DEVELOPMENT OF Mn-C PELLET CARBURANT AND RESEARCH ON RECARBURIZING MECHANISM

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Abstract

The flexibility of steelmaking production in steel making plants could be greatly improved by addition of carburant in molten steel. When the traditional carburant, such as graphite, graphite-like, coke and so on, are used, there are some problems, such as the fluctuating carbon yield and long carburization process, etc. A new type of ultra-low nitrogen Mn-C pellet carburant was developed in order to solves the problems. It has been applied in some iron and steel enterprises in China since 2002. The factory application results show that a high and stable recovery rate of carbon and manganese was reached with the new carburant. The average recovery rate of carbon is 90-95%, and the average recovery rate of manganese is more than 92%. In this paper, the Mn-C pellet phase is analyzed by XRD. The XRD results show that the carbon in Mn-C pellet mainly exists in the form of graphite carbon and Fe exists in the form of Fe_3C and Mn exists in the form of Mn_5C_2. The experimental results showed that t Mn-C pellet carburant has better performance than traditional carburant, but had no effect on the composition of harmful elements such as N,S and P.

KEYWORDS: STEELMAKING; CARBURANT; Mn-C PELLET; CAICINED COAL;ULTRO LOW NITROGEN

1 INTRODUCTION

There are two methods in the final carbon content controlling in oxygen converter steel-making. Two methods are catch carbon and recarburization. Both of them have advantages and disadvantages. At present the majority of steel plants make medium carbon steel and high carbon steel by recarburization. The carbon content is blown to 0.05~0.06% for all types of steel and then the carburant is added according to the carbon content requirement of steel type. With the extensive use of carburant, the variety and quality of carburant largely determine the properties of steel, so carburant requires high purity, low ash content and low N and S content. Traditional carburant includes electrode block, coke powder, calcined anthracite etc. Electrode block has high carbon content and strong oxidation resistance, but the production process is complex and the cost is high. Because of the high ash content and S content, low carbon content, coke powder is not good for carburizing, although it is cheap[1]. Calcine anthracite, the most commonly used now, needs to be first purified and then be graphitized. Although calcined anthracite meets the needs of steel-making basically, the recovery rate of carbon is often low and unstable. Fig.1 shows the distribution of recovery rate of C for 11 heats by adding calcined anthracite during the production of medium carbon steel and high carbon steel in Panzhihua Iron & Steel (Group) Co., Ltd.. It can be seen from the figure that the recovery rate of C is low and unstable, which leads to the difficulty of controlling the composition of molten steel. The reason is tha calcined anthracite floats on the surface of molten steel and does not dissolve completely due to its low density. Therefore, a new type of ultra low nitrogen Mn-C pellet carburant has been developed and applied Baosteel, Tainjing Steel, Chongqing Steel, Jinan steel, Xingcheng Special Steel and other enterprises in China. The application results show that the recovery rate of carbon and manganese is high and stable, the average recovery rate of carbon is 90-95%, the average recovery rate of manganese is greater than 92%. In this paper, the pellet phase is analyzed by X ray diffraction(XRD), and the recarburizing effect and mechanism of the Mn-C pellet carburant were studied.

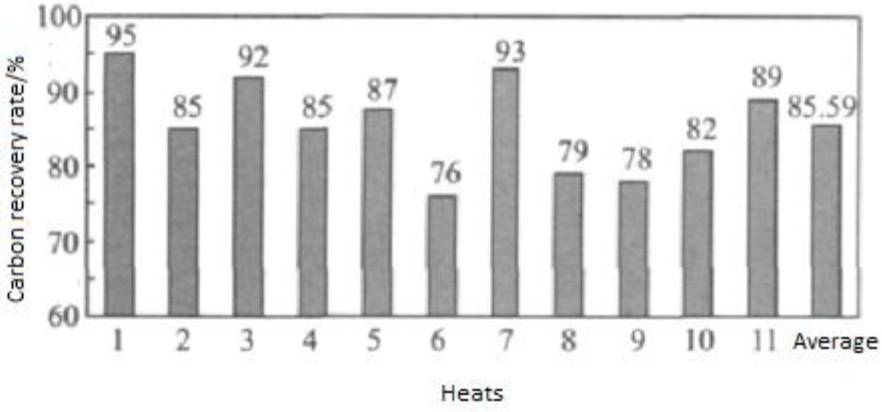

Fig.1-Recovery rate of C with anthracite[2]

2 Mn-C PELLET CARBURANT

2.1 Raw Material Composition and Product Standard

Mn-C pellet caburant was prepared by compacting the chip produced in Fe-Mn process and graphite powder with binder. The raw material composition and product standard of Mn-C pellet are shown in Table 1 and Table 2.

