Research Article

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Study on manganese volatilization behavior of Fe–Mn–C–Al twinning-induced plasticity steel

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Abstract: In the smelting process of high manganese steel, the volatilization of manganese will be accompanied. In this article, the volatilization of manganese in high manganese steel was studied by simultaneous thermal analyzer. The results show that the volatilization rate of manganese in high manganese steel increases with increasing temperature and holding time. It is proved by experimental study and data analysis that manganese volatilization follows the first-order kinetics model, and the empirical formula of manganese evaporation is derived. The volatile products of manganese were analyzed by scanning electron microscopy and X-ray photoelectron spectroscopy. It was found that the volatile components of manganese mainly consisted of MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 . Combined with thermodynamics, the mechanism of manganese volatilization is further analyzed, and two forms of manganese volatilization in high manganese steel are revealed. One is that manganese atoms on the surface of high manganese steel and oxygen atoms in the gas form different types of manganese oxides and then volatilize at high temperature. The other way is that Mn atoms vaporize into Mn vapor and evaporate in high temperature environment, and then are oxidized into different types of manganese oxides. The results of theoretical calculation and experiment show that manganese volatilization is mainly in the first form.

Keywords: high manganese steel, manganese volatilization, thermodynamics

1 Introduction

With the development of automotive steels toward lightweight, high strength, and high plasticity, high manganese steels have attracted wide attention. Twinning-induced plasticity (TWIP) steels can produce a lot of mechanical twinings in the grain after stretching [1–3]. The reason why TWIP steel can be used as an ideal type of automotive steel is because it can have high plasticity (60–95%) while maintaining ultrahigh strength (600–110 MPa) through TWIP effect [4–9]. Because of the unique mechanical properties of TWIP steel, high manganese steel has become not only the best choice for automotive steel, but also a hot material in aerospace, marine shipbuilding, petrochemical, and natural gas industries.

The Mn content in high manganese TWIP steels is usually about 20% [10,11]. TWIP steel is characterized by a high content of manganese, and a large amount of manganese will be added in smelting process. Therefore, there will be a lot of Mn volatilization in smelting process resulting in heavy Mn loss, which makes the smelting cost of high manganese steel increase greatly [12–14]. However, the volatile loss of Mn in smelting process will cause the instability of liquid steel composition, which will increase the difficulty of smelting manganese steel. At the same time, after solidification, the volatile Mn will pollute the furnace, affect the service life of refractories, and be harmful to the emission index after emission, causing potential safety hazards in the production of manganese steel [15–17]. Wang et al. [18] measured the solubility of Fe–Mn alloy at different temperatures and found that the solubility of carbon in steel decreased with the decrease of Mn content and temperature. Hong et al. [19] suggested that Mn is more volatile than P in ferromanganese melts. During the evaporation process of manganese, the evaporation rate of manganese will decrease

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because of the increase of carbon concentration. Chu and Bao [20] carried out experiments on the volatilization of manganese in alloy composition (high carbon ferromanganese alloy and ferrosilicon alloy) in vacuum and found that the higher the carbon content in the steel is, the lower the vapor pressure of manganese is, but the vapor pressure of manganese is not affected by silicon content. With the prolongation of vacuum smelting time, the content of Mn in steel decreases gradually, and the volatile Mn content increases. You et al. [13] found that the loss of Mn in steel is in the form of evaporation of oxidized slag and soot, with a loss rate of 5–25%, and Mn volatilization becomes significant with the increase of slag weight and slag alkalinity. When the slag basicity is 1.5, the volatilization of Mn can be greatly reduced. In the literature about manganese volatilization behavior of high manganese steel, the vast majority of the literature is in vacuum or decompression conditions for experimental research [21–24]. Therefore, it is very important to study manganese volatilization in high manganese steel under atmospheric pressure.

