

Development and prospects of molten steel deoxidation in steelmaking process

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Development and prospects of molten steel deoxidation in steelmaking process

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Abstract: In the long traditional process of steelmaking, excess oxygen is blown into the converter, and alloying elements are used for deoxidation. This inevitably results in excessive deoxidation of products remaining within the steel liquid, affecting the cleanliness of the steel. With the increasing requirements for steel performance, reducing the oxygen content in the steel liquid and ensuring its high cleanliness is necessary. After more than a hundred years of development, the total oxygen content in steel has been reduced from approximately 100×10^{-6} to approximately 10×10^{-6} , and it can be controlled below 5×10^{-6} in some steel grades. A relatively stable and mature deoxidation technology has been formed, but further reducing the oxygen content in steel is no longer significant for improving steel quality. Our research team developed a deoxidation technology for bearing steel by optimizing the entire conventional process. The technology combines silicon–manganese predeoxidation, ladle furnace diffusion deoxidation, and vacuum final deoxidation. We successfully conducted industrial experiments and produced interstitial-free steel with natural decarbonization predeoxidation. Non-aluminum deoxidation was found to control the oxygen content in bearing steel to between 4×10^{-6} and 8×10^{-6} , altering the type of inclusions, eliminating large particle Ds-type inclusions, improving the flowability of the steel liquid, and deriving a higher fatigue life. The natural decarbonization predeoxidation of interstitial-free steel reduced aluminum consumption and production costs and significantly improved the quality of cast billets.

Keywords: steel deoxidation; deoxidizer; metallurgical equipment; bearing steel; IF steel

1. Introduction

The physical nature of the dynamic operational process of the steel metallurgical manufacturing industry can be described as follows: under the driving and action of the carbon flow, the iron flow runs dynamically and orderly based on a specific overall plan in accordance with the set production operation instructions, and multi-objective optimization is achieved [1]. Blast furnace ironmaking is a reduction process that is used within the long steelmaking process, and it employs reducing agents (such as coal powder and coke) to remove oxygen from iron ore and produce pig iron containing carbon, silicon, manganese, and phosphorus [2–4]. The pig iron is then in a state of over-reduction, and it has a very low oxygen content [5]. Converter steelmaking is an oxidation process that requires pure oxygen to be blown into the pig iron through an oxygen lance so that the harmful elements dissolved in the pig iron can be rapidly oxidized and removed into the slag, and steel with different carbon contents can be obtained at the endpoint [6–7]. As the carbon content in the steel gradually decreases, the oxygen content gradually increases, and carbon and oxygen have a corresponding equilibrium relationship [8]. The endpoint oxygen content of the converter is usually between 300×10^{-6} and 800×10^{-6} , and in some overblown heats, it may even exceed $1000 \times$

10^{-6} . Various methods are subsequently used for deoxidation, and different deoxidation methods are adopted for different types of steel to meet the standard requirements prior to solidification [9]. A primary oxygen source and a secondary oxygen source are required throughout the entire steelmaking process according to the source of molten steel oxygen [10–12].

Oxygen is an element with obvious nonmetallic properties that has a strong affinity with iron and can be well dissolved in molten steel [13]. If the dissolved oxygen in the steel is not properly removed in an appropriate manner, carbon and oxygen tend to segregate and concentrate during solidification. This causes the carbon to oxidize again, which leads to both the formation of carbon monoxide (CO) gas bubbles in the steel and steel boiling with an increased CO bubbling intensity [14–15]. Ultimately, this increases the inhomogeneity and porosity of the steel, resulting in irreversible and severe damage. In addition, oxygen readily reacts with iron, forming FeO or Fe_3O_4 , which is distributed on the grain boundaries [16]. Deoxidizers can reduce dissolved oxygen to gas or form easily removable solid oxides [17–19], and a deoxidizer is usually added to molten steel to achieve deoxidation. The most commonly used deoxidizers include silicon, manganese, aluminum, carbon, and other elements [20]. The remaining free oxygen in the steel is mostly com-

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bined with alloying elements to form oxide inclusions, which exist in the form of bound oxygen [21]. However, due to the different deformation capabilities of various oxide inclusions in steel and their significant differences, cracks are prone to occur during the rolling process, leading to reduced plasticity and impact toughness of the steel [22–25]. Large-sized oxide inclusions also have a negative impact on the fatigue life of the steel [26–28].

To obtain high-quality steel, it is necessary to effectively remove the dissolved oxygen within the molten steel while ensuring that the bound oxygen remaining within it forms oxide inclusions that can be fully floated and adsorbed [29–30]. Developments in the steel industry over many years include early single alloying element deoxidation to the later emergence of vacuum technology and the application of composite deoxidation alloys [31]. Methods such as precipitation deoxidation, diffusion deoxidation, and vacuum deoxidation are currently used in production, and electrochemical deoxidation and reducing gas deoxidation have been experimentally explored. The total oxygen content in steel has been reduced from approximately 100×10^{-6} in the early 20th century to below 10×10^{-6} ; for steel grades with a strict oxygen content requirement, such as bearing steel, the oxygen content can be stably controlled at 5×10^{-6} . However, research has shown that deoxidation problems exist in industrial production, and these include a high alloy consumption, a low yield rate, and a limited deoxidation product removal efficiency [32]. In addition, for steel grades with an ultra-low oxygen content, the further improvement of fatigue life is no longer significant as the total oxygen content decreases. Therefore, there is an urgent need to develop new deoxidation technologies to achieve rapid, low-cost, and unpolluted deoxidation and significantly improve the performance of steel while meeting the oxygen content requirements of molten steel.

This study focuses on the development process of steel deoxidation. The current application status of deoxidation in typical steel grades (such as high-carbon bearing steel and ultra-low-carbon IF steel) is summarized, and two innovative applications of deoxidation technology are introduced. Fu-

ture development trends are presented, with the aim of providing a reference for further technological developments in steelmaking.

2. Development of molten steel deoxidation technology

2.1. Changes in steel oxygen content and deoxidation technology

2.1.1. Changes in steel oxygen content

The steel oxygen content has evolved over time with the development of steelmaking deoxidation technologies and new deoxidizers, as shown in Fig. 1 [33–37]. In the early 20th century, deoxidation was mainly conducted using single elements (such as silicon, manganese, or carbon), resulting in a wide steel oxygen content range that was generally above 100×10^{-6} [33–34]. In the 1930s, with the maturation of electrolytic aluminum technology, aluminum deoxidation technology for steelmaking emerged, which revolutionized steelmaking deoxidation technology. The United States was the first country to use aluminum as a deoxidizer, and this significantly reduced the oxygen content in steel to approximately 50×10^{-6} while ensuring the casting effect [36]. In the 1950s, Dortmund–Hörder (DH) vacuum degassing and Ruhrstahl–Heræus (RH) vacuum degassing methods were introduced, and these further lowered the steel oxygen content to about 30×10^{-6} [38]. In the 1960s to 1990s, ladle refining, injection metallurgy, and wire feeding technology were widely used in steel production, and the total oxygen content in steel with high cleanliness requirements had already approached 10×10^{-6} by the 1990s [39]. Today, with continuous improvements in the quality of raw materials used in steelmaking, the oxygen content can be stably controlled to below 5×10^{-6} through refined deoxidation control, combination deoxidation, full-process oxygen source traceability, protective casting, and the automatic addition of deoxidizing alloys.

The evolution of the oxygen content in steel mirrored transformations in the iron and steel industry, and new technologies and methods consistently appeared with each deoxidation technology advancement. Metallurgists constantly

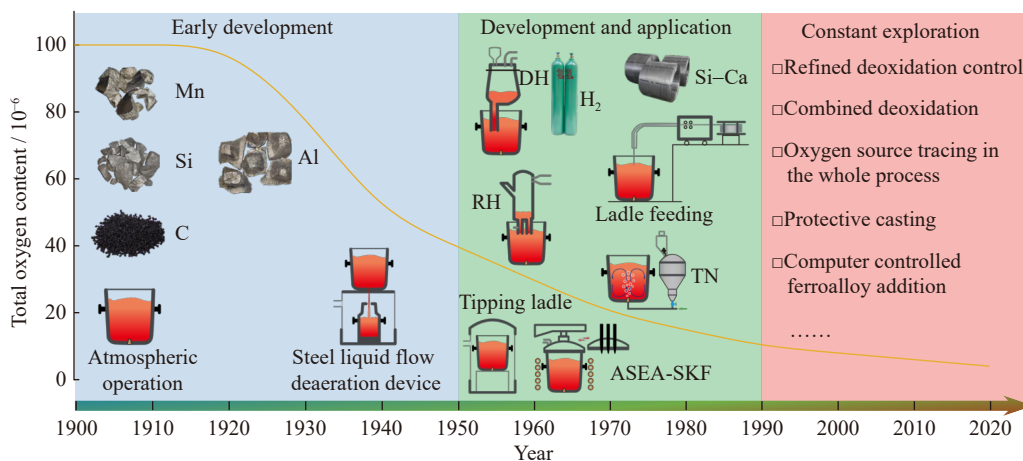


Fig. 1. Changes in steel oxygen content, deoxygenation technologies, and equipment over time.

explored and developed innovative ways to improve this process, making important contributions to the development of the steel manufacturing industry. According to the technical characteristics and application effects, the development process of steelmaking deoxidation can be divided into three stages: early development, development and application, and constant exploration, and these are presented in the following subsections.