Tab. 1 Raw material composition of Mn-C pellet

Raw material	*Mn，%*	*S，%*	*T.C，%*	*H_2O，%*
High C Fe-Mn chip	*73.18*	*0.053*	*6.99*	
low S Graphite	*-*	*0.056*	*80.47*	*2.38*

Tab. 2 The product standard of Mn-C pellet carburant

Production	*Mn，%*	*S，%*	*T.C，%*	*H_2O ，%*	*SiO_2 ，%*	*P，%*	*Particle size,mm*	*Screening, %*	*Falling strength ,%*
36Mn-C pellet	*34～38*	*≤0.050*	*34～38*	*≤0.5*	*≤7.0*	*≤0.200*	*20～50*	*≤3.0*	*80*
28Mn-C pellet	*26～28*	*≤0.100*	*40～44*	*≤1.0*	*≤7.0*	*≤0.200*	*20～50*		

2.2 Phase Analysis

A Mn-C pellet was ground into a powder and analyzed by X ray diffraction. The results are shown in Figure 2.

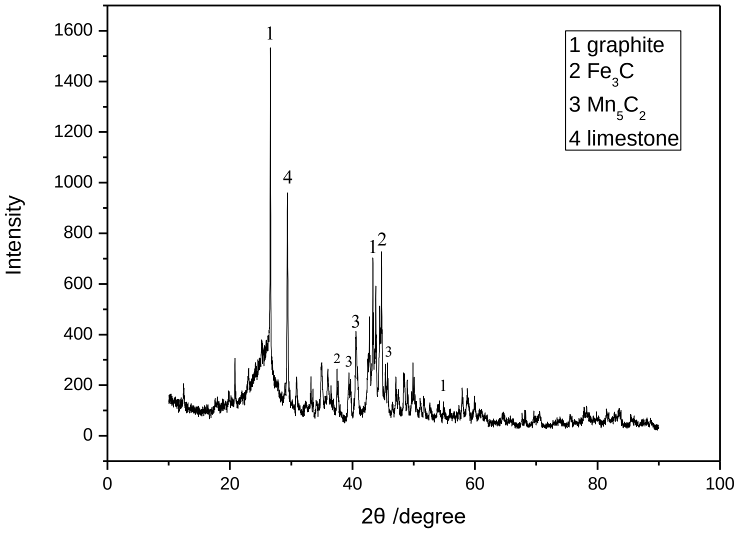

Fig.2-The XRD spectrum of Mn-C pellet

The XRD results show that the carbon in Mn-C pellet mainly exists in the form of graphite carbon and Fe exists in the form of Fe3C and Mn exists in the form of Mn_5C_2., and there is some limestone.

3 EXPERIMENT

3.1 Recarburizing contrast experiment

Carburizing contrast experiment was carried out in a medium frequency induction furnace. 95 calcined anthracite (carbon content 96.788C) and Mn-C pellet were added after melting scrap in induction furnace. Carburizing experiments of molten steel with different kinds of carbon-increasing agents were carried out with the same theoretical carburization amount. The experimental operation is as follows:

1) Weighing scrap 30kg is put into induction furnace, after melting into molten steel, temperature and oxygen content are measured with oxygen probe, temperature is controlled at 1600-1650 ℃, initial w [O] is controlled at about 650ppm, no top slag is added in the experiment, the surface of molten steel is exposed. to air

2)When the temperature and initial w [O] reach the control goal, the sample is taken for the first time with quartz tube, the recarburizing agent is added, the sample is taken with quartz tube at regular intervals. The amount of carbon added by different carburants is 0.45% of the weight of molten steel.

3)The composition of the samples are analyzed..

3.2 Mn-C pellet dissolution experiment

In order to analyze the recarburizing mechanism of Mn-C pellets in molten steel, the dissolution experiment of Mn-C pellets was carried out. The experimental operation is as follows: Mn-C pellets are fixed with molybdenum wire .and immersed in the molten steel. Then is taken out of molten steel at regular intervals. .The morphology of the pellets is observed .

