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XUDONG GAO[1*], XIN LI[2]

ANALYSIS OF GAS UTILIZATION RATE OF VANADIUM TITANIUM MAGNETITE REDUCED BY CH_4-H_2-CO MIXED GAS IN BLAST FURNACE

Gas utilization rate is a very important production parameter in the ironmaking blast furnace (BF), which can effectively reflect the utilization of fuel chemical energy. While hydrogen rich gas (such as shale gas) was injected into BF, with the introduction of CH_4 in the hydrogen rich gas, the traditional calculation formula for the utilization rate of binary mixed gas (H_2-CO) was no longer suitable for the calculation of the utilization rate of ternary mixed gas (CH_4-H_2-CO). Based on the principle of oxygen migration in the gas-solid reduction reaction, this paper established and derived the method for calculating the utilization rate of mixed gas after methane-rich gas was injected into BF (the mixed gas changes from H_2-CO type to CH_4-H_2-CO type), it is helpful to analyze the influence of CH_4 introduction in hydrogen rich gas on the utilization rate of mixed gas in reduction reaction after injecting hydrogen rich gas. In this paper, the change of gas utilization rates and physical phases of 0.5 mol Fe_2O_3, 0.5 mol V_2O_5 and 1 mol TiO_2 reduced by different amounts of H_2-CO or CH_4-H_2-CO at 700°C, 850°C and 1000°C were studied respectively, some meaningful results were obtained through comparative analysis, which provides a theoretical basis for methane rich gas injection practice of vanadium titanium magnetite blast furnace (VTM-BF).

Keywords: CH_4-H_2-CO mixed gas; Reduction reaction; Gas utilization rate; Vanadium titanium magnetite

1. Introduction

With the increasingly stringent restrictions on carbon emissions in various countries, hydrogen metallurgy has been regarded as an important development direction of ironmaking and steelmaking [1-4]. As the main carbon emission source in iron and steel smelting, the carbon emission of blast furnace ironmaking accounts for more than 60% of the entire iron and steel smelting process [5-9]. Compared with convention blast furnace, VTM-BF has higher fuel ratio and more prominent carbon emission problems [10-11]. At present, the principal method for comprehensive utilization of VTM is still BF [12-13]. Therefore, this paper mainly studies the reduction of iron, vanadium and titanium oxides in VTM after hydrogen rich gas was injected into VTM -BF, and mainly analyzes the impact of the introduction of CH_4 and H_2 in hydrogen rich gas on the utilization rate of BF gas. Utilization rate of BF gas was affected by the theoretical coal gas utilization rate (thermodynamic factor), also by the BF operation technology (dynamic factor, such as controlling the center and edge gas flows, which can change the gas residence time in the furnace and improve the BF gas chemical energy utilization rate) [14-18]. From the thermodynamic point, this paper analyzes the changes of theoretical gas utilization rate of iron, vanadium and titanium oxide reduction process which affected by the introduction of CH_4 and H_2 in hydrogen rich gas, it provides reference for the injection of hydrogen rich gas into VTM-BF.

2. Proposal and Derivation of General Formula for Utilization Rate of Mixed Gas

With the introduction of CH_4 in hydrogen gas, the reduction reactions become more complex, and the traditional calculation method of gas utilization rate was no longer suitable for calculating the utilization rate of mixed gas containing CH_4.

The traditional calculation formulas for the utilization rate of monadic gas (H_2 or CO) are as follows [19]:

$$\eta_{CO} = \frac{\varphi_{CO_2}}{\varphi_{CO} + \varphi_{CO_2}} \tag{1}$$

$$\eta_{H_2} = \frac{\varphi_{H_2O}}{\varphi_{H_2} + \varphi_{H_2O}} \tag{2}$$

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[1] CHONGQING UNIVERSITY OF SCIENCE AND TECHNOLOGY, SCHOOL OF METALLURGY AND MATERIALS ENGINEERING, CHONGQING, 401331, PR, CHINA
[2] IRONMAKING DIVISION, INSTITUTION OF CISDI GROUP CO., LTD, CHONGQING, 401122, PR, CHINA

* Corresponding author: gxd@cqust.edu.cn

The traditional calculation formula for the utilization rate of binary gas H_2-CO is as follows [20]:

$$\eta_{H_2-CO} = \frac{\varphi_{CO_2} + \varphi_{H_2O}}{\varphi_{CO} + \varphi_{CO_2} + \varphi_{H_2} + \varphi_{H_2O}} \tag{3}$$

In the form, φ_{CO}, φ_{H_2}, φ_{CO_2}, φ_{H_2O} are the amount fractions of CO, H_2, CO_2 and H_2O in the mixed gas after reduction reaction, respectively.

On the basis of existing utilization rate of monadic gas (H_2 or CO) and binary gas H_2-CO, the influence of CH_4 introduced into hydrogen rich gas on the utilization ratio of mixed gas was studied. According to the law of oxygen balance in the reaction, the mathematical expression of ternary mixed gas utilization rate is obtained as follows:

$$\eta_{CH_4-H_2-CO} = \frac{n_{H_2O} + n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{H_2} + n^0_{CO} + 4n^0_{CH_4}} \tag{4}$$

In the form, n^0_{CO}, $n^0_{H_2}$ and $n^0_{CH_4}$ are the amounts of CO, H_2 and CH_4 before reduction reaction, respectively, n_{CO}, n_{CO_2}, and n_{H_2O} are the amounts of CO, CO_2 and H_2O after reduction reaction, respectively.

