Guo Jing*, Cheng Shu-Sen and Guo Hanjie

Thermodynamics and Industrial Trial on Increasing the Carbon Content at the BOF Endpoint to Produce Ultra-Low Carbon IF Steel by BOF-RH-CSP Process

<https://doi.org/10.1515/htmp-2019-0054>

Received August 19, 2018; accepted December 09, 2018

Abstract: Thermodynamic analysis was performed to obtain the relation between the carbon content at the BOF endpoint and the dissolved oxygen content in liquid steel and the (FeO + MnO) content in the slag with the help of thermodynamic calculation software FactSage. It finds that both the [O] and (FeO + MnO) content increase with decreasing the carbon content at the BOF endpoint and the increasing rate is larger when the carbon content is lower. In addition, in the case of the higher temperature at the BOF endpoint the [O] in liquid steel increase and the (FeO + MnO) in the slag increase as well. The consumption of O₂ for decarbonization at the BOF endpoint is much more than that in RH degasser since the majority of the blowing O₂ at the BOF endpoint will produce FeO into the slag, thus it increase the metal loss and deteriorate the steel cleanness during the consequent refining process. As a result, the carbon content at the BOF endpoint should be properly increased within the RH decarbonization ability. At last, industrial trials were carried out and confirmed that total oxygen consumption decrease obviously and the (FeO + MnO) of final BOF slag decline as well with increasing carbon content at BOF endpoint from 0.042% to 0.081%. In addition, it almost does not slow down the RH process and the carbon content in final steel all met the demand of the ultra-low carbon steel. In addition, mechanical properties of IF steel with higher carbon content at the

endpoint of BOF are almost all more superior to those of heat with lower carbon content at BOF endpoint.

Keywords: BOF endpoint; decarbonization; C–O equilibrium; ultra-low carbon IF steel

Introduction

There are generally two major problems with regard to production of ultra-low carbon IF steel currently: one is the surface quality problems, the other is the continuous casting (CC) nozzle clogging [1–4]. Both of the problems have a great relationship with the cleanliness of molten steel, i. e. the amount, size and composition of inclusions in steel. (FeO + MnO) in the final slag of the converter is the main reason for the high oxidizability of the refining slag in RH. Many works [5, 6] have proved that reducing the content of (FeO + MnO) in the refining can effectively decrease the total oxygen content in the steel, improve the castability and reduce IF steel surface quality problems. On the one hand, it is necessary to strictly control the amount of slag during converter tapping to the next refining process; on the other hand, it also needs to reduce the content of (FeO + MnO) content in the BOF final slag. Therefore, the determination of the optimized carbon content at the BOF endpoint by reasonable allocation decarburization amount in converter and in RH is of high significance to improve subsequent liquid steel cleanliness.

At present, the usual operation principle of producing ultra-low carbon IF steel is to lower the carbon content in the converter as much as possible to increase the free oxygen in the molten steel so as to reduce the decarburization tasks in RH refining. For example, Baosteel [7, 8] considered that the optimum carbon and dissolved oxygen contents before RH treatment were $(300\text{--}400) \times 10^{-6}$ and $(500\text{--}650) \times 10^{-6}$, respectively; Kawasaki Steel Company [9], the United States Inland Iron and Steel Company [10] controlled the carbon content in the molten steel between 0.03% and 0.04% and

***Corresponding author: Guo Jing**, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China; Beijing Key Laboratory of Special Melting and Reparation of High-end Metal Materials, University of Science and Technology Beijing, Beijing 100083, P.R. China, E-mail: guojing@ustb.edu.cn

Cheng Shu-Sen, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China

Guo Hanjie, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China; Beijing Key Laboratory of Special Melting and Reparation of High-end Metal Materials, University of Science and Technology Beijing, Beijing 100083, P.R. China

the oxygen content between 0.050% and 0.065% at the end of converter; and Thyssen Steel [11] considered the optimal carbon content of the molten steel at the end of BOF is 0.03%, and the optimal oxygen content is 0.06%. However, the removal of carbon at the BOF endpoint in the steel is at the expense of a large amount of oxygen blowing, a substantial increase of oxygen in the steel, and an increase of (FeO + MnO) in the slag. This will not only increase the oxygen consumption and the iron loss, but also increase the difficulty of slag modification during subsequent refining process and lower the cleanliness of molten steel. Due to the rate of RH vacuumizing increases and the ultimate vacuum degree steady decreases in recent years, decarburization ability of RH has been greatly strengthened, which provides the conditions for more decarburization tasks in RH. In this paper, the thermodynamic software FactSage was used to analyze the influence of carbon content at the BOF endpoint theoretically. The theoretical calculations and industrial trials both verify that increasing the carbon content at the BOF endpoint in a proper extent is beneficial for steel cleanliness improvement as well as many other aspects.

