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# TG STUDY ON THE REDUCTION KINETICS OF HEMATITE AND IRON OXIDE-CONTAINING WASTES

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The reduction kinetics of a pure and a Ca-added hematite, as well as of two iron oxide-containing metallurgical wastes, were studied by means of isothermal TG measurements, using $H_2$ or CO as reducing agents.

Below 900 K, the wastes were far less reactive than the pure or Ca-added hematite. This phenomenon was attributed to retardation of the hematite—magnetite transformation by surface Na and Si. Above 1000 K, however, the reaction rates for the wastes and for the Ca-added hematite were higher than that of the pure hematite. The higher reactivities were attributed to the effects of the Ca on the microstructure of the product layer.

The models of nucleation and growth processes were applied to describe the isothermal TG curves at low temperatures and in the vicinity of the rate minimum, while the model for gas-film diffusion control could be used in the case of high reaction rates.

Utilization of the various metallurgical by-products and ferrous wastes may improve the productivity and economy of iron and steel processing, and is of great importance as concerns environmental protection, too. Reduction of the iron oxide content of these materials is an unavoidable step in their utilization. Therefore, the reduction of iron oxide and different iron oxide-containing materials has been investigated extensively [1–6]. However, some questions, such as the role of non-ferrous components on the reduction of wastes, as well as the kinetics of their reduction, are still not completely answered. We have therefore studied the reduction of some iron-containing metallurgical by-products, using gaseous reducing agents. The present paper discusses TG reduction studies on two wastes with high iron contents from the Dunaferr Iron Works. Results on the reduction of pure and Ca-added hematite are also discussed.

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## Experimental

The TG experiments were carried out in a specially constructed reactor attached to a Mettler semimicro recording balance [7]. $H_2$ or CO was used as gaseous reducing agent with $N_2$ as inert diluting gas. Four powder-like samples were investigated:

Sample 1: analytical grade hematite (Reanal, $s^\circ = 10\ m^2\ g^{-1}$).

Sample 2: hematite mixed with 2.5% CaO.

Sample 3: flue dust separated from the converter stack gas ($s^\circ = 34\ m^2\ g^{-1}$).

Sample 4: slimes from the Dorr settler connected to the blast furnace.

The chemical compositions of these samples were determined by means of AAS (Table 1). The iron content in the samples was present mainly as hematite; however, sample 4 also contained a considerable amount of wustite. The theoretical mass loss for total reduction of the iron oxide content is likewise given in Table 1. The surface compositions of the samples were measured with the XPS technique on a KRATOS XSAM 800 photoelectron spectrometer, using Mg $K_\alpha$ (1253.6 eV) radiation for excitation of the samples.

**Table 1** Chemical compositions of the samples

| No. | Composition, % | | | | | | Theoretical mass loss, % |
|---|---|---|---|---|---|---|---|
| | FeO | $Fe_2O_3$ | $SiO_2$ | $Al_2O_3$ | CaO | MgO | |
| 1 | — | 100.0 | — | — | — | — | 30.1 |
| 2 | — | 97.5 | — | — | 2.5 | — | 29.3 |
| 3 | 3.1 | 82.9 | 1.7 | — | 3.7 | — | 25.5 |
| 4 | 15.3 | 72.3 | 2.6 | 0.2 | — | 1.4 | 22.5 |

## Results and discussion

### *Reduction with hydrogen*

The reactivities of the samples can generally be characterized by means of non-isothermal TG measurements. Figure 1 shows the plots of the relative mass loss ($\alpha$) *vs.* temperature curves for samples 1 and 3. For the pure hematite, the first mass loss step at about 600 K ($\alpha = 3\%$) relates to a fast hematite-to-magnetite transformation. TG curves of similar character have been observed during hematite reduction by Viswanath et al. [8] and by Colombo [9]. However, for sample 3 this step could not be distinguished, and the mass loss starts only at much higher temperatures (750 K). The reason for this difference will be discussed later.

