doi:10.11835/j.issn.1671-8224.2014.01.02

To cite this article: XIONG Shuang, ZENG Hui, CAO Yang, WANG Qing-xiang. Change and control of nitrogen in molten steel production process [J]. J Chongqing Univ: Eng Ed [ISSN 1671-8224], 2014, 13(1): 11-16.

Change and control of nitrogen in molten steel production process

XIONG Shuang†, ZENG Hui, CAO Yang, WANG Qing-xiang

Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, Wuhan University of Science and Technology, Wuhan 430081, P. R. China

Received 8 January 2014; received in revised form 17 February 2014

Abstract: The change and control of nitrogen content in molten steel was investigated through the production process of “LD-BAr-LF-RH-CC”. Results show that nitrogen content reduces gradually in converter-steelmaking stage, rises rapidly from the end of converter process to the end of argon station process, continues to increase in ladle furnace process, and decreases slightly in RH refining stage. Since nitrogen is removed mainly by BOF steelmaking and vacuum refining operations, nitrogen in molten steel should be removed as much as possible in these two operations. However, nitrogen uptake should be minimized in other operations of molten steel production process.

Keywords: molten steel; production process; nitrogen content; change; control

CLC number: TF76 Document code: A

I Introduction

Nitrogen in steel exists in the form of nitride and it affects the quality of steel in two aspects. On one hand, it can improve the hot rolling performance, ductility and high temperature process ability of the steel by the refined grain precipitated from VN in the non-quenched and tempered steel that contains vanadium [1-3]. Obviously, this produces good social and economic benefits. On the other hand, as the interstitial impurity such as C and N can diffuse easily in Fe atomic lattice at low temperature, the cold forging performance of steel can be reduced.

Although nitrogen content in steel is very little, it has considerable effects on the mechanical performance of steel [4]. It not only reduces the mechanical performance of steel, but also becomes an important cause of defects such as crack, skin blowhole, and central porosity [5-6].

The pipeline steel, which is used to transport oil and natural gas, is growing rapidly at present. As oil and natural gas resources are mostly located in remote and harsh areas, the delivery pressure in pipeline is high, the medium is both complex and corrosive, and pipelines are generally assembled and girth welded in the field. All above require the pipeline steel to be strong and tough, but also to have good performance to resist fatigue, fracture and corrosion. Both of them put forward strict requirements on the nitrogen
content in these steel, thus on the denitrification and nitrogen control during steelmaking process. Consequently, it is necessary to research the change of nitrogen content and its causes, which can provide theoretical basis for improving nitrogen desorption measures and the control of nitrogen during steelmaking progress.

2 Nitrogen absorption and desorption theory of molten steel

Nitrogen has certain solubility in each state of steel. Gaseous nitrogen and dissolved nitrogen in molten steel abide by the following chemical equilibrium [7-8]:

\[
\frac{1}{2}N_2 = [N].
\]  

(1)

The solubility of nitrogen in molten steel conforms to the law of square root, namely

\[
\%N = \left( K_N \sqrt{P_{N2}} \right) / f_N,
\]  

(2)

where \( K_N \) is the equilibrium constant of nitrogen dissolution reaction in Eq. (1), \( P_{N2} \) is the partial pressure of nitrogen in the gas phase, and \( f_N \) is the activity coefficient of nitrogen in molten steel.

It can be seen from Eq. (2) that the solubility of nitrogen in molten steel is affected by temperature, partial pressure of nitrogen, and composition of molten steel.

As the dissolution of nitrogen in molten steel is an endothermic reaction, the solubility of nitrogen increases when the temperature rises. Therefore, the temperature of molten steel needs to be lowered to reduce the nitrogen content.

The solubility of nitrogen in molten steel declines with the decrease of nitrogen’s partial pressure, and vice versa. Therefore, we should reduce the partial pressure of nitrogen for the denitrification of molten steel. There are two methods to reduce partial pressure of nitrogen at present: one is to reduce the system pressure, such as VD and RH process [9-10], and the other is dilution, such as AOD process [11].

