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Integrated Reduction of the Self–Reducing Pellets on the Blast Furnace

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Комплексне відновлення самовідновних гранул на доменній печі

The objective *of the present work is to research a quantitate ratio of degree direct reduction inside of SRP and degree of indirect reduction outside of SRP on the top of the blast furnace.The reactions of direct and indirect reduction occurring during the heat treatment of self reducing pellets (SRP) have been studied. In this investigation Blast furnace (BF) sludge which contains particles of coke, has been included in the SRP blend as a source of solid reductant and iron bearing oxides.*

In the SRP as a part ot the blast furnace burden occur the reactions simultaneously: inside of SRP-direct reduction by C_{solid}; gasification of carbon and indirect reduction by CO; and outside of SRP-indirect reduction of iron bearing oxides by reducing gas coming from the hearth of blast furnace through the column of charged materials. ***The experimental*** *setup is shown in Fig. 1. It con-sists of a electrical heating furnace, which can be moved up and down. The quartz tube passes through the furnace. The reaction zone is in the middle of the furnace. Neutral argon atmosphere is created and for indirect reduction argon changed - on hydrogen. Gases of argon, hydrogen are introduced into the furnace separately. Wire of nickel alloy chromosome joins the scales test. A thermocouple is located in the tube.The crucible of wire chrome-nickel was permeable.****Metohd.*** *The experiments was performed continuously from the start temperature (~200 ˚C) to the experimental temperature (500 ˚C; 700 ˚C; 900 ˚C; 1100 ˚C) in argon free environment. Upon reaching the desired temperature argon was replaced by hydrogen during 30 minutes. After that the reduced probe of SRP was cooled in argon.* ***Results****. The integrated degree of reduction is equal 100%, which includes 98,6 % direct reduction by solid carbon under temperatures 1100°C. The chemical analysis of the reduced SRP showed the degree of integrated reduction change from 85,79 % (900 °C) to 92,50 % (1000 °C) and 84,6% (1100°C) and metallization 83,30 % (900 °C), 89,90 % (1000 °C), 80,75 % (1100 °C).These data correspond to results of degree of reduction SRP depends on temperature*

KEY WORDS: self reducing pellets; direct and indirect reduction degree.

Метою *даної роботи є дослідження кількісного співвідношення ступеня прямого відновлення всередині СРП та ступеня непрямого відновлення поза СРП на верхній частині доменної печі Досліджено реакції прямого та непрямого відновлення, що відбуваються під час теплової обробки самовідновних гранул (СРП). У цьому дослідженні шлам доменної печі (ДП), що містить частинки коксу, був включений до суміші SRP як джерело твердого відновника та оксидів, що містять залізо. У СРП у складі доменної печі одночасно відбуваються реакції: всередині СРП - пряме відновлення за допомогою твердого вуглецю; газифікація вуглецю та непряме відновлення за рахунок СО; а поза SRP - непряме відновлення заліза, що містить оксиди, за рахунок відновлення газом, що надходить із вогнища доменної печі через стовп загружених матеріалів.* ***Експеримент.*** *Експериментальна установка складається з електричної нагрівальної печі, яку можна переміщати вгору і вниз. Кварцова трубка проходить через піч. Зона реакції знаходиться посередині печі. Створюється нейтральна атмосфера аргону, а для непрямого відновлення аргон змінюється - на водень. Гази аргон, водень вводяться в піч окремо. Дріт із хромонікелевого сплаву приєднується до вагів. У трубці розташована термопара, тигель із дротяного хромонікелю був проникним.****Методика досліджень*** *Експерименти проводились безперервно від стартової температури (~ 200 ˚C) до експериментальної температури (500˚C; 700˚C; 900˚C; 1100˚C) у середовищі, вільному від аргону. Після досягнення бажаної температури аргон замінювали воднем протягом 30 хвилин. Після цього відновлений матеріал охолоджували в аргоні.* ***Результати.*** *Інтегрований ступінь відновлення дорівнює 100%, що включає 98,6% прямого відновлення твердим вуглецем при температурах 1100 ° С.2. Хімічний аналіз відновленого SRP показав ступінь зміни інтегрального відновлення від 85,79% (900 ° C) до 92,50% (1000 ° C) і 84,6% (1100 ° C) і металізації 83, 30% (900 ° C), 89,90% (1000 ° C), 80,75% (1100 ° C). Ці дані відповідають результатам ступеня зниження SRP в залежності від температури*

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КЛЮЧОВІ СЛОВА: самовідновні гранули; прямий і непрямий ступінь зменшення.

Introduction

In recent years, to optimize the reducing process in the blast furnace a great attention is paid to self reducing pellets (SRP). These materials are used already in the operating blast furnace [1-5].