2.1.2. Early development stage of molten steel deoxidation technology

The early development stage of molten steel deoxidation technology in the steelmaking process occurred in the years pre-1950. During this period, the idea of reducing the oxygen content in molten steel by adding deoxidizers had emerged in industrial production, but it was constrained by the use of a single deoxidizer type and rudimentary equipment conditions. From the late 19th century to the early 20th century, there were annual developments in the ferroalloy industry, and ferroalloys containing only one main element (such as silicon, manganese, and chromium) were successively developed and applied in steel deoxidation and alloying [40]. However, the deoxidation effect of a single-element deoxidizer was poor and removing the deoxidation products from the steel was not easy. For example, with silicon deoxidation, when the Si content in the steel was 0.2wt%, the theoretical equilibrium oxygen content was found to be 100×10^{-6} , and the melting point of the deoxidation product (SiO_2) exceeded 1700°C and it existed as large solid inclusions within the steel [41]. In the 1930s, large-scale electrolytic aluminum production significantly reduced the unit price of aluminum and created conditions for its application in steel deoxidation. By adding chunky electrolytic aluminum into the steelmaking furnace or ladle, the oxygen in molten steel could be quickly reduced to a low level. Aluminum not only acted as a strong deoxidizing element, but it also refined the grain in the steel and prevented the aging of low-carbon steel, thereby improving its low-temperature toughness and exhibiting other positive effects. However, Al_2O_3 inclusions exist as the deoxidation product of aluminum, and these easily affect the fluidity of the steel liquid and reduce the cold working and fatigue properties of the solidified steel [42–43].

With respect to steelmaking equipment, Bessemer, who was the inventor of the converter steelmaking process, envisioned the application of vacuum casting after steelmaking as early as 1865. In 1886, Toland suggested that degassing in a vacuum would help to improve the cleanliness of molten steel [44]. However, the lack of high-performance and large-capacity vacuum pumps at the time hindered the industrial application of vacuum treatment for steel. It was not until 1938 that the Bochum Veren steel plant established a steel liquid flow deaeration device, and his was applied in industrial practice to prevent secondary oxidation and hydrogen back-flow phenomena [45]. However, the deoxidation of the steel was not thoroughly investigated. Although controlling the oxygen content in the steel at an extremely low level was not achieved during the early development stage, the idea of con-

trolling steel deoxidation was proposed, and this laid the foundation for subsequent technological development.

2.1.3. Development and application stage of molten steel deoxidation technology

The period between 1950 and 1990 is considered the development and application stage of molten steel deoxidation technology within the steelmaking process. During this period, various new deoxidation equipment and processes emerged, leading to the formation of several of the deoxidation methods used in industrial production today and resulting in significant advancements in controlling the steel oxygen content. In 1955, Tix [46] proposed the vacuum pouring method, also known as the “tipping ladle” method, which involved pouring molten steel from one ladle to another in a vacuum environment (typically multiple times) to achieve the desired deoxidation effect. However, this method suffered from significant temperature loss during the vacuum treatment process, reaching 110°C [47]. Due to its inherent limitations, this method had a relatively short application period. In 1956, the Dortmund–Hörder Hüttenunion company in Germany developed a steel vacuum treatment method that was also known as the DH method [35]. This method involved inserting refractory material tubes into the molten steel, creating a vacuum, and allowing the steel in the ladle to enter the vacuum chamber under atmospheric pressure. After completing the vacuum treatment, the steel was returned to the ladle through the refractory material tubes [48]. This process was repeated multiple times to treat steel in batches within 5–15 min. The method demonstrated good degassing performance and a long refractory material lifespan, and it could also be used to make compositional adjustments in the vacuum chamber. Therefore, the DH method had been widely adopted globally. In 1959, the Ruhrstahl and Heraeus companies in Germany jointly developed the circulating vacuum treatment method for steel (also known as the RH method) [35]. This method involved inserting ascending and descending pipes into the molten steel and utilizing argon blowing through the ascending pipe to circulate the steel between the ladle and the vacuum chamber. The circulation time depended on the inner diameter of the ascending pipe and the argon blowing rate, with most treatments completed within 10–30 min [49]. In 1965, the Swedish company Svenska Kullager-Fabriken (SKF) developed the ASEA-SKF refining furnace in collaboration with Hellefors steelworks and Allmanna Svenska Elektriska Aktiebolaget (ASEA) [50]. This furnace comprised two domes, one for vacuum sealing to achieve the vacuum degassing of the steel and the other for electric arc heating to compensate for the heat loss caused by vacuum treatment. It also featured an electromagnetic stirring device to stir the steel during vacuum treatment. In 1969, the Thyssen-Niederrhein company in Germany successfully developed injection metallurgy technology (also known as the TN method) [51–52]. This method involved injecting powdered materials into the molten steel in the ladle using a carrier gas. It served various purposes, such as the adjustment of temperature and composi-

tion and the removal and modification of inclusions, and it significantly improved the thermodynamic and kinetic conditions of metallurgical reactions. In the 1970s, ladle feeding technology began to emerge, and slag deoxidation and modification gained attention in the 1980s [37,53]. By this point, the deoxidation materials and equipment currently used in modern steel production had been preliminarily applied.

2.1.4. Constant exploration stage of molten steel deoxidation technology

The constant exploration stage of deoxidation technology in the steel refining process spans from the 1990s to the present day. The molten steel deoxidation process has matured in this stage, but no revolutionary equipment or technological innovations have been proposed. Instead, the focus has been on combining and applying existing processes and ensuring fine control; however, this has only resulted in a small decrease in the total oxygen content of steel. Therefore, with the increasing demands on steel usage in the 21st century, higher requirements are being placed on the deoxidation process [54–56].

The development of metallurgical technology has diversified the functions of various reactors, enabling multi-stage operations for deoxidation in the refining process. Typically, predeoxidation is conducted during steel tapping, followed by further deoxidation in the argon station and ladle furnace (LF), and final deoxidation in the RH and VD [57]. Different steel plants have developed refined deoxidation control technologies based on their own equipment and process routes. Compared to the original single-element deoxidation, modern deoxidation processes not only allow flexible combinations of deoxidation methods, but they also involve different combinations of deoxidizers based on the steel grade. Common composite deoxidizers include Si–Al, Si–Mn, Si–Al–Ba, Si–Ca, and Si–Ba. The order of deoxidizer addition can be applied in different ways. For example, one can first apply weaker deoxidizers and then stronger ones. Another approach is applying these deoxidizers in the opposite order. The addition of deoxidizers in the sequence of weaker followed by stronger facilitates the thorough upward movement of inclusions while also ensuring a lower overall oxygen content in the molten steel. However, in certain situations, especially in low-carbon steel production, when the oxygen content at the endpoint of the converter process is excessively high, it is typically common to first introduce strong deoxidizers before adding weaker deoxidizers to reduce alloy wastage and lower the production costs. The aim of deoxidation is to reduce the oxygen content in the molten steel. Therefore, to prevent the molten steel from undergoing secondary oxidation, it is important that the process for oxygen source tracing and protective casting is complete [58].

When the total oxygen content in the steel is relatively high, the increase in the oxygen content caused by refractory erosion and local gas absorption is not significant. However, in clean steel production, it is necessary to strictly control the harmful elements, particularly the total oxygen content, and this has led to the development of technologies for improv-

ing the quality of metallurgical materials throughout the entire process and preventing the exposure of the molten steel surface. Furthermore, the advancement and popularization of sensing and detection technologies, along with the rapid development of computer, networking, and intelligent technologies, has provided greater vitality to deoxidation technology developments. By using oxygen sensors to measure the initial oxygen content in the molten steel and transmitting information such as temperature, composition, weight, and target steel grade to computers in real time, deoxidizer addition strategies and quantities can be automatically determined, effectively avoiding errors in manual judgment based on experience. The deoxidation of molten steel in local processes is currently mature, and the demand for overall oxygen control throughout the entire process is becoming increasingly apparent. However, depending on the equipment, production scale, and product level, further refinements in the application of deoxidation technology are needed.

