High-pressure DSC investigations of the transformation goethite to hematite

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Introduction

The thermal transformation from goethite to hematite can be described by the chemical equation:

$$2\ \alpha\text{-FeOOH} \Rightarrow \alpha\text{-}Fe_2O_3 + H_2O$$

On the other hand, the dehydration mechanism is much more complex and depends on the particle size of the goethite needles (figure 1) [1]. Synthetic goethite pigments (Bayferrox®) of different particle size (table 1) were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC).

The following model for the mechanism of the dehydration process was described: at an early stage of the dehydration, water leaves the crystal lattice in the [010] direction of the crystal by forming dehydration channels parallel to the crystallographic c-axis [001]. The matrix between the channels is formed by hematite (figure 2).

In cases where the crystal dimensions are relatively large (length of needles ≥ 0.3 µm), the dehydration channels within the outer crystal regions begin to grow together, forming a compact hematite layer at the crystal surface before the dehydration front within the needle reaches the crystal center, i. e. the dehydration process is not finished yet.

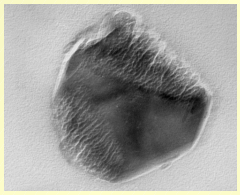
The compact surface hematite layer acts like a barrier, which hampers the further extension of the dehydration zone, because an additional amount of enthalpy must be provided to overcome the dehydration barrier and thus allows the dehydration front to proceed into the needle center, until the dehydration is completed [2]. Experimental evidence for this model consists of a second peak in the DSC plots of goethite samples.

In cases of very small needle dimensions the dehydration is finished before a dehydration barrier can be formed.

Figure 1: REM image of goethite 1; magnification: 30 000x

Table 1: Specific surface area of goethite samples (from BET-measurements in nitrogen) and characteristic particle geometry (from SEM images)

Sample	Specific surface / $m^2 \cdot g^{-1}$	Particle geometry / $10^{-18} \cdot m^3$
goethite 1	10	1.2 · 0.25 · 0.25
goethite 2	14.5	1.0 · 0.15 · 0.15
goethite 3	67	0.3 · 0.03 · 0.03
goethite 4	149	0.1 · 0.01 · 0.01



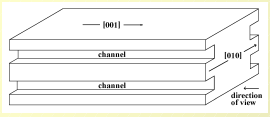


Figure 2: TEM image of a partly dehydrated goethite 1 needle cut perpendicular to the needle axis; magnification 225 000x

Experiments

Goethite samples of different particle size were investigated in a nitrogen atmosphere at ambient pressure, 35 bar, 70 bar and 150 bar by a high-pressure DSC (Netzsch 204 HP *Phoenix*®).

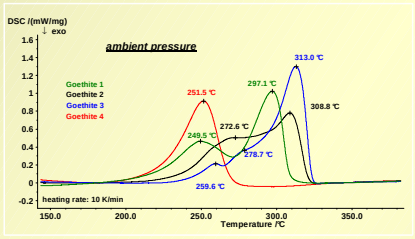


Figure 3: HP-DSC results of goethite samples (different particle sizes) in nitrogen atmoshere at ambient pressure

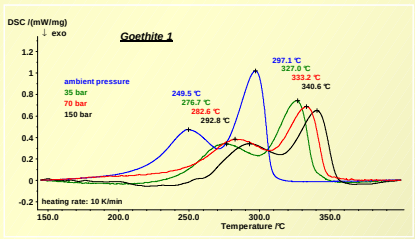


Figure 4: HP-DSC results of a goethite sample (length of needles: 1.2 µm) in nitrogen atmoshere at different pressures

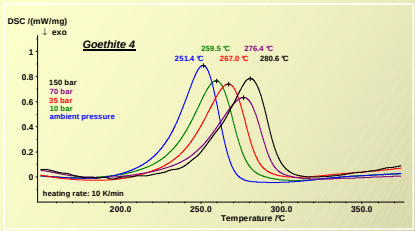


Figure 5: HP-DSC results of a goethite sample (length of needles: 0.1 µm) in nitrogen atmoshere at different pressures

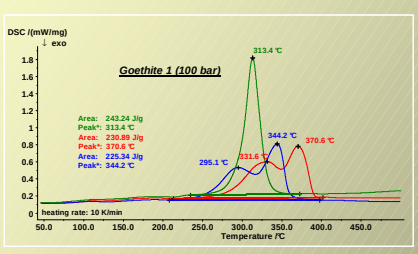


Figure 6: HP-DSC results of a goethite sample (length of needles: 1.2 µm) in nitrogen atmoshere at 100 bar (closed crucibles with holes of different cross sections)

Results

The mechanism of the transformation from goethite to hematite (figure 3) is obviously not changed by external pressure, but the transformation temperature increases to a limiting value (figure 4 and figure 5).

Varying DSC results are obtained when using aluminum pans with pierced lids of differing hole diameters (figure 6). These obviously influence the dehydration mechanism due to the water vapour pressure inside the crucible. In order to understand these effects further investigations employing a water vapour furnace and defined relative humidity are planned.

References

1. Walter, D.; Buxbaum, G.; Laqua, W., J. Therm. Anal. Cal. 2001, 63, 733-748
2. Walter, D.; Füglein, E.; Opfermann, J. R., Proceedings Book: 9. European conference on solid state chemistry, 2003, 248