The formula for calculating the utilization rate of monadic gas (CO) is derived from the calculation formula for the utilization rate of ternary gas (CH_4-H_2-CO) as follows:

$$\begin{aligned}
&\eta_{CH_4-H_2-CO} = \\
&\frac{n_{H_2O} + n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{H_2} + n^0_{CO} + 4n^0_{CH_4}} \xrightarrow{n^0_{H_2}=0 \text{ and } n^0_{CH_4}=0} \eta_{CO} = \\
&\frac{n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{CO}} \xrightarrow{n^0_{CO}=n_{CO}+n_{CO_2}} \eta_{CO} = \\
&\frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \longrightarrow \eta_{CO} = \frac{\varphi_{CO_2}}{\varphi_{CO} + \varphi_{CO_2}}
\end{aligned} \tag{5}$$

The formula for calculating the utilization rate of binary gas (H_2) is derived from the calculation formula for the utilization rate of ternary gas (CH_4-H_2-CO) as follows:

$$\begin{aligned}
&\eta_{CH_4-H_2-CO} = \\
&\frac{n_{H_2O} + n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{H_2} + n^0_{CO} + 4n^0_{CH_4}} \xrightarrow{n^0_{CH_4}=0 \text{ and } n^0_{CO}=0} \eta_{H_2} = \\
&\frac{n_{H_2O}}{n^0_{H_2}} \xrightarrow{n^0_{H_2}=n_{H_2O}+n_{H_2}} \eta_{H_2} = \frac{n_{H_2O}}{n_{H_2O} + n_{H_2}} \longrightarrow \eta_{H_2} = \\
&\frac{\varphi_{H_2O}}{\varphi_{H_2O} + \varphi_{H_2}}
\end{aligned} \tag{6}$$

The formula for calculating the utilization rate of monadic gas (H_2-CO) is derived from the calculation formula for the utilization rate of ternary gas (CH_4-H_2-CO) as follows:

$$\begin{aligned}
&\eta_{CH_4-H_2-CO} = \\
&\frac{n_{H_2O} + n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{H_2} + n^0_{CO} + 4n^0_{CH_4}} \xrightarrow{n^0_{CH_4}=0} \eta_{H_2-CO} = \\
&\frac{n_{H_2O} + n_{CO} + 2n_{CO_2} - n^0_{CO}}{n^0_{H_2} + n^0_{CO}} \xrightarrow[n^0_{CO}=n_{CO}+n_{CO_2}]{n^0_{H_2}=n_{H_2O}+n_{H_2}} \eta_{H_2-CO} = \\
&\frac{n_{H_2O} + n_{CO_2}}{n_{H_2O} + n_{H_2} + n_{CO} + n_{CO_2}} \rightarrow \eta_{H_2-CO} = \\
&\frac{\varphi_{H_2O} + \varphi_{CO_2}}{\varphi_{H_2O} + \varphi_{H_2} + \varphi_{CO} + \varphi_{CO_2}}
\end{aligned} \tag{7}$$

It can be seen that formula (4) is not only suitable for calculating the utilization rate of monadic gas (H_2 or CO) and binary gas (H_2-CO), but also suitable for calculating the utilization rate of ternary gas (CH_4-H_2-CO). So, formula (4) can be used as a general formula for calculating the utilization rate of mixed gas. The establishment of the general formula is helpful to analyze the influence of CH_4 and H_2 introduction on the utilization of mixed gas in the reduction reaction.

3. Calculation conditions

The reductions of VTM in the indirect reduction zone were studied in this paper. Under standard state, the transition temperature of H_2 and CO reduction capacity was 810°C. The gas temperature was equal to 1000°C which was determined by some literatures as the boundary temperature of high temperature zone and low temperature zone of BF [20]. Therefore, this paper studies the influence of CH_4 and H_2 on the utilization of mixed gas when iron, vanadium and titanium oxides in VTM are reduced by mixed gas (different proportions of H_2-CO or CH_4-H_2-CO) at 700°C, 850°C and 1000°C respectively. The mixed gases of different proportions were shown in TABLE 1. The calculation results in this paper were all based on FactSage 8.0 software.

TABLE 1

The composition of mixed gas

No.	**1**	**2**	**3**	**4**	**5**	**6**
H_2:CO	10:0	8:2	6:4	4:6	2:8	0:10
CH_4:H_2:CO	6:2:2	4:4:2	2:6:2	4:2:4	2:4:4	2:2:6

4. Results and discussion

4.1. Analysis of Mixed Gas Utilization Rate for Reducing Iron Oxide

When 0.5 mol Fe_2O_3 was reduced by mixed gas with different proportions (H_2-CO or CH_4-H_2-CO) at 700°C, the influence of initial gas amounts (n_{mix}) on gas utilization rates (η_{mix}) are shown in Fig. 1. The main reactions of CH_4 reducing iron oxide are shown in equations (8-10).

