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Production of Synthetic Rutile from Molten Titanium Slag with the Addition of B_2O_3

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A new process of producing synthetic rutile from molten titanium slag with the addition B_2O_3 is proposed. The process includes a molten modification process and a leaching process. The molten modification process was conducted by adding B_2O_3 into molten slag. The leaching process was conducted by adding hydrochloric acid and subsequent NaOH. The results show that CaO and MgO are leached out by hydrochloric acid and that synthetic rutile is further improved by NaOH. The optimized conditions are 2% B_2O_3 amount, 5% hydrochloric concentration, 80°C leaching temperature, and 30 min leaching time. The synthetic rutile with 86.77% TiO_2 and 1.23% (CaO + MgO) was prepared. From x-ray diffraction results, thermodynamic calculation and the theory of bond parameter function, with the addition of B_2O_3, calcium silicate is transformed into calcium borate and anosovite is transformed into magnesium borate. Calcium borate and magnesium borate are leached out by hydrochloric acid, leading to the enrichment of rutile.

INTRODUCTION

The products of titanium metallurgy mainly contain two types: titanium white and metallic titanium. Titanium white from the fluidized bed chlorination and metallic titanium are both produced from $TiCl_4$.[1,2] The fluidized bed chlorination is the main process of producing $TiCl_4$ when compared with the molten salt process.[3–5] TiO_2 and gangues react with chlorine gas at 1000°C to form corresponding volatile chlorides during the fluidized bed chlorination.[6] The melting points of $CaCl_2$ and $MgCl_2$ are 775°C and 714°C, respectively. $CaCl_2$ and $MgCl_2$ are liquid under the temperature of chlorinating titanium slag.[7] If the CaO and MgO content in the titanium-rich material is high, $CaCl_2$ and $MgCl_2$ will make reactant particles cohere and accumulate in fluidized bed easily, deteriorating the steady state of the fluidized bed. Therefore, the CaO and MgO content in titanium-rich material for fluidized bed chlorination is required to be as low as possible, usually less than 1.5% to avoid deteriorating the steady state of the fluidized bed.[8]

Researchers have tended to upgrade ilmenite to qualified titanium-rich material due to the natural rutile shortage. Several industrial processes have been developed to upgrade ilmenite to qualified titanium-rich material, including the smelting process,[9–12] the Bencher process,[12] and the acid leaching process.[12] The electric furnace smelting is regarded as the most significant process in China due to its high efficiency and low waste emission. Panzhihua, located in the Sichuan province of China, holds ilmenite reserves of 870 million tons, accounting for 35% of total reserves in the world.[13] Nevertheless, the CaO and MgO content in titanium slag from Panzhihua ilmenite is too high to be directly employed for fluidized bed chlorination. In this case, it is imperative to develop a new process of producing synthetic rutile from high CaO and MgO titanium slag.

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Table I. Technical conditions of producing the synthetic rutile from high CaO and MgO titanium slag

Researcher	Additive	Additive amount	Treating temperature, °C	Leaching agent
Jarish Basil[14]	Caustic salts	42.8% of slag mass	900	Sulfuric acid
Yufeng Guo[15]	Phosphoric acid	16% of slag mass	1000	Hydrochloric acid
Tao Jiang[16]	Sodium carbonate	42.8% of slag mass	900	Sulfuric acid
Eldger Gerald W[17]	Sulfur trioxide gas	Enough	1100	Hydrochloric acid
Michel Gueguin[18]	Chlorine gas	Enough	800	Hydrochloric acid
Krzysztof Borowiec[19]	Oxygen/smelter gas	Enough	950/700	Hydrochloric acid

In recent decades, solid and gas additives have been applied for producing synthetic rutile from high CaO and MgO titanium slag. Process features are summarized in Table I and discussed subsequently.