2.2. Several main deoxidation methods

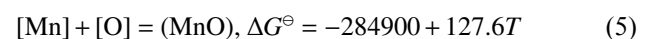
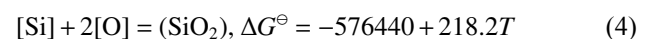
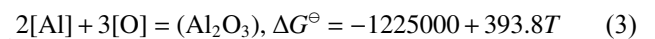
2.2.1. Precipitation deoxidation

Precipitation deoxidation is the process of adding a solid deoxidizer to the molten steel in the form of a block that contains an element with a greater affinity for oxygen than iron [59]. The deoxidizer then dissolves and reduces the dissolved oxygen within the steel. The deoxidation effectiveness of this method depends on the deoxidation capacity of the elements, the degree of oversaturation in the deoxidation reaction, the upward movement of inclusions within the steel (including the interfacial tension density difference, and particle size between the steel and inclusions) as well as the intensity of steel agitation, which can be represented by Eqs. (1) and (2):

$$m[M] + n[O] = (M_mO_n) \quad (1)$$

$$K^\ominus = \frac{a_{M_mO_n}}{a_{[O]}^n a_{[M]}^m} = \frac{a_{M_mO_n}}{f_O^n w_{[O]}^n f_M^m w_{[M]}^m} \quad (2)$$

where K^\ominus is the equilibrium constant, $a_{[O]}$ is the activity of [O], $a_{[M]}$ is the activity of [M], and $a_{M_mO_n}$ is the activity of M_mO_n , f_O is the activity coefficient of [O], f_M is the activity coefficient of [M], $w_{[O]}$ is the mass fraction of [O], and $w_{[M]}$ is the mass fraction of [M]. When pure oxides are formed, $a_{M_mO_n} = 1$, $K = 1/K^\ominus = f_O^n w_{[O]}^n f_M^m w_{[M]}^m$, where K represent the deoxidation constants. The smaller the value when reaching the reaction equilibrium, the stronger the deoxidation ability of the element. In addition, elements with stronger reducibility have a greater affinity for oxygen, allowing them to reduce the oxygen content to a lower level. At 1600°C, the reaction equations and the Gibbs free energy of commonly used deoxidizing elements with dissolved oxygen in the steel are shown in Eqs. (3)–(10) [60–63], and the calculated equilibrium relationships are shown in Fig. 2(a).



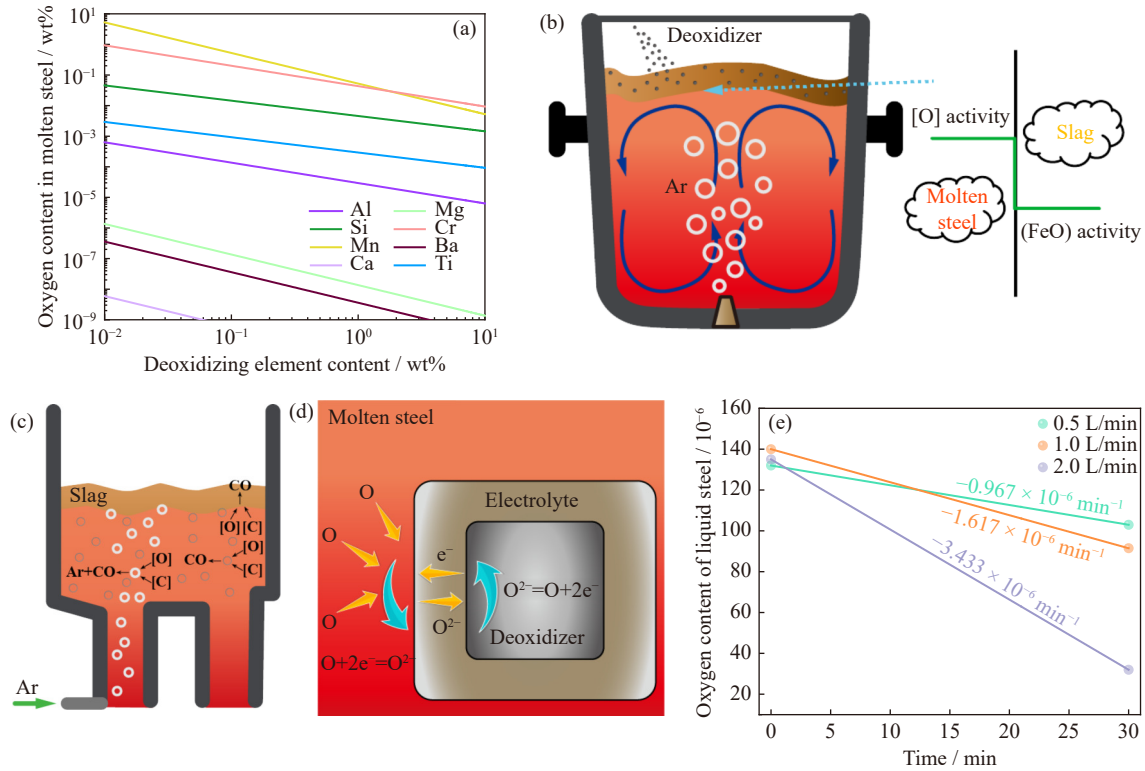
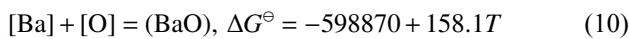
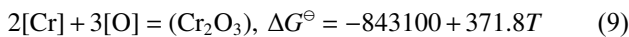
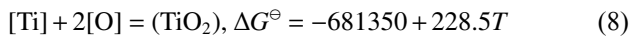
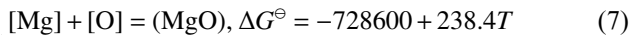
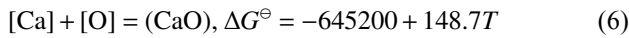


Fig. 2. Different deoxidation methods: (a) comparison of deoxidation abilities of different elements; (b) the diffusion deoxidation mechanism; (c) the vacuum deoxidation mechanism; (d) the electrochemical deoxidation mechanism; (e) hydrogen deoxidation abilities.



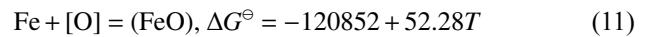
Under the same temperature and mass fraction, the deoxidation ability follows the order of $\text{Ca} > \text{Ba} > \text{Mg} > \text{Al} > \text{Ti} > \text{Si} > \text{Cr} > \text{Mn}$.

Precipitation deoxidation reactions occur rapidly and can quickly reduce the dissolved oxygen content of the molten steel to extremely low levels. However, this method has its own limitations. For example, the deoxidation product M_mO_n formed by a combination of the deoxidizer and the dissolved oxygen can seriously contaminate the steel if it is not promptly floated and removed. Therefore, when using this deoxidation method, it is necessary to consider the requirements of the steel grade and the type of inclusions and preferentially use deoxidizing elements containing deoxidation products that are easily removable. It is also important to create favorable conditions for the upward movement of inclusions.

2.2.2. Diffusion deoxidation

Diffusion deoxidation is a process that involves reducing FeO in the refining slag with a deoxidizer, thereby decreasing the FeO content in the slag. By utilizing the concentration difference between dissolved oxygen in the molten steel and FeO in the slag, oxygen in the steel is continuously diffused toward the slag, thus achieving a reduction in the dis-

solved oxygen content in the steel, as depicted in Fig. 2(b). The equilibrium relationship between oxygen in the refined slag and the steel can be expressed as Eq. (11) [64]:



After predeoxidation of the steel, it can be assumed that the reaction follows Henry's law, resulting in $f_{\text{O}} = 1$, and Eq. (12) can be transformed into Eq. (13):

$$\lg K^\ominus = \lg \frac{a_{(\text{FeO})}}{a_{[\text{O}]}} = \lg \frac{a_{(\text{FeO})}}{f_{\text{O}}w_{[\text{O}]}} \quad (12)$$

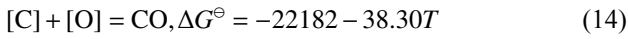
$$\lg K^\ominus = \lg \frac{a_{(\text{FeO})}}{w_{[\text{O}]}} = \frac{6320}{T} - 2.734 \quad (13)$$

When the temperature is 1873 K, the reaction at the interface between the slag and the steel reaches equilibrium, with $w_{[\text{O}]} = 0.229a_{(\text{FeO})}$ [65]. If the activity of FeO in the slag is reduced, it can disrupt this equilibrium and allow [O] to diffuse from the steel into the refining slag. The slag used for the deoxidation of molten steel must have a low mass fraction of FeO that is typically controlled to below 1.0wt%. To achieve this, an adequate amount of deoxidizer needs to be added to the slag. Deoxidizers that can be used for steel slag deoxidation mainly include ferrosilicon powder, carbon powder, calcium carbide powder (CaC_2), aluminum powder, and CaSi. To avoid the excessive loss of deoxidizers and a decrease in the steel temperature, diffusion deoxidation is usually performed in an LF, as this maintains a reducing atmosphere and provides heating. As the diffusion deoxidation reaction is slow, it is necessary for the refractory materials to be in contact with the molten steel for a considerable time, but this ac-

celerates erosion of the furnace lining. The eroded refractory materials then enter the steel and reduce its purity, and large-sized harmful inclusions are easily formed. Therefore, precipitation deoxidation and diffusion deoxidation are generally combined in practical production. In this respect, the precipitation deoxidation method is used first to quickly reduce the oxygen content in the steel to a lower level, and diffusion deoxidation is then employed as a supplementary deoxidation process to prevent the secondary oxidation of the steel.