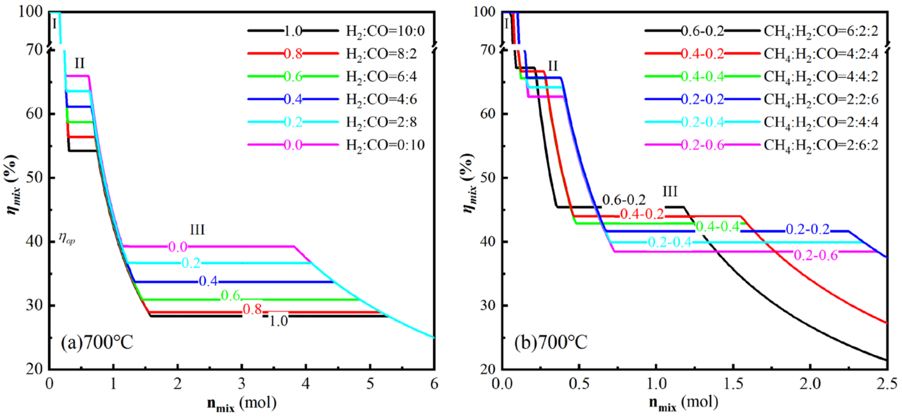

Fig. 1. Effect of mixed gas amount on gas utilization during reduction of Fe_2O_3 at 700°C

$$CH_4 + 12Fe_2O_3 = 8Fe_3O_4 + CO_2 + 2H_2O \tag{8}$$

$$CH_4 + 4Fe_3O_4 = 12FeO + CO_2 + 2H_2O \tag{9}$$

$$CH_4 + FeO = FeO + CO + 2H_2 \tag{10}$$

According to Fig. 1, it can be seen that:

1) According to the variation of η_{mix} with n_{mix} during the reduction process, the reduction process of Fe_2O_3 presents three platforms. In platforms I, II and III, with the increase of n_{mix}, η_{mix} remains constant, which indicates that there was oxygen transfer between gas and iron oxide in these three stages. The oxygen transfer process was caused by the following reduction processes: $Fe_2O_3 \rightarrow Fe_3O_4$, $Fe_3O_4 \rightarrow FeO$ and $FeO \rightarrow Fe$.
2) As can be seen in Fig. 1a, with the proportion of H_2 in the mixed gas increases, the platform III moves down and becomes longer, which indicates that the utilization rate of mixed gas reduces, and the amount of gas required for reduction to 1mol iron increases. As shown in Fig. 1b, with the increase of CH_4 proportion in the mixed gas, the platform III moves up and becomes shorter, the utilization rate of the mixed gas increases, and the amount of gas required for reduction to 1mol iron decreases. It can be seen that at 700°C, the proportion of H_2 in the mixed gas decreases and the proportion of CH_4 in the mixed gas increases, the ability of the mixed gas to reduce iron oxides increases.

This follow study focus on the effect of H_2 ratio in mixed gas on platform III. The reduction results of iron oxides at 850°C and 1000°C under different atmospheres are shown in Fig. 2.

1) The range of η_{mix} (platform III) in Fig. 2a is 32.31%~33.64%, while the range of η_{mix} (platform III) in Fig. 2b becomes