Although qualified synthetic rutile was obtained by these processes, they are highly additive and require significant energy consumption. It is necessary to explore a novel and efficient additive to modify the titanium slag to obtain synthetic rutile. B₂O₃ is a kind of fluxing agent popularly applied in the metallurgy industry. The addition of B₂O₃ greatly increases the acidity and influences the stability of the slags.[20,21] Therefore, B₂O₃ has been used to modify the Ti-bearing blast furnace slags to obtain the rutile. It has been found that small amounts of B₂O₃ can remarkably restrict the linkage between Ca^{2+} and TiO_3^{2-}, enhancing the precipitation of rutile in Ti-bearing blast furnace slags.[22,23] Therefore, it is reasonable to expect that small amounts of B₂O₃ can also restrict the precipitation of anosovite and calcium silicate in titanium slag to obtain the rutile efficiently. Furthermore, to use the sensible heat of titanium slag and avoid the reheating for the modification in Table I, B₂O₃ can be added into molten titanium slag during production of titanium slag from ilmenite, more specifically when ilmenite has been reduced to be molten iron and titanium slag in an electric furnace.

In this article, the new process consists of the molten modification process and the leaching process. The molten modification process was implemented by adding B₂O₃ into the molten titanium slag in an induction furnace to simulate the molten modification process, and subsequent leaching process was carried out to obtain synthetic rutile. The leaching process consists of hydrochloric leaching and NaOH leaching. Molten modification conditions and hydrochloric leaching conditions were optimized. NaOH leaching was selected as the necessary process to improve the synthetic rutile under predetermined conditions. Furthermore, the molten modification mechanism and hydrochloric leaching mechanism were investigated by x-ray diffraction (XRD), thermodynamic calculation, and the theory of bond parameter function.

EXPERIMENTAL

Titanium Slag and Reagents

Titanium slag from Panzhihua ilmenite was used in this work. The slag was analyzed by x-ray fluorescence (XRF). The chemical composition of the slag was as follows (wt.%): TiO₂ = 73.81, FeO = 12.21, SiO₂ = 5.89, MnO = 1.53, MgO = 2.51, Al₂O₃ = 2.83, and CaO = 1.00. The CaO and MgO content are 3.51%, which are too high to be used for fluidized bed chlorination. All the other reagents are analytical grades in this article.

Experimental Procedure

The experiment includes a molten modification process and a leaching process. In the molten modification process, B₂O₃ was added into molten titanium slag when ilmenite had been reduced to be molten iron and titanium slag. In this article, a mixture of B₂O₃ and titanium slag was placed in a cylindrical molybdenum crucible and then heated by an induction furnace to simulate the molten modification process. The modified slag was obtained after the molten modification process. The leaching process includes hydrochloric leaching and NaOH leaching. The molten modification conditions and hydrochloric leaching conditions were optimized. NaOH leaching was implemented under predetermined conditions because the process of removing SiO₂ by NaOH leaching was matured.

Molten Modification Process

The molten modification process was simulated in an induction furnace, where the temperature was controlled by the input power. When the power of the induction furnace was set at 11.00 kW, the temperature of melts in crucibles was 1700°C. A mixture sample, which was charged into a cylindrical molybdenum crucible, was heated and melted in an induction furnace with the power of 11.00 kW for 30 min to simulate the molten state of titanium slag in an electric furnace. After 30 min, the molybdenum crucible was taken out and cooled naturally in air. After being cooled to room temperature, the slag samples were grounded for the leaching process use.

Leaching Process

The leaching process includes hydrochloric leaching and NaOH leaching. The modified slag was leached with hydrochloric acid under a predetermined stirring speed of 300 rpm, liquid/solid ratio of 10.0 mL/g, and particle size range of 74–125 μm. In the hydrochloric leaching process, removing efficiencies for the impurities were evaluated by the

leaching rate of CaO and MgO. The NaOH leaching process was implemented with predetermined conditions: 8% NaOH concentration, 110°C leaching temperature, 60 min leaching time, and 5-mL/g liquid/solid ratio. After leaching, the slurry was filtered by vacuum. The residues were dried in an oven at 105°C for 12 h and calcined in air at 900°C for 30 min.