2.2.3. Vacuum deoxidation

Vacuum degassing is a process in which molten steel is placed in a vacuum-sealed environment to reduce the partial pressure of CO, thereby allowing the carbon–oxygen reactions that have already reached equilibrium under atmospheric pressure to continue toward CO formation. The aim of this process is to decrease the oxygen content in the steel. Eq. (14) represents the thermodynamic equilibrium relationship of the carbon–oxygen reaction in the steel [66]:



Due to the low concentrations of carbon and oxygen in the steel, it can be assumed that the reaction follows Henry's law, and both activity coefficients are close to 1. Therefore, the expression for the equilibrium constant in Eq. (15) can be simplified to Eq. (16), where the variables represent factors influencing the reaction.

$$\lg K^\ominus = \lg \frac{P_{CO}}{a_{[C]}a_{[O]}} = \lg \frac{P_{CO}}{f_C w_{[C]} f_O w_{[O]}} \quad (15)$$

$$\lg K^\ominus = \lg \frac{P_{CO}}{w_{[C]}w_{[O]}} = \frac{1160}{T} + 2.003 \quad (16)$$

As the deoxidation product is a gaseous oxide, it does not remain in the steel and form inclusions. The conditions for the formation of CO bubbles in the molten steel are described by Eq. (17):

$$P_{CO} \geq P_A + \rho_{steel} g h_{steel} + \rho_{slag} g h_{slag} + \frac{2\sigma}{\gamma_{CO}} \quad (17)$$

in which P_{CO} represents the pressure inside the CO bubble, Pa; P_A represents the furnace gas pressure, Pa; ρ_{steel} and ρ_{slag} represent the densities of steel and slag, kg/m³; g represents the acceleration due to gravity, m/s²; h_{steel} and h_{slag} represent the heights of the steel and slag above the CO bubble, m; σ represents the surface tension of the steel liquid, N/m; γ_{CO} represents the radius of the CO bubble, m.

To nucleate and grow, the bubbles need to overcome environmental pressure, static pressure from the steel and slag, and surface tension. The process of bubbles rising and separating from the molten steel also provides a certain degree of stirring, which helps to optimize the kinetic conditions for chemical reactions in the steel. In addition, bubbles can adsorb solid inclusions, thereby facilitating the removal of oxide inclusions and other impurities from the molten steel. Due to the limitations imposed by the buoyancy of the bubble, the vacuum effect is more pronounced on the upper part of the steel melt pool, as shown in Fig. 2(c). Therefore, high equipment requirements are necessary to accurately control the process parameters of each deoxidation stage; if these are not

applied, issues such as severe splashing caused by intense carbon–oxygen reactions, incomplete deoxidation due to insufficient reaction time, and secondary oxidation caused by the exposed molten steel surface after breaking through the bubble can easily occur. Various studies have investigated the influence that different elements in molten steel and the crucibles used in vacuum refining have on the vacuum deoxidation process [67–68], and the reaction mechanisms underlying vacuum deoxidation have been explored.

2.2.4. Electrochemical deoxidation

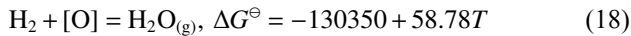
Electrochemical deoxidation is a process that utilizes oxygen ion conductors to selectively guide the oxygen in molten steel away from the metal melt, thereby achieving deoxidation [69]. The oxygen ion conductor used at steelmaking temperatures needs to possess characteristics of non-volatility, non-combustibility, and high-temperature resistance, and solid electrolyte materials meet these requirements. Oxygen probes made from such materials have been widely used in steel production. The principle behind these probes involves utilizing a zirconia-based solid electrolyte with oxygen ion conduction properties to create a concentration cell for measuring oxygen activity in the molten steel. Since the 1970s, researchers have been studying unpolluted deoxidation in copper and steel melts using zirconia-based solid electrolytes [70–72]. Depending on the driving mechanism of oxygen migration across the solid electrolyte, two methods are employed: the external potential method and the galvanic cell method. However, their basic principles remain the same, as shown in Fig. 2(d). First, oxygen in the molten steel reacts with the negatively charged surface of the solid electrolyte, generating oxygen ions. These oxygen ions then migrate through the electrolyte toward its inner surface, where they react with the deoxidizing agent to produce negative charges and oxides. However, the primary challenge linked to this deoxidation approach is the inadequately rapid deoxidation rate observed under both high and low oxygen conditions. Furthermore, the use of zirconia-based solid electrolytes comes with a high cost, leading to elevated deoxidation expenses in similar scenarios [73–74].

Researchers have proposed using slag as a replacement for solid electrolytes, where an electric field is applied between the slag and the metal to enhance deoxidation. Slag is an electrolyte with ion conductivity that contains oxygen ions, various metal cations, and different complex ion groups. Based on the principle of applying an external electric field to the solid electrolyte, the application of a direct current electric field between the metal melt and the covering slag can be used to control the direction and velocity of oxygen ion conduction in the slag system. However, extensive work is still required to apply electrochemical deoxidation technology to practical metallurgical production.

2.2.5. Reducing gas deoxidation

Hydrogen gas can reduce unstable oxides. As the main component of natural gas is CH₄, which completely decomposes into carbon and hydrogen gas at 900°C [75], hydrogen gas and natural gas can both be used as deoxidizers in steel-

making deoxidation. As early as the 1960s, researchers used natural gas for deoxidation in vacuum induction furnaces and utilized the reaction of natural gas decomposing at high temperatures to generate hydrogen [76]. The chemical reaction of hydrogen gas deoxidation can be represented by Eq. (18), and both the lower partial pressure of H_2O and the higher partial pressure of H_2 in the furnace gas can achieve ideal deoxidation effects.



Thermodynamic calculations have shown that hydrogen gas can be used as a novel deoxidizer in steelmaking, and its deoxidation effect has been verified by experiments, as shown in Fig. 2(e). Reducing gases have strong deoxidizing capabilities, and as the gas injection time increases, the oxygen content and the rate of gas deoxidation in the molten steel gradually decrease [77]. The deoxidation products of reducing gases are H_2O and CO , which do not remain as inclusions in the steel. Therefore, it is not necessary to modify the deoxidation products or remove inclusions, and this results in a notable enhancement of the cleanliness of the molten steel [29]. However, existing research results show that the deoxidation rate of hydrogen gas is slower compared to carbon deoxidation: under the same vacuum conditions, it only takes 30 min to reduce the oxygen content of steel with a carbon content of 0.1wt% to 10×10^{-6} , whereas it takes 4 h to reduce the oxygen content to 15×10^{-6} with hydrogen. Deoxidation with reducing gases tends to increase the hydrogen content of the molten steel, which requires the use of an additional vacuum treatment for dehydrogenation after deoxidation. In addition, carbon-containing reducing gases (such as methane) produce carbon through high-temperature cracking, which leads to carbon enrichment in the molten steel, making them more suitable for use in medium or high-carbon steels.

