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Softening and Melting Behavior of Ferrous Burden under Simulated Oxygen Blast Furnace Condition

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Abstract: The softening and melting behavior of sinter, pellet and mixed burden was researched through high temperature reaction tests under load simulating traditional blast furnace (T-BF) and oxygen blast furnace (OBF) conditions. The results indicated that compared with T-BF, the softening zone of sinter and pellet became wide, but the melting zone became narrow in OBF. The permeabilities of both sinter and pellet were improved in OBF. Under the condition of OBF, the temperature of softening zone of mixed burden was increased by 63 K, but the temperature of melting zone was decreased by 76 K. Therefore, the permeability of material layer was significantly improved. This was mainly caused by the change of the melting behavior of pellet. In addition, the quality of dripping iron in OBF was much better than that of T-BF.

Key words: oxygen blast furnace; softening zone; melting zone; ferrous burden

After centuries of development, the carbon consumption in blast furnace, which is the dominant route for producing pig iron, has been close to theoretical minimum value of the process^[1]. Oxygen blast furnace (OBF), as a new iron-making technology which can significantly reduce carbon consumption by recycling most of the top gas after CO₂ removal and operating the blast furnace with pure oxygen, is increasingly causing a widespread concern. It has several advantages, such as high productivity, high pulverized coal injection (PCI) rate, low coke rate, high gas reducing capability and high top gas calorific value. Therefore, it is considered to be an ironmaking technology that can most likely realize the large-scale application^[2-4].

The shape and position of the cohesive zone in a blast furnace are largely controlled by the high temperature properties of ferrous burden. It is important to have a deep or low cohesive zone in the blast furnace for an efficient operation. This can be achieved by having a minimal temperature difference between softening and melting of the ferrous burden. A lot of studies were carried out by adapting the softening and melting experiment of constant gas composition based on the traditional blast furnace (T-BF)^[5-7]. However, the research on softening and melting behavior of ferrous burden in oxygen blast furnace is scarce. Han^[8] studied the softening and melting behavior of mixed burden in the atmosphere of oxygen blast furnace. He found that the softening zone became wide, but the melting zone became narrow. The permeability of the material layer was significantly improved. However, the softening and melting experiment of constant gas composition cannot truly reflect the softening and melting behavior of ferrous burden in an oxygen blast furnace.

In the present study, the experimental conditions for programming softening and melting tests were determined, and the softening and melting behavior of sinter, pellet and mixed burden under the conditions of traditional blast furnace and oxygen blast furnace was researched, which could provide theoretical guidance for the realization of industrial application of oxygen blast furnace.

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1 Experimental

1.1 Experimental samples

Tables 1 and 2 show the chemical composition of the sinter, pellet and coke used in a blast furnace of Laiwu Iron and Steel Company. The diameter of the samples is 10.0-12.5 mm.

1.2 Experimental apparatus and method

The experimental apparatus for softening and melting under load is schematically shown in Fig. 1. It mainly consists of electric furnace, graphite crucible, silicon-carbon tube, displacement meter, differential pressure gauge and auxiliary equipments. The rated power and the highest heating temperature

		Table	1 Chemin	ai compos	nion of raw	materials			
Burden	Composition/mass [®] / ₂								
Buiden	TFe	FeO	CaO	MgO	Al_2O_3	SiO_2	${\rm TiO}_2$	S	Basicity
Sinter	54.11	9.29	12.67	2.17	2.16	5.57	0.21	0.037	2.27
Pellet	62.46	3.69	1.06	0.97	1.50	7.62	0.17	0.005	0.14
Mixed burden	57.59	7.20	8.30	1.72	1.92	6.38	_	0.025	1.30

Table 1 Chemical composition of raw materials

Table 2	Chemical	composition	of coke	mass %
I abit L	Chemicar	composition	UI CONC	111111111111111111111111111111111111111

С	Ash	Volatile	S
86.2	11.91	1.64	0.694

are 6 kW and 1873 K, respectively. The size of reaction tube is $\phi 40 \text{ mm} \times 70 \text{ mm}$. The ferrous burden was charged into the graphite crucible and (20 ± 0.1) g coke was placed over and below that. Wherein several holes existed in the bottom of graphite crucible, which was contributed to the dripping of slag and iron, and the top of graphite crucible is connected to the graphite pusher. The height of sample in the reaction tube is (65 ± 5) mm. The load of 10 N/ cm² was added in the experimental process.