RESULTS AND DISCUSSION

Mechanism of the Molten Modification Process

The mechanism of the molten modification process was investigated by XRD, thermodynamic calculation, and the theory of bond parameter function. The phases in modified slag with different B_2O_3 amounts were characterized by XRD (Fig. 1). Compared with the peaks in untreated slag, the peaks of calcium silicate weaken while the peaks of calcium borate appear in modified slag. These results indicate that calcium silicate is partly transformed into calcium borate. The peak intensities of anosovite become smaller, whereas the peak intensities of rutile are sharper with the B_2O_3 amount increasing. It implies that anosovite is transformed into magnesium borate in the molten modification process, enriching rutile.
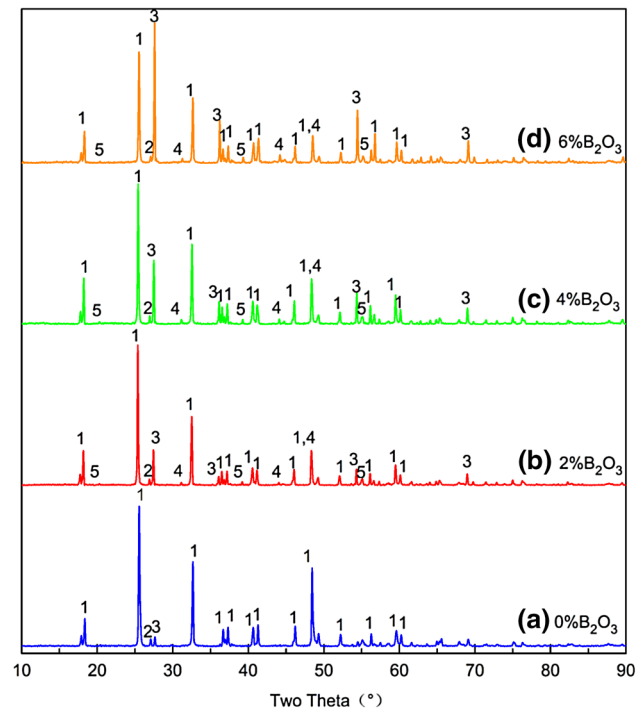
With the XRD results, possible reactions in the molten modification process can be expressed as Eqs. 1–4. Figure 2 presents the relationship between Gibbs free energy changes of reactions and temperature calculated by FactSage6.3 software.[24] The more negative value of the Gibbs free energy change means greater reaction tendency. It can be seen that the Gibbs free energy change of Eq. 3 is more negative than that of Eq. 1, indicating
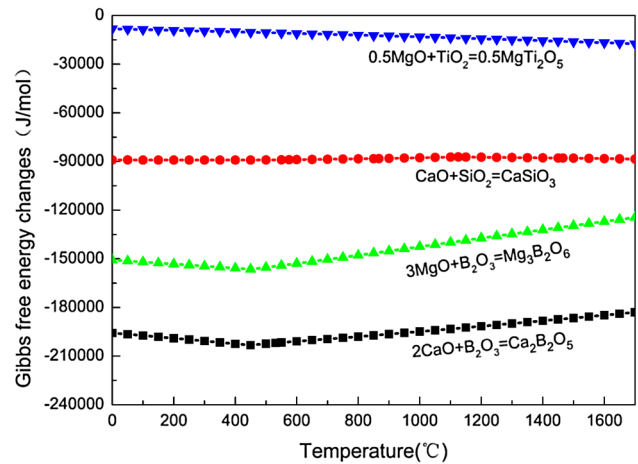
Fig. 2. Relationship between Gibbs free energy changes of Eqs. 1–4 and temperature.