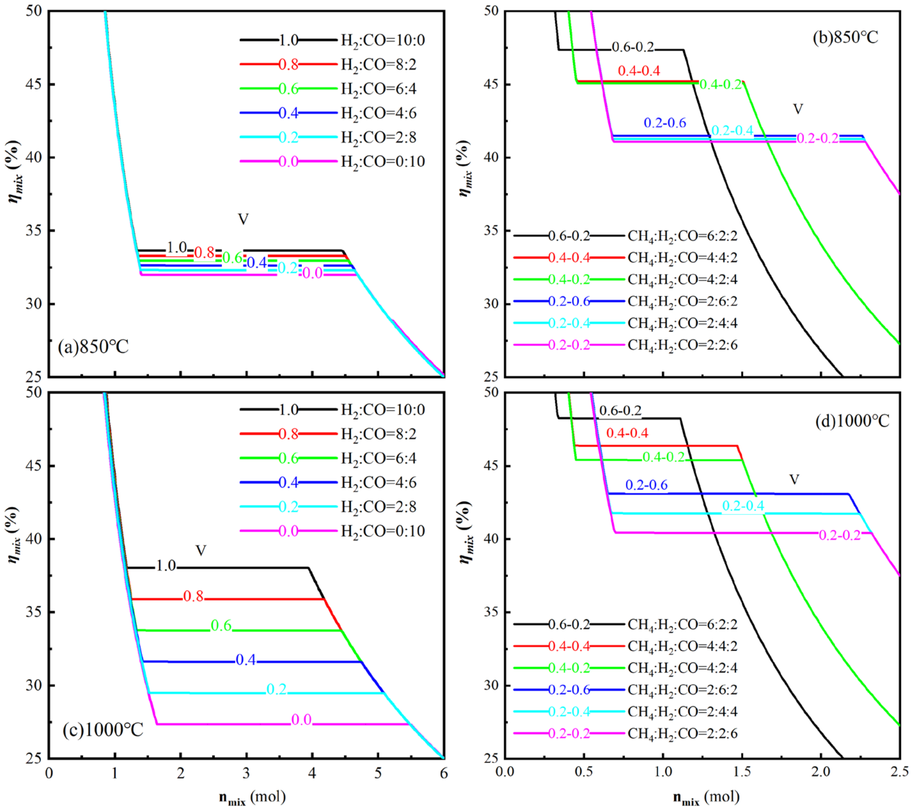

Fig. 2. Effect of the amount of mixed gas on the gas utilization rate of Fe_2O_3 reduction at 850°C and 1000°C

41.49% ~ 47.36%. The range of variation on η_{mix} at 850°C was significantly reduced compared to 700°C, which was due to the fact that the reduction capacity of CO was obviously greater than that of H_2 at 700°C, while the difference between the two reduction capacities became smaller at 850°C. The increase of CH_4 reduction capacity with the increase of temperature eventually led to the increase of η_{mix}.

2) The range of η_{mix} (platform III) in Fig. 2c is 27.35% ~ 38.03%, and the range of η_{mix} (platform III) in Fig. 2d is 43.09% ~ 48.24%. The range of change in utilization of mixed gases at 1000°C is significantly higher than that at 850°C, which is attributed to the fact that the capacity of H_2 reduction is further enhanced while that of CO reduction is gradually weakened as the temperature rises, resulting in the increasing difference in reduction capacity between the two gases. At the same time, the temperature rise leads to a further increase in the reduction capacity of CH_4, resulting in a higher η_{mix} while the mixed gas including CH_4.

When iron oxides reduced by CO, in order to ensure that the reduction reaction proceeds positively, it is necessary to have an excess of CO to maintain the $\varphi_{CO_2}/\varphi_{CO}$ ratio at equilibrium (called the "excess factor"). Similarly, when iron oxides reduced by mixed gas, there is an excess factor of mixed gases to maintain the equilibrium between reactants and products in the gas phase. In this paper, through calculated by the equip module of Factsage software, we analyzed the optimal amount of mixed gas (n_{min}) to reduce 0.5 mol Fe_2O_3 to 1 mol Fe at different temperatures, and discussed the relationship between the n_{min} and the ratio of in the mixed gas (CH_4-H_2-CO) at different temperatures was investigated. The n_{min} of mixed gas and its corresponding utilization rate (η_{min}) at different temperatures are shown in Fig. 3 and TABLE 2.

1) 700°C: With the increase of the proportion of CH_4 in the mixed gas, the n_{min} keeps decreasing and the corresponding η_{min} keeps increasing. When the proportions of CH_4 were the same, with the increase of H_2 content, the n_{min} increases and the corresponding η_{min} keeps decreasing, and the larger the proportion of CH_4, the smaller the influence of H_2 content on n_{min} and η_{min}.

TABLE 2

The optimum amounts of mixed gas and their corresponding utilization rates at different temperatures

CH_4:H_2:CO	No.	η_{min} (%)			n_{min} (mol)		
		1000°C	850°C	700°C	1000°C	850°C	700°C
0:0:10	1	27.35	31.99	39.28	5.49	4.68	3.82
0:2:8	2	29.46	32.31	36.69	5.09	4.64	4.08
0:4:6	3	31.60	32.63	33.73	4.74	4.59	4.44
0:6:4	4	33.75	32.95	30.97	4.44	4.55	4.84
0:8:2	5	35.89	33.28	28.98	4.18	4.5	5.17
0:10:0	6	38.03	33.64	28.35	3.94	4.45	5.29
2:0:8	7	39.07	40.89	43.50	2.39	2.29	2.15
2:2:6	8	40.41	41.09	41.65	2.32	2.28	2.25
2:4:4	9	41.75	41.29	39.91	2.24	2.27	2.34
2:6:2	10	43.09	41.49	38.48	2.17	2.25	2.43
2:8:0	11	44.44	41.71	37.56	2.10	2.24	2.49
4:0:6	12	44.41	44.93	45.24	1.53	1.51	1.50
4:2:4	13	45.39	45.08	43.98	1.51	1.51	1.55
4:4:2	14	46.07	45.23	42.88	1.48	1.50	1.59
4:6:0	15	47.34	45.38	42.02	1.44	1.50	1.62
6:0:4	16	47.47	47.24	46.31	1.12	1.13	1.15
6:2:2	17	48.24	47.36	45.41	1.11	1.13	1.17
6:4:0	18	49.01	47.48	44.66	1.09	1.12	1.19
8:0:2	19	49.45	48.74	47.06	0.89	0.90	0.93
8:2:0	20	50.08	48.84	46.40	0.88	0.90	0.95
10:0:0	21	50.83	49.79	47.64	0.73	0.75	0.78

2) 850°C: As the ratio of CH_4 in the mixed gases increases, n_{min} decreases continuously and the corresponding η_{min} increases continuously, At the same ratio of CH_4, with the increase of H_2 content, n_{min} decreases slightly and the corresponding η_{min} increases slightly, which is different from the case of reduction at 700°C. The greater the CH_4 content in the mixed gases, the smaller the effect of H_2 content on n_{min} and η_{min}.