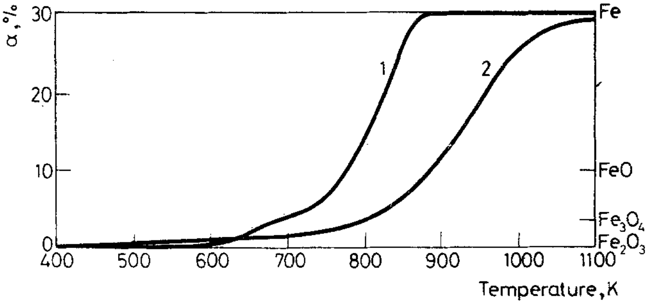

Fig 1 Anisothermal TG curves for Samples 1 and 3. Heating rate 10 deg min$^{-1}$, $p = 10$ kPa $H_2$

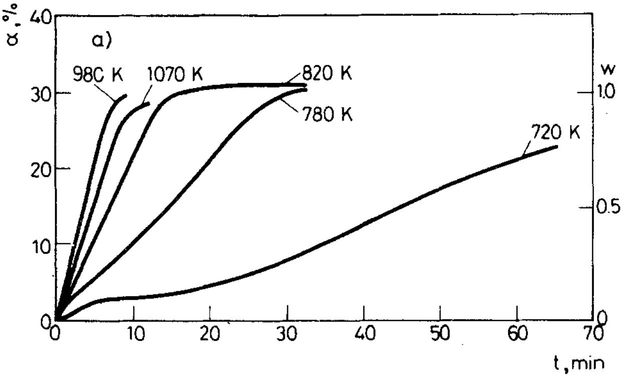

**Fig. 2/a** Conversion *vs.* time curves at $p = 10$ kPa $H_2$ for Sample 1

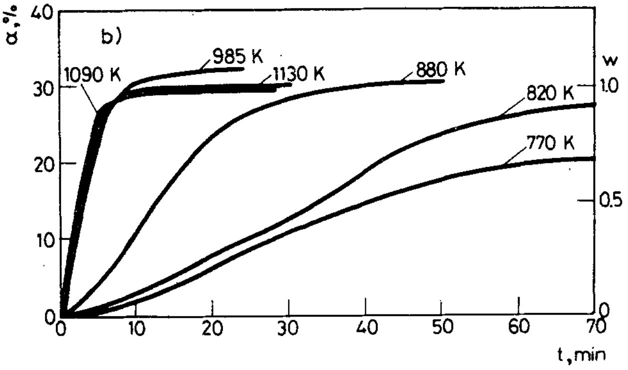

**Fig. 2/b** Conversion *vs.* time curves at $p = 10$ kPa $H_2$ for Sample 3

The reduction of the samples was studied by means of isothermal TG measurements in the temperature range 700–1120 K. Figures 2/a and b show the conversion of the reduction (fractional reduction, *w*) *vs.* time plots for samples 1 and 3, while the change in the reaction rate ($dw/dt$) with the conversion is given in Figs 3/a and b. For a comparison of the reactivities of the samples, and Arrhenius representation of the rates at $w = 0.25$ is shown in Fig. 4.

It can be seen that, below 900 K, the metallurgical wastes were far less reactive than the pure or Ca-added hematite (Fig. 4). This phenomenon can be explained by retardation of the hematite-magnetite transfomation, which is indicated by the low reaction rates at $w = 0.05$ (Fig. 3/b). Such an inhibitory effect was not observed in the case of Ca-added hematite (sample 2). On the basis of previous observations [10], and also of our ESCA measurements on the wastes, the inhibitory effect is attributed to the surface Na and Si content. A considerable amount of Na and Si was detected on samples 3 and 4 even after reduction at 1070 K for 10 minutes.

The rate minimum attributed to the change in the texture of the product layer [11] appeared at about 1070 K for the pure hematite. However, there was no decrease in the reaction rates for the wastes and for the Ca-containing hematite (Fig. 4). The higher reaction rates at this temperature can probably be explained by the effect of the Ca on the microstructure of the metallic iron formed [12].

It can also be seen that the TG curves below 1100 K for sample 1 and 900 K for sample 3 are sigmoid-shaped, pointing to the rate-controlling role of the nucleation and growth processes. For $Fe_2O_3$ at temperatures below 800 K, the transformation of hematite to magnetite is much faster than the magnetite—iron transformation.

