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THERMAL ANALYSES OF SYNTHETIC HIGH BASICITY SINTERS

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Abstract

The paper presents studies on synthetic sinters of given basicities (CaO/SiO_2 1.7–2.1). These multicomponent systems include not only doped iron oxides but calcium ferrites and numerous silicate phases as well. Investigatons were carried out by complex research methods, first of all by thermal analysis. Reduction processes of the sinters were observed by the methods of polythermal analysis in CO/CO_2 atmosphere. The effect of mineral composition on physico-chemical properties of the sinters has been determined.

Keywords: iron oxides, blast furnace sinters, reduction, thermal analysis

Introduction

In a multicomponent material, the individual phases can hardly be distinguished. As it is often the case, the identification of phases cause problems, several phases giving rise to a measured property. This become more complicated when one examines the effects of temperature and redox atmosphere on the components of the system.

Blast furnace sinters of complex mineral contents including, besides of iron oxides, also calcium ferrites and numerous silicate phases, have been examined for many years. The most important properties of the sinter, i.e. its reducibility and mechanical strength, depend mainly on the mineral composition.

Investigations on this kind of dependence are being carried out in many scientific centres [1–5]. However, many fundamental results are still missing in this area. That is why model studies have been undertaken, including examination of pure single and polycrystalline iron oxides [6–9].

Iron oxide phases in metallurgical materials are doped with different elements, such as calcium, magnesium and manganese, found in ores and sintering additives. Therefore, investigations of single crystal and polycrystalline samples of iron oxides singly doped with Ca, Mg and Mn and doubly doped with Ca and Mg have been carried out [10–13].

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More complex systems – ferrite phases [14, 15] as well as synthetic ore sinters [16] were examined.

Experimental

In this work, we have examined synthetic sinters of given basicities ($CaO/SiO_2=1.7$; 1.9; 2.1), coming from the experimental misa spiekalnicza of the T. Sendzimir Steelworks.

The methodics of the investigations includes several blocs of complex research methods which are complementary to one another. They allow us to show the dependences between reducibility and strength of the samples and their mineral composition.

The first group of this methods are chemical and spectral analytical methods including classical chemical analysis, spectral analysis in microregions, reducibility measurements according to the ISO standard, and also thermal analysis.

Phase composition was determined by means of optical and scanning microscope observations (Stereoscan S4–10), being always accompanied by the spectral analysis of the grains (Kevex energy microanalyser).

The third bloc included physical properties measurements (strength for example).

According to the ISO standard, the reducibility of the sinter is determined by a mass loss of a 0.5 kg sample, for 10–12.5 mm grain size. The sample is heated in a vertical retort, in an inert atmosphere, up to 950°C, then it is reduced in the 40–60 CO/N_2 gas mixture, flowing at the rate of 3 m^3/h.

In the Ironmaking Department of the University of Mining and Metallurgy, this method has been modified by fixing the heating rate at 5 $deg \cdot min^{-1}$ up 950°C, and by the continuous change of the reducing gas composition: from 20% CO+20% CO_2+60% N_2 at 600°C up to 40% CO+60% N_2 at 950°C.

Reducibility of the sinters determined by this method of the 1.7; 1.9 and 2 basicity samples is of 80.2, 83.3 and 81.1%, respectively. It is quite elevated as compared to the basic sinter (basicity of 1.1; Fe=51.5%; FeO=8–9%) whose reducibility is of 75.84%.

I order to follow equilibrium stages with Fe_3O_4, then with FeO the thermal analysis in the temperature range 20–1200°C, at the heating rate of 5 $deg \cdot min^{-1}$, in the $CO/CO_2=1$ atmosphere, has been carried out (Mettler thermoanalyser).

The thermogravimetry TG_1 and TG_2 as well as DTG differential runs (Figs 1, 2, 3) show two specific temperature ranges connected with the mass loss. The first, 375–580°C, in which reduction occurs from haematite to magnetite, and the second, up to 970°C with the reduction of magnetite to wustite. The quantitative analysis of the TG curve shows the increase in mass loss with basicity in

the first temperature range (mass losses are 0.23; 0.45 and 0.78% for $CaO/SiO_2=1.7$; 1.9 and 2.1, respectively). Therefore, one can believe that more basic sinters contain more haematite.

