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THERMAL ANALYSIS IN EXAMINATIONS OF REDUCTION OF MIXTURES OF ACIDIC PELLETS AND HIGH-BASICITY SINTERS

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Abstract

The aim of this work was to investigate the application of mixtures of high-basicity sinters and acidic pellets in blast furnace charges.

The ratio of high-basicity sinter and pellets depends on the nature and basicity of the latter, and is established in order to secure desired properties of the slag and sufficient reducibility and mechanical strength of the furnace charge. Such a composition of the charge leads to a considerable cost decrease related to coke saving, the elimination of fluxes and a decrease in air pollution.

Examinations of phase composition and physicochemical properties of the sinters and pellets as separate materials were carried out. The effect of the mineral composition of sinters with a basicity of 1.7–2.0 on the reducibility was determined.

Sinters of different basicities (CaO/SiO_2=1.7; 2.0) mixed with pellets from **Połtawawere reduced in a CO/CO_2** gas mixture. The reduction process was followed by thermal analysis.

Keywords: acidic pellets, blast furnace charge, blast furnace sinters, thermal analysis

Introduction

Sinters are agents which intensify the functioning of blast furnaces. In consequence of their physicohemical properties, augmentation of the production capacity and a decrease in coke consumption are possible. However, for economic reasons, the utilization of ore sinters in blast furnace charges is decreasing in favour of cheap acidic pellets. Reduction of gas and dust emission into atmosphere is also important.

The increasing fraction of pellets in the charge necessitates investigations of their mixtures with high-basicity sinters, in order to determine the optimal composition of the charge, depending on the sinter basicity and the nature of the pellets.

Previous investigations of composition, physicochemical properties and reduction course were focused on the blend components, i.e. the sinters [1–4] and pellets [5]. In this paper, we present an account of preliminary reduction studies of blends of the components. For investigation of the reduction process, methods

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of thermal analysis (TG and DTG) were applied, complemented by determinations of the chemical and phase compositions of the samples. Reduction was carried out in atmospheres normally used in blast furnaces.

Experimental

The subjects of the present investigations were metallurgical substances: sinters, pellets and mixtures of sinters and pellets.

High-basicity sinters were obtained in a sinter belt in the T. Sendzimir Steelworks. The basicities of the sinters (CaO/SiO_2) expected from the formulae were 1.7 and 2.0.

Pellets were obtained from granular fractions of Połtawa ore by drum lumping with water addition and subsequent hardening on short belts at temperatures below 800°C.

Mixtures of sinters of basicities 1.7 and 2.0 with pellets from Połtawa (30%) were subjected to further investigations.

The chemical compositions of the acidic pellets and sinters were determined by classical chemical analysis. Sodium and potassium contents were determined by atomic absorption spectroscopy.

The phase compositions of the pellets and sinters were determined by means of X-ray diffraction with an HZG-4B diffractometer, using data from the ICPDS catalogue; and by optical and scanning microscope observations with Stereoscan S4-10 equipment with a Kevex energy analyser. The observations were complemented by electron probe microanalysis on a Cameca MS-46 microprobe.

Thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) were carried out on a Mettler thermoanalyser in the atmospheres $CO/CO_2=1$ and $CO/CO_2=4$ at a gas flow of 20 l/h, in the temperature range 20–1200°C, at a heating rate of 6°C/min, with annealing of the reduction product at 1200°C for 1 h. The analysis sensitivity was 10 and 1 mg in the case of TG and 1 mg/min for DTG. Identical measuring parameters were applied in observations of the reduction course of the blend components: sinters [2, 4] and pellets [5].

The reducibility of the sinters and pellets was determined according to the standard ISO 4695.