Fig. 1. XRD patterns of titanium slag modified with different B_2O_3 amounts. (a) 0% B_2O_3, (b) 2% B_2O_3, (c) 4% B_2O_3, (d) 6% B_2O_3 1—anosovite [$M_xTi_{3-x}O_5(0 \leq x \leq 2$, M = Fe, Mg, Mn, etc.)], 2—calcium silicate ($CaSiO_3$), 3—rutile(TiO_2), 4—calcium borate ($Ca_2B_2O_5$), 5—magnesium borate ($Mg_3B_2O_6$).
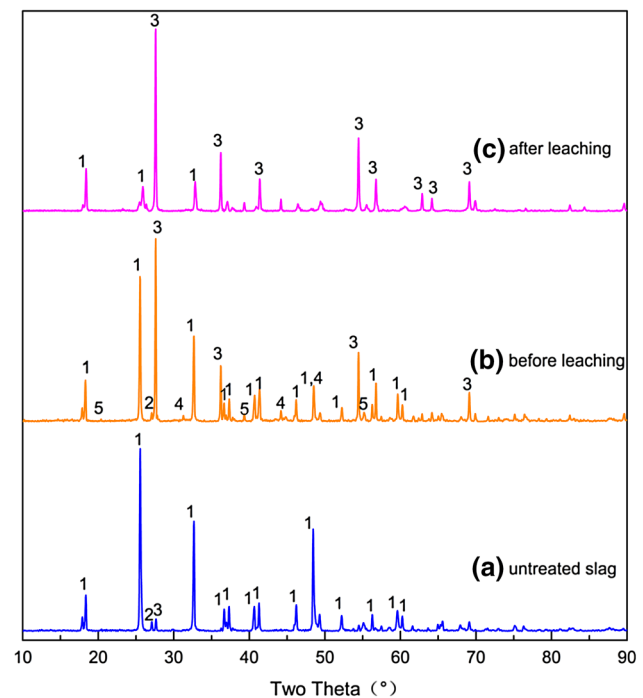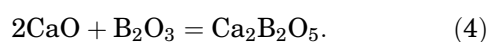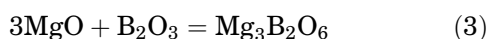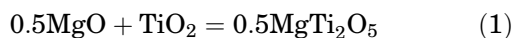
Fig. 3. XRD patterns of titanium slag. (a) Untreated slag, (b) before leaching, (c) after leaching 1—anosovite [$M_xTi_{3-x}O_5(0 \leq x \leq 2$, M = Fe, Mg, Mn, etc.)], 2—calcium silicate ($CaSiO_3$), 3—rutile (TiO_2), 4—calcium borate ($Ca_2B_2O_5$), 5—magnesium borate ($Mg_3B_2O_6$).

that MgO reacts with B_2O_3 more easily than with TiO_2. The Gibbs free energy change of Eq. 4 is more negative than that of Eq. 2, indicating that CaO reacts with B_2O_3 more easily than with SiO_2. With the addition of B_2O_3, the activity of CaO and MgO becomes small based on the molecular theory for slag structure proposed by H. Schenck,[25,26] inhibiting the precipitation of $CaSiO_3$ and $MgTi_2O_5$ and facilitating the formation of $Ca_2B_2O_5$ and $Mg_3B_2O_6$. It is in accord with the experiment mechanism shown by the results from XRD:

$$0.5MgO + TiO_2 = 0.5MgTi_2O_5 \qquad (1)$$

$$CaO + SiO_2 = CaSiO_3 \qquad (2)$$

$$3MgO + B_2O_3 = Mg_3B_2O_6 \qquad (3)$$

$$2CaO + B_2O_3 = Ca_2B_2O_5. \qquad (4)$$

The reaction mechanism in the molten modification process was also demonstrated by the theory of bond parameter function. The X_P^*Z/R_K value of the ions in the modified slag are $Ca^{2+} = 2.02$, $Mg^{2+} = 3.7$, $Fe^{2+} = 4.45$, $Ti^{3+} = 6.1$, $Fe^{3+} = 8.42$, $Al^{3+} = 9.0$, $Ti^{4+} = 9.44$, $Si^{4+} = 18.56$, and $B^{3+} = 22.67$.[27,28] The parameter X_P^*Z/R_K represents the acidity and basicity capacity of the ions in the melt, where X_P^* is electronegativity of the element