4 EXPERIMENTAL RESULTS

4.1 Recarburizing contrast experimental results

The composition of the samples were analyzed. In which, oxygen and nitrogen were analyzed with oxygen, nitrogen and hydrogen analyzer (type:ONH836). The carbon and sulfur were analyzed with carbon and sulfur analyzer. Manganese and phosphorus were analyzed by colorimetric method. The recovery rate of carbon is calculated by formula 1, and the recovery rate of manganese is calculated by formula 2.

$$\eta_C = \frac{W_S(w[C]-w[C]_i)}{100\times W_C\times w[C]_C} \qquad \text{(F-1)}$$

$$\eta_{Mn} = \frac{W_S(w[Mn]-w[Mn]_i)}{100\times W_C\times w[Mn]_C} \qquad \text{(F-2)}$$

In equation,η_C, η_{Mn} are carbon and manganese recovery rate individually, W_S is liquid steel weight(30kg), $w[C]_i$ and $w[Mn]_i$ are initial carbon and manganese content individually, $w[C]$ and $w[Mn]$ are carbon and manganese content individually, W_C is carburant weight(kg), $w[C]_C$ are carbon and manganese content in carburant.

The results of analysis and calculation are shown in fig1-fig7.

From Fig.3 and Fig.4 it can be seen that in the early period of the experiment, w[C] increase, and reached the maximum at the 8min l, then decreased. And in the early period the increase of w[C] with Mn-C pellet is more than that with calcined anthracite, and the growth rate is faster When calcined anthracite is added, the recarburizing rate is 0.047%C/min, when calcined anthracite is added, the recarburizing rate is 0.065%C/min. and the recovery rate of C is also higher. In the later period, the decrease of w[C] with Mn-C pellet is more than that with calcined anthracite.