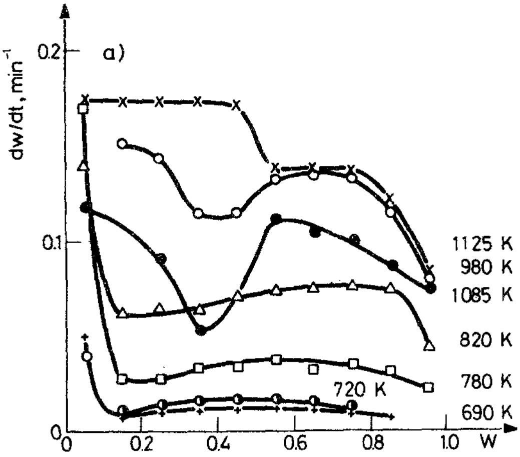

**Fig. 3/a** The change of the reaction rate with the conversion for Sample 1, $p = 10$ kPa $H_2$

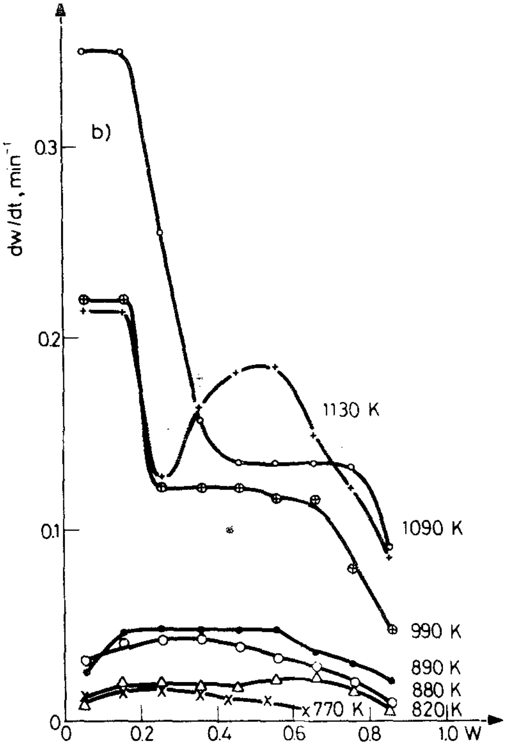

**Fig. 3/b** The change of the reaction rate with the conversion for Sample 3, $p = 10$ kPa $H_2$

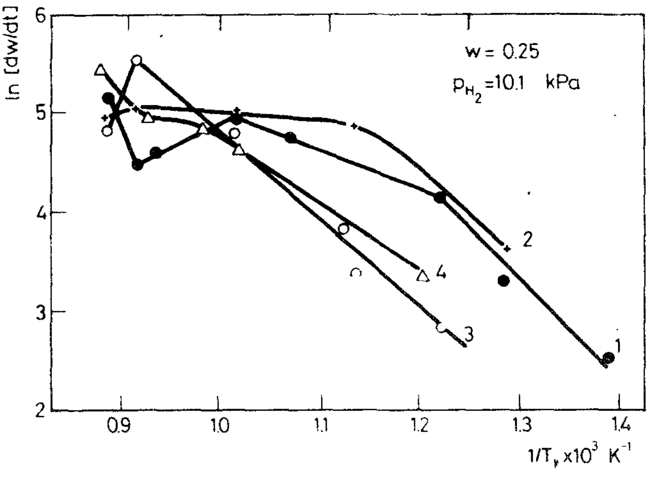

**Fig. 4** The Arrhenius representation of the reaction rate at $w = 0.25$. 1 for Sample 1; 2 for Sample 2; 3 for Sample 3; 4 for Sample 4, $p = 10$ kPa $H_2$

As proposed earlier by Viswanath et al. [8], a two-step consecutive process can be assumed:

$$3\,Fe_2O_3 + H_2 \xrightarrow{k_1} 2\,Fe_3O_4 + H_2O \tag{1}$$

$$Fe_3O_4 + 4\,H_2 \xrightarrow{k_2} 3\,Fe + 4\,H_2O \tag{2}$$

where $k_1 \gg k_2$.

In our case, in accordance with the sigmoid shape of the isotherms with a local rate maximum at $w = 0.3$–$0.5$, the second step can be described well by a nucleation model of one-dimensional growth:

$$[-\ln(1-w^+)]^{1/2} = kt \tag{3}$$

where $w^+$ is the conversion related to the amount of magnetite formed. Figure 5/a shows plots of the reduction at 720 and 780 K, as calculated via Eq. (3).

