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The-state-Art of steelmaking technology based on hydrogen metallurgy

**Сучасний стан технології виробництва сталі
на основі водневої металургії**

Abstract. This paper puts forward the viewpoint that "hydrogen steelmaking" replaces "oxygen steelmaking", and summarizes and evaluates the research status of "hydrogen steelmaking". Hydrogen metallurgy steelmaking has unique advantages in energy saving, consumption reduction and product quality improvement. On the one hand, hydrogen has a highly efficient melting effect, which can effectively reduce the energy consumption of steelmaking. "Hydrogen" in plasma state has the characteristics of high temperature and high thermal conductivity, which can be used as a highly efficient heat source to realize the melting of charge and heating of steel, and has been applied in steelmaking processes such as EAF, converter and tundish. Blowing gaseous "Hydrogen" can accelerate the homogenization in the composition and temperature, and the movement of hydrogen bubbles can be adhered to the non-metallic inclusions which can be accelerated to float out. At the same time, hydrogen reacts with oxygen in the liquid steel to release a large amount of heat, which improves the thermodynamic and kinetic conditions of the melt pool reaction. In addition, "Hydrogen" can inhibit oxidation and reduce the loss of Cr, Mn and other alloying elements by creating a reducing atmosphere. On the other hand, "Hydrogen" has a non-polluting refining effect that significantly improves the cleanliness of the steel. Based on the high activity and high reducibility of "Hydrogen", "Hydrogen" can effectively remove impurity elements such as O, C, N, S and P in steel, especially "Hydrogen" in plasma state, which can directly react with the impurity elements to generate H_2O , CH_4 , NH_3 , H_2S and PH_3 and other gaseous products that are easy to be volatilized and removed, so as to avoid the formation of non-metallic inclusions, and to realize the highly efficient and high-cleanliness steelmaking with "zero inclusions". Therefore, the development of a new generation of green, near-zero carbon, "zero inclusion" and pollution-free steelmaking process using "hydrogen" instead of "carbon" will accelerate the green, high-quality, and sustainable development of the steel industry.

Key words: hydrogen metallurgy, steelmaking, hydrogen plasma, melting, refining, green and low-carbon.

Аноатація. У статті висувається точка зору, що "водневе виробництво сталі" замінює "кисневе виробництво сталі", а також узагальнюється та оцінюється стан досліджень "виробництва сталі з використанням водню". Воднева металургія сталі має унікальні переваги в енергозбереженні, зменшенні споживання та покращенні якості продукції. З одного боку, водень має високоефективний плавильний ефект, який може ефективно зменшити енергоспоживання при виробництві сталі. "Водень" у плазмовому стані характеризується високою температурою та високою теплопровідністю, що може бути використано як високоефективне джерело тепла для реалізації плавки шихти та нагріву сталі, і вже застосовується в сталеплавильних процесах, таких як електродугові печі, конвертери та проміжні ковші. Продування газоподібним "воднем" може прискорити гомогенізацію хімічного складу та температури, а рух водневих бульбашок може сприяти прилипанню неметалевих включень, що прискорює їхнє спливання. Водночас, водень реагує з киснем у рідкій сталі, виділяючи велику кількість тепла, що покращує термодинамічні та кінетичні умови реакції розплаву. Крім того, "водень" може пригнічувати окислення та зменшувати втрати Cr, Mn та інших легуючих елементів шляхом створення відновлювальної атмосфери. З іншого боку, "водень" має ефект рафінування без забруднення, що значно покращує чистоту сталі. Завдяки високій активності та високій відновлювальній здатності "водню", "водень" може ефективно видаляти домішкові елементи, такі як O, C, N, S та P зі сталі, особливо "водень" у плазмовому стані, який може безпосередньо реагувати з домішковими елементами, утворюючи H_2O , CH_4 , NH_3 , H_2S та PH_3 та інші газоподібні продукти, які легко випаровуються та видаляються, щоб уникнути утворення неметалевих включень та реалізувати високоефективне та високочисте виробництво сталі з "нульовими включеннями". Таким чином, розробка нового покоління зелених, майже безвуглецевих, "безвключних" та екологічно чистих сталеплавильних процесів з використанням "водню" замість "вуглецю" прискорить зелений, високоякісний та сталий розвиток сталеливарної промисловості.

Ключові слова: воднева металургія, виробництво сталі, воднева плазма, плавка, рафінування, зелений та низьковуглецевий.

1. Introduction

In 2023, the output of crude steel in China was 1.019 billion tons, accounting for more than half of the global total, with remarkable achievements [1, 2]. Steel industry is characterized by resource-intensive and energy-intensive. Currently, carbon emissions account for about 16% of China's total, and it is the largest

carbon emission industry in the manufacturing industry [1, 3, 4]. Under the "dual-carbon" strategy, the iron and steel industry is the main battlefield of the industrial green development, and the problems of excessive carbon emissions have to be solved urgently to promote the green and healthy development of the iron and steel industry [3, 6, 7]. On the other hand, it is

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necessary to strengthen the research and development and industrialization of key high-end steel to solve the problem of improving the quality of key materials required for the development of high-end manufacturing industry [4, 8]. Therefore, the green and high-quality development is the main theme of the future development of the steel industry, and the active development of a new generation of green near-zero carbon steel production process will effectively solve the ecological environment pollution, product quality instability and other problems, thus boosting the high-quality sustainable development of the steel industry.

In the traditional iron and steel metallurgy process, the ironmaking process is "carbon metallurgy" which uses carbon as reducing agent and heat source, while the steelmaking process is "oxygen steelmaking" which uses oxygen as oxidant to remove impurities such as carbon, silicon and phosphorus in the hot metal. A large amount of greenhouse gas CO_2 is produced in the process of iron and steel making. At the same time, in the later stage of steelmaking, aluminum and other deoxidizing agents must be used to deoxidize and produce a large number of Al_2O_3 non-metallic inclusions to pollute the liquid steel, leading to a decline in the performance of steel materials. Green hydrogen is regarded as the key to a carbon-free economy, with the advantages of wide sources, high thermal efficiency, high energy density, clean and renewable, etc. The application of "hydrogen" in iron and steel production is expected to solve the problems that have long restricted the green, high-quality and sustainable development of steel industry [2, 7, 9, 10]. At present, hydrogen-metallurgy ironmaking technology such as hydrogen-rich blast furnace and hydrogen-based shaft furnace reduction is a hot research and development in the world, and some technologies have been applied in industrialization, which can reduce the carbon emission of ironmaking process by more than 50% [2, 7, 11]. At the same time, hydrogen metallurgy iron product (for example, the direct reduction iron - DRI) have the advantages of low content of harmful impurity elements and low carbon content, and is one of the best

iron source materials for the production of high clean steel [7, 12]. However, the current theoretical research and technical development of hydrogen metallurgy are mainly concentrated in the ironmaking field, and there are few reports in the steelmaking field. So, could the theory and technology of hydrogen metallurgy be applied to the field of steelmaking, replace the traditional "oxygen steelmaking", and fully open up a new generation of green near-zero carbon steel production process based on hydrogen metallurgy? The author thinks that this is a major issue to promote the green, high-quality and sustainable development of the steel industry.

This paper reviews the theory, technology research and application status of "hydrogen steelmaking", and puts forward a new generation of green near-zero carbon steel production process, aimed at promoting the green, high-quality and sustainable development of the steel industry.

2. The role of hydrogen in the steelmaking process

In the steelmaking process, hydrogen acts in two main forms: gaseous and plasma, each demonstrating distinct characteristics:

(1) Gaseous: Hydrogen is a monomer formed by the element hydrogen, with the chemical formula H_2 , which is the lowest molecular weight substance in nature and is also recognized as one of the most environmentally friendly energy sources. As an emerging strategic energy source, hydrogen has the advantages of abundant sources, high thermal efficiency, high energy density, clean use and renewability [2, 7, 9-10].

(2) Plasma state: Hydrogen exists in the form of hydrogen molecules in its natural state. With the increasing energy contained in hydrogen molecules, they gradually transition to the "plasma state" [13-14]. There are various forms of hydrogen molecules in this transition to the plasma state, including molecular H_2 (ground state H_2 and excited state H_2^*), atomic state H (ground state H and excited state H^*), H^+ , H_2^+ , H_3^+ , and e^- . In terms of reduction potential, the hierarchy is as follows: $\text{H}^+ > \text{H}_2^+ > \text{H}_3^+ > \text{H} > \text{H}_2$, as shown in Fig. 1 [14-16].