In the smelting process of high manganese steel, Mn volatilization directly affects the yield and composition control of Mn, which plays a key role in cost control and quality of manganese steel. Therefore, the volatilization behavior of Mn in high manganese steel was studied by differential scanning calorimetry-thermogravimetric analysis (DSC-TG). Manganese volatilization was characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The mechanism of Mn volatilization is explained in terms of saturated vapor pressure and evaporation rate. By deepening the understanding of manganese volatilization behavior in Fe–Mn–C–Al TWIP steel, it can provide theoretical guidance for the actual production of smelting TWIP steel and further save cost and improve the quality of steel.

2 Experimental

2.1 Experimental materials

A furnace of Fe–Mn–C–Al TWIP steel was prepared by vacuum induction heating furnace (vacuum degree: 10^{-2} MPa). The

main raw materials are pure iron bar (99.90%), silicon metal (99.99%), electrolytic manganese (99.90%), and aluminum metal (99.99%), and 20 kg melting material is prepared in proportion. In the smelting process, the screw pump is used to stir, and the liquid steel is poured into the mold for air cooling. The C and S elements in high manganese steel samples were determined by carbon–sulfur detector (Yanrui Instrument Co., Ltd, Chongqing, China), N and O elements by nitrogen–oxygen determinator (Yanrui Instrument Co., Ltd, Chongqing, China), and the other elements by X-ray fluorescence spectrometer (Shimadzu Enterprise Management (China) Co., Ltd, Shanghai, China). The chemical composition of TWIP steel obtained by smelting is shown in Table 1.

2.2 Preparation and process of experiment

The type of simultaneous thermal analyzer used in the experiment is NETZSCH STA 449F5 (Netzsch, Selb, Germany). Heat and mass changes of samples can be studied under exactly the same test conditions up to 1,600°C. Wherein the schematic of the experimental equipment is shown in Figure 1.

In high-temperature melting state, manganese element in high manganese steel is easy to escape from the melt. It is easy to pollute the instrument after the volatilization of manganese metal solidifies, which makes the thermocouple in the synchronous analyzer invalid and damages the equipment [11]. To reduce the equipment damage caused by manganese volatilization, a tantalum sheet crucible cover was added to the alumina crucible to absorb the oxygen inside the crucible and absorb the volatilized metal manganese.

To ensure the uniformity of multiple experiments, the spare samples were cut into cuboids measuring 2.0 mm × 2.0 mm × 1.0 mm. The sample weight was controlled at (21 ± 3) mg, and the sample was polished and stored in antirust solution. The sample was cleaned with acetone and dried with absorbent filter paper before the thermogravimetric experiment, and then the samples were cleaned with alcohol and dried by absorbent filter paper. This cleaning operation was repeated three times. In thermogravimetric experiment, the alumina crucible (lid + tantalum) was placed on the sample table. After the reading

Table 1: Chemical composition of TWIP steel (wt%)

Mn	Al	Si	C	S	N	O	Fe
23.7571	3.5383	0.0957	0.3834	0.0088	0.0056	0.0046	Bal.

Figure 1: Schematic of experimental equipment.

will be zero, put the dried sample into the crucible, read the TG signal column mass recorded as W_1 . To ensure the purity of inert gas in the furnace, the furnace is evacuated and then filled with argon. This operation is repeated three times. In the thermal gravimetric process, the purging gas flow rate is $60 \text{ mL} \cdot \text{min}^{-1}$, and the protecting gas velocity is $40 \text{ mL} \cdot \text{min}^{-1}$. After the end of the thermo gravimetry, read the TG signal column again to write W_2 . The mass changes of W_1 and W_2 recorded before and after showed the volatilization of manganese.