The heating process was protected by N_2 below 473 K, and then the reductive gas mixture with a flow rate of 12 L/min was introduced into the reaction tube. When the first iron dripped, the reductive gas mixture was switched to N_2 , and the sample was

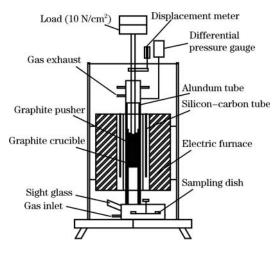


Fig. 1 Experimental apparatus

cooled to the room temperature. The vertical shrinkage, pressure drop and temperature of burden layer were all recorded automatically by computer. The contents of carbon and sulphur in dripping iron were analyzed.

1.3 Experimental condition

The flow charts of traditional blast furnace and oxygen blast furnace are shown in Figs. 2 and 3, respectively. The oxygen blast furnace is characterized by recycling top gas, which is reheated to 1173 K and then injected into the blast furnace from the stack tuyeres and main tuyeres after CO_2 and H_2O removal.

With reference to the characteristics of actual blast furnace and the research by domestic and foreign scholars^[9,10], the heating program in traditional blast furnace can be approximated to be that its heating rate is 9 K/min before 1173 K, and then it goes to the thermal reserving zone at 1173 K, and after insulation of 30 min, it heats up by 5 K/min. Currently, because oxygen blast furnace has not been put into practical operation, and in-furnace temperature field cannot be obtained, its heating program is the same as that of traditional blast furnace. In the present paper, the influence of gas composition change in oxygen blast furnace on softening and melting behavior of the ferrous burden was further investigated.

According to blast furnace mathematical model with multi-zone constraints established by Han et al.^[11], the gas composition in different zones of blast furnace is determined. The heating program and gas composition at different temperatures for softening and melting in tests are shown in Fig. 4.

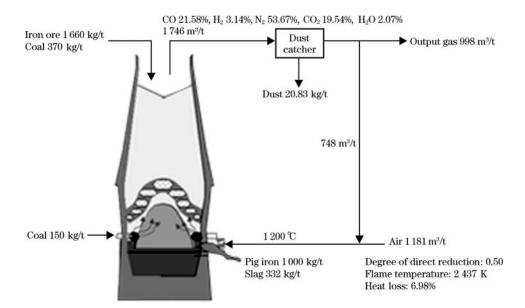
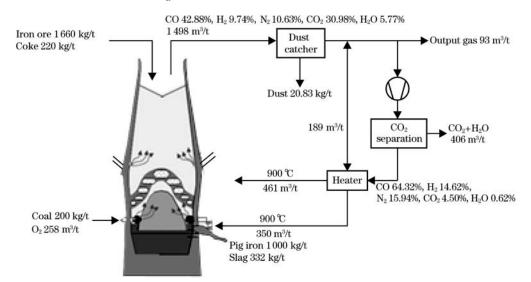
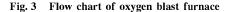


Fig. 2 Flow chart of traditional blast furnace





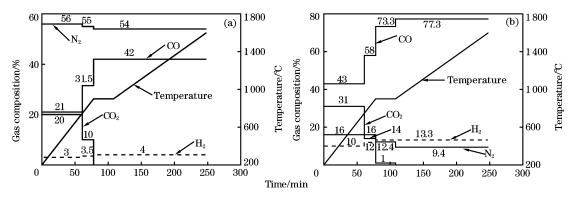


Fig. 4 Experimental condition of traditional blast furnace (a) and oxygen blast furnace (b)

1.4 Data processing

The experimental results of ferrous burden in different conditions are shown in Table 3. The key

temperature points, include $T_{10\%}$, $T_{\rm m}$, $T_{\rm d}$, $\Delta P_{\rm max}$ and S, were automatically recorded by computer, and the $\Delta T_{\rm S}$, $\Delta T_{\rm M}$ and $\Delta T_{\rm SM}$ were obtained by manual