The consumption of SRP from 60 to 80 kg/t_{NM} was used in the commercial blast furnace melt. It provides the coke rate lowering by 10-15 kg/t_{hM} and the degree of direct reduction falls by 2% [2].

The consumption of SRP could be come to 200 kg/t_{HM} in the blast furnace charge [3,4].

Results of the blast furnace operation indicated that SRP charged into the blast furnace does not reduce the gas permeability of the charge and does not

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disturb the smooth run of blast furnace. Reduction of the iron oxides contained in the SRP starts at low temperature zone and reduction to come to an end earlier as the sinter and pellets. Thus there is a tendency to a significant reduction in coke consumption.[5)]

The mechanism and kinetics of self reduction has already been modelled. These models take into consideration not only the kinetics of gasification and reduction reactions but also the mass and heat transfer phenomena [6,)].

The simultaneous reaction between reduction and gasification of carbon was examined. The obtained results are as follows: coupling phenomen between reduction and gasification existed. The starting temperature of reduction was 250 ˚C in the hematite graphite facing pair while the temperature was 420 ˚C in the single hematite.[7)]

It was calculated reduction degree at different temperatures during thermal analysis of SRP samples. Iron oxide reduction seems to start in relatively low temperature range between 500-600 ˚C. A possible explanation is that some carbon gasification catalyzed by H_2O from dihydroxylation of hydrates [8.9)].

The reduction mechanism of pellets with reducing gas can be transferred to the SRP [10,11)].

The contribution ratios of direct reduction by solid carbon and indirect reduction and carbon gasification were estimated through reduction experiment of the composite under inert atmosphere. The reduction from Fe_2O_3 to Fe_3O_4 proceeds at low temperature. During this period direct reduction proceeds because new contact points between Fe_2O_3 and carbon are formed. The contribution ratio of the direct reduction as approximately 45% during the reduction from Fe_2O_3 to Fe_3O_4–[12)]. If carbonaceous material and iron bearing oxides could be adjoin, the starting temperature of the reaction could be lowered. With the increase in the degree of contact in such mixture the starting temperature is lowered. It is an effective method to increase the rate of direct reduction [13)].

The blast furnace process differ from the processes production of iron by direct reduction. In the SRP as a part of the blast furnace burden occur simultaneously reactions: inside of the SRP –direct reduction by carbon (solid); gasification of carbon and indirect reduction by mono oxide of carbon and outside of SRP – indirect reduction by reducing gas coming from hearth of the blast furnace.

A significant number of research of a reduction processes carried out in the carbon composite agglomerates in an inert atmosphere (nitrogen, argon). From the point of a view of the use in the blast furnace process SRP it is necessary to take into account indirect reduction of iron bearing oxides by reducing gas coming from the hearth of through the column of charge materials of the blast furnace.

The purpose of this paper is to estimate the ratio of indirect and direct reduction SRP depending on the temperature in the range of 500-1100 ˚C.

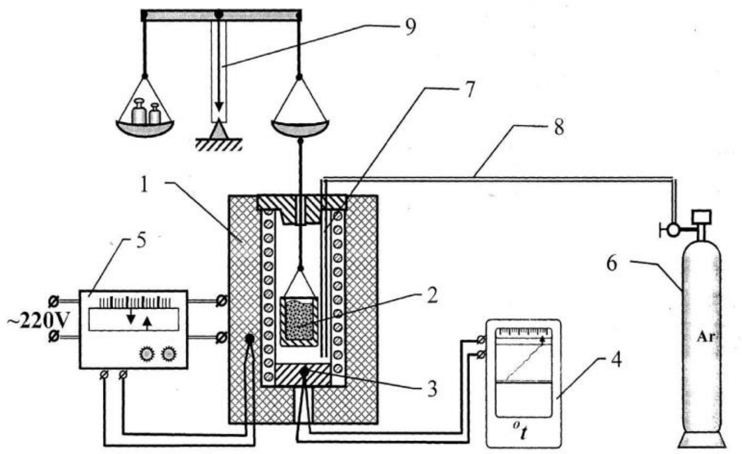

Fig. 1 Diagram of the installation for the reduction of iron ore materials:

1 - tubular heating electric furnace; 2 - crucible with the test material; 3-thermocouple; 4 -automatic potentiometer for temperature control; 5 -automatic temperature regulator in a furnace with a thermocouple; 6-gallon with inert gas; 7-alundum tube; 8-rubber tube; 9 -analytical balance.

2. Experimental Procedure.

2.1. Sample

SRP sample was selected from industrial parties. The chemical composition and physical characteristics of the sample are given below: SRP produced the mixture of a blast furnace and converter sludge in proportion (3: 2), with the addition of portland cement.

Chemical composition of SRP. %

Fe_{tot}	FeO	Fe_2O_3	SiO_2	CaO	MgO	C
43,10	8,00	52,68	7,50	14,00	8,00	9,82

Fractional size of SRP.