and Z and R_K are the valence and actual radius of the ion, respectively. When the X_P^*Z/R_K value increases, basicity decreases and acidity increases. Therefore, B^{3+} has the strongest acidity, while Ca^{2+} has the strongest basicity and Mg^{2+} has the second strongest basicity after Ca^{2+}. Therefore, CaO reacts with B_2O_3 preferentially, generating calcium borate. MgO reacts with B_2O_3 subsequently, generating magnesium borate. These results are consistent with the phase transformations in Fig. 1 and the thermodynamic calculation in Fig. 2.

Mechanism of the Hydrochloric Leaching Process

To investigate the mechanism of the hydrochloric leaching process, the modified slags phases before and after leaching were characterized by XRD (Fig. 3). Compared with peaks in modified slag before leaching, the peaks of calcium borate and magnesium borate disappear in the modified slag after leaching. The phase transformations demonstrate that the calcium borate and magnesium borate are leached out by hydrochloric acid. Meanwhile, rutile is the main phase in the final slag. These results suggest that anosovite is almost destroyed in the molten modification process by the addition of B_2O_3.
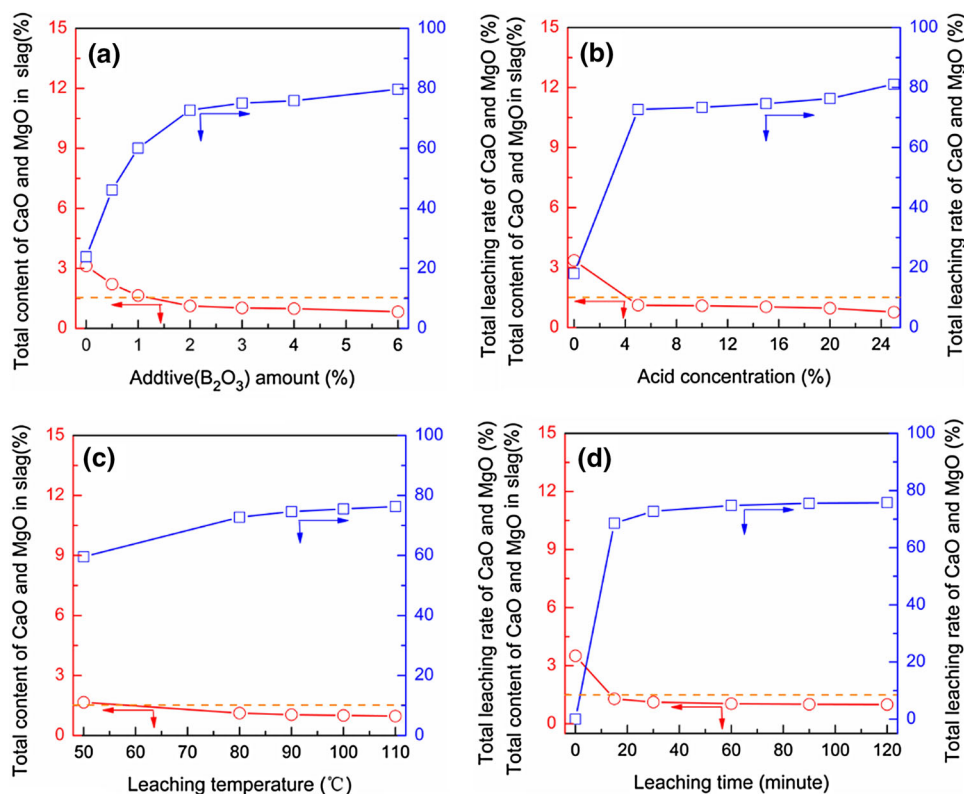

Fig. 4. Effects of experiment factors on leaching rate for the impurities in slag. (a) additive (B_2O_3) amounts, (b) acid concentration, (c) leaching temperature, (d) leaching time.

