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THERMAL ANALYSIS IN EXAMINATIONS OF METALLURGICAL MATERIALS OBTAINED FROM IRON-BEARING FINES

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Abstract

This paper present results of research performed on briquettes containing iron oxides with the aiming of establishing a relationship between their chemical and phase compositions. Briquettes obtained from industrial in-plant fines waste were subjected to experimental tests involving simulation of the temperature conditions and the redox potential of a gas phase, characteristic of both the top and central parts of a blast furnace.

The results of the analysis allowed conclusions concerning the use of briquettes as a blast furnace charge component.

Keywords: blast furnace, briquettes, reduction, thermal analysis

Introduction

The utilization of iron-bearing in-plant fines such as scale, millscale and blast furnace dust is currently an increasingly important issue for Polish steelworks. It is estimated that approximately eight million kg of iron-bearing in-plant fines is dumped annually within Polish steel and iron plants.

One method of solving this problem is to briquette these wastes with appropriate additives in order to ensure briquettes with physicochemical properties which permit their use as a blast furnace feed substitute [1].

Among the most important factors determining their utilization in metallurgical processes are suitable reducibility, resistance to crushing (compressive strength) and swelling properties in the temperature range 20–950°C and in the reducing conditions typical of the top and central parts of a blast furnace [2].

Experimental

The research was carried out on two types of briquettes made with scale, millscale and blast furnace dust. The quantitative compositions of these two blends are shown

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in Table 1. The briquetting process was carried out on a universal laboratory roll press, using a two-component binder containing molasses [3].

Table 1 Quantitative compositions of blends

Blend	Millscale/%	Scale/%	Blast furnace dust/%
1	60	20	20
2	30	50	20

The aim of the research was to determine the changes in the physicochemical properties of the briquettes in the temperature range 20–950°C and in a reductive atmosphere of N_2–CO–CO_2 with differing contents of CO and CO_2. As the temperature was raised, the amount of CO was increased from 25 to 40% in order to simulate the distribution of the CO concentration present in the top and central parts of a blast furnace.

The thermogravimetric analyses were performed on a Mettler thermoanalyser in the temperature range 20–950°C and also on equipment constructed especially for this purpose. It allowed a sample to be cooled rapidly in a reductive atmosphere by taking it out when at a suitable temperature from the heating region to the region cooled on the outside by compressed air.

The research into the chemical and phase compositions, the structure and the strength properties was carried out on both untreated and thermally treated (at 600, 750, 850 and 950°C) briquettes. Samples were identified by classical chemical analysis, EPMA (Cameca MS-46), X-ray diffraction (HZG-4B), scanning electron microscopy (Hitachi S3500N) and spectral analysis of the grains (EDS Noran Instruments).

Samples obtained were examined in order to measure their volumes by the water method. The reported results are the averages of 25 measurements. Resistance to crushing was established by determining the breaking load under compression of a briquette of standard size with the 1120 Zwick machine.

Results and discussion

The results of thermogravimetric and dilatometric analyses are given in Tables 2 and 3, respectively.

Table 2 Results of thermogravimetric analyses of briquettes under reducing conditions

Briquette	Sample mass loss/%					
	20°C	600°C	750°C	850°C	950°C	950°C+1 h
1	–	4.2	16.3	21.8	26.9	31.7
2	–	5.6	13.6	25.6	32.4	32.8

The chemical and phase analyses revealed that the main iron oxide components of such briquettes are wustite and magnetite. A SEM image of untreated briquette 2 is shown in Fig. 1.

Table 3 Increase in volume of briquettes under reducing conditions

Briquette	Volume increase/%					
	20°C	600°C	750°C	850°C	950°C	950°C+1 h
1	–	0	25	75	101	91
2	–	0	27	102	101	91

In the temperature range 20–600°C, a slight loss in mass was observed, with no subsequent changes in the volume of the briquette. The color of the briquette changed from brown to red. On heating, sharp-smelling fumes were emitted, as a result of the total pyrolysis of the oil, contaminating both the scale and the millscale. Thus, a loss in mass is likely to occur as a result both of oil pyrolysis and of the process of reduction of magnetite to wustite. This can be seen in Fig. 2, where grains of wustite may be observed on the surface of magnetite.

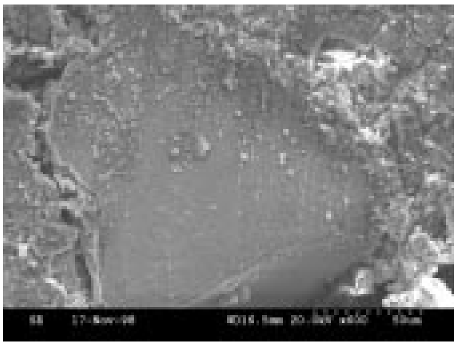

Fig. 1 SEM image of untreated briquett 2, 800×

Fig. 2 SEM image of briquette 2 after reduction at 600°C, 1000×

Above 600°C, reduction to metallic iron takes place. However, the fine-grained wustite phase undergoes the reduction processes to metallic iron earlier, and the iron whiskers formed fill the empty cavities (Fig. 3). Iron whiskers form cross-linked tangles, as can be observed in Fig. 4.