3 Results and discussion

3.1 Effect of temperature on manganese volatilization

The liquidus temperature of steel was calculated by ThermoCalc thermodynamic software (database TCFE7, Stockholm, Sweden) to be $1,407^\circ\text{C}$. The volatilization rate of manganese in the melt is expressed as equation (1).

$$[E_{\text{Mn}}]_t = \frac{[W_{\text{Mn}}]_0 - [W_{\text{Mn}}]_t}{[W_{\text{Mn}}]_0} \times 100\% = \left(1 - \frac{[W_{\text{Mn}}]_t}{[W_{\text{Mn}}]_0}\right) \times 100\%, \quad (1)$$

wherein $[E_{\text{Mn}}]_t$ represents the volatilization rate of Mn element in the steel at time t , $[W_{\text{Mn}}]_0$ denotes the mass of the initial sample in kg, and $[W_{\text{Mn}}]_t$ denotes the mass of the sample in kg at time t .

High manganese steel was taken as the experimental object, and the temperature was raised from room temperature to 40, 80, and 120°C higher than liquidus at the heating velocity of $10^\circ\text{C} \cdot \text{min}^{-1}$. Heat preservation for 1 min and then end cooling. The cooling mode is furnace cooling. Record the quality change of steel sample before and after treatment, as shown in Table 2.

Table 2 shows the liquidus temperatures of 40, 80, and 120°C . The difference in mass before and after thermogravimetry was 0.2291, 0.3436, and 0.9524 mg. The volatilization rates were 0.93, 1.51, and 4.50%, respectively. With the hoist of temperature, the volatilization rate of high manganese steel increases.

3.2 Effect of holding time on manganese volatilization

The sample was heated from room temperature to 30°C above liquidus at a heating velocity of $10^\circ\text{C} \cdot \text{min}^{-1}$. The heat preservation time of three times was 3, 5, and 10 min, and then the temperature was lowered. The cooling method is natural cooling. The change of steel sample quality before and after recording is shown in Table 3.

As can be seen from Table 3, the holding time is 3, 5, and 10 min. The difference in mass before and after heat weight was 0.3651, 0.5593, and 0.7278 mg, respectively. The volatilization rates were 1.69, 2.61, and 4.63%, respectively. At high temperature, the volatilization rate of high manganese steel increases with the extension of holding time.

Assuming that the evaporation of solute element Mn represents a reaction of first order with respect to Mn, the evaporation rate is expressed by equation (2).

$$\ln \frac{[\text{Mn}]_t}{[\text{Mn}]_0} = -k_{\text{Mn}} \cdot \frac{S}{V} \cdot t, \quad (2)$$

Table 2: Variation of steel sample quality at different temperatures

Above liquidus temperature ($^\circ\text{C}$)	Quality of steel sample before heat weight W_1 (mg)	Quality of steel sample after heat weight W_2 (mg)	Volatilization rate (%)
40	24.5909	24.3618	0.93
80	22.7709	22.4273	1.51
120	21.1529	20.2005	4.50

Table 3: Variation of sample quality under different heat preservation times

Holding time (min)	Quality of steel sample before heat weight W_1 (mg)	Quality of steel sample after heat weight W_2 (mg)	Volatilization rate (%)
3	21.5764	21.2113	1.69
5	21.4360	20.8767	2.61
10	20.8761	19.9101	4.63

wherein k_{Mn} represents the apparent evaporation rate constant ($\text{m}\cdot\text{s}^{-1}$), S represents the free surface area (m^2) of the melt exposed to the gas, V represents the melt volume (m^3), and t represents the processing time (s). According to the eq. (2), the relation curves of $\ln([\text{Mn}]_t/[\text{Mn}]_0)$ and $(S/V) \cdot t$ in high manganese steel melt are drawn, as shown in Figure 2. It can be seen from Figure 2 that the ratio of $\ln([\text{Mn}]_t/[\text{Mn}]_0)$ to $(S/V) \cdot t$ is a straight line. This confirms that under the present experimental conditions, the evaporation of Mn element in high manganese steel at high temperature can be expressed by first-order kinetics. Thus, the evaporation rate of manganese is expressed by the first-order evaporation rate constant k_{Mn} , which is determined by the slope of the function $\ln([\text{Mn}]_t/[\text{Mn}]_0)$ with respect to $(S/V) \cdot t$.