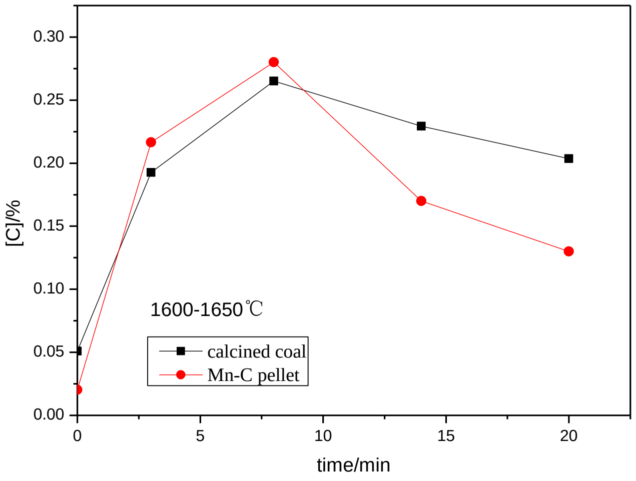

Fig 3 w[C] changes with time by adding different carburants

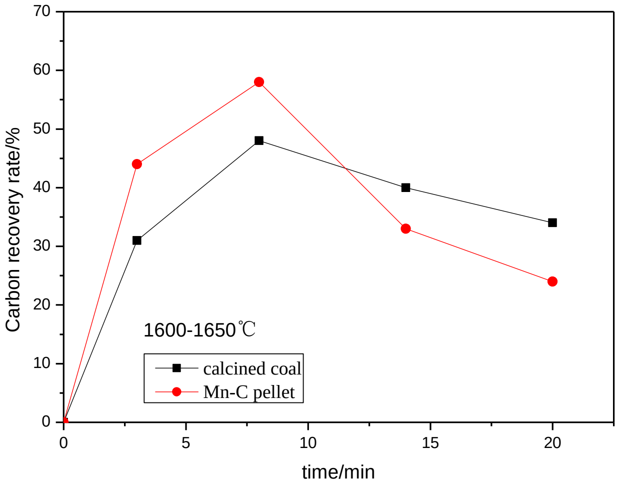

Fig 4 Carbon recovery rate changes with time by adding different carburants

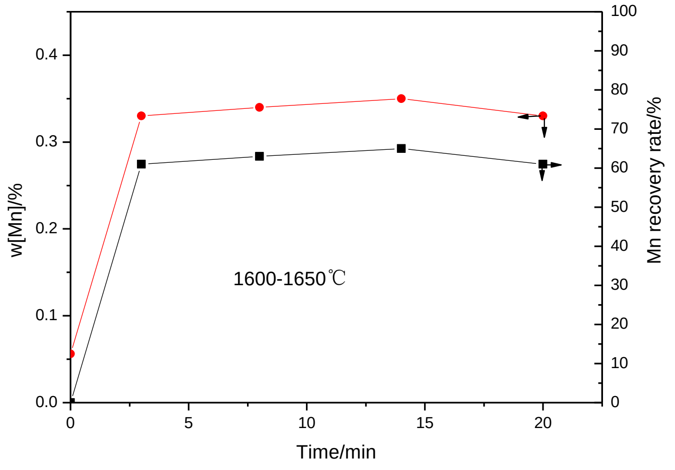

Fig5 w[Mn] and Mn recovery rate change with time by Mn-C pellet

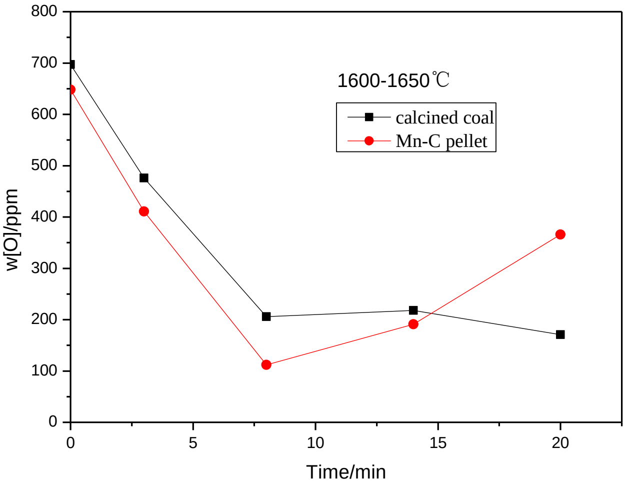

Fig 6 w[O] change with time by adding different carburants

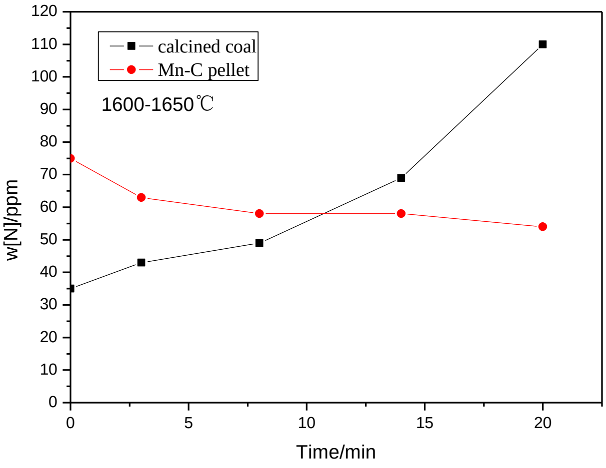

Fig 7 w[N] changes with time by adding different carburants

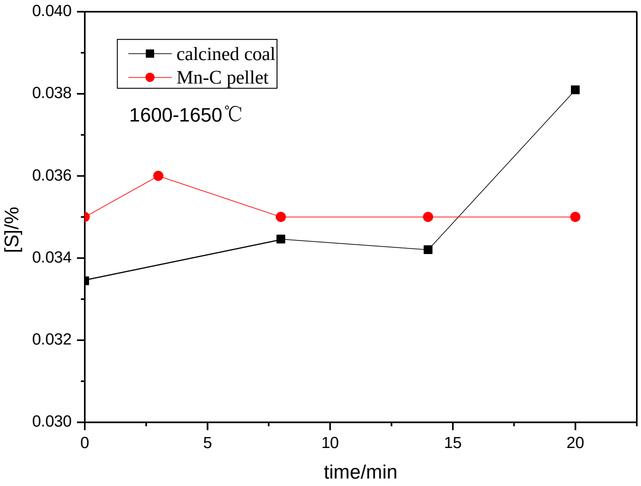

Fig 8 w[S] changes with time by adding different carburants

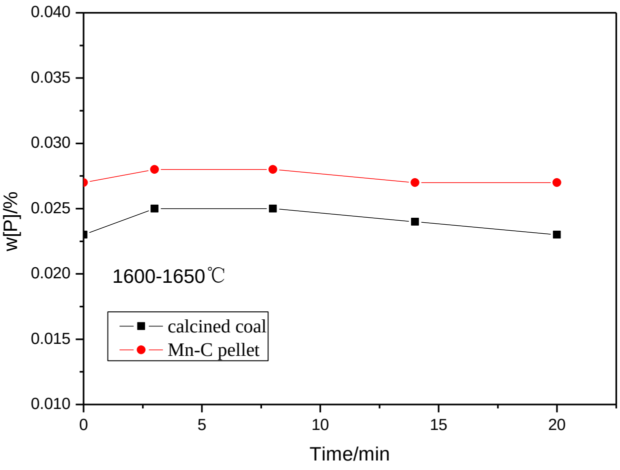

Fig 9 w[P] changes with time by adding different carburants

Fig 5shows that Mn content in molten steel with Mn-C pellet increases and tends to be stable. And the recovery rate of Mn is higher than C recovery rate.

Fig.6 shows that the change of w[O]t is opposite to that of carbon content, which decreases in early period, increases in later period. And in the early period the decrease of w[O] with Mn-C pellet is more than that with calcined anthracite, In the later period, the increase of w[O] with Mn-C pellet is more than that with calcined anthracite.

As Fig. 7 and Fig.8shown,w[N]and w[S] with Mn-C pellet is stable while that in the molten steel with calcined anthracite rise Therefore, Mn-C pellet has little effect on N and S content. However, calcined anthracite increases N and S content to a certain extent.

As Fig.9 shown, both of Mn-C pellet and 95 calcined anthracite have no effect on P content.

4.2 Mn-C pellet dissolution experimental result

Figure 10 shows the dissolution of the pellets in molten steel. When the pellet was first immersed in the liquid steel, steel shell were formed. It is discontinuous due to the formation of CO bubbles formed by carbon-oxygen reaction. The shell melted with the increase of temperature. In the outer layer of pellets, FeMn melts and binders fail, and exfoliated FeMn rapidly dissolves into molten steel, while graphite fine graphite gradually dissolves into molten steel.