Production of Synthetic Rutile by the New Process

Effect of Technical Conditions

The effects of experimental factors on removing CaO and MgO were investigated (Fig. 4). The B_2O_3 amount has the most significant influence on leaching impurities, followed by hydrochloric concentration. Leaching temperature and leaching time have important effects on leaching impurities. The leaching rate of CaO and MgO increases rapidly with B_2O_3 amounts from 0% to 2% but slowly from 2% to 6%. The leaching rate of CaO and MgO goes fast with hydrochloric concentration increasing but gradually with a hydrochloric concentration of more than 5%. The leaching rate of CaO and MgO rises with temperature increasing but tardily with temperature greater than 80°C. The leaching rate of CaO and MgO elevates sharply with leaching time increasing but increases gradually with leaching time of more than 30 min.

Therefore, considering the leaching results and energy consumption, the optimized conditions for the new process of producing synthetic rutile are 2% B_2O_3 amount, 5% hydrochloric concentration, 80°C leaching temperature, and 30 min leaching time. Synthetic rutile containing 80.54% TiO_2, 1.12% (CaO + MgO), and 7.87% SiO_2 was prepared under optimized conditions. It is obvious that the SiO_2 content is too high and the content of TiO_2 was less than 85%.

Upgrading of Synthetic Rutile

Considering the high content SiO_2 in synthetic rutile after hydrochloric leaching, NaOH leaching was introduced to improve synthetic rutile. Synthetic rutile containing 86.77% TiO_2, 1.23% (CaO + MgO), and 0.91% SiO_2 was obtained after NaOH leaching. In the new process, the qualified synthetic rutile was prepared for fluidized bed chlorination with lower energy consumption and a smaller amount of additive.

Compared with the previous processes in Table I, the new process has two advantages: the lower energy consumption and smaller amount additive. First, B_2O_3 was added into molten titanium slag when ilmenite had been reduced to be molten iron and titanium slag in the electric furnace. The modified slag was obtained after the molten modification process. The specific heat capacity for titanium slag is 900 J/(kg °C).[29–32] Therefore, the new process uses at least 419 kW h/t sensible heat of molten titanium slag and meanwhile avoids at least 197 kW h/t reheating for the modification in previous processes in Table I. Second, the B_2O_3 amount in the new process is smaller than in the previous processes in Table I.

CONCLUSION

1. The XRD results show that with the addition of B_2O_3, calcium silicate is transformed into a calcium borate and anosovite is transformed into a magnesium borate. Then, calcium borate and magnesium borate are leached out by hydrochloric leaching, enriching the rutile. It is demonstrated by thermodynamic calculation and the molecular theory that with the addition of B_2O_3, the activity of CaO and MgO become small in modified slag, inhibiting the precipitation of $CaSiO_3$ and $MgTi_2O_5$ and facilitating the formation of $Ca_2B_2O_5$ and $Mg_3B_2O_6$.
2. The optimized conditions are 2% B_2O_3 amount, 5% hydrochloric concentration, 80°C leaching temperature, and 30 min leaching time. Synthetic rutile containing 1.12% (CaO + MgO) was prepared under optimized conditions.
3. Synthetic rutile containing 86.77% TiO_2, 1.23% (CaO + MgO) was obtained with optimized conditions and predetermined NaOH leaching conditions. Compared with the previous processes, the qualified synthetic rutile was prepared for fluidized bed chlorination with lower energy consumption and a smaller amount of additive.