3) 1000°C: While the CH_4 content of the mixed gas rises, n_{min} keeps decreasing and η_{min} keeps increasing. When the CH_4 content is certain, n_{min} decreases and η_{min} increases with the increase of H_2 content, and the larger the CH_4 content, the smaller the effect of H_2 content on n_{min} and η_{min}.

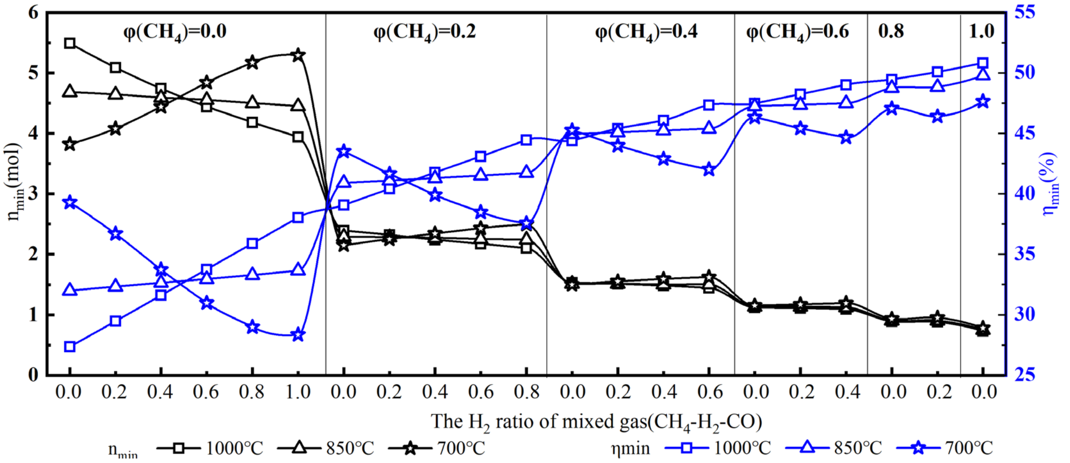

Fig. 3. The optimum amounts of mixed gas (n_{min}) and its corresponding mixed reduction utilization rate(η_{min}) at different temperatures

4.2. Analysis of Mixed Gas Utilization Rate for Reducing Vanadium Oxide

Vanadium mainly exists in complex forms such as vanadium-iron spinel in VTM, which was studied by considering vanadium oxide as V_2O_5 in this paper. The effect of gas amount on the utilization rate of the mixed gas was investigated for the reduction of 0.5 mol V_2O_5 at three temperatures of 700°C, 850°C and 1000°C with different ratios of the mixed gas as shown in Fig. 4, respectively. The main reactions of CH_4 reducing vanadium oxide are shown in equations (11-14).

$$CH_4 + 4V_2O_5 = 4V_2O_4 + CO_2 + 2H_2O \qquad (11)$$

$$CH_4 + 6V_2O_4 = 4V_3O_5 + CO_2 + 2H_2O \qquad (12)$$

$$CH_4 + 4V_2O_5 = 4V_2O_3 + CO_2 + 2H_2O \qquad (13)$$

$$CH_4 + 0.217V_2O_3 = 4.35\times10^{-2}V_{10}C_8 + 0.652CO + 2H_2 \qquad (14)$$

1) In Figs. 4(a), 4(c), 4(e), according to the variation of η_{mix} with n_{mix} during the reduction process, the reduction process of V_2O_5 also presents three platforms. The length of platform III ended at 1 mol, and the utilization rate of mixed gas at platform III was above 99% and changed very little, which is an indication that the transformation of $V_2O_5 \rightarrow V_2O_4 \rightarrow V_3O_5 \rightarrow V_2O_3$ occur easily. After the amount of mixed gas substance exceeds 1 mol and V_2O_5 is completely transformed into V_2O_3, the utilization rate of mixed gas keeps decreasing, which means that V_2O_3 cannot be further reduced. Even if the temperature rises to 1000°C, V_2O_5 can only be reduced to V_2O_3.
2) In Figs. 4(b), 4(d), 4(f), with the addition of CH_4 in the mixed of gases, the length of platform I becomes shorter. It indicates that the higher the proportion of CH_4 in the mixed gases, the smaller the amount of mixed gas are needed for the complete conversion of V_2O_5 to V_2O_3. However, while

