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APPLICATION OF THERMAL ANALYSIS TO STUDY OF PHASE COMPOSITION CHANGES IN BLAST FURNACE SINTERS

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Abstract

Applieation of thermal analysis to determine a quantity portion of iron oxides in symmetric blast furnace sinters is presented.

In the multicomponent sample, calcium ferrites and many silicate phases beside doped iron oxides phases were observed.

The dependence of sinter phase composition from basicity and relation with physicochemical properties is defined.

Keywords: blast furnace sinters, calciomagnetite, calciowustite, dilatometrical analysis, iron oxides, multicomponent systems, thermal analysis

Introduction

The subject of this work is to examine the sinters whose utilization in the blast furnace process mainly depends on their physical and chemical properties, such as reductibility and strength. They are multicomponent samples and their mineral composition can vary depending on the initial composition and sintering conditions. The reductibility of the sinter depends on the content of iron oxides phases (magnetite, haematite, wustite), as well as on the content of doping elements, such as calcium, magnesium and manganese. It can also be affected by the content of ferrite and silicate phases [1–5].

The paper presents thermal analysis applied to the quantitative determination of the iron oxides content in those complex samples. The analyse were carried out in two equilibrium states, first with calciomagnetite and then with calciowustite phase. The quantities of doping elements were measured by electron microprobe analysis. Dilatometric examinations done in the same conditions have allowed us to relate the expansibility with the mass effects. The above analyses were completed by the powder X-ray diffraction.

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Experimental

The examined samples were synthetic ore sinters made in a sinter pan of the T. Sendzimir Steelworks. Their basicity (CaO/SiO_2) was of 1.48, 1.58, 1.65 and 1.90.

The analytical methods used in this work allowed us to determine both chemical and phase compositions of the samples. The former was measured by the classical chemical analysis and electron probe microanalysis (Cameca MS-46). The latter was determined by the X-ray diffraction (HZG-4B) and scanning microscope observations (Stereoscan SH-10) accompanied by the spectral analysis of the grains (Kevex).

The thermal analyses used in this work include complex investigations which aim at relating the thermal expansion changes with the mas effects. This is helpful at determining the conditions of phase transitions in the sinter. Another goal of this study was to quantitatively evaluate the content of the calciowustite ($(FeCa)_{1-y}O$), calciomagnetite ($(FeCa)_3O_4$) and haematite (Fe_2O_3) phases.

The dilatometric measurements were carried out on an 18 AV dilatometer made by S.A.D.A.M.E.L. The samples were 4 mm diameter and 15–30 mm height. They were heated in argon in the temperature range 20–1100°C, the heating rate was 6°/min.

The 1.48, 1.58, 1.65 and 1.90 basicity sinters were examined by the TG1 and TG2 thermogravimetrical analysis (sensibility of 10 and 1 mg) DTG analysis (sensibility of 1 mg/min) and DTA (sensibility of 100 μV). A Mettler thermoanalyser was used for all the analyses, the gas flow was 15 l/h, the temperature range 20–1100°C.

Results and discussion

The X-ray diffraction has revealed an effect of basicity on the phase composition of the sinter. Phase found in the initial samples are listed in Table 1. Magnetite is the main mineral component of the sinters. Its fraction varies with the basicity from 45–55% (91.48 basicity sinter) down to about 40% (1.9 basicity sinter).

Due to the electron probe microanalysis of magnetite grains, calcium, magnesium, manganese and aluminium were found to be the doping elements (Table 2).

The results of the analysis show that basicity does not affect the content of Mg, Mn and Al. The calcium content, however, depends on both basicity and other ferrites content.

As a rule, the calcium content in magnetite increases up to 1.8% with the increase of basicity, whereas in 1.65 and 1.9 basicity samples it is comprised between 0.1 and 0.5%. This is due to the existence of ferrite phases. It is to em-

phasize that the increase of calcium concentration in magnetite beyond its solubility limit causes the formation of calcium ferrites.