Above 800 K, the two steps could not be distinguished. The local maximum in the rate curves was shifted towards higher conversions, and the processes were described by the nucleation model of two-dimensional growth:

$$[-\ln(1-w)]^{1/3} = kt \tag{4}$$

as shown in Fig. 5/b.

At high reaction rates, however, the plots of reaction rate *vs.* conversion have no local maximum, and a model of external gas film diffusion control [13]:

$$1-(1-w)^{2/3} = kt \tag{5}$$

can be applied to describe the TG curves (Fig. 5/c).

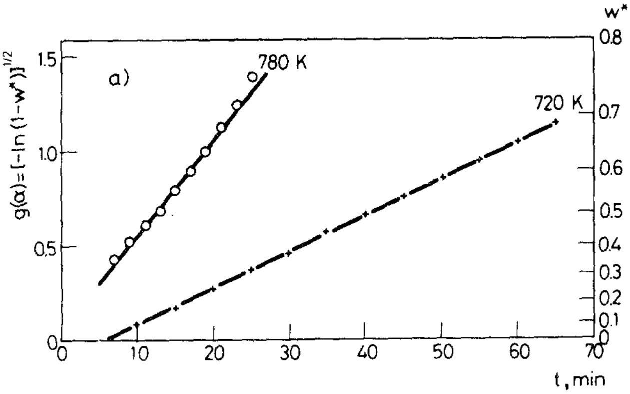

**Fig. 5/a** $[-\ln(1-w^*)]^{1/2}$ *vs.* $t$ curves for Sample 1

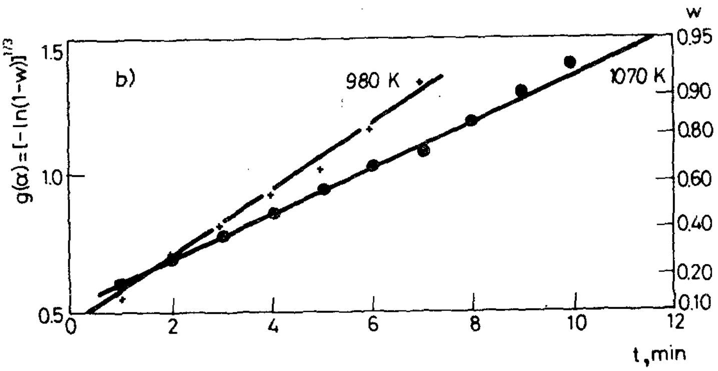

Fig. 5/b $[-\ln(1-w)]^{1/3}$ *vs. t* curves for Sample 1

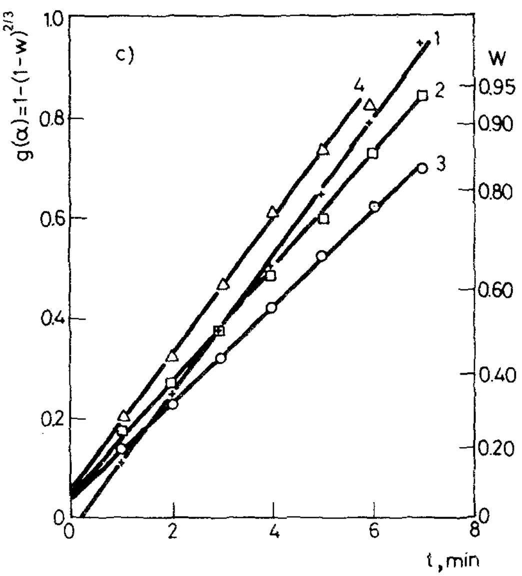

Fig. 5/c $1-(1-w)^{2/3}$ *vs. t* curves, + Sample 1, 1125 K, □ Sample 2, 1130 K, ○ Sample 3, 990 K, △ Sample 3, 1090 K

### *Reduction with carbon monoxide*

The reduction of the samples was also studied by using carbon monoxide as reducing agent, in the temperature range from 700 to 1120 K. Figure 6 shows mass loss *vs.* time curves for sample 4, while the temperature-dependence of the reaction rate at selected conversions is given in Fig. 7.