Fig 10 Photo of Mn-C pellet dissolution in molten steel for different time

5. DISCUSSION AND ANALYSIS

Recarbonization experimental results show that recarburization effect of Mn-C pellet is better than that of calcined anthracite. One of the reasons is due to addition of FeMn, the density of carburant increases, witch make it easier enter liquid steel. Another reasons is that Fine graphite dissolves faster than calcined anthracite with large particles. Third is that manganese is a deoxidizer. The deoxidization product of is a liquid solution or a solid solution composed of MnO and FeO, which is similar to an ideal solution. Whether the liquid solution or the solid solution is related to temperature and manganese content, when the temperature is low and the manganese content is high, the solid solution is formed. When a liquid solution is formed, the deoxidation reaction is:

[Mn]+(FeO)=(MnO)+[Fe] ΔG_1^0=－123307+56.48T(J/mol) （R-1）

$$K_1=\frac{a_{MnO}}{a_{FeO}a_{Mn}}=\frac{x(MnO)}{x(FeO)w[\mathrm{Mn}\}}$$

$$lg\,K_1=\frac{6440}{T}-2.95$$

As well as $\mathrm{x(MnO)+x(FeO)=1}$，get：

$$\mathrm{w(FeO)=\frac{1}{1+K_1w[Mn]}} \qquad \text{(F-3)}$$

(FeO) =Fe+[O] ΔG_2^0=120923－52.34T (J/mol) （R-2）

$$\mathrm{logK_O=-\frac{6320}{T}+2.73}$$

$$\mathrm{w[O]=K_Ox(FeO)} \qquad \text{(E-4)}$$

To take F-3 into F-4,get:

$$w[O]=\frac{K_O}{1+K_1 w[Mn]} \qquad \text{(F-5)}$$

1873K， K_1=3.29，L_O=0.23

$$w[O]=\frac{0.23}{1+3.29w[Mn]} \qquad \text{（F-6）}$$

When a solid solution is formed, the deoxidation reaction is:

$[Mn]+(FeO)_s=(MnO)_s+[Fe]$ ΔG_3^0=－137114+59.49T(J/mol) （R-3）

$$K_3=\frac{a_{MnO(s)}}{a_{FeO(s)}a_{Mn}}=\frac{x(MnO)_s}{x(FeO)_s w[Mn\}}$$

$$lg\ K_3=\frac{7162}{T}-3.11$$

1873K 时，K_3=5.21.With the same principle ,the following is got：

$$w[O]=\frac{0.23}{1+5.21w[Mn]} \qquad \text{（F-7）}$$

The relationship between w[Mn] and w[O] is obtained from foumula 6 and 7(see fig 11)。