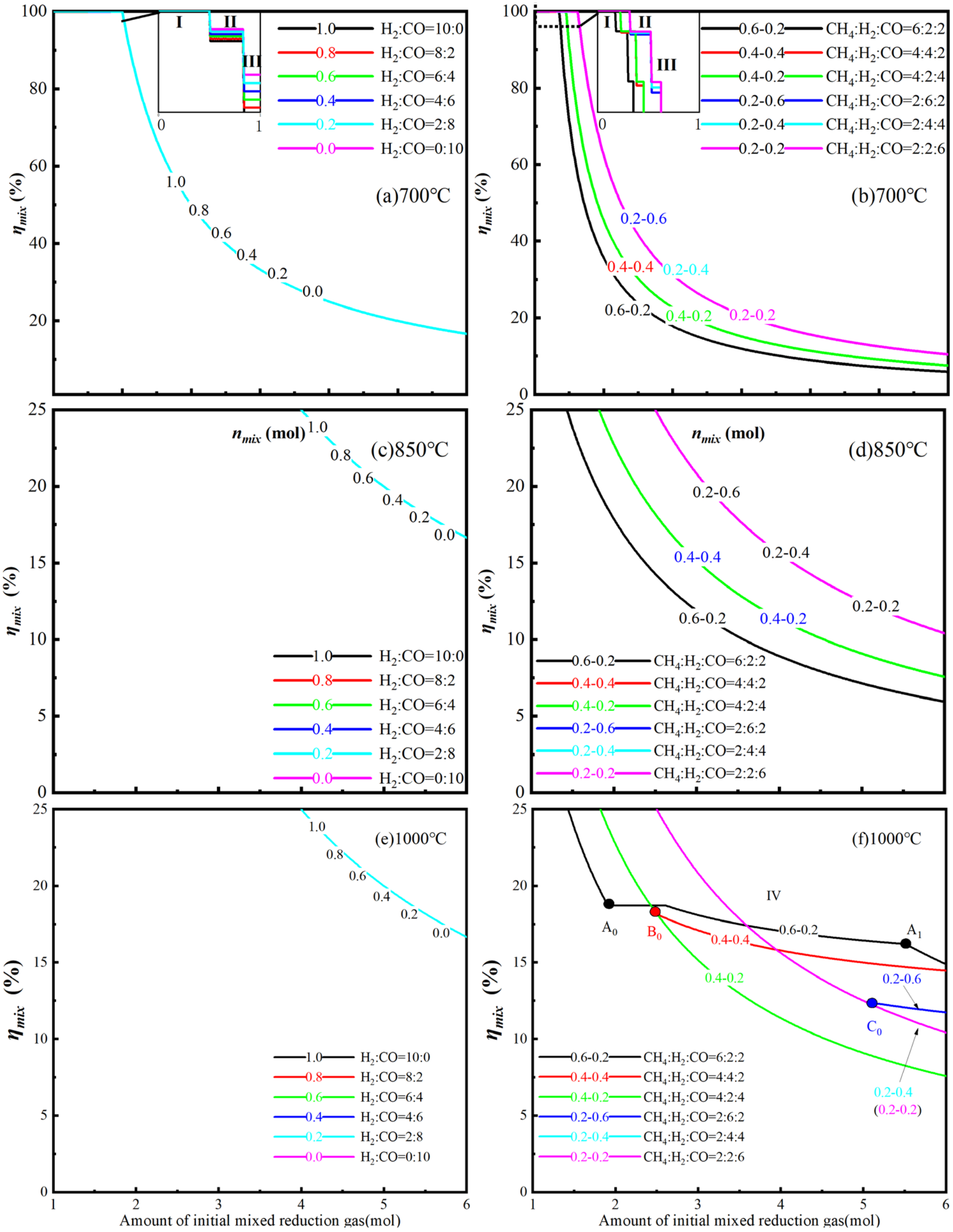

Fig. 4. Effect of mixed gas amount on gas utilization during reduction of V_2O_5 reduction at 700°C, 850°C and 1000°C

the reaction temperature at 700°C and 850°C, the elevated amount of CH_4 reduction could not make V_2O_3 be further reduced afterwards. When the reaction temperature reaches 1000°C, V_2O_5 can be further reduced to $V_{10}C_8$ (stage IV which starting at points A_0, B_0, C_0 respectively) after conversion to V_2O_3 at $CH_4:H_2:CO = 6:2:2$ and 4:4:2. When the gas amount of mixed gas ($CH_4:H_2:CO = 6:2:2$) is 5.51 mol, it can be completely converted to $V_{10}C_8$.

4.3. Analysis of Mixed Gas Utilization Rate for Reducing Titanium Oxide

The reduction of titanium oxide (TiO_2) was studied. Through calculation, it was found that H_2-CO and CH_4-H_2-CO were almost unable to reduce TiO_2 when using the mixed gases at 700°C and 850°C. However, the reduction conditions are significantly improved while 1000°C, the effects of gas amounts on the utilization rate of mixed gases for the reduction of 1 mol TiO_2 at 1000°C were investigated, as shown in Fig. 5, TABLE 3 and TABLE 4. The main reactions of CH_4 reducing titanium oxide are shown in equations (15-21).