Table 1 Phase compositions of the sinters–X-ray diffraction

Phases	CaO/SiO_2		
	1.48	1.58	1.65
Fe_2O_3	++	++	++
Fe_3O_4	+++	+++	+++
$Fe_{1-y}O$		+	+
$CaO \cdot Fe_2O_3$	++	++	++
$2CaO \cdot Fe_2O_3$	+	++	++
$CaO \cdot 2Fe_2O_3$	++	++	
$CaO \cdot FeO \cdot Fe_2O_3$			+
$CaO \cdot 3FeO \cdot Fe_2O_3$			
$3CaO \cdot FeO \cdot 7Fe_2O_3$			+
Ca_2SiO_4	++	++	++
$(CaFe)_2SiO_4$	++	++	+
$0.47MgSiO_3$			
$0.53FeSiO_3$	+	+	+

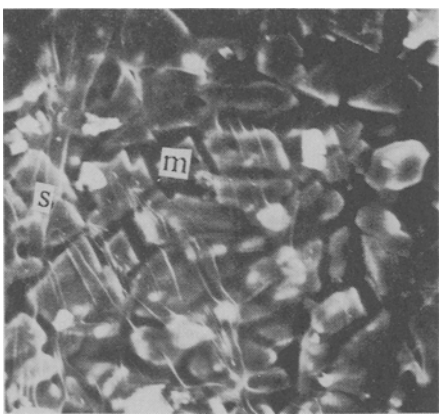

Fig. 1 Scanning image of 1.48 basicity sinter, 1200× (*m*-magnetite, *s*-glassy phase)

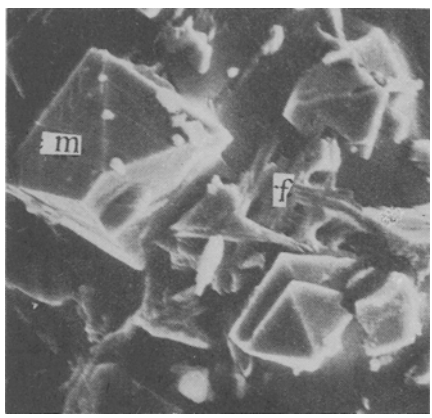

Fig. 2 Scanning image of 1.58 basicity sinter, 1000× (*m*-magnetite, *f*-calcium ferrites)

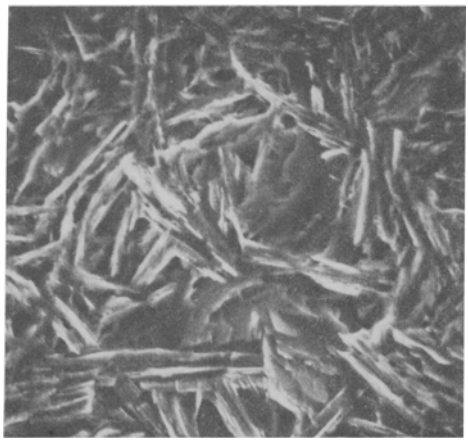

Fig. 3 Scanning image of 1.58 basicity sinter, 550×

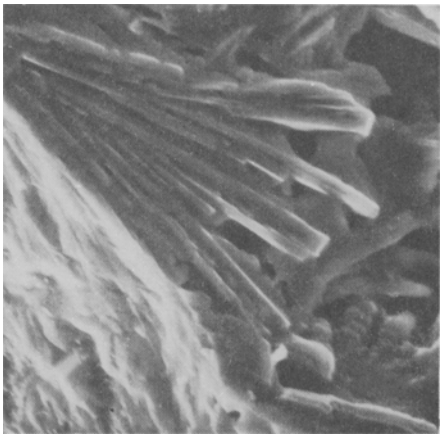

Fig. 4 Scanning image of 1.48 basicity sinter, 1100×

Magnetite in sinters occurs most frequently in the form of octahedral crystals, loosely encrusted in the silicate phase – Fig. 1. It is also possible that magnetite crystals are cemented by calcium ferrites, as shown in Fig. 2.

As found by X-ray diffraction studies, decrease of magnetite content in a sinter is accompanied by decrease of ferrite phases: from about 20% in 1.48 basicity sinters up to 39–35% for $CaO/SiO_2=1.9$.

