical analytical method and the ICP method with OPTIMA 7000DV, respectively.

3. Results and Discussion

3.1. Melting Behavior of Iron and Slag Phases at 1 473–1 573 K

Analyzed by the SEM-EDS methods, the mineral structures and compositions of the samples obtained by melting at 1 473 K and 1 573 K are shown in Fig. 4. As shown in Figs. 4(a) and 4(c), the samples mainly maintained in the oolitic structures, and the inner layer of oolith scattered and the outer border broken after melting at 1 473 K, while the inner layer of oolith has disappeared and the outer boundary was no longer clear after melting at 1 573 K. It indicate

![Fig. 4. SEM-EDS photographs of the samples obtained by melting in normal gravity: (a) SEM of the sample melted at 1 473 K, (b) EDS of iron phase in the sample melted at 1 473 K, (c) SEM of the sample melted at 1 573 K, (d) EDS of iron phase in the sample melted at 1 573 K.](image-url)
that the gangue minerals have formed into slag phase and slightly flowed, and the iron grains remained in solid state at 1 473–1 573 K, which can be further confirmed by the following experimental results in super gravity field. Simultaneously, as shown in Figs. 4(b) and 4(d), the phosphorus was mainly staying in the slag phase rather than into iron phase after melting at 1 473 K, while more phosphorus have immigrated into iron phase from slag phase after melting at 1 573 K. Consequently, separating the iron and slag phases at 1 473 K will be beneficial for keeping the phosphorus out of iron phase, but it is impossible to accomplish this task under the conventional conditions.

3.2. Concentrating of Iron and Slag Phases in Super Gravity Field

By using the high phosphorous iron ore gaseous reduction product with size of 0.11–0.15 mm, the vertical sections of the samples obtained by super gravity treatment with the gravity coefficient of $G = 300$, $G = 600$, $G = 900$ and $G = 1 200$ at 1 473 K for 10 minutes compared with the parallel sample ($G = 1$, $T = 1 473$ K, $t = 10$ min) are illustrated in Fig. 5. Obviously, the uniform structure presents in the sample obtained in normal gravity field. However, the layered structures appear significantly in the sample obtained by super gravity treatment, whose upper part is the black glassy slag phase and the bottom part is the bright white iron rich phase. It means that all the iron grains moved directionally to the bottom of the sample along the direction of super gravity according to the density difference with the slag, and then joined and concentrated as the iron rich phase. Instead, the molten slag broken through the barriers of the iron grains and concentrated at the upper of the sample along the opposite direction, in which it’s practically impossible to find any iron grain.

Figure 6 presents the mass fractions of the concentrated slag phases and corresponding iron rich phases obtained by super gravity treatment with different gravity coefficient. Compared with the sample in normal gravity ($G = 1$), super gravity field is definitely beneficial for the separation of molten slag from iron rich phase, and increasing the gravity coefficient can effectively increase the mass fraction of the concentrated slag phase. With the gravity coefficient of $G = 1 200$, the mass fraction of the slag phase is up to 40.19 wt%, while a small amount of slag were intercepted in the iron rich phase compared with the theoretical maximum value of slag phase.

3.3. Microstructure and Component of the Concentrated Iron Rich Phase in the Layered Sample

The concentrated iron rich phases in the layered samples obtained by super gravity treatment were divided into four areas along the direction of super gravity, and then characterized respectively by the metallographic microscopy, with the corresponding micrographs shown in Fig. 7. It is observed that the concentrated iron rich phase presents the porous structure, with a number of pores in the bottom area and some slag included in the pores of the upper area. According to the variations of the volume fraction and equivalent diameter of iron grains in different areas of the iron rich phases with different gravity coefficient as shown in Fig. 8, it is obvious that the volume fraction and equivalent diameter of iron grains both increase with the area approaching to the bottom of the sample along the direction of super gravity, and the peak values appear in the bottom
area (A), in which the iron grains have joined and changed to the larger crystals with little slag inclusion. Furthermore, both the volume fraction and equivalent diameter of iron grains increase significantly with the increase of the gravity coefficient from $G = 300$ to $G = 1200$.

The mass fractions of MFe measured by the chemical analytical method in the concentrated iron rich phases obtained by super gravity treatment with different gravity coefficient are shown in Fig. 9. Obviously, increasing the gravity coefficient from $G = 1$ to $G = 1200$ can enhance the purity of iron rich phase from 54.19 wt% to 90.50 wt%. It gives further evidence that the super gravity field is definitely beneficial for the concentrating of iron grains and the separating from slag phase, while some slag included in the pores of the upper area hinder the further increase of the purity of iron rich phase.