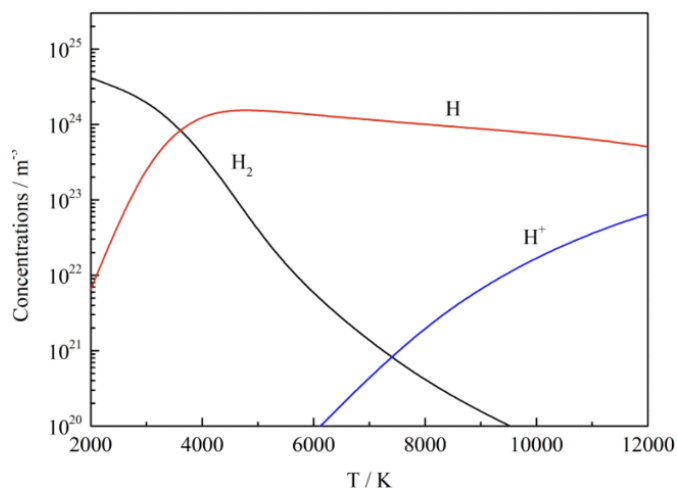


Fig. 1. Equilibrium composition of hydrogen at different temperatures at one atmospheric pressure.

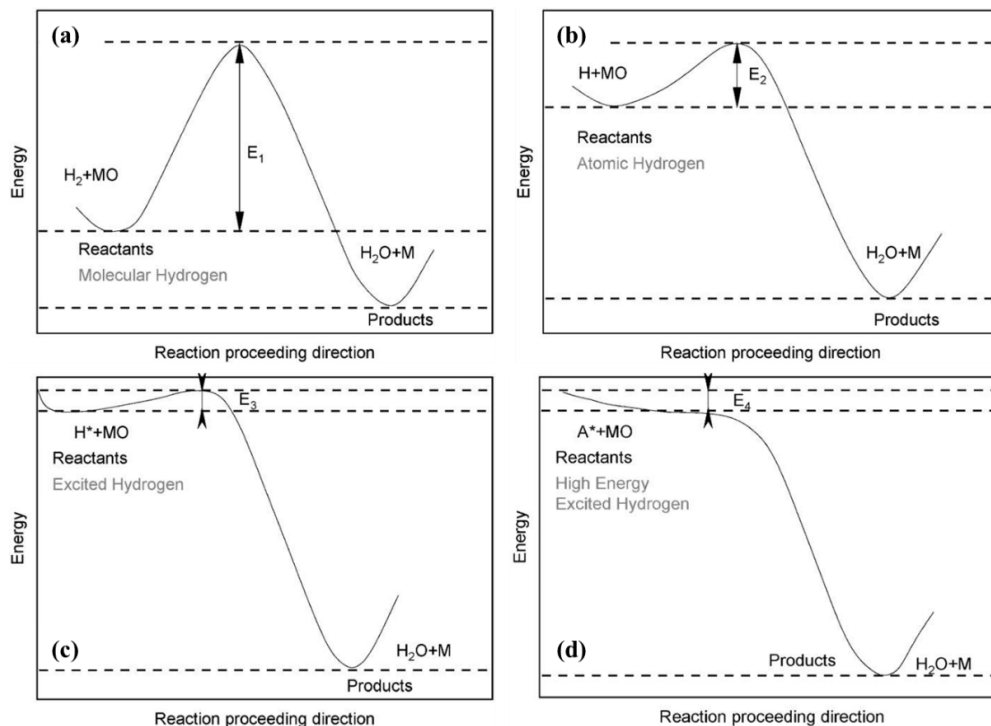


Fig. 2. The activation energy of the reaction of different types of hydrogen with metal oxides (a) molecular hydrogen; (b) Atomic hydrogen; (c) Excited hydrogen; (d) High energy excited hydrogen.

Based on the variance in reduction potential, the trend of the reaction between various hydrogen forms and metal oxides differs. Fig. 2 illustrates the schematic diagram of activation energies of different forms of hydrogen reacting with metal oxides, in which the activation energies are respectively $E_1 > E_2 > E_3 > E_4$ from the largest to the smallest. It can be seen that the closer hydrogen is to the final ionization state, the lower the activation energy of reducing metal oxides, and the easier the reaction will be [15].

In summary, the two forms of "hydrogen" in the steelmaking process have dual functions. Firstly, the reaction between "hydrogen" and metal oxide releases a significant amount of heat, which rapidly melts the charge and heats the liquid steel. In particular, hydrogen in plasma state has the characteristics of higher temperature and greater heat transfer efficiency, which can be directly used as a heat source to quickly heat the charge or liquid steel. Secondly, due to its high

reducibility, especially hydrogen in plasma state, hydrogen can efficiently remove impurity elements such as O and S from the steel. This helps prevent the formation of non-metallic inclusions that could pollute the liquid steel and enables high clean steel smelting. Additionally, hydrogen has the potential to replace common injection gases like argon and nitrogen to stir liquid steel and accelerate mixing within the melt pool.

3. The Smelting effect of "hydrogen"

3.1. The heating effect of "hydrogen"

The heating effect of "hydrogen" is a process in which hydrogen or hydrogen-containing gas is dissociated into plasma to form a high-temperature hydrogen plasma torch, which is used as a high-temperature heat source to achieve rapid melting of the charge or precise temperature control of liquid steel [13, 17]. At present, plasma heating technology has been applied in EAF, converter and tundish equipment. The system diagram is shown in Fig. 3 [18-20].

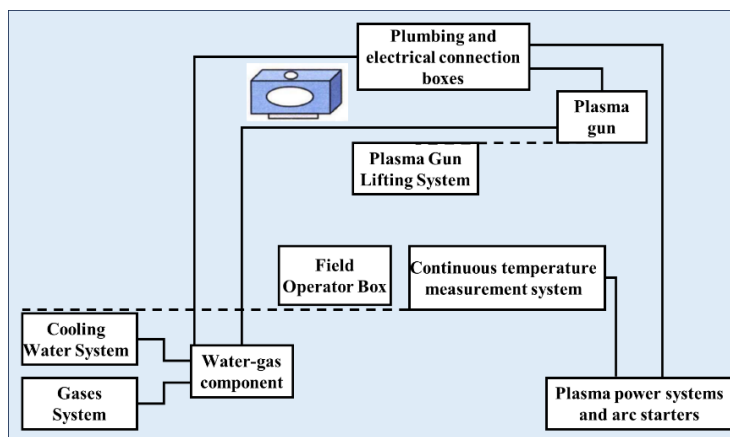


Fig. 3. Schematic diagram of the plasma heating system equipment for tundish.

The results show that the temperature in the plasma torch center increases from 10417 K to 11660 K when 5% hydrogen is added into argon. When 5% hydrogen is added to nitrogen, the temperature can be increased from 10789 K to 11254 K, and the larger the proportion of hydrogen, the higher the central temperature of the jet, and the faster the heating rate of the molten pool [17]. Taking a 100 kg multifunctional DC ladle furnace as an example, the heating rate of the molten pool is faster than that of the solid electrode by

injecting Ar-H₂ mixture into the molten pool through the hollow graphite electrode. The higher the proportion of H₂ in the mixed gas, the faster the heating rate of the molten pool [21]. In addition, hydrogen-containing gas CH₄ also has efficient heating effect, but the heating efficiency does not increase with the increase of CH₄ concentration. When 95%Ar-5%CH₄ is blown into the molten pool, the heating rate is the largest, as shown in Fig. 4 [22].

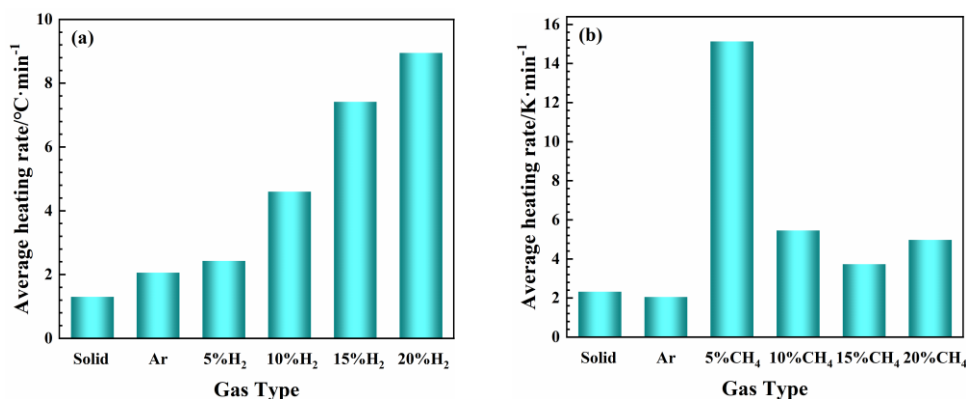


Fig. 4 Influence of hydrogen containing gas on melt pool heating rates: (a) H₂; (b) CH₄.