3. Typical steel grade deoxidation process

3.1. Controlling oxygen content of bearing steel

3.1.1. Oxygen content requirements in bearing steel

Bearings are essential key components in modern mechanical equipment, primarily used in supporting rotating parts, reducing friction, and sealing [78]. They are commonly used in industries such as aerospace, wind power, high-speed railways, and automobiles. In the early development of bearing steel smelting, the oxygen content often reached approximately 30×10^{-6} , and oxide inclusions were the nonmetallic steel inclusions. As such, the total oxygen content in the steel was often used as an important indicator to measure steel quality. From Fig. 3, it is evident that when the total oxygen content of the steel decreases, its relative fatigue life rapidly increases [79], and when the total oxygen content decreases from 30×10^{-6} to 5×10^{-6} , the fatigue life of bearing steel can be improved 100 times. The figure also shows that the ESR material has an oxygen content of approximately 14×10^{-6} , indicating that its fatigue life is excellent. Compared with other materials, there are fewer types of inclusions in ESR materials, and their sizes are smaller. This in-

dicates that the fatigue life depends on the oxygen content and the type, content, size, and distribution of the inclusions [80]. Notably, the relationship between the oxygen content of the steel and its fatigue life depends on the smelting method used. For example, steel with an oxygen content of 20×10^{-6} produced by a converter and RH refining has a much longer fatigue life than steel with an oxygen content lower than 10×10^{-6} produced in an electric furnace and RH via refining with calcium silicon wire addition. Therefore, the relationship between the total oxygen content in the steel and its fatigue life is not absolute. Nevertheless, the total oxygen content is used to determine fatigue life under the same smelting method, and it is closely related to the morphology, distribution, hardness, and other properties of the steel inclusions. However, it is still necessary to control the total oxygen content within a certain low range [81–83].

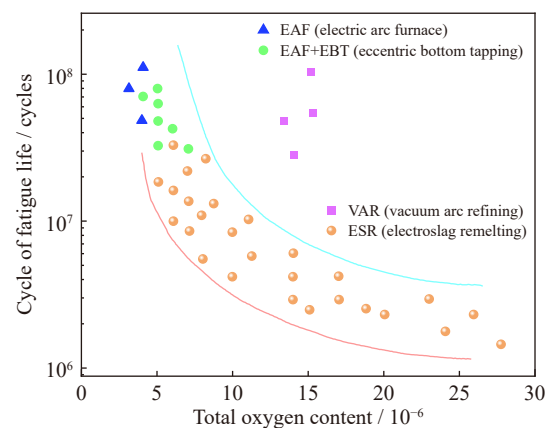


Fig. 3. Relationship between the total oxygen content in steel and fatigue life [79]. Copyright 2001 from Impact of steelmaking and casting technologies on processing and properties of steel by J.P. Birat, reprinted by permission of Taylor & Francis Ltd.

3.1.2. Controlling method for oxygen content of bearing steel

Controlling the total oxygen content in bearing steel is a coordinated process that occurs throughout the production. The production process at present primarily used aluminum deoxidation, and the final carbon and dissolved oxygen content in the converter steel were typically controlled. According to theoretical calculations, when the carbon content in the steel is controlled above 0.2wt% at 1600°C, the dissolved oxygen content in the steel is below 0.02wt%. Industrial production data statistics show that during the converter smelting process, the dissolved oxygen content in the steel increases by 135×10^{-6} for every 0.01wt% decrease in the final carbon content. Therefore, for the converter, the lower the final carbon content, the higher the dissolved oxygen content in the steel, necessitating the use of more deoxidizers; this results in increased deoxidation products within the steel, which is unfavorable for reducing the total oxygen content. Therefore, a high-carbon content level in the converter smelting process of bearing steel is recommended, with carbon content controlled within the range of 0.1wt%–0.4wt%.

The deoxidizer alloy content of the steel is controlled.

Bearing steel mostly uses aluminum deoxidation for smelting, and the oxygen activity in the molten steel decreases as the aluminum content in the steel liquid increases. When the aluminum content in the steel is 0.01wt%, the oxygen activity is approximately 2.43×10^{-4} . As the aluminum content in the steel increases, the total oxygen content in the steel first decreases and then increases. Specifically, when the aluminum content is in the range of 0.2wt%–0.4wt%, the total oxygen content of the steel is at its minimum. Therefore, an appropriate aluminum content is crucial to control the total oxygen content in steel bearing.

The composition of the appropriate refining slag is controlled. The experimental research of Kato *et al.* showed that the total oxygen content in the steel liquid decreased as the binary basicity of the slag increased [84]. In Japanese bearing steel production, high-basicity slag with a basicity greater than 3 is commonly used, which is beneficial for deoxidation and desulfurization effects during the refining process. It also ensures that the slag has good fluidity and a strong inclusion adsorption capacity, enabling the slag-steel reaction to proceed fully.

In addition, the oxidizing property of the slag is an important factor affecting the final total oxygen content in the molten steel. The oxidizing property of the slag is generally represented by (T.Fe + MnO) content, and the variation trend in the total oxygen and (T.Fe + MnO) content is consistent. Research by Matsuoka indicated that with a (T.Fe + MnO) content of the slag lower than 0.5wt%, the total oxygen content in the steel liquid can be controlled at $<10 \times 10^{-6}$ [85].

3.2. Oxygen content control in IF steel

3.2.1. Oxygen content requirements of IF steel

The key technology used to produce high-purity interstitial-free (IF) steel involves the stable control of total oxygen and inclusion contents of the steel, a significant correlation existing between total oxygen content and quality of the slab. The total oxygen content of the steel has been used as an evaluation criterion for low-carbon aluminum-killed steel cleanliness [86]. In addition, the Kawasaki Steel Corporation in Japan conducted experiments to identify the relationship between defects in cold-rolled thin sheets and the total oxygen content of molten steel in tundish [87]; the following conclusions were drawn based on sampling observations at Mizushima works: when T[O] (total oxygen content of molten steel) was below 30×10^{-6} , defects in cold-rolled thin sheets were extremely rare, and the products did not require any inspection; when T[O] ranged from 30×10^{-6} to $50 \times$

10^{-6} , defects could occur in cold-rolled thin sheets, so they underwent inspection; when T[O] in ladle steel exceeded 55×10^{-6} , cold-rolled thin sheets were automatically downgraded for use. Similarly, during the production of 0.15 mm thin sheets at the Weirton Steel Corporation in the United States, an inspection of 120 coil sheets revealed the relationship between the total oxygen content in the billets and the quality index [88]. Evidently, the lower the T[O] in the billets, the higher the quality index of the cold-rolled sheets. When the total oxygen content of molten steel was in the range of 15×10^{-6} to 20×10^{-6} , the quality index was 81, but when the total oxygen content exceeded 30×10^{-6} , the quality index dropped to only 35. Currently, high-quality IF steel requires the total oxygen content in the steel to be below 20×10^{-6} , and some companies even demand that it is below 15×10^{-6} .

3.2.2. Method for oxygen content control of IF steel

It is necessary to control the oxygen content of IF steel throughout the entire smelting process. Fig. 4 illustrates the typical process used to produce IF steel and the measures used to control the oxygen content of the molten steel. Reducing the final oxygen content during converter smelting, improving the dual hitting rate of carbon and temperature at the converter endpoint, and strictly controlling slag tapping employed during the steelmaking process are important. Converter slag has strong oxidizing properties, and when the oxygen content in the molten steel is reduced to a certain level, oxygen is transferred from the slag to the molten steel. Therefore, it is necessary to modify the top slag of the ladle, which ensures that the molten steel has an appropriate oxygen content upon arrival at the RH refining station, and this is generally controlled between 500×10^{-6} and 600×10^{-6} . An excessive oxygen content can cause boiling and splashing during the initial stage of RH treatment and make deoxidation difficult in the subsequent processes, affecting the molten steel cleanliness. However, a very low oxygen content can increase the decarburization load during RH refining [89–90]. After decarburization in the RH process, the dissolved oxygen in the steel is typically between 250×10^{-6} and 300×10^{-6} . After aluminum deoxidation, the key factors involved in controlling the total oxygen content allowed Al_2O_3 to fully float and be removed, reducing the secondary oxidation of the steel melt, and effectively utilizing the metallurgical effects of the tundish.

Takeshi reported in 1994 that the total iron mass fraction of slag at the endpoint of converter smelting of IF steel was generally 15wt%–25wt% at the Kawasaki Steel Company in

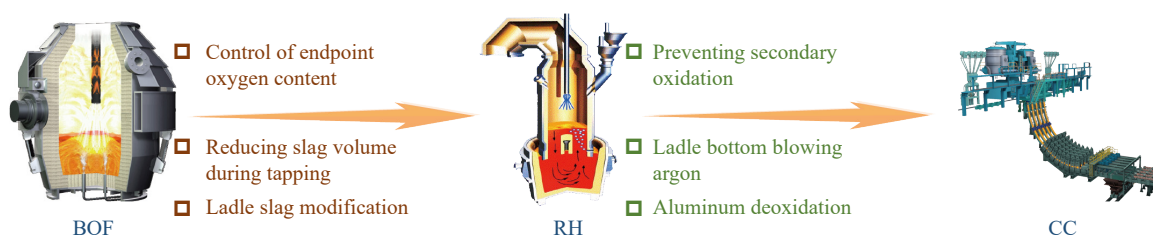


Fig. 4. IF steel production process and measures used to control oxygen content of molten steel.