Thermodynamic analysis

With oxygen blowing in the converter, the following two reactions will take place,

$$\Delta G_1^\theta = -22200 - 38.34T^{[12]} \quad (2)$$

$$\Delta G_2^\theta = -117700 + 49.83T^{[12]} \quad (4)$$

where ΔG_i^θ stands for Gibbs energy. As a result, oxygen will not only react with the carbon in the steel, but also react with Fe to form FeO into the slag. Especially a large amount of FeO is generated at the same time as decarburization when the carbon content is low at the BOF endpoint. Therefore, the carbon content at the BOF endpoint is directly related to the oxygen in the steel and the FeO (or MnO) in the slag. Due to strong mixing conditions in the converter, it can be considered that the slag-steel

equilibrium is reached so that the relationship among the carbon content, dissolved oxygen content and FeO in slag at the endpoint of BOF, can be obtained with the help of thermodynamic software FactSage. This can avoid the complex calculation of multiphase reactions and get more accurate results.

Figure 1 shows the relationship between the oxygen content, the content of (FeO + MnO) in the slag and the carbon content at the BOF endpoint in a 120-ton converter at 1,973 and 1,923 K, respectively calculated by using FactSage. As the carbon content decreases, the corresponding content of oxygen and of (FeO + MnO) gradually increase, and the increasing rate accelerates. In addition, [O] in steel at 1,973 K is higher than [O] at 1,823 K by $20\text{--}30 \times 10^{-6}$ with the same carbon content, whereas the content of (FeO + MnO) in the slag is lower by about 1.5–2.5 mass%. This is due to the fact that the free energy change of C–O reaction eq. (1) decreases with the increasing of temperature and, thus, the value of $[C\%][O\%]$ in the steel increases in the case of a constant partial pressure of CO. The Fe–O reaction, as reaction(2), is an exothermic reaction, thus, temperature increase causes the above reaction to proceed leftward and reduces the content of FeO in the slag. Therefore, increasing the temperature at the BOF endpoint is advantageous for smelting ultra-low carbon IF steel. This can not only reduce the oxidability of slag, but also increase the dissolved oxygen in the steel for RH decarbonization.

At the BOF endpoint, the target blowing O_2 amount to remove a certain amount of carbon should contain the following three parts as shown in eq. (5),

$$O_{\text{addition}} = O_{\text{de-C}} + \Delta O_{\text{in-equ}} + O_{\text{in-slag}} \quad (5)$$

Figure 1: Relations between the oxygen content, (FeO + MnO) content in the slag and the carbon content at the BOF endpoint.

where $O_{\text{de-C}}$ means the required oxygen to generate CO in the process of decarbonization, $\Delta O_{\text{in-equ}}$ indicates increased oxygen in equilibrium with the carbon in liquid steel; and $O_{\text{in-slag}}$ suggests oxygen into the slag.

For RH degasser, on account of the quiet slag-steel interface, the slag-steel interface reaction is quite weak and the amount of FeO into the slag is much smaller during decarbonization. Furthermore, the content of excess oxygen after decarbonization is almost the same ($200\text{--}300 \times 10^{-6}$) to that before decarbonization since the oxygen needed in equilibrium with carbon under vacuum condition in RH is very small. Therefore, the required blowing O_2 for removing a certain amount of carbon in RH are nearly the same as the O_2 demanded in decarbonization chemical reaction,

$$O'_{\text{addition}} = O_{\text{de-C}} \quad (6)$$

Figure 2 shows the volume of the blowing O_2 and the required oxygen amount for producing CO during decarbonization ($O_{\text{de-C}}$) by decreasing the carbon content in steel from 0.1% to different levels at BOF endpoint. The amount of the blowing O_2 raises dramatically with the decreasing carbon content, especially, it increases more obviously when the carbon content is lower than 0.04%. In addition, the required blowing O_2 content at 1,973 K is less than that at 1,923 K. According to eq. (6), the bottom curve could represent the blowing oxygen content for the same carbon content removal in RH degasser. Apparently, it is far less than the blowing oxygen content for removing the same carbon content at the BOF endpoint. When the carbon content s decreases from 0.04% to 0.03% at the

