China Steel Technical Report, No. 36, pp.6－10, (2023)

Theoretical Analysis and Technology Development of Dehydrogenation in Vacuum Degasser

HUI-JAN LIN*, KU-LING CHANG*, HAIPING SUN* and
CHING-HONG CHUNG**

**Iron & Steel Research & Development Department*
***Steelmaking Department*
China Steel Corporation

During the solidification process, the hydrogen contained in the high-temperature molten steel is likely to cause defects such as cracks and shrinkage cavities in the steel product. Therefore, when the hydrogen content in the steel is too high, hydrogen embrittlement occurs in the solidified steel, which reduces the mechanical properties of the steel. Therefore, in the production of high-grade steel, refining under vacuum was introduced to remove gas components such as nitrogen and hydrogen before casting the molten steel tapped from the converter. This is called vacuum degassing because the gas components in the molten steel are removed by reducing the balanced partial pressures when the molten steel is treated under reduced pressure.

A vacuum degassing analysis system has been developed for describing degassing phenomena in the vacuum degassing (VD) process. The effect of partial pressure in the vacuum degasser, process time, flow rate of stirring gas, effective surface area, and the composition of the steel on the removal rates of gaseous elements in steel during the VD process was investigated in this work. At the end of this work, it will be evaluated whether the VD process can be a good alternative to the vacuum degassing process in addition to the RH cycle degassing refining process

Keywords: Vacuum Degasser, Dehydrogenation, Steelmaking, Secondary Refining

1. INTRODUCTION

In the production of high-grade steel, refining under vacuum was introduced to remove gas components such as oxygen, nitrogen, and hydrogen before casting the molten steel tapped from the converter.(1-2) This is called vacuum degassing because the gas components in the molten steel are removed by reducing the balanced partial pressures when the molten steel is treated under reduced pressure. VD process is one of such processes used for removing oxygen, nitrogen, and hydrogen in molten steel to produce high-purity steel.(3) It is important to know the reaction mechanism in the VD process to ensure fast and thorough degassing of the steel.

Vacuum treatment is widely used in steel plants to reduce the hydrogen content in molten steel. Steel plates that require a dehydrogenation process are divided into UT/non-UT categories according to whether UT inspection is carried out later, and the [H] concentration of molten steel that requires UT inspection is low after the vacuum degassing process.(4) Therefore, starting from the principle of VD dehydrogenation technology, exploring its important influencing factors will have important research value for clarifying the vacuum degassing process.

2. RESEARCH METHOD

The steps of the vacuum degassing process are briefly described as follows: Steel is tapped from a converter into a ladle which is then loaded in a chamber after killing the steel. The chamber is connected to a vacuum system so that the pressure in the chamber can be reduced. Stirring gas of argon is blown into the steel from the bottom of the ladle to start the treatment of the steel under reduced pressure. The stirring gas forms numerous bubbles which are released from the top surface of the bath after rising through the steel. Stirred by the bubbles, a circulation flow in the bath is created. At the top surface, a portion of the slag layer is pushed to the side by the rising gas-metal plume that allows a part of the steel surface to be directly exposed to the gas under reduced pressure.(5) The degassing in a VD process is generally recognized to be achievable in two ways; one is the degassing by argon stirring bubbles injected into the steel from a ladle bottom and the other is the degassing at the free surface of steel in a ladle.(6)

Development of vacuum degassing analysis system: the system is developed by combining the sub-model of argon bubble-steel reaction in the molten pool and the sub-model of the molten steel reaction and dehydrogenation on the molten pool surface, and it is used to describe the degassing phenomenon of the VD process. The bubble model is used to calculate the reaction rate between the molten steel and the stirred argon gas bubbles in the molten pool; the surface model considers the surface dehydrogenation reaction at the exposed top surface of the molten pool.