$$CH_4 + 20TiO_2 = Ti_{20}O_{39} + CO + 2H_2 \tag{15}$$

$$CH_4 + Ti_{20}O_{39} = 2Ti_{10}O_{19} + CO + 2H_2 \tag{16}$$

$$CH_4 + 9Ti_{10}O_{19} = 10Ti_9O_{17} + CO + 2H_2 \tag{17}$$

$$CH_4 + 8Ti_9O_{17} = 9Ti_8O_{15} + CO + 2H_2 \tag{18}$$

$$CH_4 + 7Ti_8O_{15} = 8Ti_7O_{13} + CO + 2H_2 \tag{19}$$

$$CH_4 + 6Ti_7O_{13} = 7Ti_6O_{11} + CO + 2H_2 \tag{20}$$

$$CH_4 + 5Ti_6O_{11} = 6Ti_5O_9 + CO + 2H_2 \tag{21}$$

From Fig. 5a, TiO_2 can be completely reduced to $Ti_{20}O_{39}$ by the mixed gas (H_2-CO) when the temperature reaches 1000°C. The higher the proportion of H_2, the stronger the reduction ability. And the optimum gas amounts of mixed gas (H_2-CO) at 1000°C and their corresponding utilization rates are shown in TABLE 3. From Fig. 5b, it can be seen that the introduction of CH_4 makes TiO_2 reduced by the mixed gases easier while 1000°C. When the composition of the mixed gas is $CH_4:H_2:CO = 6:2:2$, the reduction process of TiO_2 is divided into seven platforms according to the different utilization rates of the mixed gases during the reduction process. The meanings represented by each stage are as follows: $TiO_2 \rightarrow Ti_{20}O_{39} \rightarrow Ti_{10}O_{19} \rightarrow Ti_9O_{17} \rightarrow Ti_8O_{15} \rightarrow Ti_7O_{13} \rightarrow Ti_6O_{11} \rightarrow Ti_5O_9$. TiO_2 is completely reduced to Ti_5O_9 by mixed gas which requiring 2.28 mol mixed gas, corresponds to the gas utilization rate of 3.15%. The optimum mixed gas amounts and their corresponding utilization rates are shown in TABLE 4, while TiO_2 is reduced by mixed gas (CH_4-H_2-CO) at 1000°C.

TABLE 3

The optimum amounts of mixed gas (H_2-CO) and their corresponding utilization rates at 1000°C

$H_2:CO$	0:10	8:2	6:4	4:5	2:8	10:0
Reduction product	$Ti_{20}O_{39}$					
n_{min} (mol)	3.48	4.07	4.52	4.84	5.15	5.65
η_{min} (%)	1.44	1.23	1.11	1.03	0.97	0.89

TABLE 4

The optimum amounts of mixed gas (CH_4-H_2-CO) and their corresponding utilization rates at 1000°C

$CH_4:H_2:CO$	6:2:2	4:4:2	2:6:2	4:2:4	2:4:4	2:2:6
Reduction products	Ti_5O_9	Ti_5O_9	Ti_6O_{11}	Ti_7O_{13}	Ti_8O_{15}	$Ti_{20}O_{39}$
n_{min} (mol)	2.26	4.25	1.37	2.09	1.54	0.24
η_{min} (%)	3.15	2.14	7.60	3.11	5.11	13.02

4.4. Experiments

The VTM sinter samples (100 mg, 200~220 mesh) used in this study were obtained from one of iron and steel companies in China. The main chemical composition and phase composition of the sinter are shown in TABLE 5 and Fig. 6. Then the furnace was heated from room temperature to the desired reduction temperature (700°C, 850°C and 1000°C) at a rate of 20°C/min while keeping the samples under argon. After 10 minutes stabilization

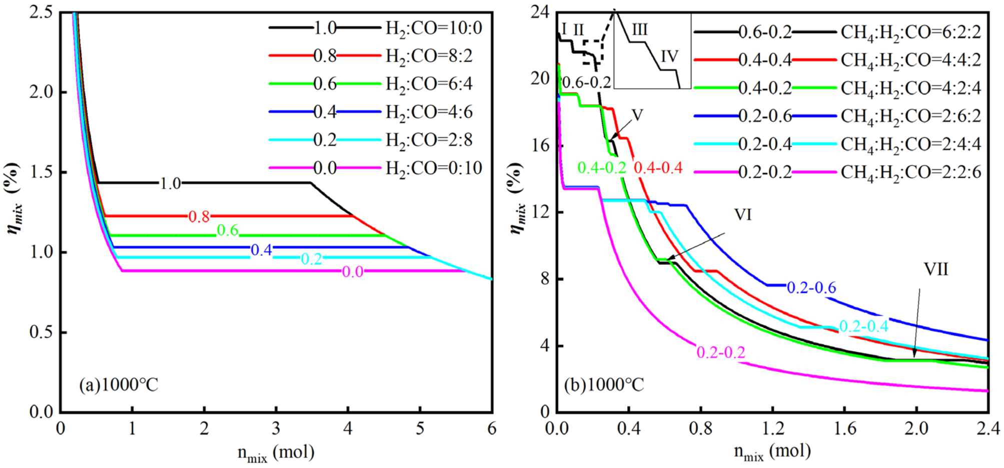

Fig. 5. Effect of mixed gas amount on gas utilization during reduction of TiO_2 reduction at 1000°C