Japan [91]. A slag-blocking technique was employed, and the thickness of the slag in the ladle was controlled below 50 mm to prevent the secondary oxidation of molten steel caused by excessive slag in the tapping process. Immediately after steel tapping, a slag modifier composed of CaCO_3 and aluminum was employed, and this reduced the total iron content in the slag to approximately 4wt%, or even below 2wt%. In 2000, Hoile reported that the oxygen and Al_2O_3 inclusion contents of steel were reduced during the converter process at Inland Steel in the United States by controlling the slag tapping and top slag treatment in the ladle [92]. During steel tapping, small-particle lime (0.468 kg/t) and aluminum and limestone (2.335 kg/t) were added, and after steel tapping, a slag modifier containing 25wt% aluminum and 65wt% limestone was added to the slag surface. The $\text{CaO}/\text{Al}_2\text{O}_3$ and FeO content of the slag were approximately 1.0wt% and 6wt%. In the RH process, temperature control was achieved with an accuracy of $\pm 5^\circ\text{C}$ by establishing a temperature model for the end-point temperature. Al was used to raise the temperature of molten steel as early as possible, and at least 6 min of stirring time was ensured after the deoxidation completion. Additionally, $[\text{T}][\text{O}]$ in the steel before deoxidation was kept below 250×10^{-6} .

4. Research on clean purification deoxidation processes

4.1. Bearing steel deoxidation technology involving whole process optimization

4.1.1. Silicon–manganese predeoxidation

Domestic and international production of bearing steel primarily adopts an aluminum deoxidation process to control the total oxygen content in steel and create high-basicity slag for adsorbing and removing inclusions. However, inevitable inclusions (such as spinel, calcium aluminate, and titanium nitride) exist in aluminum-deoxidized bearing steel. Among these, spinel and calcium aluminate have the greatest influence on the fatigue life of bearing steel and are the main causes of fatigue failure [93]. In practical production, further reduction of the total oxygen content of ultra-high-purity

bearing steel does not significantly improve its fatigue life. Even with an extremely low total oxygen content, occasional large particle inclusions exist, leading to fatigue failure in bearings. In addition, the use of the aluminum deoxidation process deteriorates the flowability of the molten steel due to the residual aluminum oxide, significantly reducing the number of continuous casting heats and increasing production costs. The high aluminum content in the molten steel promotes TiO_2 reduction in the slag, resulting in fluctuations in $\text{Ti}(\text{C},\text{N})$ inclusions quantity, which further affects the fatigue life of bearing steel.

To address these issues, our research team proposed a combination deoxidation process for smelting bearing steel, which involved predeoxidation with silicon manganese and LF diffusion and vacuum final deoxidations. The influence of different manganese–silicon ratios on the proportions and activities of various deoxidation products was calculated using the Equilib module in FactSage 7.2 (Fig. 5(a)) [94]. In GCr15 bearing steel, the mass fraction ranges of $[\text{Si}]$ and $[\text{Mn}]$ were found to be 0.15wt%–0.35wt% and 0.25wt%–0.45wt%, respectively, and the manganese–silicon ratio ranged from 0.71 to 3.0. The calculation results represent variations in the oxygen content in molten steel concerning the $[\text{Si}]$ mass fraction (Fig. 5(b)) [94]. With increasing manganese–silicon ratio, activities of SiO_2 and the equilibrium $[\text{O}]$ content decrease. However, at a manganese–silicon ratio of 4.6, SiO_2 activity reached 0.022 and did not decrease further. With a $[\text{Si}]$ mass fraction of 0.15wt%, the mass fraction of $[\text{O}]$ was 120×10^{-6} if silicon was used for deoxidation alone. However, if silicon–manganese composite deoxidation with a mass fraction of $[\text{Mn}]$ at 0.45wt% was used, the maximum manganese–silicon ratio in bearing steel was 3, which corresponded to a mass fraction of $[\text{O}]$ of only 30×10^{-6} . However, increasing $[\text{Si}]$ content further did not reduce the $[\text{O}]$ content in composite deoxidized bearing steel. When the mass fraction of $[\text{Si}]$ was 0.35wt%, the maximum manganese–silicon ratio was 1.3, and the mass fraction of $[\text{O}]$ was 62×10^{-6} .

4.1.2. Diffusion deoxidation on slag surface

Through predeoxidation with silicon manganese, the mass

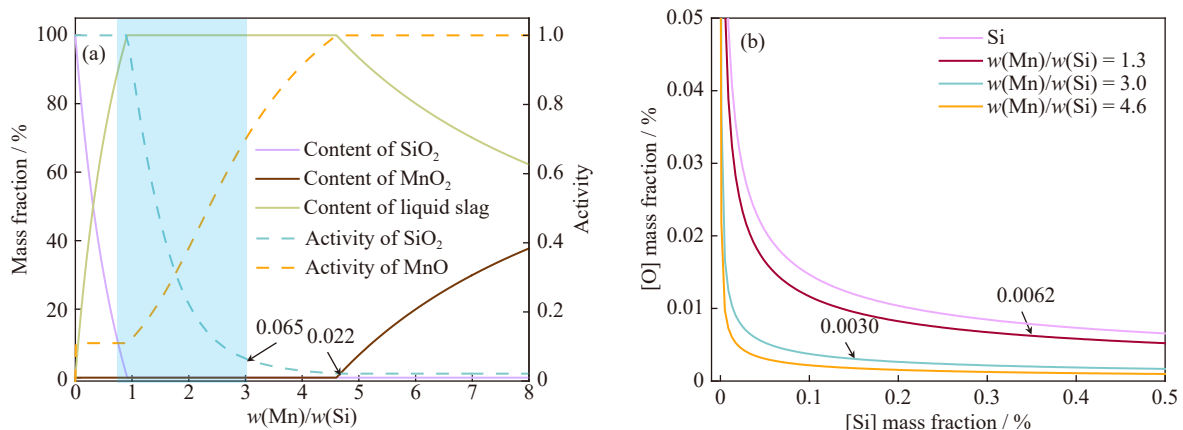


Fig. 5. Relationship between alloying elements and deoxidation effect: (a) effect of different manganese–silicon ratios on proportion and activity of deoxidation products; (b) change of mass fraction of $[\text{O}]$ in $[\text{Si}]$ equilibrium molten steel [94].

fraction of [O] in the molten steel was reduced to 30×10^{-6} . To further decrease [O] content, an adequate amount of silicon carbide was added to the slag surface during the refining process to maintain a reducing slag, promoting continuous diffusion deoxidation and achieving low oxygen control. Diffusion deoxidation occurred at the slag–metal interface; when the reduction reaction reduced the (FeO) content of the slag, [O] in the steel began to diffuse into the slag and a new equilibrium was reached [95].

Some studies have used the Phase Diagram module in FactSage 7.2 to calculate the isothermal activity lines of CaO–SiO₂–Al₂O₃–12wt%MgO quaternary system (Fig. 6 [94]) and investigate the effect of different basicity levels on the dissolved oxygen content in the steel. In the phase diagram, *R* represents the binary basicity, specifically the ratio of *w*(CaO) to *w*(SiO₂). For non-aluminum-deoxidized bearing steel, when an equilibrium between [Si], [Mn], and [O] in the molten steel is reached, the dissolved oxygen content decreases as the basicity of the refining slag increases. When the basicity of LF refining final slag is 0.8–1.0, with Al₂O₃ mass fraction below 10%, the mass fraction of the dissolved oxygen in the steel is approximately 20×10^{-6} to 30×10^{-6} . Therefore, when smelting bearing steel using the non-aluminum deoxidation process, the combination of predeoxidation with silicon manganese during LF refining and diffusion deoxidation with the refining slag effectively controls the total oxygen mass fraction in the molten steel below 30×10^{-6} .

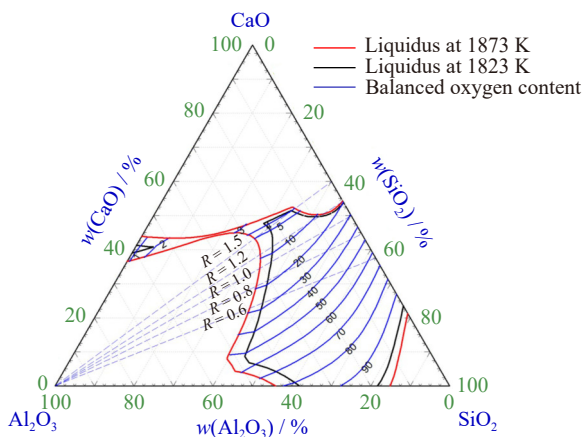


Fig. 6. Isothermal activity lines of CaO–SiO₂–Al₂O₃–12wt%MgO quaternary system [94].