endpoint of BOF, for instance, the oxygen content obtained by C–O reaction ($O_{\text{de-C}}$) is about 133×10^{-6} , the increased amount of [O] for equilibrating the carbon ($\Delta O_{\text{in-equ}}$) is about 180×10^{-6} (from 550 to 730×10^{-6}), and the increment of (FeO + MnO) in the slag is approximating 6% that corresponds to about $1,200 \times 10^{-6}$ dissolved oxygen ($O_{\text{in-slag}}$). Namely, $1,513 \times 10^{-6}$ [O] are demanded in total. However, only 133×10^{-6} [O] are required in RH process ($O_{\text{de-C}}$) to remove the same amount of carbon, which is less than a tenth of the former. Majority of the blowing oxygen at the BOF endpoint (80%) turns into FeO into the slag, which increases the difficulty of modifying the top slag in the following second refining process so that it is hard to enhance the steel cleanness. Also, it rises metal loss of converter steelmaking resulting in the smelting cost increase. As a result, the carbon content at the BOF end point should be properly increase and more decarbonization task can be carried out in RH degasser within the RH decarbonization ability.

Industrial trial and results

In order to validate the thermodynamic analysis, a large number of industrial data in a 120 ton converter and 120 ladle to produce ultra-low carbon IF steel were collected, in which carbon content in steel were determined by OES (Optical Emission Spectrometer) and (FeO + MnO) content in slag were measured by X-ray fluorescence. In addition, three heats of IF steel with controlling of different carbon content at the endpoint of BOF, 0.042%(A), 0.051%(B) and 0.081%(C) were carried out in the 120 ton converter and ladle for a more accurate comparison by controlling other parameters in similar levels such as hot metal quality and heat treatments. It should be pointed out that the vacuum power of RH should be increased corresponding in a proper manner in the case of carbon content increase.

Figure 3 shows relationship between the oxidizability of final BOF slag and the content of [C] in the steel in a 120 ton converter. It can be seen that the oxidizability of the slag increases with the reduction of carbon content at both temperatures, which is in great agreement with thermodynamic calculations in Figure 1.

Figure 4 shows relations between the carbon content at the BOF endpoint and the total oxygen consumption both in 120 ton BOF and RH in the case of ultra-low carbon IF steel with final product carbon content lower than 40×10^{-6} . A total of 370 industrial data are displayed in the figure corresponding to that in Figure 3(a). When the

Figure 2: Relation between carbon content at the endpoint of BOF and the volume of blowing oxygen.

Figure 3: Relation between industrial carbon content in liquid steel and oxidizability in slag at different temperature regions at the BOF endpoint in a 120 ton converter.

Figure 4: Relationship between C content at BOF endpoint and total oxygen consumption of 120 ton BOF and RH.

carbon content at the BOF endpoint decreases, the total oxygen consumption in whole smelting process markedly increases. For example, the carbon content at the BOF endpoint is 0.08% and the required total blowing oxygen amount in BOF and RH are between 6,000 and 7,000 m³, while the total oxygen consumption are between 6,500 and 8,000 m³ in the case of [C%] = 0.03 at the BOF endpoint 0.03%, namely, the latter is 500–1,000 m³ higher than the former. Therefore, higher carbon strategy is applied for decarbonization at the endpoint of converter, and the total oxygen consumption is apparently lower than that with a lower carbon strategy at BOF endpoint.

Figure 5 shows the variation of carbon content in IF steel during BOF-RH-CC process. Although the carbon at BOF endpoint in Heat B and Heat C were more than that in Heat A, the carbon content in the steel after RH was lower than that in Heat A, and they three have all been to

Figure 5: Carbon content evolution of three heats of IF steel during BOF-RH-CC process.

a low carbon level ($< 40 \times 10^{-6}$) in the final products meeting the IF steel composition demand. Table 1 lists comparison of oxidability in final BOF slag, total oxygen consumption both in BOF and RH and RH vacuum time for the three heats of IF steel with different carbon at the endpoint of BOF. In comparison that of Heat A, the BOF slag oxidability of Heat B and Heat C decreased by 1.6%

Table 1: Comparison between some typical parameters of three heats of IF steel with different carbon content at BOF endpoint.

