Mechanism and Control Study on Metallized Pellet Bonding with High Temperature

Jie QIN[a,*], Gong-Guo LIU[b]

Pangang Group Research Institute Co., Ltd., State Key Laboratory for Vanadium Titanium Resources Comprehensive Utilization, Pabzhihua 617000, China

[a]qinjie110110@126.com, [b]cquart2@126.com

*Corresponding author

Keywords: Metallized Pellets, Bonding at High Temperature, Oxidation.

Abstract. The problem of metallized pellet bonding at high temperature, which appeared in the production of Pangang pilot plant for resources comprehensive utilization, is analyzed. It shows that it is the main cause leading to the metallized pellet bonding of low melting silicate phase bonding, and it is caused by metallized pellet re-oxidation. Experiments are carried out to investigate the influence of different anti-oxidation ways on pellet metallization rate, and to verify it with the method of nitrogen protection. Results show that metallized pellet bonding could be avoided effectively by nitrogen protection, which could ensure smooth pilot production of metallized pellet.

Introduction

In order to improve the utilization level of V-bearing titaniferous magnetite resources and recovery Fe, V and Ti from the magnetite iron ore efficiently, the 100,000/tpy V-bearing titaniferous magnetite comprehensive utilization pilot plant has been constructed by Pangang Group in 2010. In the pilot plant rotary heath furnace (RHF) and electric arc furnace (EAF) are the core devices and the main process is direct reduction in RHF-melting and deep reduction in EAF-desulfurization of hot metal- vanadium recovery-iron ingot. This is a new process and through running of the pilot plant could supply lots of data for the technical and economic target which can provide support for the industrialization of the process.

The temperature of the metallized pellets produced by RHF is around 800～1000℃ and the pellets are conveyed to the feed bins of EAF by heat preservation tanks. In real production, if the pellets stay in the tanks or the bins for a long time, they will bond with each other and form large scale materials that could block exports of the tanks and bins, and the normal production is restricted seriously. So it is necessary to study the mechanism of the pellets bonding at high temperature and find out effective measures to solve this problem.

Study on the Mechanism of Metallized Pellets

Pellets Bonding Phenomenon

The experiment materials are V-bearing iron ore concentrate and anthracite. The components content of the materials are shown in table1 and table 2. Table 3 shows the analysis result of the bonding metallized pellets which have been stored in tanks and bins for certain time. We can see that metallic iron almost oxidized completely and exist as Fe_2O_3. Besides, the carbon content decreases sharply and nearly to zero.

Tab.1 Components content of V-bearing iron ore concentrate/%

Components	TFe	FeO	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	V_2O_5	TiO_2
Content/%	54.75	33.29	41.29	3.96	0.55	3.56	3.59	0.59	12.68

Tab.2 Components content of anthracite powder/%

Components	C	Ad	Vdaf	S
Content/%	76.64	14.90	8.24	0.44

Tab.3 components content of the metalized pellets/%

Sample number	TFe	FeO	MFe	Fe_2O_3	$C_{残}$	Metallization rate
A reference sample	58.28	16.50	45.44	<0.5	3.34	78.0
Bonding sample 1	52.7	1.29	<0.5	73.82	0.033	/
Bonding sample 2	52.6	0.56	<0.5	74.45	0.021	/
Bonding sample 3	54.2	20.91	4.25	48.08	0.022	7.8

Bonding Mechanism of the Metallized Pellets at High Temperature

Metallized pellets have the feature of high porosity, and they will have high reaction activity under high temperature. If the metallized pellets expose to the air directly the oxidation reaction will happen between metallic iron and oxygen to form iron oxides and release heat at the same time. The oxidation reaction is slow at room temperature but the reaction rate speed up quickly when the temperature over 200℃. If pellets contain certain amount carbon in them, the domino effect of iron oxidation and heat releasing will lead 'self-ignition' of the metallized pellets and the metallic iron produced by direction reduction will become to Fe_2O_3 under this condition [1]. So the re-oxidation of metallized pellets not only reducing the metallization rate of the pellets but also contribute to the melting of silicate with low melting point and make the pellets bond into blocks when they squeeze with each other in the transport process.

Through petrographic analysis of the bonding metallized pellets we get the phase compositions and their volume fractions. The data are shown in table 4. It can be seen that there is high metallic iron content in the pellets that have been protected, however, in the bonding pellets the iron element exits in the form of titanium hematite which is corresponding to the data shown in table 3.This means the bonding pellets have been oxidized and the SEM photos of the bonding areas of the pellets are shown in figure 1and figure 2, and the electron probe microanalysis results are shown in table5 and table 6. It can be seen from table 5 that at the edge of sample 2 the main phases are hematite, magnetite, and silicate. Similar to sample 2, from table 6 we can know that main phases at the edge of sample 3 are titanium hematite and silicate.