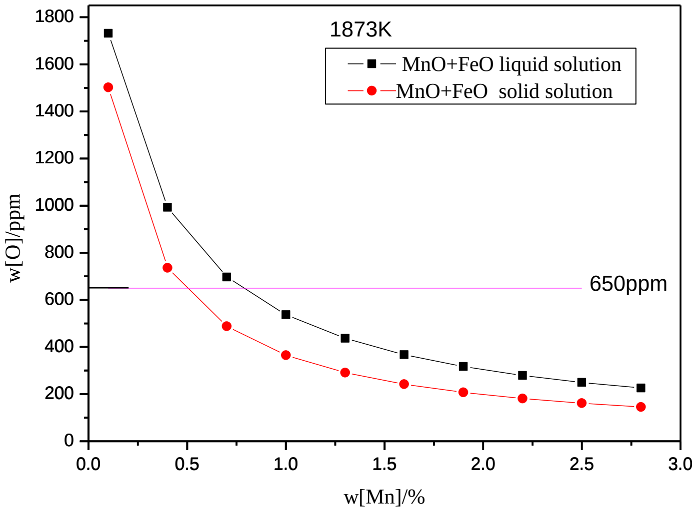

Fig11 The relationship between w[Mn] and w[O] with different deviation products

It can be seen that when the oxygen content is 650 ppm, and the solid solution is formed, the manganese deoxidation reaction can take place as long as the content of manganese in molten steel is more than 0.47%, which can be achieved around the pellets. Manganese reduces the oxidation of carbon around the pellets, while in the area away from the pellets, carbon is more easily oxidized because of the principle of selective oxidation, and carbon acts as an inhibitor of manganese oxidation.

When carbon and manganese are added into the molten steel simultaneously, the oxygen can be reacted with them. at the same time, but the degree of oxidation varies with the change of temperature and composition. who has priority to react with oxygen depends on the oxygen potential. The element with lower oxygen potential has priority to react with oxygen There is a competitive oxidation relationship between carbon and manganese. When the temperature and manganese content is fixed, when w[C] is smaller, the oxygen level is higher and manganese is priority oxidation. With the increase of carbon content in the steel, oxygen potential controlled by carbon decrease. When the oxygen potential controlled by carbon is equal to the oxygen potential controlled by manganese, the balance is established. If the carbon content continues to increase, the oxygen potential controlled by carbon is lower than the oxygen potential controlled by manganese, manganese is priority oxidation. Reaction carbon and oxygen:

$[C]+[O]=CO \quad \triangle G^0=-22364-39.63T$ J/mol

$$K_{\text{C}-\text{O}}=\frac{P_{CO}}{a_C a_O}=\frac{P_{CO}}{f_C f_O w[C]w[O]}$$

When P_{CO}=100KPa，w[C] is not very large， $f_C f_O \approx 1$

$$K_{\text{C}-\text{O}}=\frac{P_{CO}}{a_C a_O}=\frac{1}{w[C]w[O]}$$

$$w[O]=\frac{1}{K_{\text{C}-\text{O}}w[C]} \qquad \text{(F-9)}$$

1873K，$K_{C\text{-}O}$=494,

$$w[O]=\frac{1}{494w[C]} \qquad \text{(F-10)}$$

To take F-10 into F-6 and F-7, the equilibrium relationship between w[Mn]与 w[C]are obtained at 1873K：

When a liquid solution is formed： $\frac{1}{494w[C]}=\frac{0.23}{1+3.29\text{w[Mn]}}$ （F-11）

When a solid solution is formed： $\frac{1}{494w[C]}=\frac{0.23}{1+5.21\text{w[Mn]}}$ （F-12）

The relationship between w[Mn]and w[C] in steel can be obtained from formula 11and12 (see Fig. 11). In the Fig,