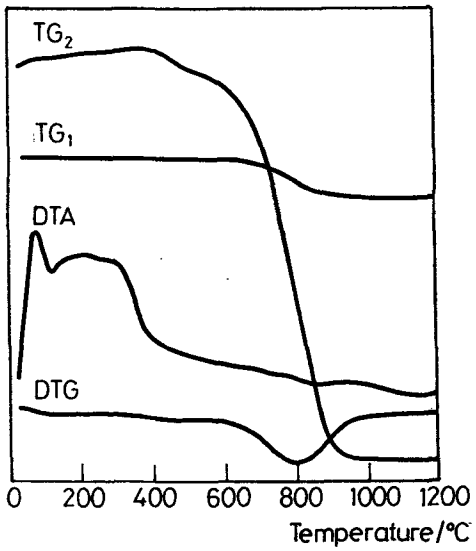

Fig. 1 Reduction of the 1.7 basicity sinter-thermal analysis curves

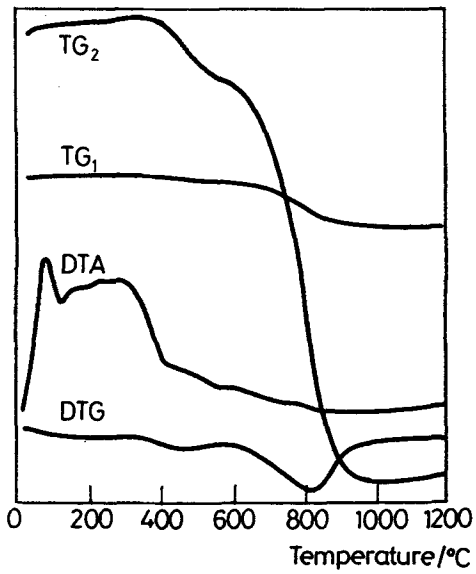

Fig. 2 Reduction of the 1.9 basicity sinter-thermal analysis curves

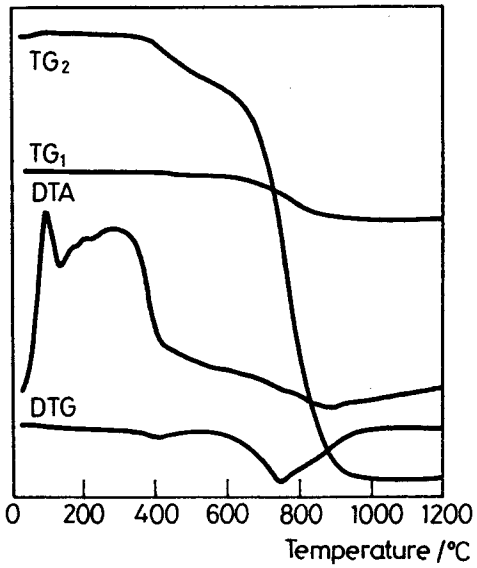

Fig. 3 Reduction of the 2.1 basicity sinter-thermal analysis curves

Differential thermal analysis (DTA) shows a strong exothermic effect at low temperature range. At elevated temperatures, thermal effects are not discernable.

The DTG run at the second mass loss step indicates that the dominant process is the reduction of magnetite to wustite, accompanied by the 0.5% mass loss.

Reduction processes of high basicity sinters (1.9 and 2.1) occur at similar temperatures, with mass loss of 4.93 and 5.22%. However, in this case, the DTG curves are more complicated because of overlapping thermal effects – reduction to wustite and reduction of calcium ferrites. Determination of partial mass effects of the mentioned reactions becomes still more difficult as the iron oxides in the substrata as well as in the products of the reaction are the doped phases.