Tab.4 Phase compositions and their volume content of the bonding metallized pellets/%

Sample number	Iron anosovite	Metallic iron	Silicate	ulvite	fayalite	Titanium magnetite	Titanium hematite
Bigger part of sample 1	15-18	56-61	24-27				
Smaller part of sample 1	5-8	42-47	26-29	20-23			
Core part of sample 2			14-17			8-11	73-78
Edge of sample 2	5-7		16-19	2-4		3-5	67-72
Core part of sample 3			5-8		15-18	3-5	71-76
Edge of sample 3			10-13		4-6	12-15	66-71

Note:sample1 refers to the pellet that have been protected in the sealed iron box, sample 2 refers to the bonding pellet that stored in tanks, and sample 3 refers to the bonding pellet that stored in the bins.

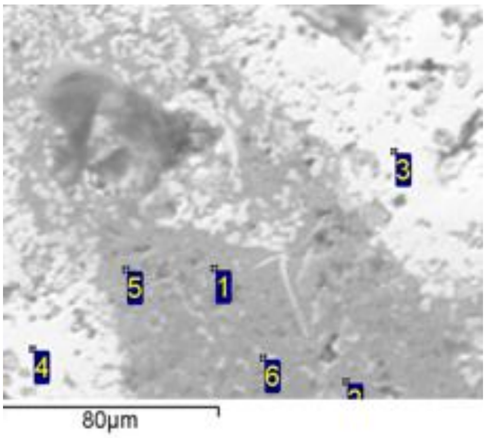

Fig.1 Photo of the edge of sample 2

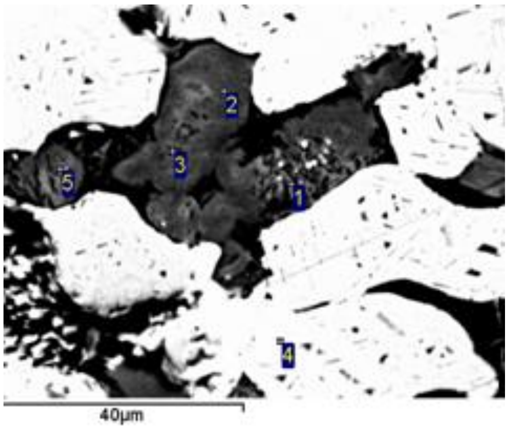

Fig.2 Photo of the edge of sample 3

Tab.5 Mass percent of the points in the edge of sample 2 tested by electron probe/%

Number	Phases	O	Mg	Al	Si	Ti	Fe
1	Silicate	42.91	19.31	13.34	24.44		
2	Silicate	40.73	36.46		22.81		
3	Hematite	24.28					75.72
4	Magnetite	20.29					79.71
5	Silicate	42.60	25.18		32.21		
6	Silicate	35.12	18.40	9.01	24.96	12.51	

Tab.6 Mass percent of the points in the edge of sample 3 tested by electron probe/%

Number	Phases	O	Mg	Al	Si	K	Ca	Ti	Fe
1		33.12	12.06		19.88				34.94
2		36.48	6.39	1.93	19.55	1.45	1.25	1.20	31.76
3		34.42	12.61		18.66		0.91		33.40
4	Titanium hematite	24.90		2.44				8.62	64.03
5		30.75		5.25	9.58		1.29	6.30	46.83

From the analysis of the phase compositions about the bonding pellets we get that the main phases at the bonding areas are titanium magnetite, titanium hematite and silicate. The iron element in metallized pellet should be re-oxidized at high temperature and releases large amount of heat which would make the temperature of the pellet rise up sharply and parts of the silicate with low melting point will melt and bond with each other at the action of gravity. Value of the heat released by the pellets re-oxidation has been estimated and the related data of the pellet without oxidation are shown in table 3(A reference sample).

Enthalpy of the Fe element oxidized in to FeO and Fe_2O_3 are -266.68kJ/mol and -822.62 kJ/mol. Suppose there are 30% of the MFe are oxidized into FeO and 30% into Fe_2O_3 then 1.65×10^6J of heat will be released from 1kg metallized pellet. One tank could store pellet around 6t and would release heat of 9.9×10^9J. On the other side, heat is dissipating at the same time. The tank is a cylinder with the size of φ1.9m×2.0m and inner wall of the tank has been knotted 50mm thick stamp mass. Ignoring the thickness of steel plate of the tank, considering the heat dissipation of stamp material only, setting the thermal conductivity as 1.0 W/(m•K)and different in temperature between inside and outside of the tank as 500K, the heat dissipating will reaches to 3.4×10^9J during 8 hours.

Difference between heat released by the pellets and that of dissipated by the tank is the part that would warm up the pellets and make the temperature rise sharply ($Q_{releasing}$-$Q_{dissipating}$ = Q_{rising}). The specific heat formula of the metallized pellets is shown as Eq.1:

$$C_{\mathrm{p}} = \sum a_i C_{pi} \tag{1}$$

C_p—Isobaric heat capacity of each component, α_i—Mole fraction of each component.