The argon gas bubbles are injected from the bottom of the steel ladle, because the static pressure changes with the depth of molten steel during the floating process, when reaching the surface of the molten pool, the bubble radius will expand to about 18 times, and the volume expansion will be about 5000 to 6000 times. The amounts of these changes near the surface of the molten pool are more severe, as shown in Figure 1(a).

The "0s" line in Figure 1(b) shows that due to the high [H] content at the beginning of the VD treatment, the H_2 in the stirring bubbles increases faster during the bubbles ascent to the top of the molten pool, and the H_2 content in the bubbles arrives at the top surface at higher concentrations. When the processing time increased to 300s or 900s, the increase of H_2 in the bubbles became slower. In addition, as can be seen from Figure 1(c), the dehydrogenation reaction of the VD process is almost all carried out through the top surface of the molten pool.

3. RESULTS AND DISCUSSION

3.1 Pressure and Time Effects

According to Sieverts' Law, the solubility of diatomic gases in metals is proportional to the square root of the partial pressure of the gas according to thermodynamic equilibrium, that is to say, for dehydrogenation, the equilibrium [H] concentration in molten steel is proportional to $P_{H_2}{}^{1/2}$.(7) Thus, the driving force for transforming the gaseous elements in molten steel into gaseous products in gas can be increased by reducing the internal pressure of the gas. In addition, when the pressure in the chamber is low, the size of the stirring bubbles that reach the top surface of the molten steel pool will be further expanded, providing a larger surface area of the bubbles, and also providing a stronger stirring power to promote the reaction at the top surface of the molten steel pool. The change of hydrogen content with treatment time under various pressures in a VD process is shown in Figure 2(a). Since hydrogen is removed from

