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THERMAL ANALYSIS IN EXAMINATION OF REDUCTION OF BLAST FURNACE PELLETS

J. Orewczyk, S. Jasieńska and S. Iwanczenko

Faculty of Metallurgy and Materials Science, University of Mining and Metallurgy
30–059 Cracow, al. Mickiewicza 30, Poland

Abstract

This paper presents applications of thermal analysis to observe the course of reduction of acidic pellets, metallurgical substances whose reducibility and strength are basic parameters of use in blast furnace processes. Both parameters depend on the mineral composition of the samples. The investigations included determination of the chemical and phase compositions of the initial samples and reduction products.

Research was conducted on acidic pellets from Połtawa (Poland), applied in the T. Sendzimir Steelworks (Poland), in comparison with pellets from Brazil, Canada and Lebedyn (Russia).

Keywords: acidic pellets, blast furnace charge, thermal analysis

Introduction

Blast furnace pellets are metallurgical substances which are used together with high-basicity sinter as blast furnace charges. Obtained by lumping fine ore fractions, they are characterized by homogeneity and high iron content. In Poland, the proportion of acidic pellets in blast furnace charges has recently increased, due to the low cost and little danger to the environment.

Acidic pellets from Brazil, Canada, Russia (Lebedyn) and Poland (Połtawa) were examined in order to determine their chemical compositions and physico-chemical properties. Conditions of the reduction acidic pellets were determined after thermal analysis with a Mettler thermal analyser. A two-stage reduction process was observed in a CO/CO_2 atmosphere. The pellets were reduced to wustite (CO/CO_2=1), and then to metallic iron (CO/CO_2=4).

The present investigations allow determination of the effects of the composition of the blast furnace charge, consisting of both acidic pellets and high-basicity sinter, on the reduction rate [1–3].

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Experimental

The subject of the examinations were acidic pellets of ores from Brazil, Canada, Russia (Lebedyn) and Poland (Połtawa), obtained by lumping granular fractions of these ores with water addition in a drum pelletizer, and subsequent hardening on short belts at 800°C.

Several blocks of complex, complementary research methods were used in examination of the samples. This made it possible to reveal the dependence between the phase compositions of the materials and their physico-chemical properties.

The chemical compositions of the samples were determined by classical chemical analysis together with atomic absorption spectroscopy. X-ray diffraction analyses, and optical and scanning microscopy observations were carried out, as well as electron probe microanalysis. The course of the reduction was observed in 2 stages: oxide reduction to wustite (CO/CO_2=1) and then to metallic iron (CO/CO_2=4).

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out on a Mettler thermoanalyser in the temperature range 20–1200°C, in a gas flow at 20 l h^{-1}, a heating rate of 6°C min^{-1}, and an annealing time of the reduction product at 1200°C of 1 h. The softening temperatures (start and finish) corresponding to a transition between a 'dough-like' state to a liquid, before and after 65% reduction, were determined according to the BN-85/0604-16 standard. These parameters are very important as regards the existence of a cohesion zone in the blast furnace. The course of the reduction in the blast furnace depends on the width of this zone.

Results and discussion

The chemical compositions of the analysed pellets from Brazil, Canada, Russia (Lebedyn) and Poland (Połtawa) are presented in Table 1. Table 2 lists the phase compositions of the samples determined by X-ray powder diffraction, and quantitative evaluation of the phases present.

Table 1 Results of chemical analysis of pellets

Pellets	CaO/SiO_2	Fe_{met}	FeO	CaO	SiO_2	MgO	Na_2O	K_2O
				%				
1. from Brazil	0.93	64.29	0.80	3.32	3.55	0.46	0.014	0.008
2. from Canada	0.13	66.5	0.1	0.4	3.1	0.05	0.011	0.008
3. from Russia	0.17	64.69	1.67	0.95	5.45	0.60	0.045	0.056
4. from Poland	0.069	59.68	2.86	0.79	12.55	0.89	0.028	0.016

Table 2 Phase compositions of acidic pellets, determined by X-ray diffraction

Phase content/ %	Pellets from Brazil			Pellets from Canada			Pellets from Russia (Lebedyn)			Pellets from Poland (Połtawa)		
	before reduction	after reduction CO/CO_2=1	after reduction CO/CO_2=4	before reduction	after reduction CO/CO_2=1	after reduction CO/CO_2=4	before reduction	after reduction CO/CO_2=1	after reduction CO/CO_2=4	before reduction	after reduction CO/CO_2=1	after reduction CO/CO_2=4
Hematite	72.0			85.0			75.0			69.0		
Magnetite	6.8	3.7		6.5			12.5			9.5		
Wustite	2.5	72.0	3.8		84.0			83.0	7.6		80.7	6.1
Fe	3.5	2.4	85.0–89.0			93.0			58.6	1.5		81.6
Ca ferrites	3.0	12.5		4.0	4.2	6.5	3.3	14.0	29.3	1.5	16.2	2.2
CaO	2.0				2.7							
$CaO{\cdot}SiO_2$	2.0		4.0							1.5		
$3CaO{\cdot}SiO_2$										2.0		
SiO_2		4.2		2.5–4.5	8.9		9.0	2.9	4.3	15.0	3.0	
Ca_2SiO_4		5.0										
Al_2O_3			4.3									
Al			3.0									
$CaO{\cdot}Al_2O_3$	6.5											
Others	≅10											

Ca ferrites: $CaFeO_4$; $CaFe_4O_7$; $Ca_3Fe_{15}O_{25}$

The predominant mineral component of the pellets before reduction is hematite (69–85%). It occurs in the form of rounded grains linked together by hematite bridges (Fig. 1). The content of the hematite phase varies from 6.5% for the Canadian pellets up to 12.5% for the pellets from Russia (Lebedyn). The fraction of calcium ferrites, mainly $CaFe_4O_7$, $CaFe_2O_4$ and $Ca_3Fe_{15}O_{25}$, varies from 1.5% up to 4.0% for the pellets from Poland (Połtawa) and Canada, respectively. A silicate phase was also found and, in the Brazilian pellets, an aluminium containing phase.