Size, mm	40-20	20-15	15-10	10-5	5-0
Yield, %	37,00	45,00	12,00	1,80	4,20

The SRP have been produced on the pelletizer 5,5 m. with productivity 25-30 ton per in an hour. After an probe exposure during 28 day the compressive strength of SRP was in average 90 kg/pellet.

The bulk weight g/cm^3-1,4.

Reaction behavior SRP involving with reduction of iron bearing oxide has been investigated with size of SRP ranked between 10-15 mm was set in reaction crucible and in reaction tube.

2.2. Research facility

The experimental setup is shown in Fig. 1. It consists of a electrical heating furnace, which can be moved up and down. The quartz tube passes through the furnace. The reaction zone is in the middle of the furnace. Neutral argon atmosphere is created and for indirect reduction argon changed - on hydrogen. Gases of argon, hydrogen are introduced into the furnace separately. Wire of nickel alloy chromosome joins the scales test. A thermocouple is located in the tube.The crucible of wire chrome-nickel was permeable.

The reduced sample of SRP was to cool in Ar gas until room temperature was reached.

2.3.Experimental Procedure reduction of SRP by Hydrogen. Thermogravimetric method was used to measure the degree of a reduction depends on the temperature. The SRP fraction 10 - 15 mm was used. The furnace temperature was varied in the range 500-1100 ˚ C. The heating rate of the sample was varied in the range of 27.7 - 29.5 ˚ C/min.

In this investigation chemical analysis of reduced samples after thermal treatment was feasible. An attempt to calculate reduction and metallization degree was done using results from chemical analysis and the change in mass due to oxygen removal from iron oxides of SRP separately due to direct reduction and indirect reduction. Reduction degree has been defined as follows.

$$RD\ (\%) = (\frac{\Delta m_{red}}{m_{initial}}) \times 100\%$$

Where RD – is reduction degree, %

Δm - is the change in mass due to oxygen removal from iron oxide;

$m_{initial}$ – initial mass of sample.

The SRP samples from heated to temperature: room (20˚C) and 1000 ˚C were studied using the methods of manual microscopy and petrography of ore using a notarizing microscopy the MIN – 9 microfotometric device PME – 1. An ore, slag and carbonaceous components were determined by reflectance, colour, polarization effect and internal reflex.

Results and discussion

Results of SRP reduction process study shown in table 1 and figure 2. The experiments were performed continuously from the start temperature (~200˚C). The sample was placed in an furnace and heated to the experimental temperature under argon, and then replacement by hydrogen reducing gas, at this temperature for 30 min. This cycle is to be repeated for the temperatures: 500 ˚C;700 ˚C; 900 ˚C; 1100 ˚C.

Fig 2 shows the dependence the reduction degree of the iron oxides of SRP on the temperature. The direct reduction degree of the SRP is 7,6%, at the temperature 500˚C.

Fig 2 shows the change in the indirect reduction degree of iron oxides of SRP by reducing gas-hydrogen on the outside surface of SRP. The degree of indirect reduction is 8,9 % at the temperature 500˚C.

Integrated degree of direct and indirect reduction is equal 16,5 %. Initial probe of SRP contains 43,1 % Fe_{tot}; and 8 % FeO that it is corresponded to content of 34,88 % Fe_3O_4. Thus Fe_2O_3 could be reduced to Fe_3O_4. The following calculation let us to understand that integrated degree of reduction 16,5 % corresponds approximately to reduction of Fe_2O_3 to Fe_3O_4. It occurs due to reaction $3Fe_2O_3 = 2\ Fe_3O_4 + {}^1\!/_2 O_2$. The content of oxygen in Fe_2O_3 to transfer for Fe_3O_4 could be : $\frac{52,68\times144}{480} = 15,8\%$ that corresponds approximately integrated degree of reduction (16,5 %) to get experimentally at temperarure 500°C (table 1).

Where: 52,68 – content of Fe_2O_3 in initial sample of SRP

144 – content of oxygen in 3 Fe_2O_3 according to reaction

480 – molecular mass of Fe_2O_3 according to reaction.

As to direct reduction of Fe_2O_3 to Fe_3O_4 by solid carbon which proceeds at temperature 200 – 500 ˚C, the gasification rate is very small. During this period direct reduction prossesds due to contact between Fe_2O_3 and partical of carbon of wich are formed continuously due to expansion of iron oxides. The contribution part of the direct reduction by carbon during the reduction from Fe_2O_3 to Fe_3O_4 {7,6 : 16,5}*100%= 46,06 % where:7.6% degree of direct reduction and 16.5% integrate reduction of SRP. It corresponds result to report earlier[12)].

Table 1.

Results of the integrated reduction of self-reducing pellets.