Lumps of scale undergo reduction to sponge-like iron. This is illustrated in Fig. 5.

At the same time, an increase in volume of the briquettes is observed; for briquettes thermally treated at 950°C, this amounts to 101±1%. Thermal treatment of briquettes for 1 h at 950°C under reducing conditions brings about a 10% decrease in briquettes volume as a result of the sintering of the products.

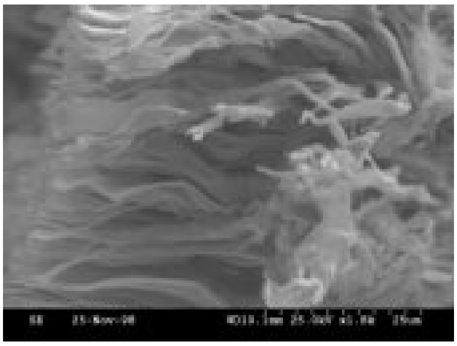

Fig. 3 SEM image of briquette 1 after reduction at 750°C, 1800×

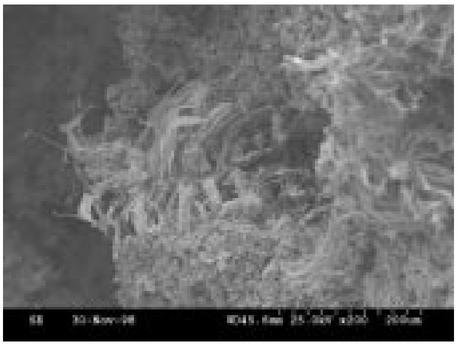

Fig. 4 SEM image of briquette 1 after reduction at 850°C, 200×

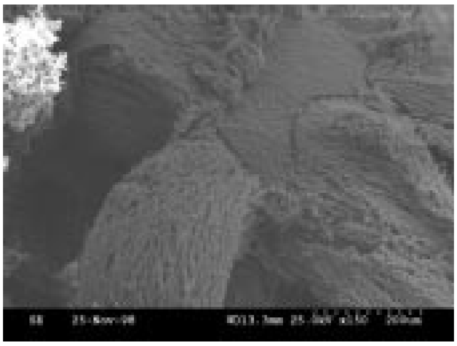

Fig. 5 SEM image of briquette 1 after reduction at 950°C, 5000×

Both the results of thermogravimetric, dilatometric and chemical composition analyses and the changes in structure and phase composition allow an evaluation of the factors influencing the briquette strength properties, which determine their use as a component of blast furnace feed.

Changes in the resistance of the briquettes to crushing under reduction conditions as a function of temperature are presented in Table 4.

Table 4 Resistance to crushing of briquettes after thermochemical treatment

Briquette	Resistance/N/briquette					
	20°C	600°C	750°C	850°C	950°C	950°C+1 h
1	580	720	220	135	220	305
2	670	265	75	100	185	122

The texture of briquette 2, which contains almost the same amount of blast furnace dust as briquette 1, but a higher amount of scale and a smaller amount of millscale, is more heterogeneous and is characterized by large grain scale surrounded by aggregates of linked fine-grained phases. Within briquette 2, there is no interrelation between the large grain scale (Fig. 6) and the iron whiskers formed during the reduction of the fine-grained fraction of millscale and blast furnace dust. As a result of the facts that the reduction processes take place first in the fine-grained phases and that the morphology of the iron formed is different, the resistance of briquette 2 is decidedly lower, which makes it impossible to use this type of briquettes as a blast furnace feed component.

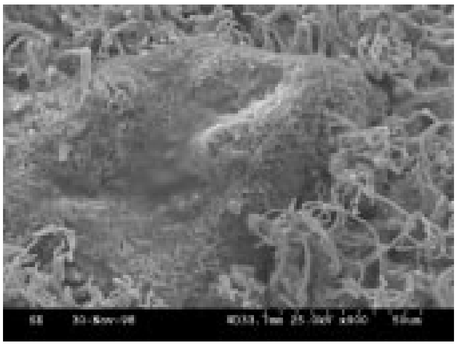

Fig. 6 SEM image of briquette 2 after reduction at 950°C, 1500×

Conclusions

When heated, these briquettes undergo both a mass loss and a change in volume comparable to that of blast furnace feed. The reductions of iron oxides to wustite and metallic iron takes place below 750°C. Above this temperature, the briquettes undergo a loss in mass and increases in volume and porosity, as a result of spongy-like iron produced on the surface of the scale grains and the formation of iron whiskers and needles, which are specific morphological forms usually observed on the interface of wustite grains in the areas of lowest environmental resistance.

Thermochemical treatment does not cause disintegration of the briquettes, but their resistance to crushing decreases with increasing scale content.

Among the methods used to test reduction processes of complex systems, thermal and thermogravimetric analysis and dilatometry are valuable tools for the examination of multicomponent samples.

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