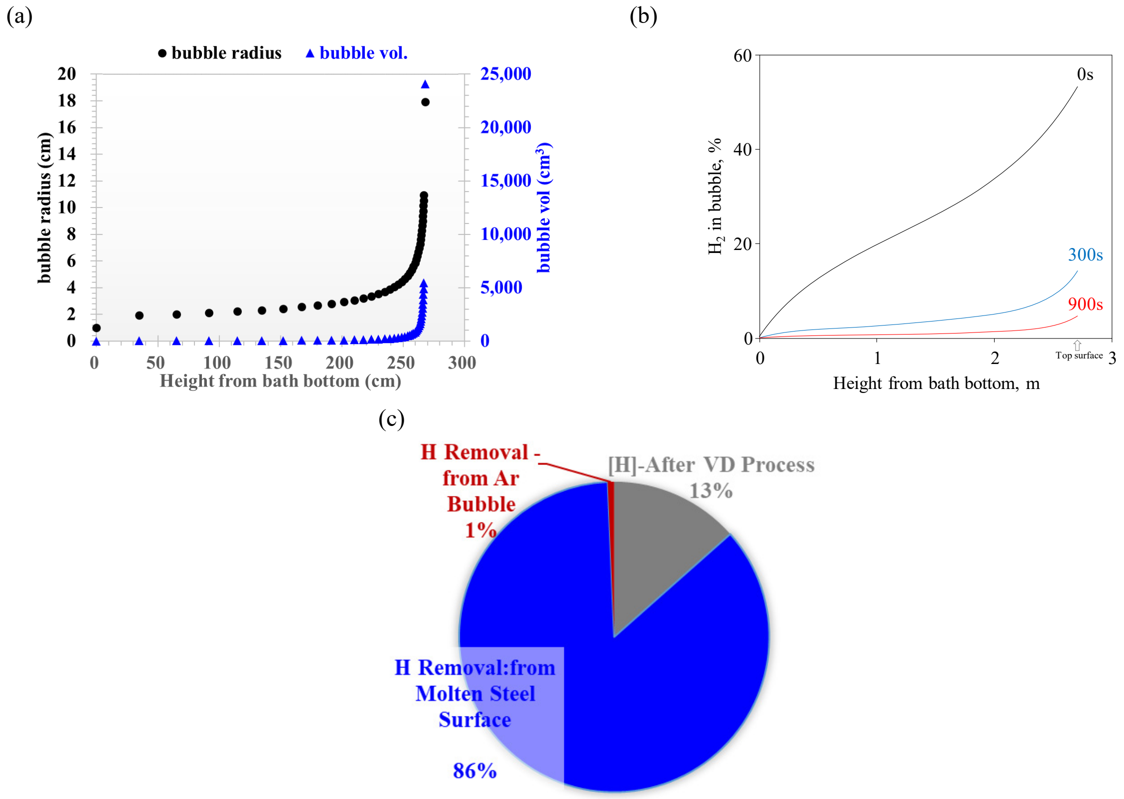

Fig.1. The rising process of the bottom stirring bubbles: (a) the change of radius and volume of the bubbles, (b) the change of hydrogen content in bubbles, and (c) the dehydrogenation mechanism and corresponding ratio in a VD.

the steel by the reaction of $2[H]=H_2$ at the gas-steel interface, hydrogen in the steel decreases under low-pressure conditions. The removal rate of hydrogen is faster when the pressure in the chamber is lower because the reduction of H_2 pressure enhances the reaction. In addition, the longer the ladle is kept in the medium-high vacuum, the [H] in the molten steel will gradually decrease, the industrial test results are shown in Figure 2(b).

3.2 Effect of Bottom Stirring Gas Flow

Increasing the flow rate of stirring argon gas may promote the removal rates of the gaseous elements from the steel in several ways. Firstly, the stirring power is increased by increasing the flow rate to promote the removal rates of the gaseous elements from the steel top surface by enhancing the mass transfer in the steel. Secondly, the number of the stirring gas bubbles is increased by increasing the flow rate which may increase the removal rates of the gaseous elements from the steel by the stirring gas bubbles. And lastly, the increase in the flow rate of stirring argon gas at the bath bottom means more argon is released from the top surface of the steel bath into the vacuum chamber. More argon entering the chamber brings more dilution of the gaseous products of the degassing reactions such as N_2 and H_2. The dilution reduces the partial pressures of N_2 and H_2 and therefore further promotes the removal rates of the gaseous elements from the steel top surface. The calculation and industrial test results of the changes of hydrogen content with treatment time in the VD process for various flowrates of stirring argon are shown in Figure 3(a) and (b), respectively. Hydrogen decreases with the treatment time and it decreases faster when the flow rate of stirring argon gas is higher.

3.3 Effect of Effective Surface Area

The slag, leftover from the BOF, may present at the top surface of the steel bath during the VD process; to cover the bath surface and to retard the degassing reaction. However, a portion of the slag layer at the bath surface is pushed to the side by the rising gas-metal plume that allows a part of the steel surface to be directly exposed to the gas under reduced pressure. The exposed surface is considered as the effective surface area for the