In actual production, according to the characteristics of steel and metallurgical quality requirements, reasonable selection of heating power and time, and other process parameters to control the heating efficiency of hydrogen plasma can not only meet the requirements of melting heating rate and end temperature [13, 23], but also effectively reduce the loss of refractory materials and improve the service life of smelting equipment [24]. In addition, hydrogen plasma torch has the characteristics of high impact force, which can not only improve the fluidity of liquid steel and accelerate the floating of inclusions, but also increase the temperature of slag layer and reduce the viscosity of slag layer, so as to improve the adsorption capacity of slag layer to inclusions, and help improve the cleanliness of liquid steel [25]. However, at this stage, plasma heating also has some problems, such as expensive equipment, short service life, difficult arc-starting, and electromagnetic radiation generated by plasma heating process has great interference on weak current systems [26].

3.2. The Stirring Effect of "Hydrogen"

Gas injection is a commonly used method to enhance metallurgical reactions in the steelmaking process [27-31]. It serves to stir the liquid steel, promoting homogenization of its composition and temperature, as well as facilitating the formation of small bubbles that accelerate the removal of impurities. Hydrogen injection not only creates smaller and more dispersed bubbles for enhanced stirring, but also generates significant chemical heat by reacting with dissolved oxygen or blown oxygen in the molten steel [27, 32-34]. Additionally, hydrogen can aid in decarbonization and contribute to low-oxygen or no-oxygen smelting in converters, thereby reducing carbon emissions [27, 34]. Furthermore, it provides a reducing atmosphere that

inhibits over-oxidation and minimizes loss of metal elements during steelmaking. Any residual hydrogen dissolved in the molten steel can be effectively removed during subsequent vacuum refining processes without compromising final product quality (Fig. 5 (a)) [16, 33-35]. Taking production data from Pangang Group Xichang Steel & Vanadium Co., Ltd. 210-ton converter as an example [35], at an blowing intensity of 0.1 m³·min⁻¹·t⁻¹, hydrogen injection yields an extra 16174.72 kJ compared to argon injection (Fig. 5 (b)) and increases scrap charging ratio by 8.17% (Fig. 5 (c)). Moreover, higher bottom-blowing intensities correspond to greater extra calorific value and scrap charge ratios; CO₂ emission reductions also correlate with increased hydrogen intensity at the bottom blow (Fig. 5 (d)).

The practice has demonstrated that hydrogen blowing can effectively address the issues of "insufficient temperature" and "slag dilution" in the AOD converter smelting process of high manganese stainless steel based on its advantages in efficient stirring, rapid heating, and providing a reducing atmosphere. Specific measures are outlined as follows [36].

During the first decarburization stage (Fig. 6 (a)), to prevent the potential hazards of hydrogen and oxygen reacting and causing explosions, they are separately injected into the converter from the side. The reaction between hydrogen and oxygen generates a significant amount of heat within the converter, while unreacted hydrogen is completely consumed by the top-blown oxygen, effectively raising the temperature of molten steel without relying on carbon and reducing carbon emissions. Additionally, blown hydrogen can facilitate the reduction of hexavalent chromium in slag, thereby improving chromium recovery rates.

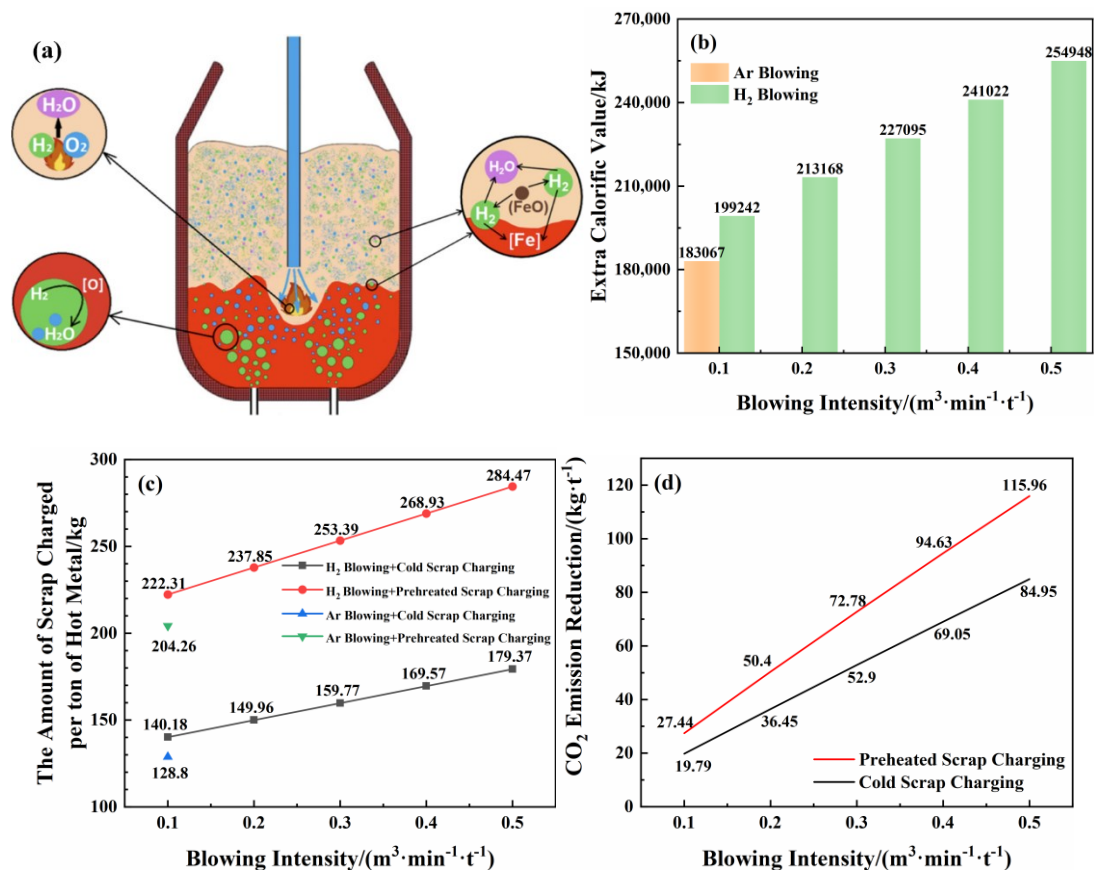


Fig. 5. Metallurgical effects of hydrogen blowing in converter: (a) Metallurgical behavior of hydrogen in the converter; (b) Extra calorific value; (c) Scrap charge; (d) CO₂ emission reduction.

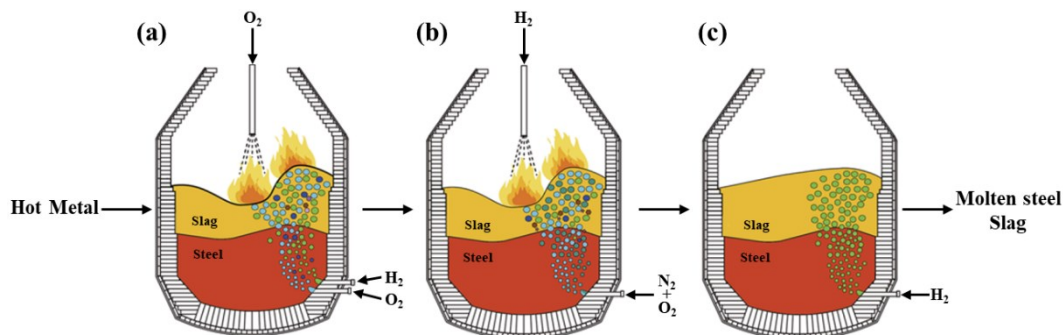


Fig. 6. Schematic diagram of hydrogen blowing smelting of high manganese stainless steel: (a) The first decarburization stage; (b) The second decarburization stage; (c) The reduction stage.

During the second decarburization stage (Fig. 6 (b)), oxygen and nitrogen blown into the converter from the side enhance the decarburization process; any remaining oxygen is eliminated by reacting with hydrogen from the top, generating heat and sustaining the molten steel temperature.

During the reduction stage (Fig. 6 (c)), hydrogen is injected into the side to intensify mixing within the molten pool for more uniform composition and temperature of molten steel as well as promote reduction reactions.

In summary, hydrogen injection in the steelmaking process not only further strengthens the stirring effect and improves the kinetic conditions of steelmaking; but also will react with the dissolved oxygen in the molten

steel and the oxygen sprayed, release a lot of heat, maintain or increase the temperature of the molten steel, and improve the thermodynamic conditions of steelmaking. The dissolved hydrogen is subsequently removed by vacuum degassing without affecting the metallurgical quality of the steel.

4. The refining effect of "hydrogen"

Hydrogen, especially hydrogen in plasma state, has extremely high chemical activity and reducibility, and can react quickly with impurity elements such as O, N, S and P and C in liquid steel to generate gas products that are easily removed by vacuum (Fig. 7 [37]), to avoid the formation of non-metallic inclusions contaminating the molten steel due to the addition of deoxidizers and slag-making agent, and the increase

of oxygen in the molten steel due to oxygen blowing and decarburization. The green, near-zero-carbon, high-clean steel smelting with “less oxygen or non-oxygen” and “zero inclusions” is realized [37-44]. A small

amount of dissolved hydrogen in steel can be reduced to very low levels (1×10^{-6}) by means of vacuum degassing, thus completely eliminating adverse effects such as hydrogen embrittlement [33-34].