Burden	$T_{10\%}/\mathrm{K}$	$T_{\rm m}/{ m K}$	$\Delta T_{\rm S}/{\rm K}$	$T_{\rm d}/{ m K}$	$\Delta T_{\rm M}/{ m K}$	$\Delta T_{\rm SM}/{ m K}$	$\Delta P_{ m max}/ m Pa$	S/(kPa•K)
Sinter (T-BF)	1508	1738	230	1811	73	303	2342.2	118.54
Sinter (OBF)	1497	1737	240	1801	64	304	1911.0	103.73
Pellet (T-BF)	1376	1581	205	1718	137	342	3263.4	379.96
Pellet (OBF)	1300	1718	418	1731	13	431	1117.2	8.15
Mixed burden (T-BF)	1411	1596	185	1687	91	276	2861.6	215.82
Mixed burden (OBF)	1440	1688	248	1703	15	263	1813.0	19.84

Table 3 Experimental results of ferrous burden in different conditions

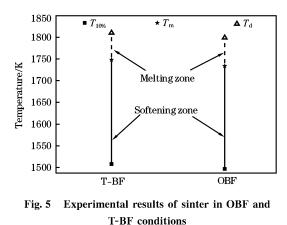
computation. Among them, $T_{10\%}$ is softening starting temperature, at which the burden layer has contracted by 10% (volume percent); $T_{\rm m}$ is softening finishing temperature, at which the pressure drop of the burden layer has reached 490 Pa, and $T_{\rm m}$ is also defined as the melting starting temperature; $T_{\rm d}$ is the dripping temperature which is recorded manually when the first iron drips; $\Delta T_{\rm S}$, $\Delta T_{\rm M}$ and $\Delta T_{\rm SM}$ are defined as softening zone ($T_{\rm m} - T_{10\%}$), melting zone ($T_{\rm d} - T_{\rm m}$) and cohesive zone ($T_{\rm d} - T_{10\%}$), respectively; $\Delta P_{\rm max}$ is the maximum pressure drop; and S is the permeability index, which reflects the total pressure drop across the cohesive zone and can be calculated by Eq. (1).

 $S = \int_{T_m}^{T_d} (\Delta P_{\max} - \Delta P_T) dT$ (1) where ΔP_T is the pressure drop at the temperature of T.

2 Experimental Results

2.1 Softening and melting behavior of sinter

The experimental results of sinter under the conditions of T-BF and OBF are shown in Fig. 5. Compared with traditional blast furnace, the softening starting temperature was decreased by 11 K, but the temperature of softening zone was increased by 10 K in the oxygen blast furnace condition. It is generally acknowledged that the softening of ferrous burden is mainly caused by the onset of liquid phases. As the temperature rose, the liquid gradually formed at the interface of low melting point oxide, and then it would wet the surrounding oxide particles due to reduction of the interfacial free energy. When all the oxide particles in the core of the burden were wet by the liquid, the core had a reduced mechanical strength, and the resistance to deformation would be determined by the iron shell^[12]. Under oxygen blast furnace condition, the reduction potential of the reduction reaction is improved for adding H₂ into the reductive gas, and the crystal stock of metallic iron is generated due to the formation of smaller particles of metallic iron. Therefore, the softening starting temperature of sinter is slightly lower,



1-BF conditions

which is caused by sintering of metallic iron.

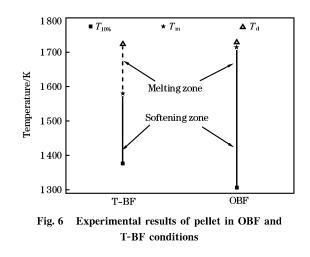
The permeability of burden layer is mainly determined by the melting behavior of ferrous burden, which is measured by the melting starting temperature and melting zone. With the increase of temperature, the liquid oxide volume fraction increases. Meanwhile, the melting point of iron was lowered by gas carburizing. The carburization process also coarsens the structure of iron shell at the periphery of the burden. This leads to the formation of cracks in iron shell and the exudation of the liquid material from the ferrous burden. This temperature is defined as melting starting temperature. The exuded liquid material reacts with carbon present in the adjacent coke layer and the remaining iron oxide is reduced by a direct reduction reaction. This also leads to the closing of the passageway for the gas through the bed, ultimately resulting in the marked increase in pressure drop over the bed. The final meltdown occurs when iron melts. The temperature, at which this phenomenon appears, is commonly known as dripping temperature.