3.4. Concentrating of Phosphorous Phase in Super Gravity Field

The SEM-EDS mapping of phosphorous phases in different areas of the layered sample obtained by super gravity treatment are shown in Fig. 10. It is obvious that most of phosphorous phases were concentrated in the iron-slag interface and few were intercepted and stopped in the slag inclusion in the upper area of iron rich phase. Furthermore, these concentrated phases are mainly in the form of columnar crystals with the size of 0.15–0.30 mm. Combined with the corresponding energy disperse spectrum data given in Table 2, the phosphorous phases are mainly comprised of phosphorus (18.32–19.63 wt%), calcium (38.87–40.03 wt%), oxygen (38.15–39.78 wt%) and a small amount of silicon (0.91–1.72 wt%), it is in evidence that the phosphorus still exist in the form of apatite phase. The concentration of the apatite crystals occurred in the interfacial area during the melting process at 1473 K in super gravity field can be explained as the following reasons: Since the temperature was not high enough for the active iron-slag interface reaction\(^20\) or phosphate compound formation reaction,\(^27\) thus the phosphorus mainly maintained in the form of fine and dispersed apatite crystals (0.001–0.01 mm). Moreover, as the density of apatite is between that of slag and iron, the fine apatite crystals moved with molten slag along the opposite direction of super gravity, and collided with each other and formed into larger columnar crystals (0.015–0.03 mm), and then most of larger apatite crystals concentrated in the iron-slag interface after super gravity treatment.

The mass fractions of P measured by the ICP method in the concentrated iron rich phases with different gravity coefficient are shown in Fig. 11 (solid lines), which is decreased with the increase of the gravity coefficient obviously. Compared with the sample in normal gravity ($G = 1$), the mass fraction of P in iron rich phase decreases from 1.089 wt% to
0.217 wt% by super gravity treatment with the gravity coefficient of $G = 1200$. Considering that the phosphorus residue in the iron rich phase may be caused by the slag inclusion, the iron rich phases were further processed by fine grinding and magnetic separation to remove the visible slag inclusion, and the mass fractions of P were measured again by ICP method, with the results further shown in Fig. 11 (dash

Table 2. Energy disperse spectrum data (wt%) of phosphorous phases in different areas of the layered sample obtained by super gravity treatment with $G = 900$.

<table>
<thead>
<tr>
<th>Position</th>
<th>area</th>
<th>P</th>
<th>Ca</th>
<th>O</th>
<th>Fe</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-slag interface</td>
<td>Fig. 10(a): A</td>
<td>19.63</td>
<td>38.87</td>
<td>39.78</td>
<td>—</td>
<td>1.72</td>
</tr>
<tr>
<td>Upper area of iron rich phase</td>
<td>Fig. 10(b): B</td>
<td>18.32</td>
<td>40.03</td>
<td>38.15</td>
<td>2.59</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Fig. 10. SEM-EDS mapping of phosphorous phases in different areas of the layered sample obtained by super gravity treatment with $G = 900$: (a) interface, (b) upper area of iron rich phase.

Fig. 11. Mass fractions of P in the concentrated iron rich phases obtained by super gravity treatment with different gravity coefficient.
lines). Obvious, after removing the slag inclusion in the iron rich phase, the mass fraction of P can be further decreased to 0.061 wt%. It gives further evidence that the phosphorus mainly exist in apatite phase rather than incorporating into iron grains at 1 473 K, and most of the apatite crystals can be separated from the iron rich phase and concentrated in the iron-slag interface by super gravity treatment.

4. Conclusions
It was confirmed by the experiment results that concentrating of iron, slag and apatite phases from high phosphorous iron ore gaseous reduction product by super gravity at 1 473 K was a feasible and effective method. The layered structures appear significantly in the samples obtained by super gravity treatment, all the iron grains moved along the direction of super gravity and concentrated at the bottom of the sample, and the molten slag broken through the barriers of iron grains and concentrated at the upper of the sample, meanwhile, the fine and dispersed apatite crystals moved with molten slag, collided and formed larger columnar crystals, and then concentrated in the iron-slag interface.

Increasing the gravity coefficient is definitely beneficial for the separating and concentrating of iron grains, slag phase and apatite phase. With the gravity coefficient of G=1 200, the mass fraction of MFe in the iron rich phase is up to 90.50 wt%, and that of P is decreased to 0.217 wt%, it is further decreased to 0.061 wt% after removing the slag inclusion in iron rich phase. So some works on extremely separating by super gravity are needed to further remove the slag inclusion in the concentrated iron rich phase.

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