Ferrites of the binary system are the prevailing constituents in the 1.48–1.58 basicity sinters. Above $CaO/SiO_2=1.58$ appear ferrites of the ternary system $CaO–FeO–Fe_2O_3$, $CaO·3FeO·Fe_2O_3$ and $3CaO·FeO·7Fe_2O_3$.

In the 1.58 –1.65 basicity range the content of $2CaO·Fe_2O_3$ calcium ferrite increases which worsens both reducibility and strength of the sinter.

Ferrites crystallize most often in the form of elongated columns or needles. This structure which cements the sinter is represented in Fig. 3. A 'crater', exposed in a fracture, is shown in Fig. 4. The crater is surrounded by a weakly crystallized glassy (vitreous) phase, whereas its surface is formed of needle-

Table 2 Spectral analysis in microregion of magnetite phase in the sinter

Sinter	CaO/SiO_2	FeO/	Fe/	Ca/	Mn/	Mg/	Al/	Si/
					%			
1	1.48	7.83	65.3–67.2	0.1–0.3	0.1–0.7	0.1–0.2	0.1	–
2	1.58	5.80	66.6–67.6	1.6–3.0	0.1–0.3	0.2–0.4	–	–
3	1.65	5.36	68.1–69.7	0.1–0.5	0.1	0.2–0.3	0.1	–
4	1.90	7.54	67.1–68.8	0.2–0.3	0.2	0.1–0.3	–	–

Table 3 Spectral analysis in microregion of ferrite phases in the sinter

Sinter	CaO/SiO_2	FeO/	Fe/	Ca/	Mn/	Mg/	Al/	Si/
				%				
1	1.51	6.95	45.5–47.9	9.5–10.0	0.1–0.3	0.1–0.2	0.3	1.3–2.0
2	1.58	5.80	37.8–39.5	26.4–27.5	0.2–0.3	–	–	0.1–0.2
3	1.65	5.36	49.2–51.6	8.4–9.3	0.1	0.1–0.3	0.3–0.5	2.2–2.4
4	1.80	7.98	53.4–59.5	9.2–9.8	–	–	0.2–0.3	1.6–2.0

shaped precipitations of calcium ferrite of the binary system. Ferrites occur also, as shown in Fig. 2, close to the magnetite phase. This can be due to a tendency of creation of calcium ferrites in sites where calcium concentration in magnetite exceeds the solubility limit. The results of spectral analysis (Table 3) show the presence of manganese, magnesium, aluminium and silicon. Mg, Mn and Al contents do not depend on the basicity of the sinter, Silicium occurs in form of precipitations of silicate phases within the grains. The silicate components of sinters occur in the form of crystalline silicate phases or rapidly quenched glassy phases. After X-ray diffraction the following phases have been found: calcium orthosilicate Ca_2SiO_4, olivines $(CaFe)_2SiO_4$ as well as Mg and Fe containing phase $0.47MgSiO_3.0.53FeSiO_3$. Increase of the basicity causes