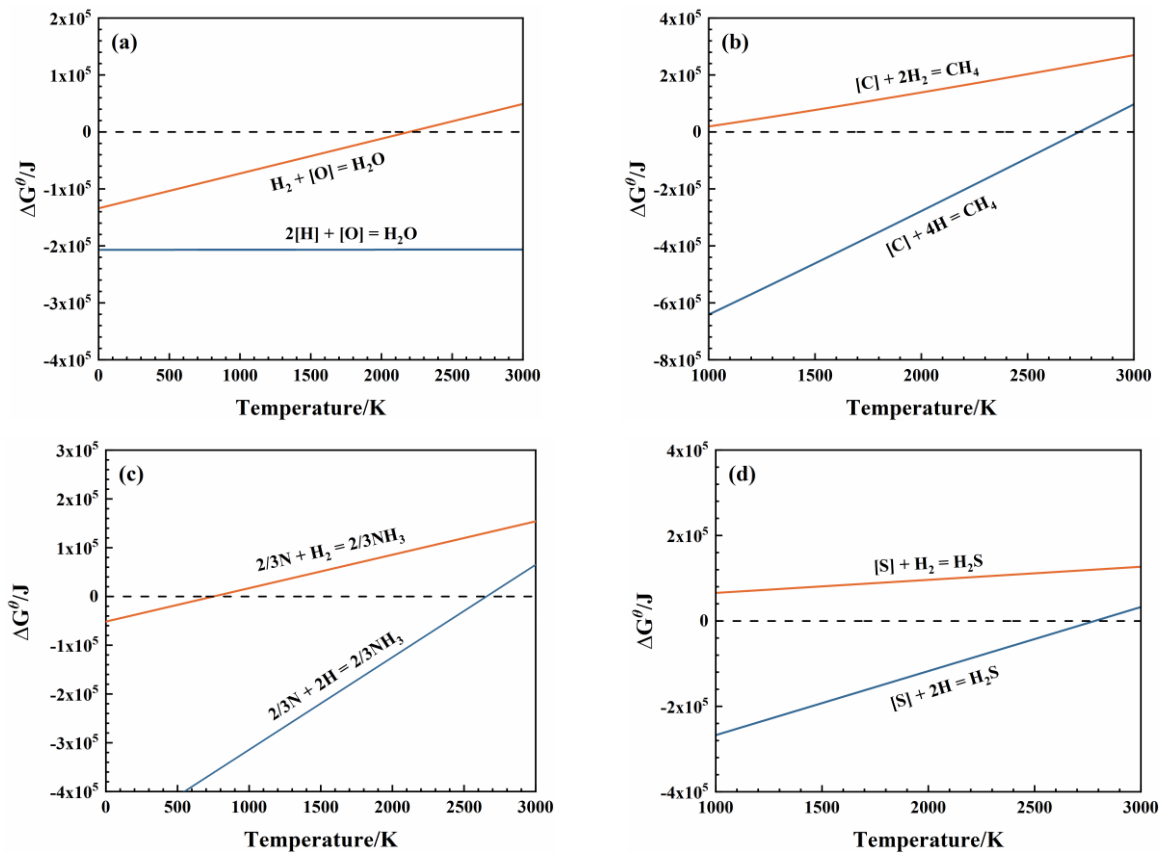


Fig. 7. Gibbs free energy of the reaction of “hydrogen” with impurity elements in steel: (a) Hydrogen-oxygen reaction; (b) Hydrogen-carbon reaction; (c) Hydrogen-nitrogen reaction; (d) Hydrogen-sulfur reaction.

4.1. “Hydrogen” deoxidation

As we all know, high oxygen content is the cause of large-size inclusions in steel. The traditional deoxidation methods are difficult to completely remove inclusions [45]. Hydrogen reacts with dissolved oxygen in the molten steel to produce water, which can directly discharge the molten steel and effectively reduce the oxygen content in the steel [36, 46-48]. At the same time, the injection of gaseous hydrogen into the liquid

steel can also stir the liquid steel to strengthen mass transfer, increase the diffusion rate of dissolved oxygen to the interface between hydrogen bubble and liquid steel, and improve the kinetic conditions of hydrogen deoxidation [27, 33-34]. However, with the refining process, the driving force of dissolved oxygen mass transfer to the hydrogen bubble-liquid steel interface decreases, and the deoxidation rate and hydrogen utilization rate both decrease, as shown in Fig. 8 [49].

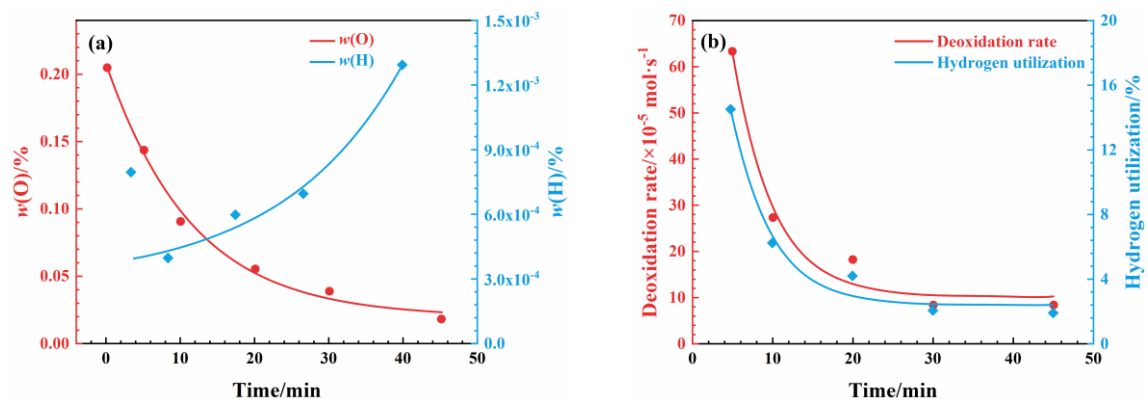
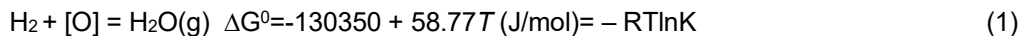


Fig. 8. Effect of hydrogen blowing time on the rate of deoxidation and hydrogen utilization: (a) Oxygen and hydrogen content in steel; (b) Deoxidation rate and hydrogen utilization rate.

In the process of hydrogen deoxidation, due to the low solubility of hydrogen in molten steel, the atomic hydrogen deoxidation reaction is limited, and the deoxidation is mainly controlled by the reaction rate of molecular hydrogen and dissolved oxygen. The molecular

hydrogen deoxidation reaction equation is shown in (1) and (2). It can be seen that when the steelmaking temperature is constant, hydrogen deoxidation is controlled by P_{H_2O}/P_{H_2} , and it is independent of the [H] content in steel and pressure [49-50].



$$[\%O] = \frac{P_{H_2O}}{P_{H_2}} \frac{1}{f_O \cdot K} \quad (2)$$

Although hydrogen deoxidation is not affected by pressure, when the C content in steel is high and the environmental pressure is low, the carbon-oxygen reaction product CO continues to be discharged from the molten steel, resulting in the carbon-oxygen reaction continuing, and the deoxidation means is transformed into carbon deoxidation. When carbon deoxidation is dominant, the tiny bubbles formed by blowing hydrogen can provide a nucleation interface for CO, adsorb CO and discharge molten steel, and cooperatively promote deoxidation [46, 49-50].

Therefore, by controlling the pressure and promoting the alternating deoxidation of carbon and hydrogen, high purity steel smelting can be achieved, the specific steps are shown in Fig. 9 [50]:

(1) In the late stage of converter smelting, [C%] is low and [O] is excessive in steel. At the same time of hydrogen blowing deoxidation, the hydrogen bubble can provide the carbon-oxygen reaction interface and reduce the nucleation resistance, and the carbon-

oxygen reaction products are removed with the hydrogen bubble floating up, as shown in Fig. 9 (a);

(2) Tapping and ladle bottom blowing H_2 . Without an external oxygen source, [C] has competitive deoxidation with H_2 , and carbon and hydrogen deoxidation is carried out alternately. As in (1), the H_2 bubbles can provide reaction interfaces and reduce nucleation resistance, and the reaction products can discharge out of the molten pool via the H_2 bubbles, as shown in Fig. 9 (b);

(3) Before vacuum refining, adding sufficient amount of carbon powder, carbon deoxidation capacity is enhanced and dominant, and the deoxidation product CO is removed by floating into the hydrogen bubble, as shown in Fig. 9 (c);

(4) In the vacuum treatment stage, high vacuum leads to carbon deoxidation capacity is stronger than hydrogen, only C can complete deep deoxidation, while dissolved hydrogen in steel is also removed at this stage, as shown in Fig. 9 (d).