Results and discussion

The chemical compositions of the analysed sinters and pellets are given in Table 1, and the X-ray diffraction results in Table 2. The predominant mineral component of the examined sinters was calcium-doped magnetite, the content of which varied from 70 to 30% for the sinters with basicities of 1.7 and 2.1 respectively. The results of electron probe microanalysis revealed that the magnetite in the sinter is a doped phase, mainly with calcium (calcium content 1.4–1.8% in the sinter with CaO/SiO_2=1.7, and 1.2–1.4% when CaO/SiO_2=2.1). Other dopants found in the magnetite were manganese, magnesium and aluminium. Calcium, however, was the doping element which most considerably affected the reducibility of the magnetite [6].

Table 1 Results of chemical analysis of initial substances

Sinters	Fe_{met}/	FeO/	CaO/	SiO_2/	MgO/	MnO/	Al_2O_3	Na_2O/	K_2O/	Other/
	%									
CaO/SiO_2=1.7	52.6	7.54	12.73	7.49	0.88	0.59	1.29			16.88
CaO/SiO_2=2.1	52.9	7.22	12.52	5.96	0.97	0.54	0.87			19.02
Połtawa pellets	59.68	2.86	0.79	12.55	0.89			0.028	0.016	23.186

Table 2 Results of powder X-ray diffraction analysis

Sinters	Fe_2O_3/	Fe_3O_4/	FeO/	Fe_{met}/	Calcium ferrites/
	%				
CaO/SiO_2=1.7	18.0	60.0	7.0		13.0
CaO/SiO_2=2.1	32.0	40.0	7.0		20.0
Połtawa pellets	69.0	9.5		1.5	1.5

Sinters	SiO_2/	$CaO{\cdot}SiO_2$/	$2CaO{\cdot}SiO_2$	$3CaO{\cdot}SiO_2$/	$(CaFe)SiO_4$/	$0.47MgSiO_3$ $0.53FeSiO_3$/
	%					
CaO/SiO_2=1.7			ca 1.0		ca 1.0	
CaO/SiO_2=2.1						ca 1.0
Połtawa pellets	15.0	1.5		2.0		

With increasing basicity, the fractions of secondary haematite and calcium ferrites increased. In the silicate phase in the basicity range 1.7–2.1, calcium and iron olivines predominated; these crystallize in the form of longitudinal plates or needles, forming a strong binder, cementing together magnetite and haematite crystals (Fig. 1). A similar role is played by some calcium ferrites: mainly $CaFe_4O_7$, $CaFe_3O_5$ and $CaFe_5O_7$. As the basicity increased, the role of binder for calcium-doped magnetite, haematite and calcium-doped wustite grains was taken over by calcium ferrites, the fraction of which in the sinter increased with increasing basicity. The reduction conditions during sintering are favourable for the formation of small amounts of calcium-doped wustite, whose content is 7% in the samples with basicities of 1.7–2.1. In the sinters, calcium-doped wustite crystallizes in the form of irregularly shaped precipitations, mostly near the grains of calcium-doped magnetite and calcium ferrites.

Fig. 1 Scanning image of sinter with basicity 2.0; 1000×

The sinters with basicities of 1.7 and 2.1 displayed a good reducibility, with rates measured according to ISO ($dR/dt_{o/Fe=0.9}$) of 1.53 and 1.90% per min, respectively. This is related to the presence of calcium-doped magnetite, secondary haematite and calcium ferrites in the sinters. The above rates are higher than that for the self-fluxing sinter ($CaO/SiO_2 \cong 1.1$) which is 1.05% per min. The self-fluxing sinter is regarded as a reference sinter; it is used in industry as the only iron-containing component of the blast furnace charge.

The predominant mineral component of Połtawa pellets is haematite, occurring in the form of rounded grains linked by haematite bridging bonds (Fig. 2). The reducibility of Połtawa pellets according to ISO is 0.74% per min.

Fig. 2 Scanning image of a Połtawa pellet; 1000×

The reducibility of the high-basicity sinters is better than that of the self-fluxing sinter. They can also be blended with acidic pellets in such a ratio that the reducibility of the mixtures obtained is equal to or better than that of the self-fluxing sinter.