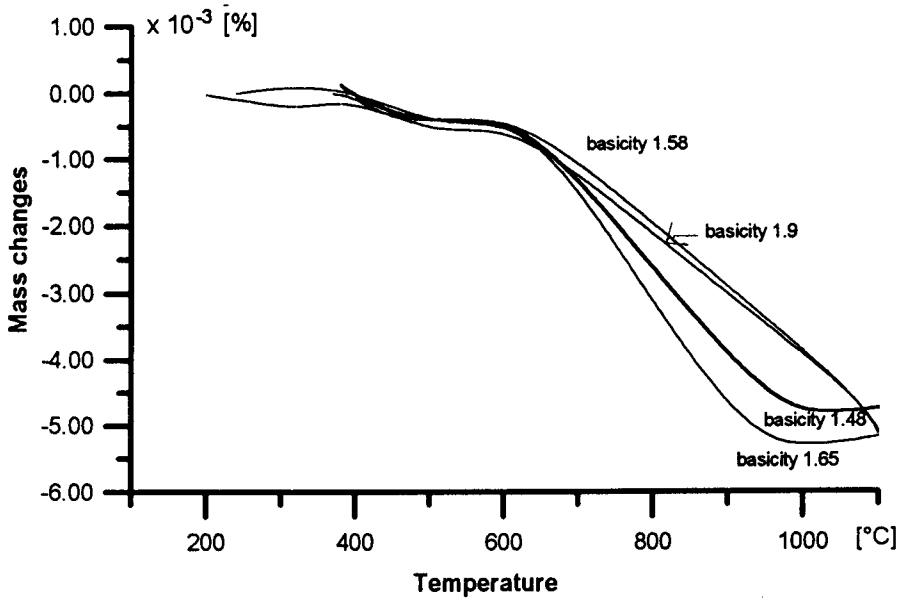

Fig. 5 Mass changes of the sinter in CO/CO_2 atmosphere

decrease of olivines content and disappearing of $0.47MgSiO_3 \cdot 0.53FeSiO_3$ phase.

In order to determine the iron oxides content in such complex samples, thermogravimetrical analyses have been done. The initial samples contained haematite, calciomagnetite and calciowustite. The product of the analyse carried out in an equilibrium atmosphere with the magnetite phase, is calciomagnetite. When measurements were done in the $P_{CO}/P_{CO_2}=1$ atmosphere, the final product is calciomagnetite, whereas in the CO/CO_2 the final product is calciowustite.

The runs of TG_1, TG_2 and DTG curves of the sinters in the CO/CO_2 atmosphere indicate a two stage mass loss (Fig. 5). The former, between 360 and 560°C, corresponds to haematite reduction to calciomagnetite, the latter, from 600°C, being result of calciomagnetite (both initially present in the sample and reduced from Fe_2O_3) reduction to calciowustite. Thermal effects of the above processes are not very clear on the DTA curves.

Average calcium contents in calciowustite and calciomagnetite (equal 0.2%) have been determined by spectral analysis in microregions. The departure from stoichiometry is assumed to be of Fe/O=0.9 [6, 7]. Table 4 presents both haematite and magnetite concentrations in the initial samples, calculated after these measurements.

Table 4 Haematite and calciomagnetite content in the sinter, after thermogravimetrical analysis in CO/CO_2 atmosphere

CaO/SiO_2	Fe_2O_3 / %	$(FeCa)_3O_4$ / %
1.48	16.02	49.99
1.58	15.81	47.31
1.65	12.36	56.55
1.90	10.14	58.35

Table 5 Calciowustite and magnetite content in the sinter, after thermogravimetrical analysis in an equilibrium atmosphere with $(FeCa)_3O_4$ phase

CaO/SiO_2	$(FeCa)_{1-y}O$ / %	Fe_2O_3 / %
1.48	9.89	3.81
1.58	6.10	6.55
1.65	7.35	5.34
1.90	6.54	9.56

Thermogravimetrical curves taken in an argon flow depend on the basicity of the sinter – Fig. 6. They run almost steadily in case of 1.48 basicity sinter, for higher basicities one observes instant mass losses. Thermal effects are