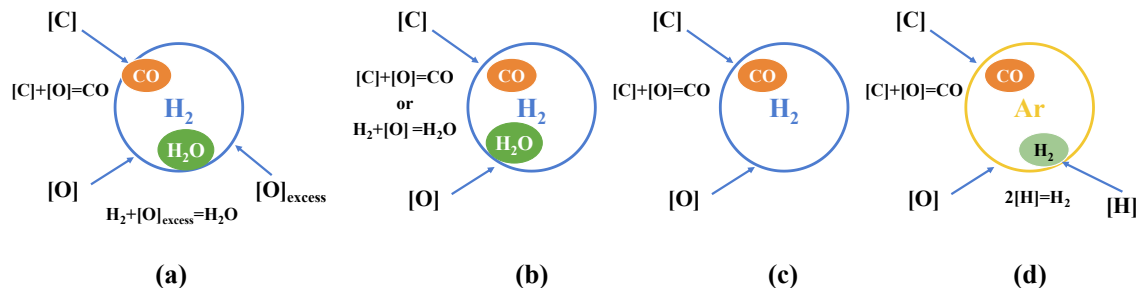


Fig. 9. Method of smelting high-clean steel in converter: (a) H_2 bottom blowing at the later stage of converter smelting; (b) Tapping and ladle bottom blowing H_2 ; (c) Adding carbon powder into ladle; (d) RH vacuum treatment.

Based on the characteristics of high-efficiency hydrogen deoxidation and the easy floating of hydrogen bubbles, the "micro-hydrogen bubble" refining technology has been developed. Due to its simple operation and remarkable deoxidation and inclusion removal effects, it has attracted more attention [30-31, 51-53]. The specific technical route is as follows: First, a large amount of hydrogen or hydrogen-containing gas is injected into the liquid steel for refining, which in addition to efficient deoxidation, while the dissolved hydrogen in steel reaches more than 8×10^{-6} ; After that, in the vacuum refining process, the dissolved hydrogen in steel is vacuumed to form tiny bubbles (1 mm) with inclusions as heterogeneous nucleation points, which

are carried and adhered to the inclusions to float to the slag for removal. In addition, the generated hydrogen bubble reduces the nitrogen partial pressure and strengthens the nitrogen removal effect of the liquid steel. Practice has proved that the micro-hydrogen bubble refining effect is obvious, $w(O) \leq 20 \times 10^{-6}$, $w(H) \leq 2 \times 10^{-6}$, $w(N) \leq 60 \times 10^{-6}$ in steel, and the cleanliness has been significantly improved, as shown in Fig. 10 [51]. To sum up, the key of the micro-hydrogen bubble method is to improve the solubility of hydrogen in molten steel, and pressure metallurgy can be used to increase the amount of hydrogen dissolved in molten steel in the actual production [54-55].

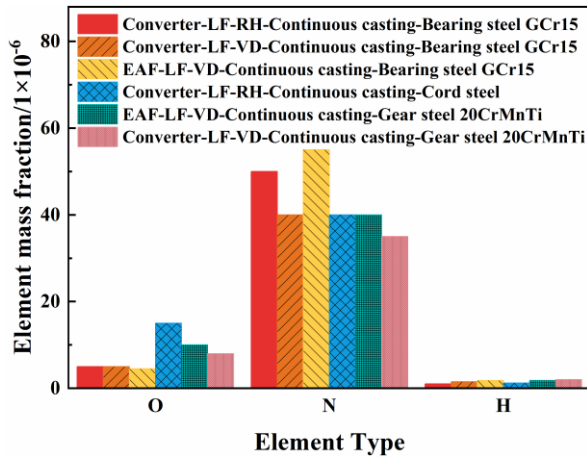


Fig. 10. Effect of micro hydrogen bubble method on the content of O, N and H elements in steel.

The above analysis is not difficult to see that after hydrogen deoxidation, the oxygen content in steel is still high, and the deep deoxidation effect is poor. The activation energy of hydrogen plasma and oxygen in steel is lower, and the deoxidation reaction is easier to carry out [37]. Therefore, hydrogen plasma has the potential of deep deoxidation. Take the deoxidation of hydrogen plasma based on argon-hydrogen mixture as an example, as shown in Fig. 11 [40-41].

Hydrogen plasma deoxidation is mainly divided into two stages, namely: 1) rapid deoxidation stage, the deoxidation rate is fast, and the oxygen content in liquid iron is rapidly reduced to a low level; 2) In the deep deoxidation stage, the deoxidation rate is slow, and the minimum oxygen content after deoxidation can be below 5×10^{-6} . The deoxidation rate and limit of the whole hydrogen plasma deoxidation process increase significantly with the increase of the concentration of

hydrogen plasma particles, the lowest can be about 1×10^{-6} , with strong deoxidation capacity and no other types of inclusions generated.

In addition, hydrogen-containing reducing gases such as CH_4 and liquefied petroleum gas also have deoxidation capacity [45, 56-59]. In steelmaking environment, CH_4 can be decomposed into C and H_2 ($\text{CH}_4 = \text{C} + 2\text{H}_2(\text{g})$), and then react with [O] in steel, deoxidation products (CO and H_2O), H_2 and undecomposed CH_4 can be removed by floating up with bubbles. Studies have shown that [56], at 1600°C , CH_4 has a significant deoxidation effect, and can be used as an initial deoxidizer to deoxidize liquid steel, as shown in Fig. 12. Similarly, hydrogen-containing reducing gases such as liquefied petroleum gas will decompose at high temperatures to generate C and H_2 for deoxidation refining of liquid steel [59].

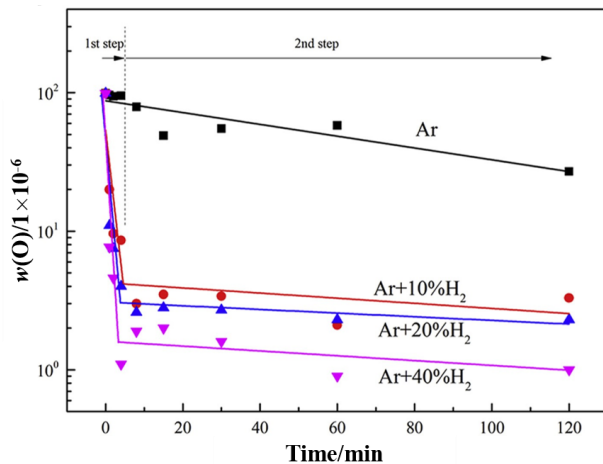


Fig. 11. Oxygen content trend with time in hydrogen plasma melting process.

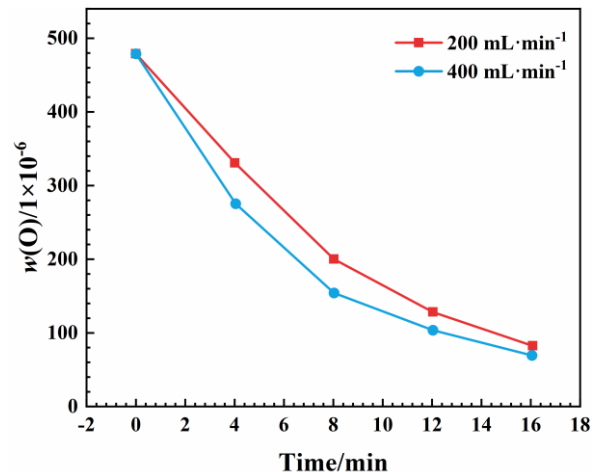


Fig. 12. Oxygen mass fraction of molten steel during CH_4 deoxidation.

4.2. "Hydrogen" decarbonization

Carbon is an important element that affects the mechanical and corrosion properties of steel, and is one of the most concerned indexes in steelmaking process. At present, oxygen blowing is one of the most common way for decarbonization, but it will increase CO_2 emissions and lead to a substantial increase in oxygen in steel, which greatly increases the difficulty of

deoxidation in subsequent refining processes and increases the proportion of large-size harmful non metallic inclusions in steel [60]. Therefore, it is very difficult to achieve high purity smelting by this refining method. It is found that carbon in steel is extremely difficult to react with gaseous hydrogen at steelmaking temperature, but it is very easy to react with hydrogen in plasma state to generate CH_4 gas and directly discharge liquid

steel. While decarbonizing and controlling carbon, there is no residue of inclusions polluting liquid steel and “zero” CO₂ emission, as shown in Fig. 7(b) [37-38, 43, 61].