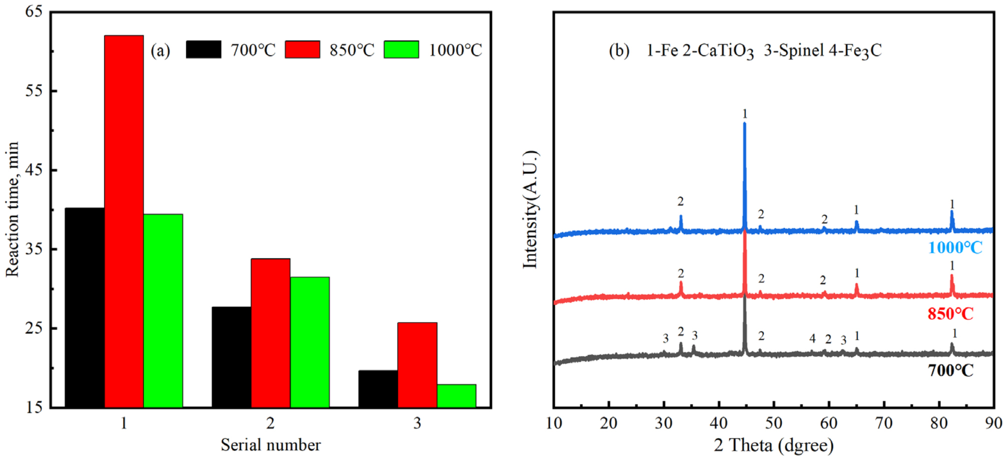

Fig. 6. The reaction times and XRD patterns of vanadium-titanium sinter reduction products at different temperatures

at the required reaction temperature, the argon gas was switched to reduction gas. After reacting for a certain time, the reduction gas was switched back to argon again, and samples were cooled in argon to room temperature. In all experimental runs, a constant flow rate was maintained, as 100 mL min^{-1} (21°C and 1 atm). The compositions of the reducing gas (according to the composition of BF hearth gas in a steel plant in China) are shown in TABLE 6.

TABLE 5

The main chemical composition of the VTM sinter, wt%

TFe	FeO	SiO_2	MgO	Al_2O_3	TiO_2	CaO	V_2O_5	R
50.72	7.61	5.58	2.98	3.04	5.27	11.08	0.38	1.99

TABLE 6

The composition of the reducing gas

No.	1	2	3
$CO:H_2:N_2$	47:04:49	42:09:49	37:14:49

The reaction times required for complete reduction of vanadium-titanium sinter under different hydrogen rich atmospheres at 700°C, 850°C, and 1000°C are shown in the Fig. 6a. It can be seen that, the increase in H_2 ratio leads to a decrease in reaction time. The XRD patterns of vanadium-titanium sinter reduction products at 700°C, 850°C, 1000°C are shown in the Fig. 6b while the composition of the reducing gas is 37:14:49. As shown in the figure, the main phases of VTM sinter after reduction are: $CaTiO_3$, Fe, $CaTiO_3$, while Fe_3C is generated only at 700°C. It indicates that iron oxide in vanadium-titanium sinter can be completely reduced, while vanadium and titanium oxide are difficult to be reduced within the temperature range of 700~1000°C.

5. Conclusions

Based on the principle of oxygen migration in iron-making production, the general calculation formula for the utilization rate of mixed gas (CH_4-H_2-CO) is established and derived, the formula can be further extended to calculate the utilization rate of gases containing various alkanes. The gas utilization rates and physical phases change process of iron, vanadium and titanium oxide reduction under mixed gas (H_2-CO and CH_4-H_2-CO) are analyzed and compared. The main conclusions are as follows:

(1) When 0.5 mol Fe_2O_3 is reduced by mixed gas (CH_4-H_2-CO), as the proportion of CH_4 in the mixed gas increases, n_{min} keeps decreasing and η_{min} keeps increasing. When 700°C, the proportion of CH_4 in the mixed gas is fixed, with the increasing of H_2 proportion, n_{min} increases and η_{min} decreases. While 850°C and 1000°C, the proportion of CH_4 in the mixed gas is fixed, with the increasing of H_2 proportion, n_{min} decreases and η_{min} increases.

(2) When 700°C, 850°C and 1000°C, while the 0.5 mol V_2O_5 is reduced by mixed gas (CH_4-H_2-CO), the reactions of $V_2O_5 \rightarrow V_2O_4 \rightarrow V_3O_5 \rightarrow V_2O_3$ are easy to proceed, but V_2O_3 is difficult to further reduce. At 1000°C, While $CH_4:H_2:CO = 6:2:2$ and 4:4:2, V_2O_5 can be further reduced to $V_{10}C_8$ after being converted to V_2O_3.

(3) It was found that H_2-CO and CH_4-H_2-CO were almost unable to reduce TiO_2 when using the mixed gas at 700°C and 850°C. TiO_2 can only be reduced to $Ti_{20}O_{39}$ using mixed gas (H_2-CO) at 1000°C. While mixed gas (CH_4-H_2-CO) at the ratios of 2:2:6, 2:4:4, 4:2:4, 2:6:2, 6:2:2, the final products are $Ti_{20}O_{39}$, Ti_8O_{15}, Ti_7O_{13}, Ti_6O_{11} and Ti_5O_9, respectively.

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