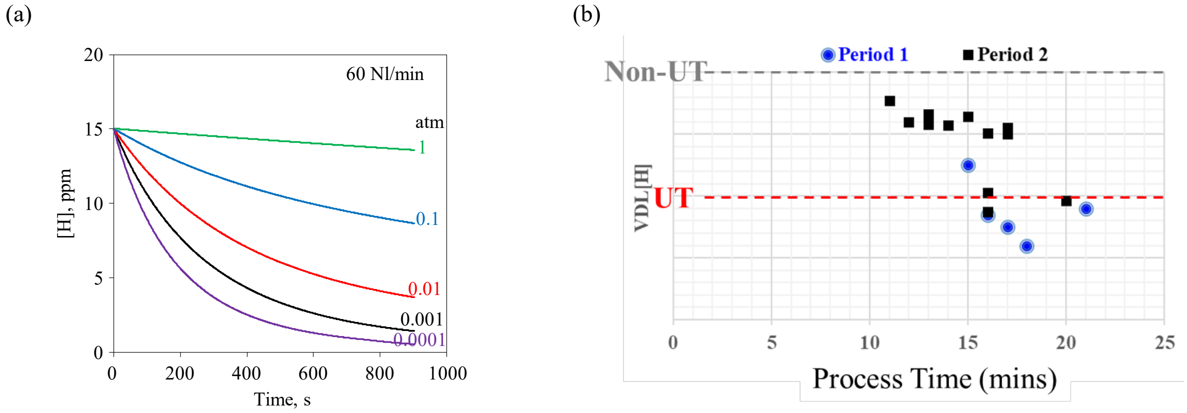

Fig.2. (a) The effect of vacuum chamber pressure on [H] with time; (b) the effect of dehydrogenation process time on VD[H].

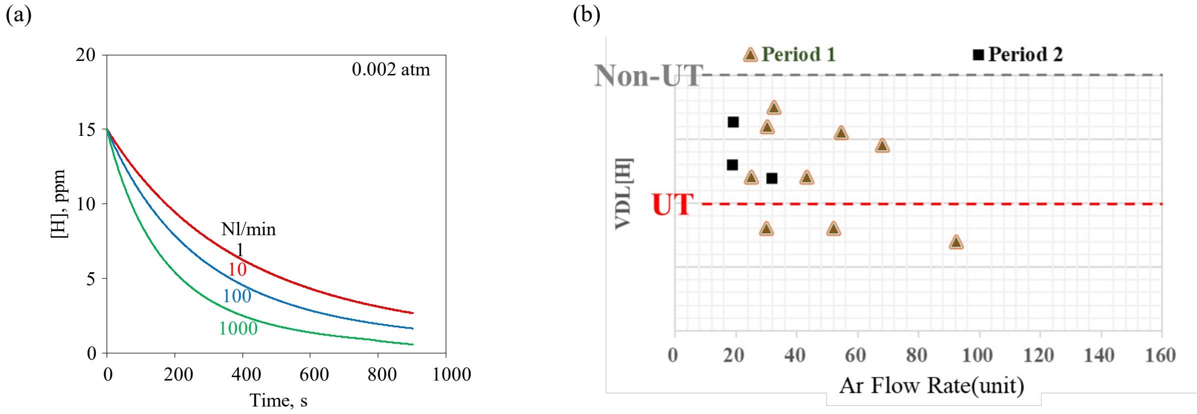

Fig.3. The influence of bottom stirring flow rate on (a) [H] change with time and (b) VD[H].

degassing reaction. The effect of the effective surface area on the removal rates of the gaseous elements in steel during the VD process was investigated by varying the fraction (A(%)), shown in Figure 4(a). The hydrogen removal rate increases with the increase of the effective surface area A (%); however, the increase of the hydrogen removal rate decreases gradually with the increase of A (%).

In the vacuum degassing station, a pinhole camera is used to photograph a local area of the molten steel surface and distinguish the slag and molten steel by adjusting the image contrast. And calculate the area ratio of exposed molten steel in each image. By calculating the ratio of the exposed molten steel area to the local area captured by the entire pinhole for the images detected in each time period, the results show that the exposed effective surface area of molten steel is less than 5% in nearly 90% of the images, shown in Figure 4(b); as a result, the [H] of the heat is high after the VD degassing process. Considering that the main mechanism of dehydrogenation is removing hydrogen through surface reaction, it is suggested that a slag raking step is required to remove the refining slag covering the surface of the molten pool to facilitate the dehydrogenation reaction.

