

APPLICATION OF THERMAL ANALYSIS FOR THE INVESTIGATION OF CALCIUM FERRITES

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Investigations of metallurgical materials such as blast furnace sinters and pellets require the syntheses of the standard phases contained in these materials.

Synthetic pure and calcium-doped iron oxides were studied. Calcium ferrite phases originated in the intergranular space and strongly affected the reducibility of the sinter, besides haematite and magnetite.

Studies of the formation and physicochemical properties of the synthetic calcium ferrites CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$, identified in polycrystalline calciomagnetite and calciowustite samples, are described.

Experimental

The calcioferrites CaFe_2O_4 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ have been obtained by thermal dissociation [1-6] and following the sintering of stoichiometric $\text{CaCO}_3\text{-Fe}_2\text{O}_3$ mixtures at 1150° in air [7]. The products were subjected to microscopic and diffractometric examination and also to microregion spectral analysis.

In order to determine the conditions of ferrite formation, thermal analyses were carried out with a Q-15000 Paulik-Paulik-Erdey derivatograph. TG, DTG, DTA analyses were performed in air atmosphere, using 500 mg samples. The temperature was increased at a rate of 7.5 deg/min.

As can be seen in Fig. 1, the TG and DTG analyses of a 1:1 molar mixture of $\text{CaCO}_3\text{-Fe}_2\text{O}_3$ in the temperature range $525\text{-}880^\circ$ indicate the complex character of the weight loss (16.4%) process. The process involving a slow increase in the weight loss rate between 325 and 825° turns into the next step with an altered rate up to 880° . The complexity of the weight loss process is confirmed by DTA. There are initially endothermic effects con-

nected with the weight loss, followed by exothermic ones without weight changes (maximum at 970°).

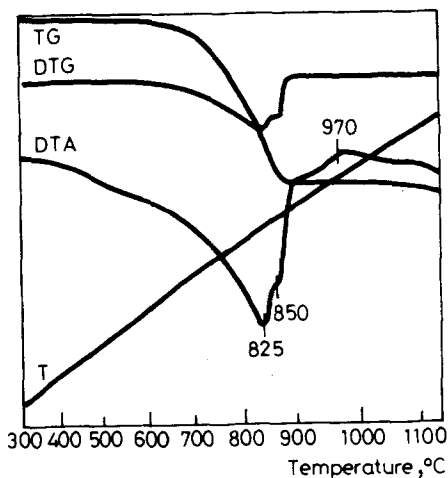


Fig. 1 Thermal curves of 1:1 molar mixture of $\text{CaCO}_3\text{-Fe}_2\text{O}_3$

Table 1 Results of spectral analysis in the microregion

Ferrite	Ca, %	Fe, %	Grain size, μm
CaFe_2O_4	18.4	50.8	8-16
$\text{Ca}_2\text{Fe}_2\text{O}_5$	28.2	40.1	4-12

The ferrite CaFe_2O_4 crystallizes in a rhombohedral system, forming 8-16 μm needle or column-shaped grains. Table 1 lists results of spectral analysis in the microregions, with the internal standards applied.

TG, DTG and DTA curves for a 2:1 molar mixture of $\text{CaCO}_3\text{-Fe}_2\text{O}_3$ are shown in Fig. 2. The TG and DTG analyses indicate a one-step weight loss of 23.6%, connected with the thermal decomposition of CaCO_3 , in the temperature range 650-900°. The corresponding section of the DTA curve reveals an endothermic effect with extremum at 885°. At higher temperatures, an exothermic effect (maximum at 1100°) can be observed.

The weight loss processes are related to the thermal decomposition of CaCO_3 . The samples crumble while decomposing and the ferrite is formed. The most stable and the least reducible is $\text{Ca}_2\text{Fe}_2\text{O}_5$ [8], which forms at higher temperatures than CaFe_2O_4 . Both ferrites appear in the intergranular

space of calciomagnetites and calciowustites obtained by reduction or synthesis [9, 10]. The parallel thermal analyses demonstrate the complexity of both above-mentioned processes. The purpose of the present paper was to separate the component reactions.

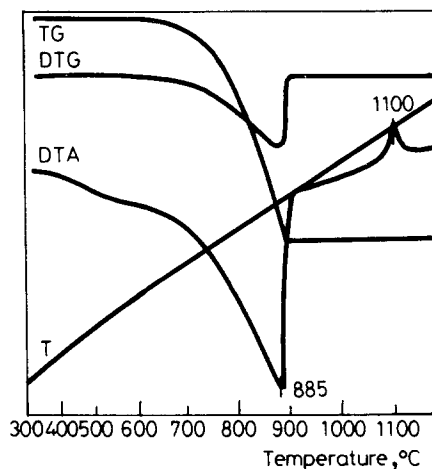


Fig. 2 Thermal curves of 2:1 molar mixture of CaCO₃-Fe₂O₃

Conclusions

The investigations allowed the following findings:

- the reaction proceeding with weight loss are connected exclusively with the thermal decomposition of CaCO₃;
- the ferrites CaFe₂O₄ and Ca₂Fe₂O₅ originate in samples that crumble subsequent to CaO formation; the latter ferrite forms at higher temperatures than the former one;
- the ferrites form in the solid phase; the melting process starts at 1150°.

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Zusammenfassung — Die Untersuchungen einiger metallurgischer Stoffe wie z.B. Hochofensinter und Pellets bedingen eine künstliche Herstellung von Standardphasen, die in den genannten Materialien vorkommen.

Es wurden synthetische reine und mit Calcium versetzte Eisenoxide untersucht. Calciumferrit wurde neben Haematit und Magnetit als diejenigen Phasen befunden, die im intergranularen Raum entstehen und die Reduzierbarkeit der Sinter stark beeinflussen.

Es werden hier Untersuchungen von Herstellungsprozessen als auch der physikalisch-chemischen Eigenschaften der synthetischen Calciumferrite CaFe_2O_4 und $\text{Ca}_2\text{Fe}_2\text{O}_5$ beschrieben.