Direct Concentration of Iron, Slag and Britholite-(Ce,La,Pr,Nd) at 1 473 K in a Super Gravitational Field

Fuqiang WANG, Jintao GAO,* Xi LAN and Zhancheng GUO*

State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, 100083 China.

(Received on August 16, 2016; accepted on September 13, 2016; J-STAGE Advance published date: October 20, 2016)

The investigations of concentrating iron, slag and britholite-(Ce,La,Pr,Nd) from gaseous reduced Bayan Obo ore were conducted at 1 473 K in a super gravitational field. The results showed that the iron grains concentrated at the bottom area along super gravitational direction, whereas the gangue formed the slag in the upper area along the opposite direction, as well as the REEs enriched into britholite-(Ce,La,Pr,Nd) with a typical hexagonal structure and concentrated in the bottom slag. Moreover, the effects of gravity coefficient on both iron-slag separation and the concentration of REEs precipitates were investigated further.

KEY WORDS: super gravitational field; concentration; iron; slag; britholite-(Ce,La,Pr,Nd); Bayan Obo ore.

1. Introduction

The Bayan Obo ore formed by hydrothermal replacement of the sedimentary carbonate rocks in the Inner Mongolia is a rich Fe–LREEs–Nb deposit,1) which accounts for one-third of the rare-earth reserves around the world.2) Although the content of RE₂O₃ (rare-earth oxides) in the ore body is up to 5–6 wt%, it was difficult to separate the REEs2) and the oxides, and then most rare earth oxides compounded and precipitated into the strip cefluosil ([7(Ca,Ce,La,Nd)₅O₁₀]•(F,O)₁₀) after slow cooling since the phosphorus had been almost all REEs were smelted into the slag during the high-temperature process.2,5,6) Hence, to effectively separate and recover the REEs from the ore, many techniques have been developed and also providing a potentially feasible process of gaseous reduction combined with low-temperature separation of iron and slag in a super gravitational field for utilizing the low-grade Bayan Obo ore.

2. Experimental

The Bayan Obo run-of-mine ore was employed in this study, its chemical compositions measured by XRF method are shown in Table 1, and its mineralogical compositions determined by XRD method are shown in Fig. 1, respectively. The contents of TFe (total iron) and RE₂O₃ are 27.12 wt% and 6.35 wt%, and the minerals consist of hematite, fluorite, barite, aegirine, bastnaesite-(Ce,La,Pr,Nd) and quartz. After pulverizing to powders less than 150 μm, the ore was filled in a boat-shaped magnesia crucible and reduced in a resistance tube furnace (GSL-1700X) with a gas flow of 0.2 L/min H₂ (99.999%) and 0.1 L/min N₂ (99.999%) at 1 733 K for 4 h. It was indicated that more than 93% of iron oxides were reduced into MFe (metallic iron) with the mass fraction of 32.14 wt% in the reduced ore. But the bastnaesite-(Ce,La,Pr,Nd) and monazite-(Ce,La,Pr,Nd) remained the original state.

The super gravitational field was generated by a modified centrifugal apparatus (DL-8M) as depicted in Fig. 2. The heating furnace was heated by resistance wire, and the temperature was adjusted to a speed of 1 196 r/min, 1 465 r/min or 1 892 r/min (G = 1 000) at the constant 1 473 K for 10 min, respectively. The centrifugal apparatus was activated and adjusted to a speed of 1 196 r/min, 1 465 r/min, 1 692 r/min or 1 892 r/min (G = 1 000) at the constant 1 473 K for 10 min, respectively. Afterward, the apparatus was shut off and the sample was water quenched. Meanwhile, the parallel experiment was conducted at 1 473 K for 10 min in normal gravity.