Molten steel also contains O, S, Si, Cr, Ni, Mn, C, Mo and other elements, and the combined influence among elements cannot be ignored [12]. Elements such as Cr, Mn, and Mo are not conducive to the denitrification as they reduce the activity of nitrogen. Elements such as C, Si, and N can improve the activity of the nitrogen, so they are conducive to the denitrification. O, S and some other elements are special, however. On one hand, they can improve nitrogen activity, which is conducive to denitrification; on the other hand, they can increase the gas-liquid interfacial diffusion resistance of nitrogen as surface active substance, which is not conducive to denitrification [13].

3 Production tests and results

The production tests of change and control of nitrogen content during steel production process for the pipeline steel grade X70 have been conducted in a steelmaking plant which has top and bottom combined blown converters with a capacity of 250 t. The production process is “LD-BAr-LF-RH-CC”. 127 heats have been tested from February 15 to March 27, 2011. Molten steel samples of each heat was taken at the late period of converter blowing process by the sublance, at the endpoint of converter process, at the end of Ar station, at the end of LF process, at the end of RH process, and in tundish. The nitrogen content results of the samples are listed in Table 1.
Table 1  Average nitrogen content ([N]) at each sampling point during the production process of the pipeline steel grade X70

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>[N]/(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Converter sublance</td>
<td>21.5</td>
</tr>
<tr>
<td>Converter endpoint</td>
<td>17.8</td>
</tr>
<tr>
<td>Ar station endpoint</td>
<td>57.4</td>
</tr>
<tr>
<td>LF endpoint</td>
<td>83.3</td>
</tr>
<tr>
<td>RH endpoint</td>
<td>62.9</td>
</tr>
<tr>
<td>Tundish</td>
<td>60.4</td>
</tr>
</tbody>
</table>

4  Change and analysis of nitrogen content during steel production process

Based on Table 1, statistical results of nitrogen content changing in the 127 heats pipeline steel grade X70 during the process of “LD-BAr-LF-RH-CC” are as shown in Fig. 1.

Fig. 1  Statistical curve of nitrogen content changing in the pipeline steel grade X70 during production process

As can be seen in Fig. 1, nitrogen content of molten steel reduces gradually in the converter process, rises rapidly from steel tapping to argon station process, continues to increase in ladle furnace process, and decreases in RH refining process.

Denitrification in converter process mainly relies on CO bubbles that generated from carbon oxygen reaction. Due to good thermodynamic and kinetic conditions in converter, the carbon oxygen reaction reacts fiercely and the nitrogen content of molten steel decreases by the denitrification of CO bubbles.

Molten steel absorbs a significant amount of nitrogen from steel tapping to argon station process. This is because molten steel contacts with air aggressively and absorbs a lot of nitrogen during steel tapping process and the following argon blowing process, which is designed to enhance the reactions between molten steel and slag, carburant, alloying agent, etc. If the tapping hole is not round, or scattered flowing occurs, or argon blows too violently, nitrogen absorption of molten steel will be more severe. In addition, most of the oxygen in molten steel is removed by slag and alloying agent during tapping steel, the carbon oxygen reaction stagnates and CO bubbles reduce instantly by a large margin. As a result, the nitrogen content of the molten steel increases. Carburant and high nitrogen alloys such as MnFe can also increase nitrogen content of molten steel. Therefore, the nitrogen content of alloy needs to be monitored and alloys with low nitrogen content should be used in low nitrogen steel smelting.

The main reason of nitrogen absorption in LF process is that nitrogen in the air goes into molten steel by being ionized into nitrogen ions in the arc region, as the surface of the molten steel in arc area becomes bare due to the breakdown of slag layer by arc. In addition, a certain amount of ferroalloys or carbon powder are added into molten steel in LF refining for composition adjustment. To strengthen the reaction, a large amount of argon is used for stirring. These can also cause additional exposure of molten steel to the atmosphere, resulting in nitrogen absorption.

Fig. 1 shows that nitrogen in molten steel can be removed to a certain degree in the RH vacuum treatment process. This can be explained by Eq. (2). As $2[N] = N_2$, the reaction will generate in the direction of the nitrogen gas when the nitrogen pressure in RH vacuum chamber is less than the equilibrium pressure.
of [N] in the molten steel, and [N] will escape from molten steel in the form of nitrogen gas. Finally, nitrogen content decreases.