Figure 3 shows the correlation between temperature and rate constant. From Figure 3, it can be seen that the rate constant of manganese evaporation in the melt increases with increasing temperature.

The volatilization rate of Mn in molten steel increases with increasing temperature. These findings are shown in Figure 4, which shows a graph of $\ln(k_{\text{Mn}})$ versus the reciprocal $1/T$ of temperature. There are different activation energy values under different temperature conditions. Through the regression analysis of the experimental data, it is proved that the dependence of evaporation rate on melt

temperature can be expressed by Arrhenius equation, as shown in equation (3).

$$\ln k_{\text{Mn}} = -\frac{E_{\text{Mn}}}{RT} + C_1, \quad (3)$$

where E_{Mn} represents the apparent activation energy of evaporation of solute element Mn ($\text{J}\cdot\text{mol}^{-1}$), R is the gas constant $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and C_1 is the temperature independent constant ($\text{m}\cdot\text{s}^{-1}$). The apparent activation energy of solute Mn evaporation is obtained from the slope of $\ln k_{\text{Mn}}$ to $1/T$, as shown in Figure 4. Under the experimental conditions, the value of E_{Mn} is $513.69 \text{ kJ}\cdot\text{mol}^{-1}$.

In conclusion, the volatilization of Mn in high manganese steel will be affected by temperature when the pressure and specific surface area are determined. Therefore, the relationship between the rate constant of Mn volatilization and temperature in high manganese steel is expressed as equation (4).

$$k_{\text{Mn}} = B \cdot e^{C \cdot T} \quad (4)$$

where B is the proportional coefficient and C is the constant of the experimental parameters. In this experiment, $B = 2.86889 \times 10^{-26} (\text{m}\cdot\text{s}^{-1} \cdot \text{K}^{-1})$ and $C = 0.02424$ were selected by multiple regression analysis. The relationship between the volatilization rate constant and temperature of Mn element is expressed as equation (5).

Figure 2: The relationship between $\ln([\text{Mn}]_t/[\text{Mn}]_0)$ and $(S/V) \cdot t$ in high manganese steel melt. **Figure 3:** Variation of manganese volatilization rate constant at different temperatures.

Figure 4: Relationship between $\ln(K_{Mn})$ and $1/T$.

$$k_{Mn} = 2.86889 \times 10^{-26} \cdot e^{0.02424T} \quad (5)$$

Combined with equations (1), (2), and (5), the empirical formula of manganese volatilization can be arranged into equation (6).

$$\ln(1 - [E_{Mn}]_t \cdot 100\%) = -8.60667 \times 10^{-23} \cdot e^{0.02424T} \cdot t, \quad (6)$$

By comparing the manganese volatilization rate in the experiment with the manganese volatilization rate calculated by the empirical formula, the comparison results are shown in Figure 5. It can be seen from Figure 5 that the calculated results are in good agreement with the experimental results.

3.3 Thermodynamics of manganese volatilization

The reason why metal elements can volatilize from molten steel is that the saturated vapor pressure of metal elements

Figure 5: Comparison between the volatilization rate of manganese in experiment and that obtained by calculation.

is too high in a specific temperature range. The higher the saturated vapor pressure of the element, the easier the element will volatilize from the matrix. The equation for the formation of manganese vapor in manganese steel in the molten state is the equation (7), the equilibrium constant of reaction is equation (8) and the standard Gibbs free energy is expressed as equation (9) [25].

$$K = \frac{Mn_g}{Mn_l} = \frac{P_{Mn}^0}{\alpha_{Mn}}, \quad (8)$$

$$\Delta G_{Mn}^\theta = 241,780 - 104.46T = -RT \ln K, \quad (9)$$

wherein Mn_l is manganese in the iron matrix, Mn_g is volatile manganese vapor, K is equilibrium constant and P_{Mn}^0 is equilibrium vapor pressure of manganese in units: Pa, α_{Mn} is the activity of manganese in liquid steel, T is the absolute temperature (K), and R is the constant $8.314 \text{ Pa}\cdot\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. By means of equations (7)–(9), the expression of the equilibrium vapor pressure of manganese related to the activity of manganese in liquid steel and the temperature can be obtained, as shown in equation (10).