Therefore, the melting starting temperature depends mostly on the thickness of the iron shell. The higher the reduction degree, the higher the melting starting temperature should be. However, the dripping temperature is mainly determined by the exuded unreduced iron oxide and the properties of iron shell. High reduction degree can be achieved in oxygen blast furnace and traditional blast furnace conditions due to its good reducibility, which results in the similar thickness of iron shell; thus, the melting starting temperature is almost identical, whereas the dripping temperature decreases from 1811 K in traditional blast furnace to 1801 K in oxygen blast furnace. This is because the carburization reaction is greatly promoted under the condition of oxygen blast furnace, which decreases the melting point of iron in sinter. Therefore, the melting zone becomes narrow in the oxygen blast furnace, compared with traditional blast furnace. The permeability of burden layer has been improved in oxygen blast furnace condition, which can be confirmed by the permeability index from Table 3 (the S value reduces from 118.54 kPa • K in traditional blast furnace to 103.73 kPa • K in oxygen blast furnace).

2.2 Softening and melting behavior of pellet

The experimental results of pellet in oxygen blast furnace and traditional blast furnace conditions are shown in Fig. 6. Compared with traditional blast furnace, the softening starting temperature sharply decreases from 1376 to 1300 K, and the softening zone of pellet is twice as wide as that of traditional blast furnace in oxygen blast furnace. It can be seen that the crystal stock and sintering of metallic iron have a greater influence on the softening behavior of pellet compared with that of sinter.

In addition, it is well known that the reducibility of pellet is poor due to its dense structure and low porosity, but the CO and H_2 contents in gas have been remarkably improved under the condition of oxygen blast furnace, whose reducibility and penetration are better. Therefore, thicker iron shell can be generated at the periphery of pellet, which has a larger capacity to resist deformation. The generation of



low-melting liquid phase caused by unreduced wustite is decreased with the increase of reduction degree of pellet, and the erosion to iron shell is alleviated. Therefore, compared with traditional blast furnace, $T_{\rm m}$ and $T_{\rm d}$ are increased by 137 and 13 K, respectively, and the melting zone is approximately onetenth. The permeability index decreases from 379.96 to 8.15 kPa • K obviously. The permeability of burden layer is significantly improved in oxygen blast furnace condition.

Meanwhile, the softening zone of sinter and pellet becomes wide, and the melting zone becomes narrow in oxygen blast furnace condition, but the atmosphere has a greater influence on the softening and melting behavior of pellet than that on sinter.

2.3 Softening and melting behavior of mixed burden

The experimental results of different ferrous burdens in traditional blast furnace and oxygen blast furnace conditions are shown in Fig. 7. The softening starting temperature of mixed burden is found between those of sinter and pellet in T-BF and OBF conditions, and the mixing of sinter and pellet results in the drop in the softening zone and melting zone for the

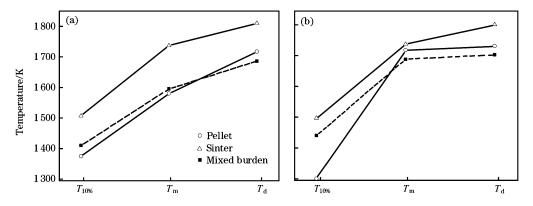


Fig. 7 Experimental results of different ferrous burdens in T-BF (a) and OBF (b) conditions

mixed burden. In addition, compared with traditional blast furnace, the temperature of softening zone of mixed burden is increased by 63 K, but the temperature of melting zone is decreased by 76 K. The maximum pressure drop and the permeability index are decreased from 2861. 6 Pa and 215. 82 kPa • K to 1 813.0 Pa and 19.84 kPa • K, respectively (Table 3). The burden permeability is obviously improved in oxygen blast furnace condition. This is mainly caused by the change of the melting behavior of pellet. Kaushik and Fruehan^[13] researched the mechanism of burden interaction and melt exudation phenomenon; it found that the melt dripping was predominantly observed in olivine fluxed pellets. Therefore, compared with traditional blast furnace, the melting behavior of mixed burden, which could reflect permeability of burden layer in blast furnace, is improved due to the improvement of high temperature properties of the pellet.