3.4 Influence of Molten Steel Composition

The effect of the initial steel composition on the removal rates of hydrogen in steel during the VD process was investigated in this section. The activity of element H in molten steel can be calculated according to Henry's law, as shown in formula (1).$^{(7)}$

$$a_H = f_H \times [H] \quad\text{..}(1)$$

Among them, a_H is the activity of hydrogen in molten steel, f_H is the activity coefficient of hydrogen, and [H] is the hydrogen concentration in molten steel. The activity coefficient of element H in molten steel can be calculated from formula (2):

$$\log f_H = \sum_j e_H^j * [j] \quad\text{...}(2)$$

The interaction parameter e_H^j for H is shown in Table 1. Comparing the two steel types: SM570 and SN490C, the content of C and Si in SN490C is higher than that of SM570. According to the calculation, SN490C with higher [C] and higher [Si] can obtain a higher [H] activity coefficient, thus resulting in a lower [H] concentration in the molten steel, in other words, it will be easier to desorb hydrogen from such molten steel, and this tendency is confirmed by the industrial test results in Figure 5(a). Besides, in the SN490C steel with high manganese, it is found that VD[H] has a downward trend as the value of [C]+[Si]-[Mn] increases, that is, high [C], high [Si] and low [Mn] heat lead to easier dehydrogenation of molten steel as shown in Figure 4(b).4. conclusion

The vacuum degassing analysis system was applied to the VD process for the explanation and analysis of the vacuum degassing process and related thermodynamic reactions, and for understanding the degassing reaction. It is found that the degassing reaction mainly occurs on

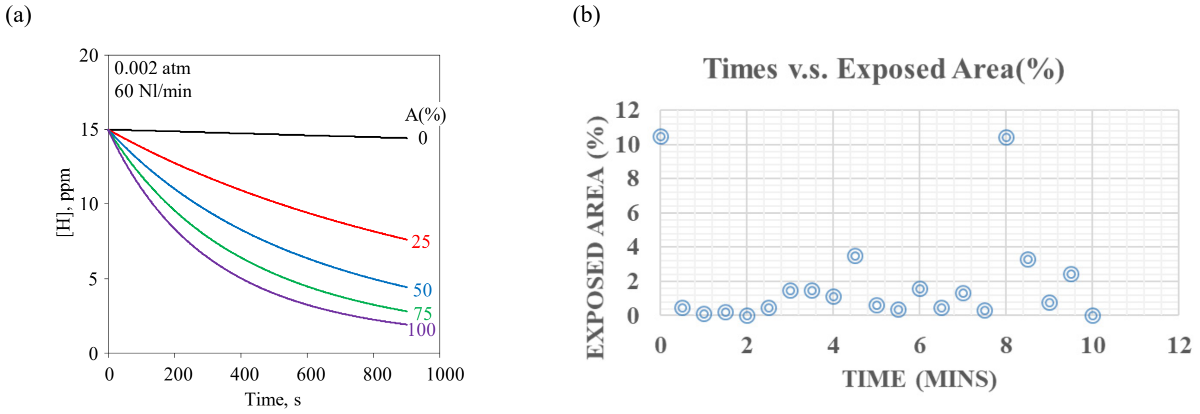

Fig.4. (a) Effect of a fraction of exposed area at the top surface (A%) on change of [H] with time in VD process, (b) the proportion of molten steel exposed area on the pinhole detection surface changes with time.

Table 1 Interaction parameters of hydrogen with major components in molten steel.