$$P_{Mn}^\theta = 101,325 \times \alpha_{Mn} \times e^{\frac{241,780 - 104.46T}{-8.314T}}, \quad (10)$$

When Wagner model is used to solve the thermodynamic calculation problems in steel, the general interaction coefficient is often used in the calculation process for general low alloy, but it is not suitable for high manganese steel with high manganese and high aluminum characteristics. Therefore, the interaction coefficient which is most suitable for high manganese steel will be used to calculate the activity of high manganese steel.

$$\log_{10}\alpha_{Mn} = \log_{10}f_{Mn} + \log_{10}[\% Mn], \quad (11)$$

$$\log_{10}f_{Mn} = \sum e_{Mn}^j [\% j], \quad (12)$$

where α_{Mn} indicates the activity of Mn element in the steel; f_{Mn} denotes the activity coefficient of Mn element

Table 4: Interaction coefficients applicable to high manganese steel

Interaction coefficients	Numerical value	References
e_{Mn}^N	$-59.6(\pm 2.87)/T + 0.011(\pm 0.0015)$	[26]
e_{Mn}^{Al}	0	[27]
e_{Mn}^C	$6631.83/T - 5.7995$	[28]
e_{Mn}^{Si}	0	—
e_{Mn}^S	-0.048	[20]
e_{Mn}^{Mn}	0	—
e_{Mn}^O	-0.037	[29]

Figure 6: Effect of temperature on the vapor pressure and evaporation rate of manganese.

in steel; [% Mn] denotes the concentration of Mn in the steel; [% j] represents the concentration of elements in steel; and e_{Mn}^j represents the coefficient of primary interaction of Mn in steel with elements in the steel. The interaction coefficients of elements in high manganese steel are listed in Table 4.

According to equations (6)–(12), the temperature effects on the volatilization rate of manganese in high manganese steel solution and the saturation vapor pressure of manganese can be graphed as shown in Figure 6.

As can be seen from Figure 6, with increasing temperature, the vapor pressure of manganese element in steel augment and the evaporation rate of manganese aggrandize. This is in line with the experimental data.

3.4 Characterization of manganese volatiles

Figure 7 is a picture of alumina crucible (with tantalum plate) before and after thermo gravimetry. The comparison

of Figure 7(a) and (b) shows that in the experiment after adding tantalum, the volatile manganese component adhered to the tantalum sheet, thus reducing the contamination of the crucible by the volatilized manganese component.

The morphology of manganese volatiles attached to tantalum sheets was observed by Zeiss-Ultra 55 field-emission scanning electron microscope (Zeiss, Oberkochen, Germany), as shown in Figure 8. According to the surface scanning graph in Figure 8(a) and linear scanning graph of Figure 8(b), it can be obtained that manganese volatiles contain manganese and oxygen elements.

XPS technique was used to further study the chemical states of surface elements and elements of manganese volatiles on tantalum tablets. The measurement spectrum of the sample contains signals of manganese element and oxygen element in the manganese volatile component, as shown in Figure 9(a). Figure 9(b) and (c) shows high-resolution XPS spectra of Mn 2p and O 1s. Figure 9(b) provides a data fit corresponding to an area of Mn 2p. According to references [30,31], the peaks with binding energies of 640.7 and 650.8 eV are attributed to Mn 2p_{3/2} and Mn 2p_{1/2} of Mn₂O₃ (Mn³⁺); the peaks with binding energies of 641.7 and 651.9 eV are attributed to Mn 2p_{3/2} and Mn 2p_{1/2} of Mn₃O₄ (Mn^{2+,3+}); the peaks with binding energies of 641.9 and 653.08 eV are attributed to Mn 2p_{3/2} and Mn 2p_{1/2} of MnO₂ (Mn⁴⁺); and the peaks with binding energies of 643.1 and 647.6 eV are attributed to Mn 2p_{3/2} and Mn 2p_{1/2} of MnO (Mn²⁺).