5 Control of nitrogen in the steel production process

The control of nitrogen content must be done throughout hot metal pretreatment, converter smelting, refining treatment and continuous casting. Theoretically, they both have certain denitrification ability during hot metal pretreatment, converter smelting and RH vacuum refining process, but denitrification should be mainly accomplished in converter smelting process in terms of the denitrification efficiency and process optimization. The main task of later processes, such as steel tapping, refining and continuous casting, is to prevent or reduce nitrogen absorption.

Measures to improve denitrification efficiency in converter process are as follows: raise the lance position properly when converter smelting starts; increase the (FeO) content of slag to ensure that bulk materials in the furnace melt fully as soon as possible and cover the surface of molten steel evenly to avoid direct contacting between molten steel and the air; use whole argon mode for bottom blowing converter to avoid nitrogen content rising caused by nitrogen supply at the initial stage of bottom blowing; increase hot metal ratio appropriately to reduce nitrogen brought by steel scrap; increase the amount of slag appropriately to avoid the slag getting dry and keep the thickness of slag layer enough to reduce the nitrogen absorption during blowing process; improve terminal hit rate to reduce point blow; keep positive pressure in furnace to reduce nitrogen absorption; and keep steel tapping hole round to prevent steel scattered flowing.

Measures for controlling the nitrogen absorption in LF process are as follows: make foaming slag with appropriate thickness during refining process to ensure submerged arc heating and to prevent nitrogen absorption caused by the surface of molten steel exposed [14]; seal ladle and smoke hood to keep reducing atmosphere in the furnace and reduce the contact between molten steel and the air; and use low nitrogen alloys for the alloying treatment whenever possible.

Measures for optimizing denitrification during RH process are as follows: increase the vacuum level and extend the vacuum refining time; use carbon oxygen reaction under the vacuum conditions and increase the lifting gas flow to improve the denitrification rate [15]; put the main nitrogen control measures in the converter steelmaking process for smelting low or ultra-low-nitrogen steel; and control the vacuum conditions during RH refining process to reduce nitrogen absorption.

Technical measures for preventing nitrogen absorption in continuous casting are as follows: seal the gap between ladle bottom nozzle and long nozzle by argon blowing to prevent the air seeping into when molten steel in the ladle comes into tundish [16]; seal the tundish and use the operation of large amount slag when molten steel is in the tundish; and seal the gap between slide plate and submerged nozzle by argon blowing when molten steel comes into the mold from tundish.

6 Conclusion

1) The nitrogen content in molten steel reduces in converter smelting stage, increases rapidly from steel tapping to argon station, continues to increase in ladle furnace process, and decreases slightly in RH refining stage.

2) Denitrification in converter process mainly relies on CO bubbles generated from carbon oxygen reaction. Due to good thermodynamic and kinetic conditions in converter, the carbon oxygen reaction reacts fiercely and the nitrogen content of molten steel decreases by
the denitrification of CO bubbles.

3) Molten steel absorbs a significant amount of nitrogen from steel tapping to argon station process. This is because molten steel contacts with air aggressively and absorbs a lot of nitrogen during steel tapping process and the following argon blowing process, which is designed to enhance the reactions between molten steel and slag, carburant, alloying agent, etc. In addition, carburant and high nitrogen alloys can also increase nitrogen content of molten steel.

4) The main reason of nitrogen absorption in LF process is that nitrogen in the air goes into molten steel by being ionized into nitrogen ions in the arc region, as the surface of the molten steel in arc area becomes bare due to the breakdown of slag layer by arc. In addition, a large amount of argon is used for stirring to strengthen the LF refining, which also results in nitrogen absorption.

5) Nitrogen in molten steel can be removed to a certain degree in the RH vacuum treatment process. The reason is that [N] will escape from molten steel in the form of nitrogen gas when the nitrogen pressure in RH vacuum chamber is less than the equilibrium pressure of [N] in molten steel.

References