2.4 Quality of dipping iron

The carbon and sulfur contents in dripping iron of pellet and mixed burden in T-BF and OBF conditions are shown in Table 4. Compared with traditional blast furnace, the carbon content in dripping iron of pellet and mixed burden decreases from 3.09% and 2.97% to 2.44% and 2.92% in oxygen blast furnace condition, respectively. The reason is that the carbon content of dripping iron is determined by two aspects. One is carburization of CO to iron before melting. The other is the carburization of coke in the process of melting zone and iron dripping. And the latter is the key factor to determine the final carbon content of dripping iron. Previous research pointed out that the highest carbon content of solid sponge iron at equilibrium was 1.5%through theoretical calculation, while due to the limitation of reaction kinetics, the carbon content cannot reach such a high level^[14]. In addition, Inayoshi and Hayashi^[15] found that under the condition of H₂ replacing half of CO in gas, when the temperature reached 1673 K, the carbon content in sinter was only 0.6%. As shown in Table 3, the melting zone of pellet in oxygen blast furnace is about 10.5 times more than that of the traditional blast furnace, and it is 6.1 times for mixed burden. Therefore, the contact time of ferrous burden and coke is longer in traditional blast furnace condition, and the carburization is also more effective; in addition, the dripping temperature of pellet is higher than that of mixed burden, resulting in the significantly higher re-

	Table 4 Content of carbon and sulphur in						
	drippi	mass%					
	Burden	С	S				
_	Pellet (T-BF)	3.09	0.047				
	Pellet (OBF)	2.44	0.030				
	Mixed burden (T-BF)	2.97	0.082				
	Mixed hurden (OBF)	2 92	0.030				

duction of carbon content in dripping iron of pellet than that of mixed burden.

The sulfur content in dripping iron reduces from 0.047% and 0.082% to 0.030% under condition of oxygen blast furnace. The fundamental reaction of the desulphurization of slag can be expressed by Eq. (2), and its desulfurization capacity is usually measured by distribution coefficient of sulfur (L_s) , which is shown by Eq. (3)^[14].

$$[FeS] + (CaO) = (CaS) + (FeO)$$
(2)

$$L_{\rm S} = K_{\rm S}^{\theta} \times \frac{\gamma_{\rm [S]}}{\gamma_{\rm (CaS)}} \times \frac{\gamma_{\rm (Ca())} w_{\rm (Ca())}}{\gamma_{\rm (Fe())} w_{\rm (Fe())}}$$
(3)

where, $K_{\rm S}^{\theta}$ is the equilibrium constant, which is a function of absolute temperature; $\gamma_{\rm [S]}$ is the activity coefficient of sulphur in the iron; $\gamma_{\rm (CaS)}$, $\gamma_{\rm (FeO)}$, and $\gamma_{\rm (CaO)}$ are the activity coefficient of CaS, FeO and CaO in the slag, respectively; and $w_{\rm (CaO)}$ and $w_{\rm (FeO)}$ are the contents of CaO and FeO in the slag, respectively.

Therefore, there are two possible reasons for explaining the reduction of sulphur in dripping iron under the condition of oxygen blast furnace. On one hand, as the reduction potential of the gas has been greatly improved and the reduction degree of ferrous burden is greatly increased, the FeO content of slag is reduced and the distribution coefficient of sulfur is increased. Thus, the desulfurization capacity of slag is enhanced. On the other hand, the melting zone of pellet and mixed burden was shortened sharply in oxygen blast furnace, and the resulphurization caused by the contact of metallic iron and coke decreases obviously.

3 Conclusions

(1) Under the condition of oxygen blast furnace, the softening starting temperature and dripping temperature of sinter decrease from 1508 K and 1811 K to 1497 K and 1801 K, respectively, but the melting starting temperature is almost unchanged. Therefore, the softening zone became wide, while the melting zone became slightly narrow, and the permeability of burden layer was improved to some extent.

(2) The softening zone of pellet in oxygen blast

furnace condition is twice as wide as that in the traditional blast furnace condition, but the melting zone is approximately one-tenth. Therefore, the permeability of the burden layer is significantly improved.

(3) Under the condition of oxygen blast furnace, the temperature of softening zone of mixed burden is increased by 63 K, but the temperature of melting zone is decreased by 76 K. Therefore, the permeability of material layer is significantly improved.

(4) The quality of dripping iron of pellet and mixed burden is obviously improved in oxygen blast furnace condition. The carbon content in dripping iron of pellet and mixed burden decreases from 3.09%and 2.97% to 2.44% and 2.92%, respectively, and the sulfur content in dripping iron decreases from 0.047% and 0.082% to 0.030%.

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