Thermal analysis (TG and DTG) was used to observe the reduction process of the blend: 70% high-basicity sinter and 30% Połtawa pellets. The examinations

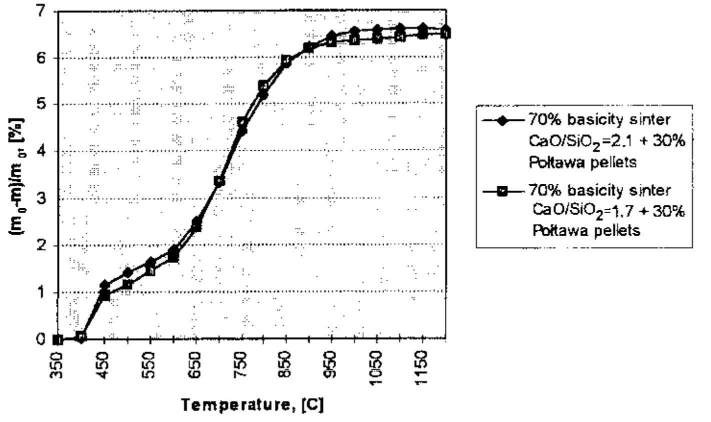

Fig. 3 Thermogravimetric analysis (TG) of mixtures of high-basicity sinters and Połtawa pellets; atmosphere; $CO/CO_2=1$

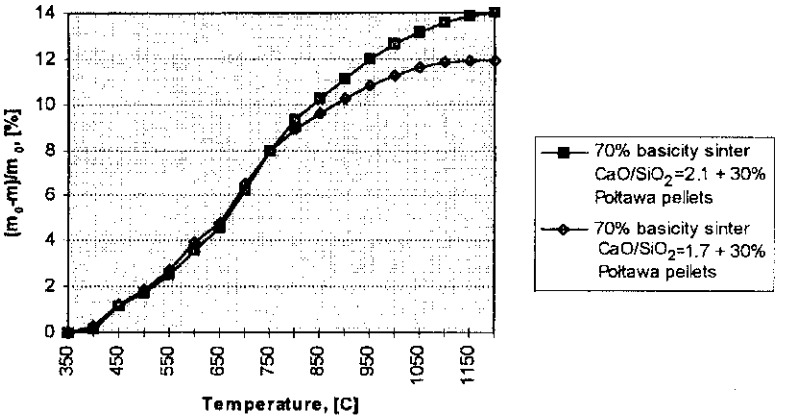

Fig. 4 Thermogravimetric analysis (TG) of mixtures of high-basicity sinters and Połtawa pellets; atmosphere $CO/CO_2=4$

concerned two stages of the process: reduction in equilibrium with wustite phase ($CO/CO_2=1$) and reduction to iron ($CO/CO_2=4$).

The reduction runs on mixtures containing the sinters with basicities of 1.7 and 2.1 (Fig. 3) resemble each other for the first stage of the process (reduction to wustite). Reduction to metallic iron (Fig. 4) is more efficient when the higher-basicity sinter (2.1) is used in the mixture.

Special behaviour was observed during annealing of the mixtures at 1200°C for 1 h. In the sample containing the sinter with a basicity of 2.1, 0.6% of additional reduction occurred, whereas only 0.05% was found after annealing in the case of sinter with a basicity of 1.7.

Conclusions

– Examinations of the reduction processes of blends of superfluxed sinter and acidic pellets facilitate the establishment of the optimal composition of the blast furnace charge.

– Blast furnace charges involving sinters with basicities of 1.7 and 2.1 are characterized by good reducing properties. Measurements according to the standard ISO 4695 indicate that these are better than those of the 'reference' self-fluxing sinter with basicity (CaO/SiO_2) 1.1.

– Blends composed of 70% the sinters with basicities of 1.7 and 2.0 and 30% of Połtawa pellets were subjected to examination. They all had good reducing properties. The replacement of part of the superfluxed sinters with less expensive acidic pellets has the aim of economic and ecological advantages.

– Thermal TG and DTG analyses were applied for rapid observations of the reduction process.

– The best results were attained when the sinter with a basicity of 2.1 was blended with acidic pellets.

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