Temperature, oC	Summary duration of experiment, min	Summary loss of mass, g	Reduction by carbon in argon athmosphere			For time of reduction of hydrogen			Integrated reduction degre, %
			Duration, min	loss of mas,g	Degree of reduction	Duration, min	loss mass, g	Degree of reduction,%	
500	48,0	0,76	18,0	0,35	7,6	30	0,41	8,9	16,5
700	55,0	3,44	25,0	1,61	34,9	30	2,87	62,2	97,1
900	61,5	4,93	31,5	2,40	48,7	30,1	2,53	51,3	100,0
1100	62,0	4,61	56,0	4,55	98,6	6	0,064	1,4	100,0

The degree of the iron oxides SRP reduction by hydrogen shows 8,9 % at temperature 500 ˚C. The reduction mechanism of burnt pellets by reducing gas could be transferred to the reduction of SRP. The degree of direct reduction by carbon and indirect reduction of iron oxides by hydrogen of SRP are equal 34,9 % and 62,2, % correspondingly at the temperature 700 ˚C. After reduction $Fe_2O_3 \rightarrow Fe_3O_4$ the total contents of magnetite could be 178,6 g/mol and oxygen (O_2) – 49,2 g/mol.

The integrated degree of the SRP reduction at the temperature 700 °C is equal 97,1%. The contribution part of the direct reduction is 34,90 and 48,70% at the temperature 900 °C and 98,60% at the temperature 1100 °C.

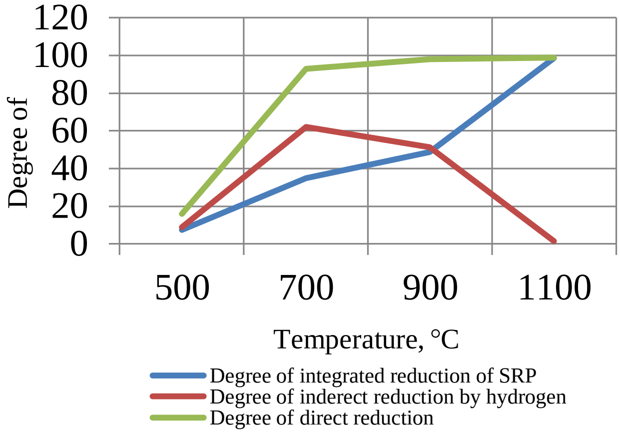

Fig.2 Depends of degrees of the SRP reduction on the temperature

Table 2.
Chemical analysis of reduced SRP

Temperature, °C	Content of the component,%					Content of oxide oxygen,%	Degree of reduction, %	Degree of metalization, %
	Fe_{total}, %	FeO	Fe_2O_3	Fe_{metall}	Carbon-residual			
1100 °C	60,00	11,80	2,05	48,45	0,67	0,10	84,60	80,75
1000 °C	59,25	3,95	5,30	53,30	0,85	0,19	92,50	89,90
900 °C	62,20	7,85	4,70	51,85	0,63	0,35	85,70	83,30

Fig 2 shows that indirect degree of the SRP reduction is higher than direct reduction up to 900˚C when indirect and direct reduction of SRP are equal approximately. When the temperature is higher then 900˚C the direct reduction degree of iron bearing oxides of SRP increase from 53,1 % to 100 % at the temperature 1100˚ it occurs due to reaction of gasification of carbon inside of the SRP ($C+CO_2=2CO$). Chemical analysis of reduced samples of SRP showed the higher degree of reduction and metallization in range of temperature from 900˚C to 1100˚C.

4.Conclusions

The following results are obtained.

1. The reduction F_2O_3 to Fe_3O_4 proceeds by direct reduction (degree of direct reduction is 46, 06%) and indirect reduction by hydrogen (degree of reduction 53,94% under temperature 500°C. The content of oxygen in F_2O_3 to transfer for Fe_3O_4 is equal 15,8% that is approximately corresponds to integrated degree of reduction – 16,5%. The same way integrated degree of SRP is equal 97,1% (t°C- 700°C) which includes 34,9 % by direct reduction and 62,2% indirect temperature 700 °C; integrated degree t°C=900°C 97,1% which includes 48,7 % by direct reduction and 51,3 % indirect reduction. At temperature - 1100°C, direct reduction – 98,6%, and indirect – 1,4%.

The integrated degree of reduction is equal 100%, which includes 98,6 % direct reduction by solid carbon under temperatures 1100°C.

2. The chemical analysis of the reduced SRP showed the degree of integrated reduction change from 85,79 % (900 °C) to 92,50 % (1000 °C) and 84,6% (1100°C) and metallization 83,30 % (900 °C), 89,90 % (1000 °C), 80,75 % (1100 °C).These data correspond to results of degree of reduction SRP depends on temperature.

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