4.1.3. Vacuum final deoxidation

RH refining deoxidation primarily involves the dissolved free and combined oxygen removal within inclusions in the molten steel. The kinetic conditions of this process are favorable, and the rate of carbon–oxygen reaction depends mainly on the mass transfer of carbon and oxygen in the steel. Ling and Zhang [96] showed that [C]/[O] was a determining factor affecting the mass transfer rate. After LF refining, [C] mass fraction in the steel was approximately 1wt%, while [O] content was approximately 20×10^{-6} to 30×10^{-6} . At this time, [C]/[O] was much larger than 0.52, and [O] mass transfer rate in the steel became the limiting factor of carbon–oxygen re-

action. In the initial stage of the reaction, dissolved oxygen was the main source of oxygen in the reaction, and vigorous stirring greatly accelerated the mass transfer rate of oxygen. Therefore, carbon–oxygen reaction rate was fast in the early stage of RH refining, and CO content in the off-gas rapidly increased. It was found that if the vacuum extraction rate was too fast, it could lead to severe splashing. As carbon–oxygen reaction progressed, the oxygen content in the mixing zone and the reaction rate significantly decreased. In actual production, the use of prevacuuming and staged pressure drop modes shortened the overall vacuum extraction time and prevented severe splashing in the early treatment stage, improving refining efficiency.

Guo *et al.* conducted a composition analysis of the top slag in the ladle, showing that the slag basicity remained essentially unchanged before and after RH refining, while the mass fractions of FeO and MnO changed. The mass fraction of FeO decreased by 0.441wt% while MnO increased by 0.023wt% [97]. After RH refining, the total oxygen content in the molten steel significantly decreased from approximately 20×10^{-6} to approximately 8×10^{-6} . During continuous casting production, slight oxidation of the molten steel occurred in the ladle and tundish during casting, resulting in total oxygen content being higher in the cast billet than during the RH refining stage. In addition, the favorable thermodynamic and kinetic conditions of the RH process had a certain effect on the removal of nitrogen from the molten steel. However, the increased nitrogen content during continuous casting indicated the occurrence of gas absorption in the molten steel, highlighting the need for further optimization of the entire process to protect casting, improve the sealing performance of the casting vessel, and reduce the exposed molten steel surface.

4.1.4. Application effect

The process flow shown in Fig. 7 can produce non-aluminum-deoxidized bearing steel. Controlling the oxygen content throughout the entire process primarily included three stages: predeoxidation with silicon manganese during converter steelmaking, diffusion deoxidation with silicon-based deoxidizers added to the slag during LF refining (where the oxygen content is controlled below 35×10^{-6}), and deep deoxidation through the vacuum carbon–oxygen reaction during RH vacuum refining. Ultimately, the total oxygen mass fraction in the steel is controlled between 4×10^{-6} and 8×10^{-6} , and [Al]_s mass fraction in non-aluminum-deoxidized bearing steel is below 0.008wt%. Under conditions where the mass fractions of Al₂O₃ and TiO₂ are 4wt% and 0.40wt%, respectively, the equilibrium mass fraction of [Ti] is only 6×10^{-6} , allowing for stable low-titanium control and a significant reduction in the titanium nitride content. The oxide density of aluminum-deoxidized bearing steel is higher than non-aluminum-deoxidized bearing steel; calcium aluminate and TiN-type inclusions are higher in the latter, but the sulfide content is higher in the former. Compared to aluminum deoxidation processes, non-aluminum-deoxidized bearing steel primarily contains ductile inclusions. Silicates are the most common oxide inclusions, followed by spinel,

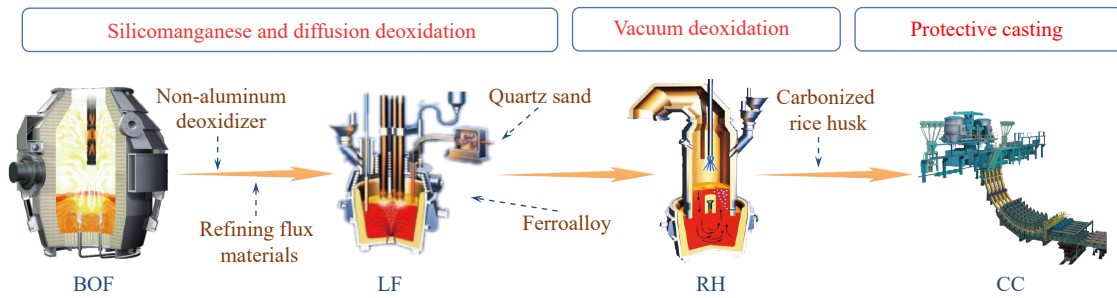


Fig. 7. Flow chart of bearing steel deoxidation technology optimized throughout the whole process.

and only a small amount of calcium aluminates exist, which significantly reduces Ds-type inclusion content. These inclusions are mostly low-melting-point inclusions, which improve the fluidity of the molten steel and address issues relating to the continuous casting of small square billets. The fatigue life of two deoxidation methods for bearing steel was determined using an ultra-high-cycle fatigue testing machine, and results revealed that non-aluminum-deoxidized bearing steel, even with a high oxygen content, exhibited a fatigue life similar to (or slightly better than) aluminum-deoxidized bearing steel with extremely low oxygen content.

4.2. IF steel predeoxidation production technology with natural decarburization

4.2.1. Process of adding carbon powder with predeoxidation technology

During the ultra-low-carbon steel production process, steel enterprises aim to control the decarburization endpoint oxygen content within a reasonable range while ensuring rapid decarburization. However, some steel plants discovered that the carbon content was low, but the oxygen content was high at the converter endpoint and RH station, and over-oxidation was often accompanied by high converter endpoint temperatures. Although it was found that a higher dissolved oxygen content shortened the decarburization reaction time to a certain extent, it resulted in an excessively high oxygen content at the decarburization endpoint and an increase in the aluminum consumption and the quantity of Al_2O_3 inclusions, which ultimately affected the surface quality of cold-rolled sheets, and caused a degradation in steel performance [88]. Therefore, enterprises face the major problem of determining how to reasonably control the decarburization endpoint oxygen content under high oxygen and low-carbon conditions.

The most commonly used predeoxidation methods include the addition of medium or high-carbon ferromanganese during the RH process or a small amount of aluminum in the early stage of the decarburization reaction. However, the first method is problematic due to the unstable control of the manganese content in the decarburization endpoint steel and the high production costs, while the main problem with the second method is the increase in Al_2O_3 inclusions and unstable temperature control.

In this context, our research team proposes a process for reducing the oxygen content in the decarburization endpoint during RH vacuum treatment by introducing carbon powder into the vacuum chamber (as shown in Fig. 8 compared to the traditional process). Carbon powder is added to the steel in batches in 4–8 min, and the main products of this predeoxidation process are CO and CO_2 . Under vacuum conditions, the generated gases are discharged in the vacuum chamber, which reduces the oxygen content in the steel and achieves pollution-free deoxidation. Moreover, compared to the energy-intensive production of aluminum grains, carbon powder is a more environmentally friendly deoxidizer. Therefore, carbon powder predeoxidation not only improves the quality of the steel but also reduces carbon emissions.