Heat	Heat A	Heat B	Heat C
C at BOF endpoint/%	0.042	0.051	0.081
(FeO + MnO) in final BOF slag/%	26.9	25.3	24.6
Total oxygen consumption/m ³	7,236	6,921	6,583
RH vacuum time/min	30	32	27

and 2.3%, respectively. Correspondingly, total oxygen consumptions of Heat B and C decrease by 315 and 653 m³, respectively. What's more, the total RH vacuum time of Heat B and Heat C are 32 and 27 min, respectively compared to 30 min of Heat A, Table 2 shows some mechanical properties of IF steels after the similar heat treatment and rolling process. They all meet the needs of IF steel, particularly, mechanical properties of heat C are almost all more superior to those of Heat A for IF steel deformation except. Therefore, all the foregoing results indicate almost no negative effect on the normal productivity of melting process and final product properties after increasing C content of BOF endpoint in a reasonable extent.

Table 2: Mechanical properties for IF steels produced by three heats.

Heat	Heat A	Heat B	Heat C
Average plastic strain ratio r_m	2.54	2.42	2.53
Hardening index n	0.24	0.25	0.25
Yield strength δ_s /MPa	148	136	133
Tensile strength δ_b /MPa	293	288	284
Elongation λ /%	45.0	47.0	47.5

Conclusion

- (1) With the decrease of carbon at BOP endpoint, the oxygen in steel and the (FeO + MnO) in the slag gradually increase. For decarbonization at the endpoint of BOF, majority of oxygen reacts with the metal and then the reaction products FeO and MnO enter the slag which makes it difficult to improve molten steel cleanliness during the consequent refining and at the same time increases the iron loss.
- (2) Industrial data verify that the oxygen consumption for decarbonization will notably decrease in the whole prices (BOF + RH) when the carbon content at BOF endpoint appropriately increase. When the carbon content at BOF endpoint increase from 0.42% to 0.081%, (FeO + MnO) in the final BOF slag decrease from 26.9% to 24.6%, and total oxygen consumption in 120 ton BOF + RH process

decreased from 7,236 to 6,583 m³. Moreover, the total vacuum time of RH do not extend by improving vacuum power of RH in a proper manner.

- (3) The carbon content in final steel products of the heats with higher carbon content at the endpoint of BOF are all less than 40×10^{-6} which meet the demand of the composition in ultra-low-carbon IF steel. In addition, their mechanical properties are almost all more superior to those of heat with lower carbon content at the endpoint of BOF.

Acknowledgements: The authors express their thanks to National Science Foundation for Young Scientists of China (51704021), China Postdoctoral Fund (2018M630071), fundamental Research Funds for the Central Universities (FRF-TP-16-079A1) and Joint Funds of National Natural Science Foundation of China (U1560203) for their kind financial support. This study is also supported by Beijing Key Laboratory of Special Melting and Preparation of High-end Metal Materials.

References

- [1] Y. Kondo, H. Tanei and N. Suzuki, ISIJ Int., 51 (2011) 1696–1702.
- [2] Y.M. Che, T. Zhu, H.M. Zhang, M. Dong and X.A. Cheng, Iron Steel, 41 (2006) 63–66.
- [3] S. Basu, S.K. Choudhary and N.U. Girase, ISIJ Int., 44 (2004) 1653–1660.
- [4] G.Y. Qian and G.G. Cheng. Proceeding of AIST Tech 2014, May 5–8, 2014, Indianapolis, pp. 1823–1828.
- [5] K. Tanizawa, F. Yamaguchi and K. Inaoka, La Metallurgia Italiana, 84 (1992) 17–22.
- [6] T. Ehara and Y. Kurose. 1996 Steelmaking Conference Proceedings, 1996, Iron and Steel Society, Pittsburgh, Warrendale, pp. 485–486.
- [7] J. Cui, L.X. Zhu and Y.Y. Zhen, Proceedings of China Iron&Steel Annual Conference, 2001, Beijing, pp. 564–569.
- [8] L.X. Zhu, X. Jiang and C. Xu, Iron Steel, 35 (2000) 15–18. (in Chinese)
- [9] T. Takechi, ISIJ Int., 34 (1994) 1–8.
- [10] A. Jungreithmeier, E. Pissenberge and K. Burgstaller, Iron Steel Technol., 4 (2004) 41–48.
- [11] W.Q. Chen, Iron Steel, 31 (1996) 79–82. (In Chinese)
- [12] The Japan Society for the Promotion Science, Steelmaking Data Sourcebook, Gordon and Breach Science Publishers, Tokyo (1986), pp. 111.