C_{pi}——heat capacity calculation formula of each component.

One tank could contain 6 t metallized pellets and the heat which rising up the temperature of the pellets can be calculated as follow:

According to the formula of $Q_{releasing}$-$Q_{dissipating}$ = Q_{rising} and using value test method we get that T=2146K, which means temperature of the inner pellets can reach about 1873℃.

Take the samples shown in table 5 (number 1 and 6) and samples shown in table 6 (number 2) as examples to estimate the melting point of silicate. According to CaO-Al_2O_3-$SiO_2$and MgO-Al_2O_3-SiO_2 ternary phase diagram, melting points of the three samples are all below 1500℃, besides, there are other phases contained in the pellets so the melting point of the silicate should be lower than 1500℃. In a word, the pellets will be re-oxidized at high temperature and release large amount of heat which can make the pellets temperature rising sharply, then oxidizing reactions become speedier and more heat release, and the pellets get higher temperature. With the temperature rising parts of the silicate will melt and bond into block at the gravity action.

Study on Anti-oxidation Technology of the Metallized Pellets

Re-oxidation is the cause of metallized pellets bonding, therefore lab experiments have been carried out to study the effects on the metallization rate by different anti-oxidation methods. Based on the results of the metallization rate the anti-oxidation measures and the corresponding parameters can be confirmed.

Experimental materials are V-bearing iron ore concentrate and anthracite. The components content of the materials are shown in table1 and table 2. High temperature resistance furnace is applied as the equipment. Experimental parameters and results are shown in table 7. It can been seen from table 7 that nitrogen sealing has the best effect for prevent reducing of the metallization rate of the pellets at the conditions of reduction temperature is 1350℃, reduction time are 30mins and C/O is 1.2 and the metallization rate reaches to 95.58%. Coal sealing takes the second place and the metallization rate is 94.28%. For the air cooling and water cooling process there exist re-oxidation phenomena of the metallized pellets.

Tab.7 Experimental scheme and results

Reduction temperature/℃	Reduction time/min	C/O	Protecting measures	Metallization rate/%
1350	30	1.2	Coal sealing	94.28
1350	30	1.2	Air cooling	91.01
1350	30	1.2	Water cooling	93.69
1350	30	1.2	Nitrogen sealing	95.58

Practices of the Nitrogen Sealing Applied to Protect Metallized Pellets in the Pilot Plant

According to the experimental results and considering the actual conditions of the plant, measures of blowing nitrogen into the tanks and bins and sealing them with lids at same time have been taken to protect the metallized pellets. Concrete measures are shown as follows: 1) Installing gas blowing device at the outlet of the tank and blowing nitrogen into the inner tank by the device during discharging process, so the air could be fully separated from the pellets. 2) Sealing the tank outlet with lid after the tank is full of pellets. 3) Installing gas blowing device at the imports of the bins and blowing nitrogen into the inner bins by the device during the pellets stay in the bins. 4) Sealing the imports of the bins with lids after the bins is full of pellets.

Adopting these measures has achieved good results. Under same production conditions metallized pellets with high temperature do not bond with each other in the tanks and bins which evidently improves the production efficiency and provides guarantee for the pellet hot charging. The metallization rate of the pellets maintains at a high level (shown in table 8) and it has been increased by 43% compering with the pellets that do not take any protective measures (metallization rate is 28.5%).

Tab.8 metallization rate comparison between the protected metallized pellet and the non-protected metallized pellets/%

Sample number	Conditions	TFe	FeO	MFe	Fe_2O_3	Metallization rate
1#	Samples put in sealing container	55.26	19.11	40.41	<0.5	73.1
2#	Samples come from the tank that sealed by nitrogen and lid	54.86	19.96	39.33	<0.5	71.7
3#	Samples come from the tank that open the outlet and do not take any protection measures	53.06	28.95	15.13	24.02	28.5

Conclusions

The pellets will be re-oxidized at high temperature and release large amount of heat which can make the pellets temperature rising sharply, then oxidizing reactions become speedier and more heat release, and the pellets get higher temperature. With the temperature rising parts of the silicate will melt and bond into block at the gravity action.

Measures of nitrogen sealing, coal sealing and water cooling can restrain re-oxidation of the metallized pellets and the nitrogen sealing could get better results. Metallization rate of the pellets protected by nitrogen could reach to 95.58%.Coal sealing takes the second place and the metallization rate is 94.28%. For the water cooling,the metallization rate can achieve 93.69%.

In the real production, blowing nitrogen into the tanks and bins, meanwhile, covering the outlets with lids are good measures to prevent bonding of the pellets. Compering with the not protected pellets the metallization rate of the pellets that have been protected is improved by 43%.

Reference

[1] Xia. Chen, Lei. Zhang, Fei. Wang. Transporting, storing and applying in the BOF of the direct reduction iron [J].IRON &STEEL SCRAP OF CHINA, 2006, (2):22-23.