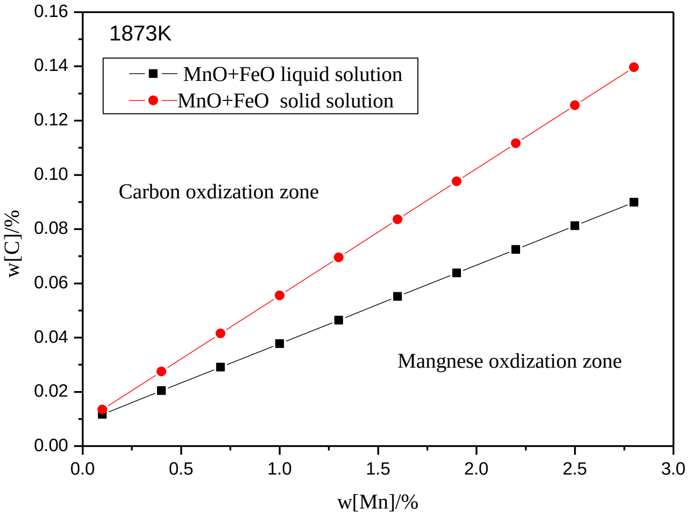

Fig11 The relationship between w[Mn] and w[C] with different deoxidation products

the manganese priority oxidation zone is located below the carbon-manganese equilibrium line, in this zone, [Mn] oxidizes with priority. [C] oxidizes with priority over the equilibrium line, which can inhibit the oxidation of [Mn]. When Mn-C pellet carburant is added, the FeMn in the outer layer of the pellet melts into liquid steel(see Fig 12), and there is a higher w[Mn] around the pellet. However, when the carbon powder peeling off from the surface layer of the pellet enters the liquid steel, the carbonization rate is lower than that of Mn. Therefore, [Mn] can oxidize with. priority in this region, which inhibits the oxidation of carbon. The reaction between [C]and [O] is

inhibited ,thus the gas film produced by carbon oxygen reaction on the surface of carbon particles is reduced, and the dissolution of carbon is accelerated. With the recarbonizing process going , the pellets gradually become smaller, and the manganese around the pellets diffuses into the steel. The manganese in the steel tends to be uniform. As the carbon particles dissolve in the process of floating, the carbon content increases, [C] can oxidize with priority to [Mn]. This is why, under experimental conditions, carbon decreases later, but manganese does not.

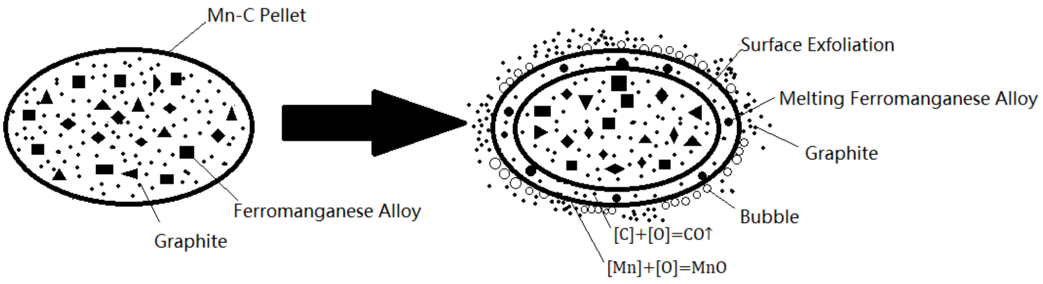

Fig12 Mn-C pellet dissolution mechanism model

6.CONCLUSSION

In this work the recarburizing effect and mechanism of the Mn-C pellet carburant were studied. The specific gravity of carburant increases by addition of FeMn alloy, and it could make carburant to stay in molten steel for a long time. Similar to the effect of core-coating line, graphite powder can be added to the liquid steel with the help of FeMn. At the moment of pellet peeling, there is a higher content of manganese around the graphite particle. Because manganese has deoxidization effect, on the one hand, the reaction between oxygen and carbon is inhibited in molten steel duo to selective oxidation, therefore ,reduces the burning loss of carbon. On the other hand, it reduces the gas film produced by carbon oxygen reaction on the surface of graphite particle, and accelerates the dissolution of carbon. Manganese in manganese carbon pellet is beneficial to recarburization.

REFERENCES

1. Wang Y M，Han C H，Wang F． Study on molding techniques of graphite － like carbon additive for steel - making ［J］. Gansu Technol，2005，27(1): 9-10．
2. Chen Jun, Development and Application of Carbon-Manganese Alloy Carburizing Materials for Converter [J]. Steelmaking, 2012, 28(5):16-19.