The gravity coefficient was calculated via Eq. (1):

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

where, \( G \) is the gravity coefficient, \( g \) is the normal-gravitational acceleration (g = 9.8 m/s²), \( \omega \) is the angular velocity (rad/s⁻¹), \( N \) is the rotating speed (r/min), \( R \) is the distance between centrifugal axis and sample center (R = 0.25 m).
The recovery ratio of MFe and RE$_2$O$_3$ were calculated via Eqs. (2) and (3), respectively.

\[
\varepsilon_{\text{MFe}} = \frac{m_1 \times \omega_{\text{MFe},-1}}{m_1 \times \omega_{\text{MFe},-1} + m_3 \times \omega_{\text{MFe},-S}} \times 100\% \quad \text{...... (2)}
\]

\[
\varepsilon_{\text{RE}_2\text{O}_3} = \frac{m_3 \times \omega_{\text{RE}_2\text{O}_3,-S} + m_1 \times \omega_{\text{RE}_2\text{O}_3,-1}}{m_3 \times \omega_{\text{RE}_2\text{O}_3,-S} + m_1 \times \omega_{\text{RE}_2\text{O}_3,-1}} \times 100\% \quad \text{...... (3)}
\]

where, $\varepsilon_{\text{MFe}}$ and $\varepsilon_{\text{RE}_2\text{O}_3}$ are the recovery ratio of MFe and RE$_2$O$_3$ in the samples, $m_1$ and $m_3$ are the mass of iron and slag (%), $\omega_{\text{MFe},-1}$ is the mass fraction of MFe in the iron (wt%), $\omega_{\text{MFe},-S}$ is the mass fraction of MFe in the slag (wt%), $\omega_{\text{RE}_2\text{O}_3,-1}$ is the mass fraction of RE$_2$O$_3$ in the iron (wt%), and $\omega_{\text{RE}_2\text{O}_3,-S}$ is the mass fraction of RE$_2$O$_3$ in the slag (wt%).

The samples prepared at different gravity coefficients were sectioned symmetrically along the super gravitational direction into two parts. One was polished and measured by SEM-EDS method to determine the microstructures, mineral compositions and distributions of the REEs precipitates. While the other was crossly halved along the iron-slag interface and weighed respectively by electronic balance to gain the mass of the iron and slag, and then the mass fractions of MFe in the irons were measured by the chemical analytical method (GB/T6730.65-2009), while those of REEs in the slags were determined by X-ray fluorescence spectrometer (XRF1800), respectively.

### 3. Results and Discussion

The macrographs of the samples obtained at different gravity coefficients are shown in Fig. 3. Obviously, the sample obtained in normal gravity maintained as a whole, and some pores presented within as shown in Fig. 3(a). However, the layered structures with an explicit interface appeared significantly in the sample obtained by super gravity as shown in Fig. 3(b). Combined with the SEM-EDS analysis of different areas in the layered sample as shown in Fig. 4, it was evidenced that the iron grains concentrated at the bottom area along super gravitational direction due to the greater density, whereas the molten slag passed through the gaps among iron grains and migrated to the upper area against super gravitational direction. Furthermore, there was neither iron grains included in the slag nor the slag inclusions intermixed in the iron from a microscopic view as shown in Figs. 4(a) to 4(d).

What’s more, the REEs precipitates appeared as a typical hexagonal prism with the hollow structure inside, and the size of REEs precipitates was up to 500–1 000 μm as shown in Figs. 4(c) and 4, which was much larger than the fine equiaxed precipitates (30 μm) reported in previous study. Combined with the energy dispersive spectrum as shown in Fig. 4(g), all the REEs co-existing with some Ca, Si, P, O and F enriched into the crystal where defined as britholite-(Ce,La,Pr,Nd) due to the similarity of ionic radii and the interchangeableness of the REEs, which was further verified by the SEM area mapping results given in Fig. 5. Consequently, all the britholite-(Ce,La,Pr,Nd) concentrated in the bottom slag along super gravitational direction due to the greater density.

Furthermore, the fine flake-like particles of fluorite in size of 30 μm appeared in the middle-lower slag rather than presented in other minerals at 1 473 K as shown in Figs. 4(b) and 4(f), which facilitated the following separation of fluorite particles from the slag by some eligible methods.

Considering that the Bayan Obo ore powders were adequately reduced in current study, and most iron oxides transformed into the alpha iron, while almost all REEs minerals got out of the paragenetic gangue minerals during
Fig. 4. SEM-EDS photographs of different areas in the layered sample obtained by super gravity with $G = 1000$ and $t = 10$ min: (a) SEM of the upper slag, (b) SEM of the middle-lower slag, (c) SEM of the bottom slag, (d) SEM of the iron, (e) EDS of the slag, (f) EDS of the fluorite, (g) EDS of the REEs precipitates, (h) EDS of the iron. (Online version in color.)