Results of the spectral analysis in microregions allow us to state that the magnetite in the initial sinters (basicity of 1.7 and 1.9) is doped with calcium (0.7–1.3%), magnesium (0.1–0.4%) and manganese (0.2–0.4%). In some grains, the presence of aluminium was found. The calcium concentration in magnetite of the high basicity sinter is elevated and equals 1.2–1.5%. The wustite phase obtained after reduction contains 0.2–0.4% of calcium, 0.1–0.3% of magnesium and 0.2–0.3% of manganese.

Table 1 High basicity sinters – results of the spectral analysis in microregions

Sinter	Fe/	Ca/	Mg/	Mn/	Al/	Si/	Grain size/	Phase
			%				μm	
1.7	63.2–64.4	1.2–1.3	0.3–0.4	0.3–0.4	0.1	0.1	10–25	CM
	65.0–66.0	0.7–0.8	0.2	0.2–0.3	0.1	0.1	10–25	
	48.6–49.0	8.6–9.2	0.1	0.1	0.3–0.5	1.8–2.3	2–8	F
	44.0–46.4	8.9–9.3	0.1	0.1	0.4–0.6	2.5–2.7	2–6	
	14.7–15.2	22.8–23.4	0.1	–	0.4–0.5	12.2–13.1	3–6	K
	14.8–15.8	20.4–22.7	0.1–0.2	–	0.6–0.7	11.8–12.5	4–8	
1.9	74.9–75.9	0.4–0.5	0.2–0.4	0.2	0.1–0.2	–	4–20	W
	73.3–73.9	0.4–0.5	0.2–0.4	0.2–0.3	0.1–0.2	–	20–60	
	68.7–70.9	0.8–1.3	0.1	0.1–0.2	0.1	–	20–80	CM
	45.8–49.7	12.9–13.5	0.3	0.1*	0.2	2.8–3.5	2–6	F
	14.4–17.0	21.4–26.1	0.1	–	0.8–1.1	11.4–13.8	2–10	K
	0.9–9.3	34.7–38.8	0.1–0.3	–	0.1–0.3	13.5–15.3	2–8	
2.1	68.4–69.0	1.2–1.5	0.1–0.4	0.2–0.4	0.1*	–	20–40	CM
	60.8–61.2	6.3–7.2	0.1	0.2	0.2	0.8–0.9	6–10	F
	56.0–56.2	7.7–8.4	0.1	0.1	0.2	1.1–1.2	6–10	
	43.4–52.2	10.5–12.4	0.1–0.2	0.1	0.2–0.4	1.8–2.8	4–10	
	18.6–31.9	19.3–20.2	0.1	–	0.5	8.6–9.9	4–6	K
	17.6–18.4	16.7–19.8	0.1	–	0.9–1.0	8.1–10.1	4–10	
	12.9–13.9	22.8–26.9	0.1	–	0.3–0.5	11.3–13.6	4–6	

Symbols: CM - magnetite, H - heamatite, W - wustite, F - calcium ferrites, K - silicates phases; * - found in some grains only

Table 2 Wustite phase after reduction of high basicity synthetic sinters– results of the spectral analysis in microregions

Basicity of the sinter	Fe/	Ca/	Mg/	Mn/	Al/	Phase
			%			
1.7	74.9–75.8	0.2–0.4	0.1	0.2	0.1*	W
1.9	75.1–75.9	0.1–0.2	0.2	0.2–0.3	0.1	W
2.1	74.3–76.0	0.2	0.1–0.3	0.3	0.1	W

* - found in some grains only

Table 3 Phase composition of high basicity synthetic sinters, %–X-ray diffractometry

Phase	Basicity of the sinter		
	1.7	1.9	2.1
Heamatite Fe_2O_3	~7	~15	~33
Magnetite Fe_3O_4	~70	~70	~45
Wustite $Fe_{1-y}O$	~10	~4	~7
Other crystalline phases:	~13	~11	~15
Calcium ferrites			
CF	+	-	-
C_2F	-	-	-
CF_2	+	+	+
CWF	-	+	+
CW_3F	+	+	+
C_3WF_4	-	-	+
Silicates:			
$(Fe, Ca)_2SiO_4$	+	+	-
$(Fe, Mg)SiO_3$	+	+	+