Because metal plasma guns are expensive and difficult to be maintained, hydrogen plasma is currently formed in the refining process mainly through the dissociation of hydrogen or hydrogen-containing gases by hollow graphite electrode plasma guns. The use of graphite electrode will cause carbonization of liquid steel to a certain extent and increase carbon content [25, 62]. Carbonization only occurs at low carbon

content in the steel, and the greater the concentration of hydrogen plasma particles in plasma, the weaker the carbonization phenomenon and the smaller the carburization degree. For example, the proportion of hydrogen increases from 10% to 20%, and the carbonization rate of molten steel decreases from $3.73 \times 10^{-6}/\text{min}$ to $3.1 \times 10^{-6}/\text{min}$, as shown in Fig. 13 (a) [63]. When the carbon content of molten steel is high, the hydrogen plasma decarburization effect is very significant and is completely unaffected by carbonization, as shown in Fig. 13 (b) [38].

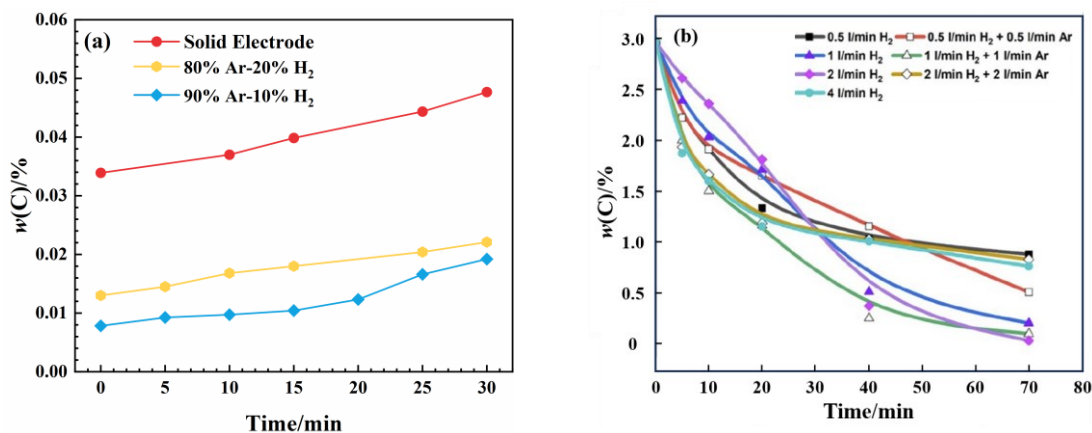


Fig. 13. Effect of hydrogen plasma on C content in steel: (a) Low carbon steel; (b) High carbon steel.

Although gaseous hydrogen cannot directly decarbonize steel, compared with argon, blowing hydrogen is more likely to form small dispersed bubbles, which can provide a nucleating interface for CO, adsorb CO and discharge liquid steel, accelerate the reaction of carbon residue and oxygen in steel, and further reduce the content of C in liquid steel [46, 49-50], as shown in Fig. 14.

In summary, “hydrogen” has excellent decarbonization ability, especially hydrogen plasma, can achieve deep decarbonization, but under low carbon conditions, the degree of decarbonization is affected by plasma gun material and hydrogen plasma particle concentration, etc. In actual production, it is necessary

to rationally optimize the production process according to the carbon content requirements of steel grades.

4.3. “Hydrogen” denitrification

Similar to decarbonization, nitrogen in steel cannot be removed by reacting with gaseous hydrogen to form gaseous products at steelmaking temperature, as shown in Fig. 7 (c) [37]. However, the small dispersed bubbles formed by blowing hydrogen increase the interface reaction area and promote the diffusion of nitrogen in steel to the hydrogen bubble interface to form nitrogen, thus reducing the N content in steel [51]. Nitrogen in liquid steel can be reduced to 0.002% by injecting hydrogen at normal pressure, as shown in Fig. 15 [49].

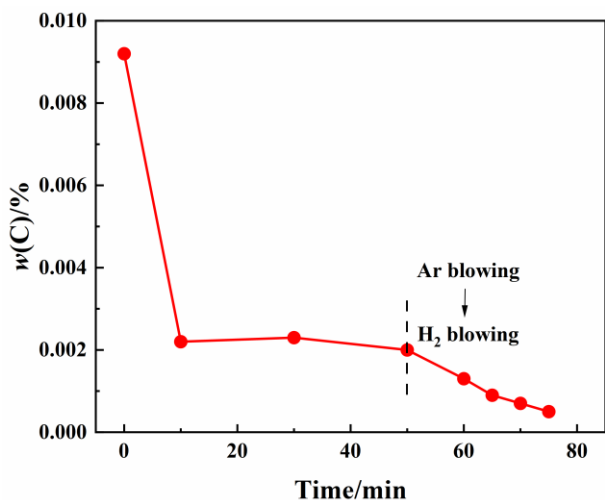


Fig. 14. Effect of hydrogen blowing on the C content in steel.

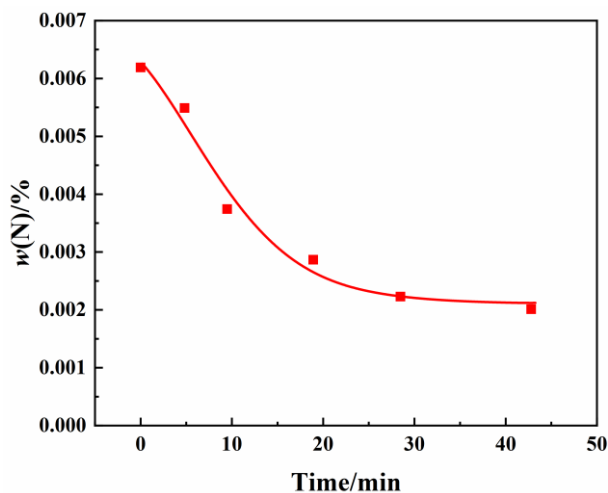


Fig. 15. Variation of elemental N content in steel with time.

In contrast, hydrogen plasma can easily react with [N] in steel to generate NH_3 , which can discharge liquid steel and effectively reduce the N content in steel. Therefore, in EAF smelting, ladle refining, VOD refining or RH refining, hydrogen can be added to argon/nitrogen to form hydrogen-containing plasma to achieve

efficient nitrogen removal [43, 64]. In addition, the use of hydrogen-containing reduction gas such as CH_4 instead of hydrogen to dissociate hydrogen plasma also has the effect of nitrogen removal, as shown in Table 1 [19, 42, 65-66].

Table 1. Examples of changes in nitrogen content in plasma melted steel.

Experimental equipment	Alloy Melt	Gas	Effect of nitrogen removal
20 kVA DC Electric Arc Furnace	Pure Iron	$\text{Ar-N}_2\text{-H}_2$	Compared to Ar-N_2 , $w(\text{N})$ decreases in $\text{Ar-N}_2\text{-H}_2$
150 kg Electric Arc Furnace (Two AC Plasma Torches)	Molten Steel	90% Ar -10% H_2	$w(\text{N})$ decreases to 1×10^{-4}
		95% Ar -5% CH_4	$w(\text{N})$ decreases to 15×10^{-6}
2 ~ 5 kg Crucible (Plasma Furnace with Single Plasma Torch)	Stainless Steel	Ar-H_2	$w(\text{N}) < 0.05\%$
	Pure Iron		$w(\text{N})$ reduced from 0.05% to 0.015%
	25% Cr-Fe		$w(\text{N})$ reduced from 0.11% to 0.065%
150 kg Plasma Furnace	Carbon Saturated Low Alloy Steel	CH_4	$w(\text{N})$ reduced from 0.21% to 0.15%
	Low Alloy Steel	Kerosene	$w(\text{N})$ reduced from 0.18% to 0.11%
Plasma Arc Melting Furnace	Pure Iron	Ar-1\%H_2	$w(\text{N})$ can be reduced to $2 \sim 3 \times 10^{-6}$
		Ar-5\%H_2	$w(\text{N})$ can decrease to as low as 1×10^{-6}

4.4. "Hydrogen" desulphurization

At present, slagging desulphurization and addition of desulphurization agents are the most commonly used desulphurization methods, but the desulphurization efficiency of such methods is relatively low, and sulfide inclusions are easily formed, which deteriorates the mechanical properties of materials. In contrast, hydrogen desulfurization produces H_2S gas, which can directly exclude liquid steel without inclusion residue, and can realize ultra-low sulfur steel smelting [37-39, 41]. Like hydrogen decarbonization and nitrogen, gaseous hydrogen cannot react with sulfur in steel, as shown in Fig. 7 (d) [37]. However, the fine dispersed hydrogen bubbles formed by blowing hydrogen not only increase the content of dissolved hydrogen in steel, but also accelerate the reaction of sulfur with the locally dissolved hydrogen, and the reaction product H_2S can be removed with the hydrogen bubbles to achieve desulfurization. However, when the sulfur content of molten steel is low, the desulfurization effect of hydrogen injection is extremely limited [46, 49], as shown in Fig. 16 (a). In contrast, hydrogen plasma desulfurization has a more significant effect, similar to hydrogen plasma deoxidation, and the degree and rate of desulfurization are greatly improved with the increase of hydrogen plasma particle concentration, as shown in Fig. 16 (b) [39, 41].