According to an earlier study [32], the peak with binding energy of 530.8 eV in Figure 9(c) is attributed to the O 1s of metal oxides Mn₃O₄, MnO, Mn₂O₃, and MnO₂ (O²⁻). The oxygen peak at the binding energy of 532.3 eV reflects the oxygen vacancy. The peak at the binding energy 533.6 eV reflects the presence of weakly bound oxygen on the surface of the manganese volatile component films, which has been shown to be carboxyl

Figure 7: Picture of aluminum oxide crucible before and after thermo gravimetry: (a) before thermo gravimetry and (b) after thermo gravimetry.

Figure 8: Picture of manganese volatiles by scanning electron microscope: (a) surface scanning graph and (b) linear scanning graph.

Figure 9: XPS spectra of manganese volatiles. (a) Survey spectra, (b) Mn 2p spectrum, and (c) O 1s spectrum.

or adsorptive oxygen [33,34]. Therefore, the volatile products of manganese are mainly Mn_3O_4 , Mn_2O_3 , MnO , and MnO_2 .

3.5 Manganese volatilization mechanism

The volatile components of manganese in high manganese steel were analyzed by SEM and XPS. Manganese volatilization is mainly composed of Mn_3O_4 , Mn_2O_3 , MnO , and MnO_2 , which indicates that the volatilization of manganese is affected by oxygen content. You et al. [13] found the oxidation of manganese and the loss of manganese in refining under the oxygenation conditions of high carbon ferromanganese, and put forward the empirical formula of manganese loss, as shown in equations (13) and (14). The empirical formula shows that the volatilization rate of manganese at high temperature is directly related to the oxygen content, which is consistent with the experimental results.

$$\frac{(W_{\text{Mn}})_{\text{evap}}}{W_{\text{metal}}} = \beta \times \sum_i^n \left\{ \frac{P_{(\text{Mn})_i}}{\sqrt{T_i}} \times (t_{(i+1)} - t_{(i)}) \right\}, \quad (13)$$

$$\beta = 10^{4.776} \times \frac{\left(\frac{Q_{\text{O}_2(B)}}{Q_{\text{O}_2(B)} + Q_{\text{intert}(B)}} \right)^{2.604} \times \left(\frac{Q_{\text{O}_2(T)}}{Q_{\text{O}_2(T)} + Q_{\text{O}_2(B)}} \right)^{1.811}}{[\% \text{ C}]^{0.608}}, \quad (14)$$

where $(W_{\text{Mn}})_{\text{evap}}$ is an amount of manganese loss in units of kg; W_{metal} is the amount of the melt in kg; i is the order of sampling, $t_{(i+1)} - t_{(i)}$ is the time interval between samples in min; $P_{(\text{Mn})}$ is the vapor pressure of manganese in atm; β is the vaporization coefficient, Q_{O_2} and Q_{inter} represent the velocity of oxygen and inert gas in $\text{m}^3 \cdot \text{min}^{-1}$; T and B represent top blowing and bottom blowing, respectively; and $[\% \text{ C}]$ represents the carbon content in the melt.

To elucidate the mechanism of manganese volatilization, the Gibbs free energies of different manganese oxides are listed in Table 5 [35]. Gibbs free energies of