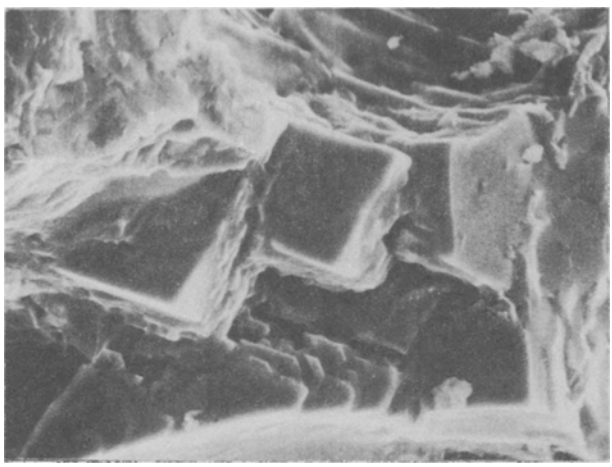

Photo 1 Secondary haematite at the surface of magnetite crystallites in the 1.7 basicity sinter. Scanning electron microscope, 800×

Photo 2 Calcium orthosilicate precipitations in the vicinity of the ferrites of ternary system in the 1.9 basicity sinter. Scanning electron microscope, 4600×

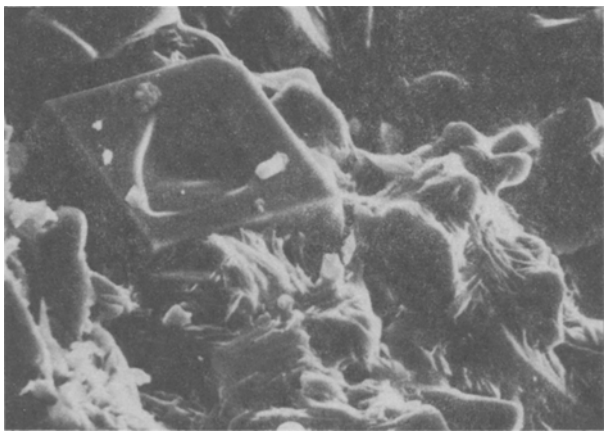

Photo 3 Large magnetite crystallites accompanied by microlitical olivine (CaFeAlMg)[SiO_4] precipitations which form, together with elongated calcium ferrite specimens, binding agent in this 1.7 basicity sinter. Scanning electron microscope, 1100×

Conclusions

The increase in basicity from 1.7 to 2.1 favours the following processes:

– decreasing silicate fraction
– increasing ferrite phases fraction
– increasing haematite phase concentration necessary that the ferrites could form.

The examined sinters are characterized by high reducibility. Increase in calcium fraction in magnetite leads to a higher structure defects concentration, causing this way increase in reducibility of a sinter.

The easily reducible calcium ferrites of the ternary system are formed beyond the solubility limit of calcium in magnetite. They crystallize as alternating long specimens which bind together the haematite and magnetite grains in this high basicity sinter.

The following phenomena have been confirmed by the thermal analysis:

– increase in haematite fraction with increase in basicity (mass effect at 375–580°C)

– increase in ferrite phases fraction in the temperature range of magnetite reduction to wustite.

Thermal analysis is a powerful method in the examination of multicomponent systems.

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Zusammenfassung — Vorliegend werden Untersuchungen an synthetischem Sintergut bestimmter Basizität (CaO/SiO_2 1.7–2.1) vorgestellt. Diese Mehrfachkomponentensysteme umfassen nicht nur versetzte Eisenoxide sondern auch Calciumferrite und zahlreiche Silikatphasen. Die

Untersuchungen wurden mittels komplexer Forschungsmethoden, in erster Linie mittels Thermoanalyse durchgeführt. Die Reduktionsprozesse des Sintergutes wurden mittels Polythermoanalyse in einer CO/CO_2-Atmosphäre beobachtet. Weiterhin wurde der Einfluß der Zusammensetzung des Minerales auf die physikochemischen Eigenschaften des Sintergutes ermittelt.