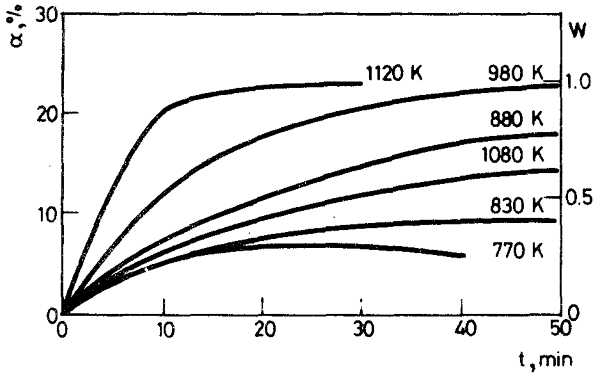

**Fig. 6** Mass loss *vs.* time curves for Sample 4 at $p = 10$ kPa CO

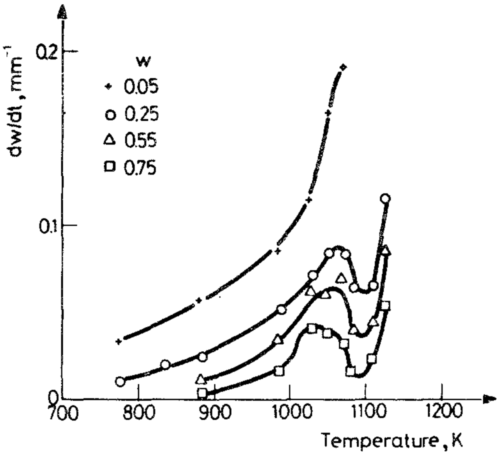

**Fig. 7** The change of the reaction rates with temperature for Sample 4 at $p = 10$ kPa CO, $w = +0.05$, ○ 0.25, △ 0.55, □ 0.75

It is clear that sigmoid-type curves were not observed even at low temperatures. However, a slight mass gain can be seen in the TG curves after a certain reaction time, which indicates carbon deposition [14] or the formation of iron carbide [15]. The reduction rate minimum can be observed at 1070 K for all samples studied. The highest reaction rates were measured for the pure hematite.

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**Zusammenfassung** — Die Kinetik der Reduktion von reinem sowie Ca-angereichertem Hämatit als auch von zwei eisenoxidhaltigen metallurgischen Nebenprodukten wurde mittels isothermen TG-Messungen untersucht. Dabei wurde CO und $H_2$ als Reduktionsmittel verwendet.

Unterhalb 900 K waren die Abfallprodukte weitaus weniger reaktiv als reines oder Ca-angereichertes Hämatit. Dies wurde der verzögerten Transformation Hämatit-Magnetit durch Na und Si an der Oberfläche zugeschrieben. Oberhalb 1000 K waren die Reaktionsgeschwindigkeiten für die Nebenprodukte und für Ca-angereichertes Hämatit höher als die für reines Hämatit. Die grössere Reaktivität wurde dem Einwirken von Ca auf die Mikrostruktur der Reaktionsprodukteschicht zugeschrieben.

Zur Erklärung der isothermen TG-Kurven bei niedrigeren Reaktionsgeschwindigkeiten und niedrigeren Temperaturen konnten Kristallkernbildungs- und Kristallkernwachstumsmodelle, für höhere Reaktionsgeschwindigkeiten gasschichtdiffusionskontrollierte Modelle erfolgreich angewendet werden.

**Резюме** — Методом изотермической ТГ в атмосфере водорода и окиси углерода изучена кинетика восстановления чистого и легированного кальцием гематита наряду с двумя металлургическими отходами, содержащими окись железа. Ниже 900 металлургические отходы намного менее реакционноспособны, чем чистый и легированный гематит. Это явление обусловлено задержкой превращения гематит — магнетит, вызванный поверхностными натрием и кремнием. Однако, выше 1000 К, скорости реакции для металлургических отходов и легированного кальцием гематита были выше, чем для чистого гематита. Их более высокая реакционная способность вызвана влиянием кальция на микроструктуру образующегося слоя. Модельные процессы образования центров кристаллизации и роста кристаллов были использованы для описания изотермических кривых ТГ при низких температурах и вблизи минимума скорости реакции, тогда как модель контролируемой диффузии газ — пленка должна быть использована в случае высоких скоростей реакции.