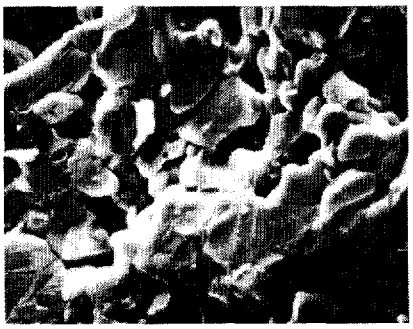

Fig. 1 Scanning image of 0.69 basicity pellets from Połtawa. Magnification 1100×

The reduction course was examined by TG and DTG analyses in an equilibrium atmosphere with the wustite phase (CO/CO_2=1), with subsequent reduction to metallic iron (CO/CO_2=4). Mass changes in the samples are shown in Figs 2 and 3. In reduction in the CO/CO_2=1 atmosphere (Fig. 2), the run of the curves indicates a two-stage mass loss. The first occurs in the temperature range from 400–450 to 550–600°C, which corresponds to the reduction of hematite to magnetite, and the second, from 600 to 750–800°C, is due to the reduction of magnetite to wustite.

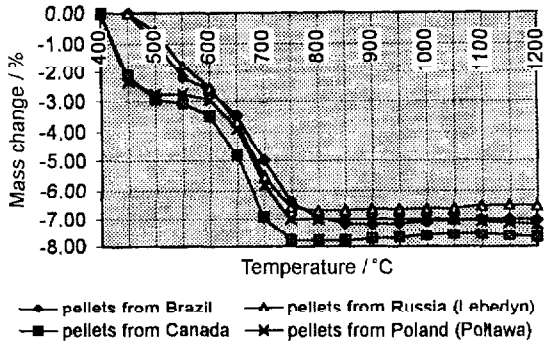

Fig. 2 Mass change in acidic pellets during reduction in CO/CO_2=1 atmosphere

In the CO/CO_2=4 atmosphere (Fig. 3), one can observe another run of the curves. The reduction of hematite to magnetite occurs first, in the temperature range from about 400 to 650°C. The mass loss is then greater than that observed in the CO/CO_2=1 atmosphere. In the second stage (about 650 to 800°C), the reduction of magnetite to wustite takes place. The third stage, that of wustite reduction to iron, occurs within the temperature range 800–950°C [4]. At temperatures above 1000°C, both the Russian (Lebedyn) and the Polish (Połtawa) pellets display a mass gain, due to iron oxidation to wustite. This is confirmed by the X-ray diffraction results (Table 2).

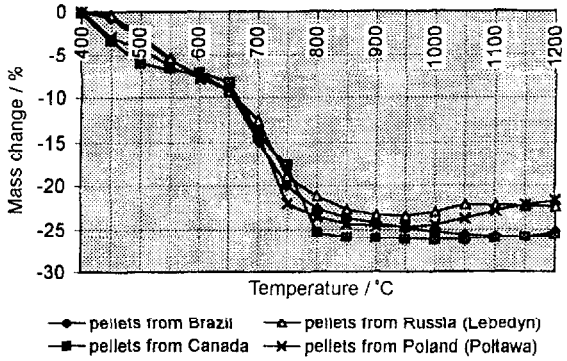

Fig. 3 Mass change in acidic pellets during reduction in CO/CO_2=4 atmosphere

After reduction in the CO/CO_2=1 atmosphere, the predominant phase component of the pellets is wustite (72–84%); the fraction of calcium ferrites also increases (12.5–16%). After reduction in the CO/CO_2=4 atmosphere, the pellets are mainly composed of iron (from 58 to 93% for the Russian (Lebedyn) and Canadian pellets, respectively). It should be emphasized that the higher the hematite content of the pellets, the more the iron in the reduction product. An exception was the Russian (Lebedyn) pellets, which contained about 29% of calcium ferrites, mostly $CaFe_2O_4$, formed after reduction in the CO/CO_2=1 atmosphere.

Table 3 Results of softening measurements

Pellets	Before reduction			After reduction		
	T_s	T_f	ΔT	T_s	T_f	ΔT
From Brazil	1220	1290	70	1060	1270	210
From Russia (Lebedyn)	1120	1350	230	1100	1380	280
From Poland (Połtawa)	1190	1270	80	1080	1210	130

T_s softening start temperature
T_f softening final temperature

Table 3 presents the temperatures of softening start and finish, and the softening range, for the acidic pellets. The results indicate that the pellets from Brazil and Poland (Połtawa) exhibit optimal parameters from the point of view of the blast furnace process, i.e. the highest temperatures of softening start and finish, and the narrowest softening range. In the case of the Polish (Połtawa) pellets, applied in the T. Sendzimir Steelworks (Poland), the temperature of the softening start approximates to those of 1.7–2.5 basicity sinters [3]. This is an advantageous phenomenon, as the softening range of the substances in the blast furnace does not widen.

Conclusions

– Thermal analysis applied to study the reduction of multicomponent systems is an efficient technique for examinations of complex samples such as acidic pellets.

– Acidic pellets are characterized by varied mineral compositions.

– The predominant mineral component of the pellets in their initial state is hematite.

– The properties of the acidic pellets, such as the temperatures of softening start and finish, are comparable to or better than those of the high-basicity sinters, which means that good results may be expected when blast furnace charges made from mixtures of these two metallurgical substances are used.

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