Component (j)	C	Si	Mn	P	S
e_H^j	0.06	0.027	-0.002	0.015	0.017

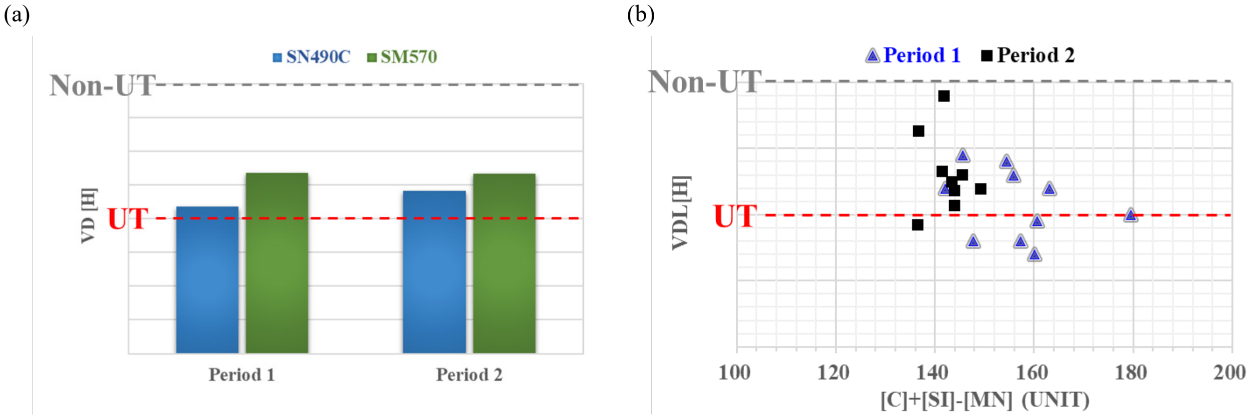

Fig.5. (a) Comparison of [H] of SN490C and SM570 after the VD process; (b) Effects of [C], [Si], and [Mn] of SN490C on the dehydrogenation process.

the surface of the molten pool, in comparison, the direct degassing of the stirring gas is not significant. In addition, the effects of vacuum pressure, stirring gas flow rate, effective surface area, and steel composition on VD dehydrogenation were also studied.

The industrial test results show that with the increase of the vacuum dehydrogenation process time and the increase of the flow rate of the bottom stirring gas, the removal rate of hydrogen can be promoted. In addition, the composition of molten steel with high carbon, high silicon, and low manganese will increase the activity coefficient of hydrogen in the molten steel, which is beneficial to the dehydrogenation reaction, so that the final [H] concentration will be decreased.

For non-UT inspection steel types that need to control [H], VD vacuum dehydrogenation technology can meet the concentration requirements of molten steel [H] after refining; for UT inspection steel types, under the control of appropriate process conditions, such as: the state of raking slag before entering the VD degassing process, the [H] concentration target after refining can also be achieved. Overall, the VD vacuum dehydrogenation technology can become another option for the vacuum degassing process besides the RH cycle degassing refining process.

REFERENCES

1. Tutarova, V. D., Shapovalov, A. N., & Kalitaev, A. N. (2017). Removal of hydrogen in the vacuum treatment of steel. Steel in Translation, 47, pp. 153-158.
2. Kor, G. J. W., & Glaws, P. C. (1998). Ladle refining and vacuum degassing. The Making, Shaping and Treating of Steel, 2, pp. 661-713.
3. Steneholm, K., Andersson, M., Tilliander, A., & Jönsson, P. G. (2013). Removal of hydrogen, nitrogen, and sulphur from tool steel during vacuum degassing. Ironmaking & Steelmaking, 40(3), pp. 199-205.
4. Yasuda, K., Ishikawa, N., Fujishiro, T., Hara, T., Tada, E., & Kimura, M. (2022). In Situ Investigation of Hydrogen-Induced Cracking Behavior in Linepipe Steel Under Different Environments. Corrosion, 78(11), pp. 1117-1125.
5. Kor, G. J. W., & Glaws, P. C. (1998). Ladle refining and vacuum degassing. The Making, Shaping and Treating of Steel, 2, pp. 661-713.
6. Kleimt, B., Köhle, S., Johann, K. P., Jungreithmeier, A., & Molinero, J. (2000). Dynamic process model for denitrogenation and dehydrogenation by vacuum degassing. Scandinavian journal of metallurgy, 29(5), pp. 194-205.
7. Ravichandar, D., Balusamy, T., Gobinath, R., & Balachandran, G. (2018). Behavior of Hydrogen in Industrial Scale Steel Melts. Transactions of the Indian Institute of Metals, 71(10), pp. 2505-2515.