Fig. 5. Area mapping of the REEs precipitates in the bottom slag obtained by super gravity. (Online version in color.)

Table 2. Variations in mass fractions and recovery ratios of MFe and RE$_2$O$_3$ in the samples obtained at different gravity coefficients.

| Gravity coefficients | $G = 1$ | $G = 400$ | $G = 600$ | $G = 800$ | $G = 1000$ |
|-----------------------|---------|-----------|-----------|-----------|------------|
| Mass fractions of MFe in iron (wt%) | 33.28 | 91.64 | 94.47 | 95.91 | 96.39 |
| Recovery ratios of MFe in iron (%) | 97.13 | 98.11 | 98.70 | 99.10 | 99.10 |
| Mass fractions of RE$_2$O$_3$ in slag (wt%) | 6.65 | 8.89 | 9.54 | 9.86 | 9.95 |
| Recovery ratios of RE$_2$O$_3$ in slag (%) | 96.10 | 97.27 | 97.86 | 98.05 | 98.05 |

gaseous reduction process, which significantly facilitated the separation and recovery of iron and REEs in the supergravity process. As the variations of mass fractions and recovery ratios of RE$_2$O$_3$ and MFe in the samples with gravity coefficient are shown in Table 2, it was illustrated that the RE$_2$O$_3$ content in slag and the iron purity enhanced significantly with increasing gravity coefficient. In the case of $T = 1473$ K, $G = 1000$ and $t = 10$ min, the mass fraction of MFe in iron was up to 96.39 wt%, while that of RE$_2$O$_3$ in slag was up to 9.95 wt%. The recovery ratios of MFe and RE$_2$O$_3$ were up to 99.10% and 98.05%, respectively.

4. Conclusions

Under the condition of super gravity at 1 473 K, the iron grains concentrated along super gravitational direction at the bottom area, while the gangue formed the slag along the opposite direction in the upper area, as well as all the REEs enriched into the britholite-(Ce,La,Pr,Nd) and concentrated in the bottom slag. Moreover, increasing gravity coefficient was definitely beneficial for the iron-slag separation and the concentration of britholite-(Ce,La,Pr,Nd) in the slag.

Acknowledgement

This study is supported by the National Natural Science Foundations of China (No. 51404025 and No. 51234001).

REFERENCES

1) K. F. Yang, H. R. Fan, M. Santosh, F. F. Hu and K. Y. Wang: Ore Geol. Rev., 40 (2011), 122.
2) J. C. Li, Z. C. Guo, T. Yang, Z. C. Yue and C. H. Ma: High Temp. Mater. Process., 34 (2015), 263.
3) Y. Kanazawa and M. Kamitani: J. Alloys. Compd., 408–412 (2006), 1339.
4) A. Jordens, Y. P. Cheng and K. E. Waters: Miner. Eng., 41 (2013), 97.
5) B. Zhang, C. J. Liu and C. L. Li: Miner. Eng., 65 (2014), 17.
6) Y. G. Ding, J. S. Wang, G. Wang and Q. G. Xue: ISIJ Int., 52 (2012), 1772.
7) J. Ren, S. Song, A. L. Valdivieso and S. Lu: J. Miner. Process., 59 (2000), 237.
8) J. C. Li and Z. C. Guo: Metall. Mater. Trans. B, 45 (2014), 1272.
9) D. C. Noe, J. M. Hughes, A. N. Mariano and J. W. Drexler: Cryst. Mater., 206 (1993), 233.
10) J. T. Gao, L. Guo and Z. C. Guo: Metall. Mater. Trans. B, 46 (2015), 2180.
11) J. T. Gao, L. Guo and Z. C. Guo: ISIJ Int., 55 (2015), 2535.
12) J. T. Gao, Y. W. Zhong and Z. C. Guo: ISIJ Int., 56 (2016), 1352.
13) J. T. Gao, Y. W. Zhong, L. Guo and Z. C. Guo: Metall. Mater. Trans. B, 47 (2016), 1080.
14) J. T. Gao, Y. W. Zhong and Z. C. Guo: Metall. Mater. Trans. B, 47 (2016), 2459.
15) N. Krishnamurthy and C. K. Gupta: Extractive Metallurgy of Rare-earths, CRC Press, FL, (2004), 195.