REFERENCES

1. W.S. Zhang, Z.W. Zhu, and C.Y. Cheng, *Hydrometallurgy* 108, 177 (2011).
2. S.S. Liu, Y.F. Guo, G.Z. Qiu, and T. Jiang, *Trans. Nonferrous Met. Soc. China* 23, 1174 (2013).
3. Y. Chang, *Non-Ferr. Min. Metall.* 25, 37 (2009).
4. H. Chen, *Mod. Mach.* 37, 68 (2010).
5. G. Deng, *Gang Tie Fan Tai* 32, 1 (2011).
6. A. Adipuri, Y. Li, G.Q. Zhang, and O. Ostrovski, *Int. J. Miner. Process.* 100, 166 (2011).
7. J.G. Speight, *Lange's Handbook of Chemistry*, 16th ed. (New York: McGraw-Hill, 2005), pp. 126–163.
8. G. Deng, *Titanium Metallurgy* (Beijing: Metallurgical Industry Press, 2010), pp. 56–146.
9. M. Guéguin and F. Cardarelli, *Miner. Process. Extr. Metall. Rev.* 28, 1 (2007).
10. P.C. Pistorius, *J. S. Afr. Inst. Min. Metall.* 108, 35 (2008).
11. A.F.S. Schoukens, D.J. Morris, and F.S. McComb, U.S. patent 6,733,561 B2 (2004).
12. D. Filippou and G. Hudon, *JOM* 61, 36 (2009).
13. F.X. Wu, X.H. Li, Z.X. Wang, L. Wu, H.J. Guo, X.H. Xiong, X.P. Zhang, and X.J. Wang, *Int. J. Miner. Process.* 98, 106 (2011).
14. B. Jarish and S. Lambert, U.S. patent 4,038,363 (1977).
15. Y.F. Guo, S.S. Liu, T. Jiang, G.Z. Qiu, and F. Chen, *Hydrometallurgy* 147, 134 (2014).
16. H.G. Dong, T. Jiang, Y.F. Guo, J.L. Chen, and X.X. Fan, *Hydrometallurgy* 113, 119 (2012).
17. G.W. Elger, R.A. Stadler, and P.E. Sanker, U.S. patent 4,120,694 (1978).
18. M. Gueguin, U.S. patent 5,063,032 (1990).
19. K. Borowiec, A.E. Grau, M. Gueguin, and J.F. Turgeon, U.S. patent 6,733,561 B2 (1998).
20. H.M. Wang, G.R. Li, Q.X. Dai, Y.C. Lei, Y.T. Zhao, B. Li, G.M. Shi, and Z.M. Ren, *ISIJ Int.* 46, 637 (2006).
21. X. Yu, G.H. Wen, P. Tang, and H. Wang, *Ironmak. Steelmak.* 36, 623 (2009).

22. Y.Q. Sun, J.L. Liao, K. Zheng, X.D. Wang, and Z.T. Zhang, *JOM* 66, 2168 (2014).
23. Y.Q. Sun, Z.M. Li, L.L. Liu, X.D. Wang, and Z.T. Zhang, *ISIJ Int.* 55, 158 (2015).
24. http://www.factsage.com/. Accessed 26 Aug 2016.
25. N. Iwamoto, *Trans. JWRI* 4, 231 (1975).
26. X.H. Huang, *Metallurgy Principle for Iron and Steel*, 3rd ed. (Beijing: Metallurgical Industry Press, 2013), pp. 163–193.
27. N.Y. Chen, *Bond Parameter Function and Its Application*, 1st ed. (Beijing: Science Press, 1976), pp. 5–28.
28. S. Ren, J.L. Zhang, X.D. Xing, B.X. Su, Z. Wang, and B.J. Yan, *Ironmak. Steelmak.* 41, 500 (2014).
29. H. Kotzé and P.C. Pistorius, *J. S. Afr. Inst. Min. Metall.* 110, 57 (2010).
30. H. Kotzé (Ph.D. Dissertation, University of Pretoria, Pretoria, 2007).
31. J.H. Zietsman and P.C. Pistorius, *J. S. Afr. Inst. Min. Metall.* 104, 693 (2004).
32. G. Lin, *Iron Steel Scrap China* 25, 30 (2007).