4.2.2. Study of the oxygen reaction behavior during the predeoxidation process

Fig. 9 presents variations in the steel oxygen content during the RH decarburization process with different process flows. Under experimental conditions, the difference in the oxygen content between the two processes reached 72×10^{-6} when 50 kg of carbon powder was added. The oxygen content in the steel decreased by 120×10^{-6} in a 0–3 min period, but the oxygen content variation patterns were essentially the same for both processes. From 3–8 min, the oxygen content

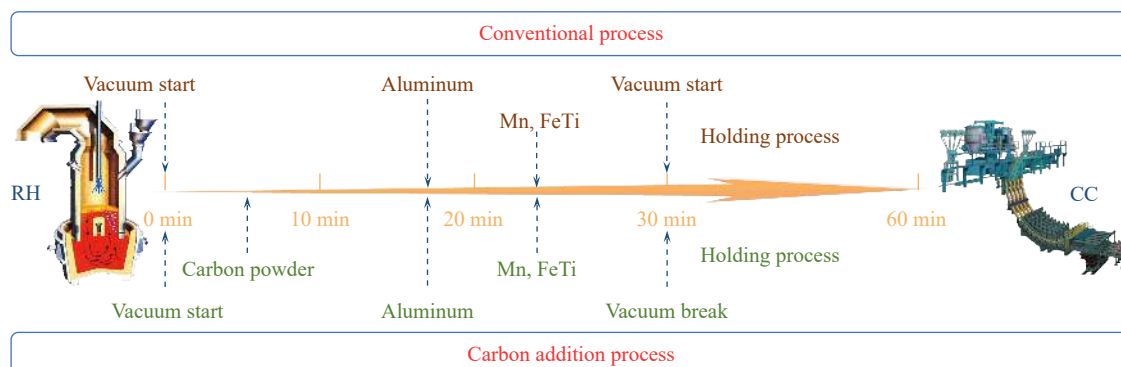


Fig. 8. Different processes used to produce IF steel.

of the carbon powder deoxidation process was significantly lower than that of the conventional process, with a maximum difference in the oxygen content of 69×10^{-6} . From 8 min until the end of decarburization, the oxygen content in the steel continued to decrease, but the reduction rate was no longer significant. This was mainly because after 8 min of the decarburization reaction, the carbon content in the steel had already decreased to a low value, and the rate of the carbon–oxygen reaction was very low at this point. The impact of the carbon powder predeoxidation process on the oxygen content in the molten steel primarily occurred between 3–8 min after the addition of carbon powder, where it rapidly reacted with dissolved oxygen in the steel, achieving the purpose of predeoxidation.

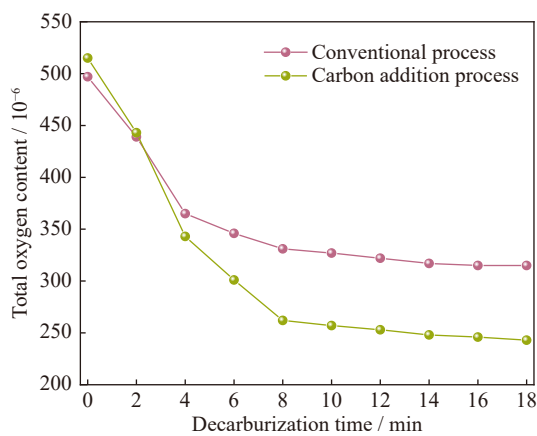


Fig. 9. Changes in the total oxygen content during the RH decarburization process using the conventional process and the predeoxidation process [97]. Reprinted by permission from Springer Nature: *Int. J. Miner. Metall. Mater.*, Carbon and oxygen behavior in the RH degasser with carbon powder addition, J.L. Guo, L.H. Zhao, Y.P. Bao, et al., Copyright 2019.

A comparative analysis of the total iron and MnO con-

tents in the starting and ending slags was conducted under two different process conditions. In the conventional process, the total iron and MnO contents decreased from 10.98wt% to 9.71wt%, with a reduction of 1.27wt%, whereas in the carbon powder deoxidation process, the total iron and MnO contents decreased from 11.32wt% to 8.44wt%, with a reduction of 2.88wt%. This indicates that the oxidative nature of the top slag differed significantly between the two processes, with a greater reduction in the total iron and MnO contents in the latter. Therefore, carbon powder deoxidation had a positive effect on reducing the oxygen content in the steel at the end of decarburization and improving the oxidative nature of the top slag.

4.2.3. Industrial experimentation

The decarburization endpoint oxygen content of the carbon powder predeoxidation process is significantly lower than in the conventional process. To further clarify the impact of the predeoxidation process on the cleanliness of the steel, a continuous industrial production verification was conducted for 100 heats. A comparison of the decarburization endpoint oxygen content, RH process aluminum consumption, and total oxygen content in the cast billet was conducted, and the results are shown in Fig. 10. Compared to the conventional process, the predeoxidation process achieved an average reduction of 89×10^{-6} in the decarburization endpoint oxygen content, reaching 239×10^{-6} . The aluminum consumption for deoxidation was reduced by 54 kg per heat, resulting in an average savings of 15.70wt%, and the total oxygen content in the cast billet was reduced by an average of 3×10^{-6} , leading to a further reduction in oxide inclusions in the steel. Therefore, adopting the predeoxidation process not only reduced aluminum consumption and carbon emissions during production but also significantly improved the quality of the cast billet.

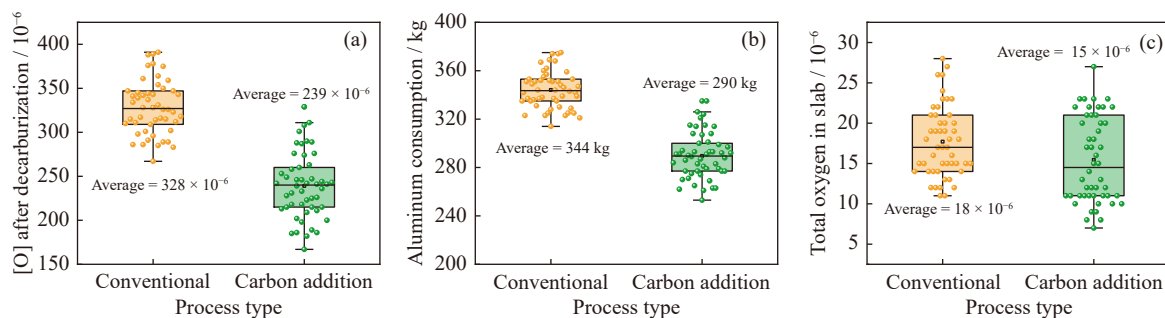


Fig. 10. Comparison between conventional and predeoxidation processes: (a) oxygen content at the end point of decarburization, (b) Al consumption, and (c) total oxygen content of the slab.

5. Conclusions and prospects

Oxygen is obtained from two main sources during the steel production process: direct entry into the steel melt as primary oxygen and secondary oxygen derived from the decomposition of materials in contact with the molten steel. Excessive oxygen content in the steel has a severe impact on the final product quality, necessitating deoxidation during the

smelting process. With the development of deoxidizers and advancements in metallurgical reactors, the total oxygen content in steel has been reduced from approximately 100×10^{-6} to approximately 10×10^{-6} , and some steel grades can stably maintain levels below 5×10^{-6} . Several deoxidation methods have been established, including precipitation, diffusion, vacuum, electrochemical, and reducing gas deoxidations. Among these methods, vacuum deoxidation relies on car-

bon–oxygen reaction to rapidly reduce the oxygen content of the molten steel, and there are no remaining resulting deoxidation products in the steel melt to form inclusions. However, due to a limited understanding of vacuum equipment and high costs, the potential of vacuum deoxidation has not been fully realized.

Our research team developed a bearing steel deoxidation technology based on comprehensive process optimization that combines silicon–manganese predeoxidation and LF diffusion, and final vacuum deoxidations. Industrial experiments were successfully conducted on IF steel using the natural decarburization predeoxidation technique. The bearing steel deoxidation technology controls the oxygen content of the bearing steel within a range of 4×10^{-6} to 8×10^{-6} while altering the type of inclusions, eliminating large-sized Ds-type inclusions, improving molten steel fluidity, and achieving higher fatigue life. The natural decarburization predeoxidation technique not only reduces aluminum consumption and production costs but also significantly improves the quality of the cast billet.

With continuous increases in the performance requirements of steel materials, the limitations of traditional deoxidation processes have become increasingly apparent. However, metallurgists have made valuable explorations, but greater technological advancements in the following areas are required: first, the large-scale promotion and application of new deoxidation technologies required, particularly technologies relating to pollution-free deoxidation methods, such as vacuum carbon deoxidation and methods used to reduce gas deoxidation. These methods enhance the cleanliness of steel, reduce the quantity of oxide inclusions, and fundamentally eliminate the contamination of the molten steel by deoxidation products. Second, it is necessary to conduct process optimization by developing personalized deoxidation processes based on the specific requirements of different steel grades regarding inclusions. Efforts should be made to minimize the generation of inclusions that significantly affect the performance of a particular steel grade or reduce the quantity and size of such inclusions. Finally, it is necessary to control the size, dispersion, and composition of oxide inclusions and to make them act as nucleation sites for precipitates, such as sulfides and nitrides. This would alter the steel's microstructure and grain size, rendering the remaining oxide inclusions harmless.

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Conflict of Interest

Yanping Bao is an editorial board member for this journal and was not involved in the editorial review or the decision to

publish this article. The authors have no competing interests to declare that are relevant to the content of this article.

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