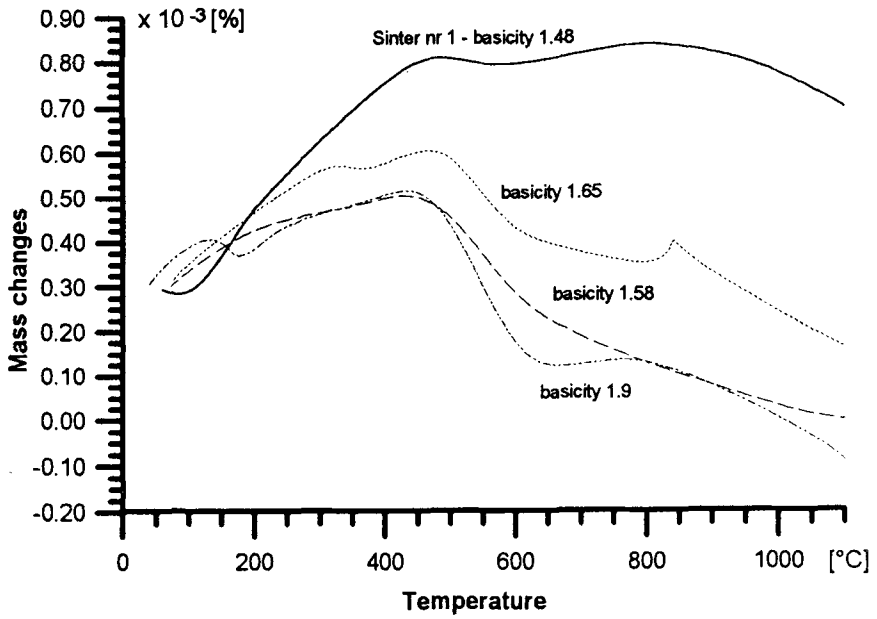

Fig. 6 Mass changes of the sinter in an equilibrium atmosphere with $(FeCa)_3O_4$ phase

marked on the DTA curves. Table 5 shows the calciowustite phase content in the sinter, calculated after the mass gain assigned by thermogravimetrical analysis. It is affected by the oxidation reaction of calciowustite to calciomagnetite. At higher temperatures a mass loss occurs, due to the haematite reduction to magnetite. Its value has been used to calculate the haematite content in the sinter. The apparent difference between haematite contents calculated after thermogravimetrical analysis carried out in various atmospheres comes from calcium ferrite reduction occurring in CO/CO_2 atmospheres. This is confirmed by a complex run of the DTG curve. Thus, haematite content calculated from thermogravimetrical analysis in argon seems to be more reliable.

The results of thermogravimetrical analysis were then confronted with those coming from the dilatometry, both having been done in the same conditions – Table 6. One can state that at low temperatures (up to 530–600°C, depending on the kind of a sinter) occur positive dilatation effects and mass gains, accompanied by a balanced exothermal effect on the DTA curve. At higher temperature dilatation effects are negative and thermogravimetrical curves show mass losses.

Positive dilatation effects can also be related to phase recrystallization processes, particularly the silicate glassy phase. Negative dilatation effects can be due to cast texture of the sinter (which lessens the porosity). Confronting mass effects with the dilatometrical analysis facilitates interpretation of phase transitions during sintering and explains some physico-chemical properties of sinters.

Table 6 Results of dilatometrical measurements

Sinter	CaO/SiO_2	T/°C	Dilatation
1	1.48	217–333	+
		333–505	+
		505–600	+
		600–717	–
		717–819	–
		819–944	–
		944–966	+
		966–1050	–
		1050–1072	–
		1072–1100	+
2	1.58	220–365	+
		365–430	+
		430–520	–
		520–740	–
		740–875	–
		875–1080	–
		1080–1100	–
3	1.65	183–575	+
		575–722	–
		722–866	0
		866–919	–
		919–986	–
		986–1069	–
		1069–1100	–
4	1.90	141–236	+
		236–688	+
		688–800	–
		800–866	–
		866–952	–
		952–1038	–
		1038–1066	–
		1066–1100	–

Conclusions

The results of experiments allowed us to make the following conclusions:

– thermal analysis is an efficient method to study complex multicomponent systems;

– iron oxides content in 1.48–1.90 basicity sinters, calculated after thermal analysis is as follows: 6–10% $(FeCa)_{1-y}O$, 47–58% $(FeCa)_3O_4$, 4–10% Fe_2O_3;

– mass and thermal effects of calcium ferrites reduction processes in CO/CO_2 atmosphere make difficult a univocal interpretation of the results;

– dilatometrical examinations of high porosity multicomponent samples allow to find a tendency of samples behaviour and not an explanation of the properties of individual phases;

– properties of magnetite phase depend on calcium content, while effect of magnesium, manganese and aluminium are negligible.

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Zusammenfassung — Vorliegend wird eine Anwendung der Thermoanalyse zur Bestimmung des Mengenanteiles von Eisenoxiden in Sintergut von Gebläseschachtöfen vorgestellt.
In den Mehrfachkomponentenproben werden neben versetzten Eisenoxidphasen auch Calciumferrite und viele Silikatphasen beobachtet.
Die Abhängigkeit der Zusammensetzung der Sinterphase von Basizität und die Beziehung zu den physikalisch-chemischen Eigenschaften wird definiert.