Table 5: Gibbs free energies of different manganese oxides

Manganese oxide reaction formula	Gibbs free energy reaction formula $[\Delta G]$, ($\text{J} \cdot \text{mol}^{-1}$)
$\text{Mn}_{(\text{s})} = \text{Mn}_{(\text{g})}$	$253,914 - 111.91T + RT \lg P_{\text{Mn}}$
$2\text{Mn}_{(\text{s})} + \text{O}_{2(\text{g})} = 2\text{MnO}_{(\text{s})}$	$-777,720 + 152.84T - RT \lg P_{\text{O}_2}$
$\frac{3}{2}\text{Mn}_{(\text{s})} + \text{O}_{2(\text{g})} = \frac{1}{2}\text{Mn}_3\text{O}_{4(\text{s})}$	$-699396.5 + 173.13T - RT \lg P_{\text{O}_2}$
$\frac{4}{3}\text{Mn}_{(\text{s})} + \text{O}_{2(\text{g})} = \frac{2}{3}\text{Mn}_2\text{O}_{3(\text{s})}$	$-645060.45 + 172.61T - RT \lg P_{\text{O}_2}$
$\text{Mn}_{(\text{s})} + \text{O}_{2(\text{g})} = \text{MnO}_{2(\text{s})}$	$-518,816 + 181T - RT \lg P_{\text{O}_2}$

Figure 10: Gibbs free energy of different manganese oxides at different temperatures.

different manganese oxides at different temperatures are shown in Figure 10.

As can be seen from Figure 10, it is very difficult for solid metal manganese to evaporate directly into manganese vapor at high temperatures. Manganese reacts with oxygen to form different oxidation products, including Mn_3O_4 , MnO , etc. As can be seen from Figure 10, the degree of formation of these manganese oxides from easy to difficult is MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 . Under the same conditions, the volatilization of high manganese steel is mainly the oxidation products of Mn_3O_4 , Mn_2O_3 , MnO , and MnO_2 , which is confirmed by experiments.

Figure 11: Schematic of manganese volatilization in high manganese steel.

The mechanism of manganese volatilization in high manganese steel can be inferred from the above results, as shown in Figure 11. The process of manganese volatilization in crucible can be divided into solid layer, interfacial reaction layer, and gas layer. Manganese volatilization in high manganese steels can be divided into two types: the first is that the metal Mn atoms on the metal surface react with the oxygen atoms in the gas at the reaction interface layer to produce different manganese oxides. The reaction process is shown in Process 1 in Figure 11. This process can be seen easily from the Gibbs free energy shown in Figure 10. Then under the action of high temperature, the manganese oxides in the reaction interface will continuously evaporate to the gas layer and finally condense on the crucible lid. The second form of manganese volatilization is that the metal Mn on the surface of the high manganese steel passes directly through the reaction layer and volatilizes directly into the gas layer under the action of high temperature. The reaction process is shown in Process 2 in Figure 11. As can be seen from Figure 10, this form of manganese volatilization is very difficult and very small. In this form, the volatilized manganese vapor can easily react with oxygen to form different manganese oxides after reaching the gas layer, so it is difficult to detect elemental manganese in the volatile components of manganese. To sum up, in the two forms of manganese volatilization, the majority of the manganese volatile forms in high manganese steel is in the form of manganese oxides.

4 Conclusions

(1) The volatilization behavior of manganese in high manganese steel was studied by using synchronous thermal analyzer. It was found that the quality difference and the rate of volatilization increased with the increase of temperature and holding time. The volatilization of manganese follows the first-order kinetics, and an empirical formula for the evaporation rate of manganese in high manganese steel is derived under the experimental conditions. The measured values are in good agreement with the calculated values.

(2) The morphology of manganese volatiles was characterized by SEM. It was found that manganese volatile components contained manganese and oxygen elements by surface scanning and line scanning. XPS was used to further characterize the volatiles of manganese. The main components of manganese volatiles were MnO , Mn_3O_4 , Mn_2O_3 , and MnO_2 .

(3) There are two mechanisms of manganese volatilization in high manganese steel. The first is that the metal Mn atoms on the metal surface react with the oxygen atoms in the gas to form different manganese oxides at the interface layer, and then the manganese oxides volatilize at high temperature. The second is that the metal Mn on the surface of high manganese steel volatilizes directly in the gas layer under the action of high temperature, and then the manganese vapor in the gas is oxidized into different manganese oxides. According to theoretical calculation and experimental results, the mechanism of manganese volatilization is the first form.

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