4.5. "Hydrogen" dephosphorization

For most types of steel, the high content of phosphorus in steel is very easy to cause serious

segregation in the solidification process of steel, thus reducing the impact performance of steel and deteriorating the service performance of steel, so it is necessary to remove phosphorus as much as possible in the smelting process [67]. Commonly used dephosphorization methods such as lime powder blowing will seriously erode the furnace lining and seriously deteriorate the safety of the furnace lining [68]. In contrast, hydrogen plasma can react with phosphorus in steel to generate PH_3 gas and directly discharge liquid steel, which can control phosphorus in steel at a lower level, as shown in Fig. 17 [38]. However, PH_3 will decompose into P and H_2 in a high temperature environment, so it is necessary to reasonably control the smelting temperature, refining time and vacuum degree during the dephosphorization of hydrogen plasma to prevent the "phosphorus return" of liquid steel.

In summary, "hydrogen" can react with impurity elements such as O, C, N, S and P in steel to generate gaseous products, achieve high efficiency, less slag and "zero inclusions" pollution-free refining, in which plasma hydrogen can be deeply refined, and can completely avoid the oxygen decarbonization process, and greatly reduce the CO_2 emissions of smelting processes such as electric arc furnace and converter. At the same time, the cleanliness of the liquid steel is greatly improved. Therefore, "hydrogen" refining will be an important refining way for the preparation of green high-quality high-end special steel in the future.

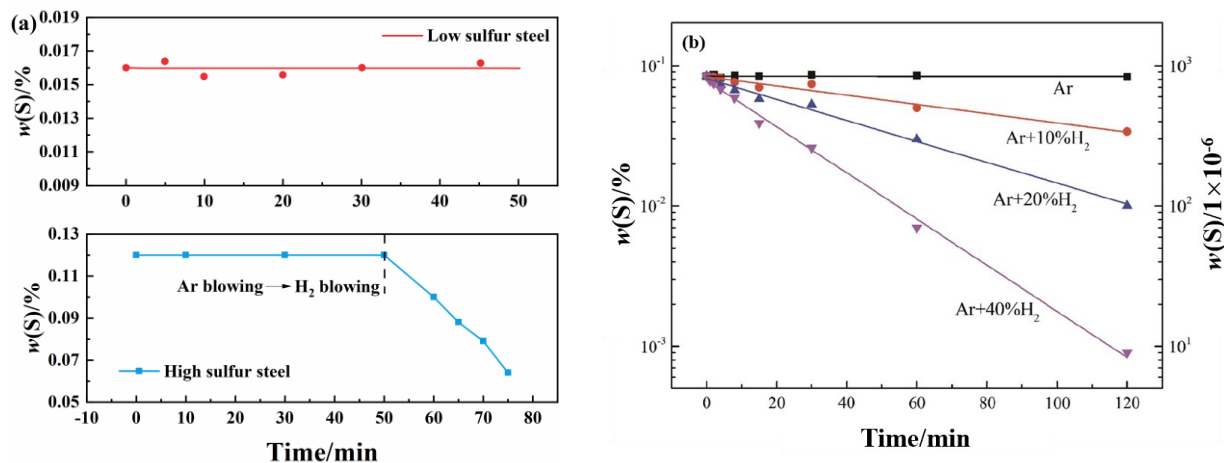


Fig. 16. Effect of "hydrogen" on the S content of steel: (a) Hydrogen; (b) Hydrogen plasma.

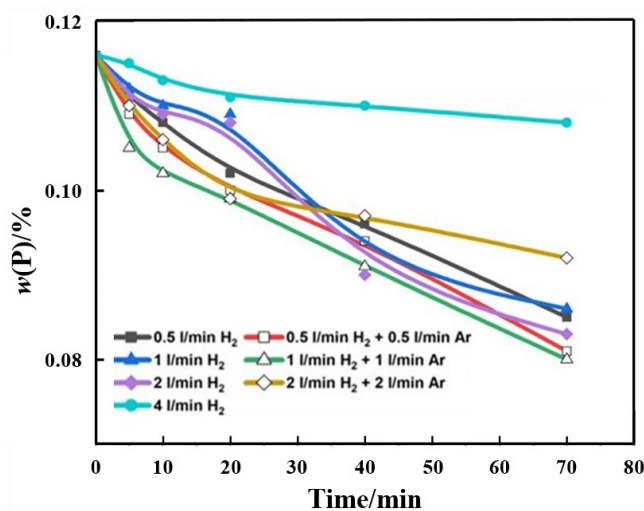


Fig. 17. Effect of hydrogen plasma on the P content of steel.

5. Prospects for a new generation of hydrogen metallurgy steelmaking processes

"Hydrogen" is the clean energy with the greatest development potential in the 21st century, and it is the best substitute for coal and other fossil fuels [9, 10]. The use of "hydrogen" in the process of steelmaking has outstanding advantages, which can not only achieve rapid melting and high-clean refining, but also significantly reduce CO₂ emissions in the process of steelmaking [27, 34-35]. Under the background of the implementation of the environmental protection strategy, the steel preparation process has gradually evolved into three categories: "BF-BOF" process, "Scarp-EAF" process, "DRI-EAF" process. Among them, the "DRI-EAF" process has the natural properties of low carbon and even zero carbon, and its CO₂ emission reduction ability is obvious to all. At present, hydrogen metallurgy mainly focuses on the ironmaking process, as shown in Table 2 [2, 69], and there are few reports on the theoretical research and production application of hydrogen metallurgy steelmaking. Therefore, hydrogen metallurgy through the entire iron and steel metallurgy production process is the development direction to promote the green, high-quality and

sustainable development of the iron and steel industry.

Therefore, based on the outstanding advantages of hydrogen metallurgy steelmaking, which is characterized by green, low carbon, rapid melting and high efficiency and high cleanliness refining, a new generation of green and near-zero carbon steel production process with hydrogen plasma electric furnace and hydrogen plasma refining furnace as the core is proposed (Fig. 18). Its core includes low carbon ironmaking, low carbon and low oxygen steelmaking and "zero inclusion" pollution-free refining and other hydrogen metallurgy technologies. The main processes include:

1. The use photovoltaic, wind power and other clean energy power (green electricity) to produce hydrogen by water electrolysis (green hydrogen);
2. Using hydrogen-rich gas such as pure hydrogen, natural gas and petrochemical waste hydrogen as reducing agent, low carbon or no carbon pure DRI is produced by hydrogen-based shaft furnace;
3. The use of green electric furnace (hydrogen plasma furnace) [43] and pollution-free refining furnace [44] (hydrogen plasma ladle refining furnace) to achieve near-zero carbon emission steelmaking;

4. Through continuous casting and rolling, the required steel was produced; Some high-end special steels adopt the new generation of gradient ultrafast cooling mold casting and controlled atmosphere

electroslag remelting and other special metallurgical technologies, and then produce high-end special steel products that meet the requirements through forging and heat treatment.

Table 2 Research status and objectives of hydrometallurgy

Project Sponsor	Project name/Key technology	Goals/Achievements
Europe	ULCOS	CO ₂ emission are reduced by 50%
Japan	COURSE50	Hydrogen is used as a reducing agent to reduce carbon emissions by 10%
Korea	COOLSTAR	Direct reduced iron is produced by hydrogen reduction
Austrian	H2FUTURE	To produce hydrogen by electrolysis of water, the hydrogen yield is 1200 cm ³ /h
German	Thyssenkrupp hydrogen-based ironmaking experiment	Hydrogen production from electrolyzed water for the reduction of iron ore and steelmaking, with the aim of achieving a 30% reduction in carbon emissions by 2030 and zero carbon emissions by 2050
Sweden	HYBRIT	Electrolysis of water to produce hydrogen and use of hydrogen to produce direct reduced iron
US	MIDREX	Using hydrogen volume fraction exceeds 50% of the reducing gas preparation of iron oxide
China Baowu Steel Group Corporation	Hydrogen-rich carbon cycle in blast furnace, Hydrogen reduction and Hydrogen production technology of nuclear energy, etc.	Carbon peak by 2023, carbon reduction by 30% by 2035, and carbon neutrality by 2050
HBIS	Energiron-ZR (zero reforming) technology replaces carbon metallurgy, and hydrogen metallurgy research agreements are signed with all parties	Construction of 1.2 million tons of hydrogen metallurgy project, 70% of hydrogen used for the production of direct reduced iron
Angang Steel Group Limited	Wind power + photovoltaic power - electrolytic water hydrogen production - hydrogen metallurgy technology	Total carbon emissions by 2035 will be 30% lower than peak
Baogang Group	Carrying out research on low-carbon metallurgical technologies and industrialized applications	Photovoltaic hydrogen production - Pipeline transport of hydrogen - green hydrogen metallurgy
JISCO	The Hydrogen Metallurgy Research Institute was established, and the demonstration base of "Coal-based hydrogen metallurgy + Dry grinding and dry separation of iron from Jiusteel" was built	Founded "coal-based hydrogen metallurgy theory" and "Shallow hydrogen metallurgy magnetization roasting theory"
Zhongjin Taihang Mining Co., LTD	Coke oven gas dry reforming reduction + PERED shaft furnace process combination	Hydrogen-based direct reduced iron project with an annual output of 300000 t
Jianlong Group	Hydrogen-based melting reduction smelting high purity cast iron and development of hydrogen-rich melting reduction CISP new process	Annual CO ₂ emissions are reduced by 112000 t
Nippon Steel Group	Hydrogen was extracted by producing ethylene acetate symbiotic product from natural gas	It is planned to produce 50 t of direct reduced iron per year
Jinnan Steel	Blast furnace hydrogen-rich injection	Hydrogen injection in 2000 m ³ blast furnaces

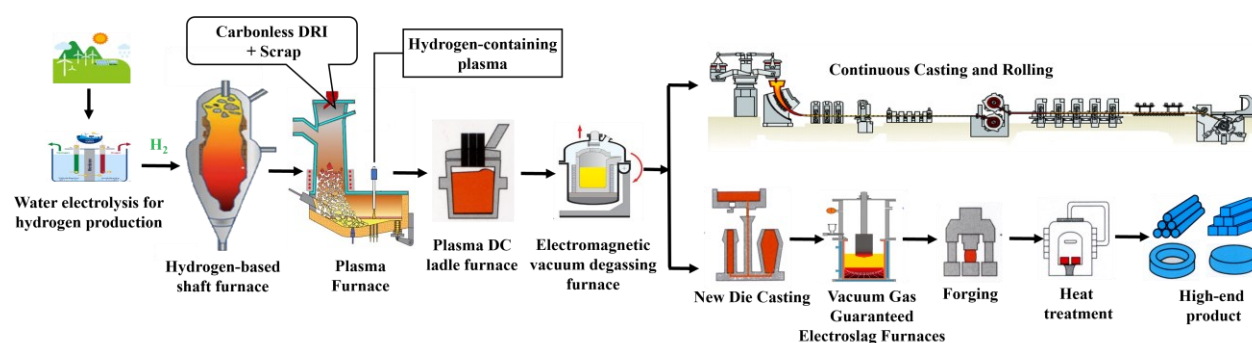


Fig. 18. New-generation ferrous metallurgical process with zero-carbon hydrometallurgy.

Fig. 19 shows the comparison between the new process and the traditional process. It can be seen from the figure that the oxygen content in the traditional process is reduced to a very low level after the iron-making stage, but it is significantly increased in the stage of oxygen blowing and decarburization in steelmaking. The deoxidizing agent such as aluminum needs to be added for subsequent deoxidation, and the deoxidizing products pollute the liquid steel as non-metallic inclusions. It will eventually lead to a decrease in the cleanliness of the liquid steel. In contrast, in the whole new process, the oxygen content has been in a continuously decreasing state, the steelmaking process basically does not need to deoxidize or use pollution-free hydrogen plasma deoxidize, and the steel is basically free of inclusions, so ultra-high clean steel can be manufactured. In terms of the change of the carbon content, the carbon content of hot metal in the traditional process of ironmaking stage reaches about 4.5%, and in the steelmaking stage, a large amount of oxygen is blown to decarbonize, resulting in a large amount of carbon consumption, and the CO₂ emission per ton of steel is as high as 1.8 t. The new process

uses hydrogen reduction, and the whole process only needs to add an appropriate amount of carbon to the liquid steel according to the target carbon content of the steel grade, without the decarbonization process, that is, to achieve near zero CO₂ emissions. In terms of temperature, compared with the traditional process, the temperature in the ironmaking stage of the new process is significantly reduced, and the temperature in the steelmaking stage is also reduced. From the perspective of solid waste gas emission, the slag amount of the new process in the ironmaking stage is only 1/5 of the traditional process, and the slag amount in the steelmaking stage is only 1/10 of the traditional process. Therefore, compared with the traditional BF-BOF process, the new process has a remarkable effect on energy saving and emission reduction. It is estimated that the new process will reduce CO₂ emissions by more than 95%, reduce oxygen consumption by more than 95%, save energy by 30-50%, shorten production cycle by more than 50%, reduce cost by 30-50%, reduce nitrogen content in steel by 10-50%, reduce oxygen content by 10-50%, and reduce non-metallic inclusions by 50-90%.

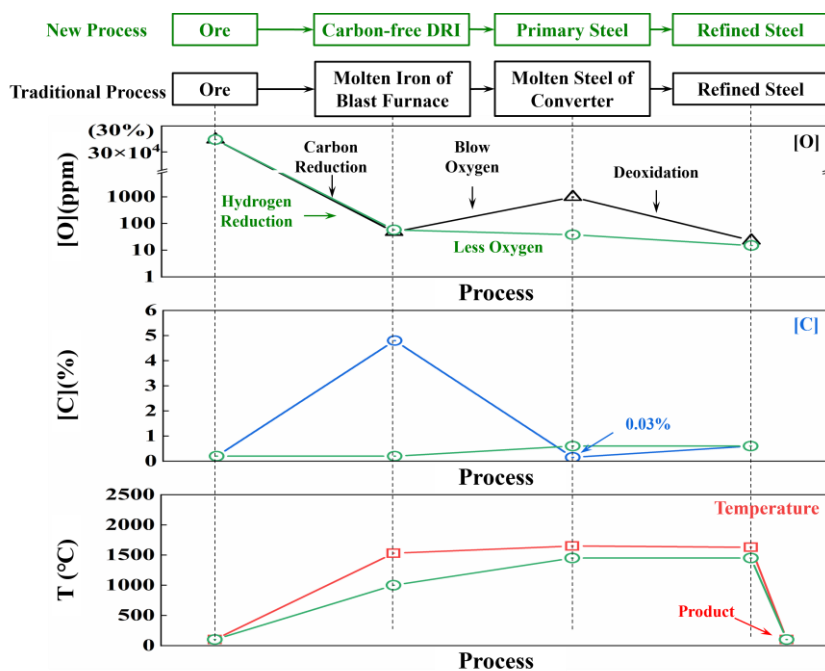


Fig. 19. Comparison of oxygen content, carbon content and temperature in the new process with the traditional blast furnace-converter long process.

The development of the above-mentioned innovative new processes is one of the important ways for China to accelerate the implementation of green development and upgrade the quality of steel products. Therefore, strongly develop the basic theoretical research of hydrogen metallurgy steelmaking, develop key equipment such as new green electric furnace (hydrogen plasma electric furnace) and pollution-free refining furnace (hydrogen plasma ladle refining furnace), and develop an innovative new steelmaking technology characterized by "hydrogen steelmaking" instead of "oxygen steelmaking". It will effectively solve important problems such as ecological environmental

pollution and unstable product quality in the steel industry, so as to promote the green, high-quality and sustainable development of the iron and steel industry.

6. Conclusion and prospect

"Hydrogen steelmaking" replacing the traditional "oxygen steelmaking" is an innovative theory and technology in the current steelmaking field, overcoming the theory and key technologies of hydrogen metallurgy steelmaking, and fully opening up a new generation of green near-zero carbon steel production process based on hydrogen metallurgy, which is an important means to promote the green, high-quality and sustainable development of China's iron and steel industry

and implement the goal of “double carbon” and “high-quality development”.

(1) Hydrogen plasma has the advantages of high temperature and high thermal conductivity, and can be used as an efficient heat source to achieve rapid melting of charge or precise temperature control of liquid steel, which has been preliminarily applied in steelmaking processes such as EAF, converter and tundish.

(2) The injection of hydrogen can promote the homogenization of the composition and temperature of the molten steel, and the hydrogen bubble can adhere to non-metallic inclusions during the floating process, and the “hydrogen” can also react with dissolved oxygen and sprayed oxygen to release a lot of heat, improving the thermodynamic and kinetic conditions of the molten pool reaction.

(3) “Hydrogen” can create a reducing atmosphere, which can inhibit the over-oxidation of liquid steel,

reduce the iron loss in the steelmaking process, and the loss of other metal elements such as Cr and Mn.

(4) “Hydrogen” can efficiently remove impurities such as O, C, N, S and P, especially hydrogen plasma, which can directly generate highly volatile gas products such as H₂O, CH₄, NH₃, H₂S and PH₃, to avoid the formation of non-metallic inclusions, and achieve “zero inclusions” of high cleanliness steelmaking, which is the development direction of future steelmaking technology.

(5) A new generation of green near-zero carbon steel production process based on hydrogen metallurgy is the key to accelerate the green, high-quality and sustainable development of China's iron and steel industry and the implementation of the goal of “double carbon” and “high-quality development”, and is currently a major issue in the field of iron and steel metallurgy.

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