Composite Fe_xO_y/TiO_2 powders – microstructure and magnetic properties

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AIM: Preparation and characterization of magnetically modified TiO_2 powders to improve the separation from liquids.

Sample preparation

- 0.36 g $FeSO_4.7H_2O$ dissolved in 100 ml of water in a 600-800 ml beaker
- one gram of anatase (TiO_2) was added and a solution of sodium hydroxide dropped slowly under mixing until the pH reached the value 10-12
- suspension diluted up to 200 ml with water and treated for 10 minutes in standard kitchen microwave oven (700 W, 2450 MHz) at the maximum power
- magnetically responsive composite with iron oxides captured using an appropriate magnetic separator or NdFeB magnet and dried at cca 60°C

sample	Fe content wt. %	FeO content wt. %	SSA m^2g^{-1}	Mean diameter µm
anatase	< 0.001	< 0.001	84.9	3.88
magn. modified anatase	6.47±0.25	0.43±0.05	173	3.51

Table 1: Total content of Fe, Fe^{II} (expressed as content of FeO), the specific surface area, and mean diameter of non-magnetic and magnetic anatase particles.

Experimental techniques

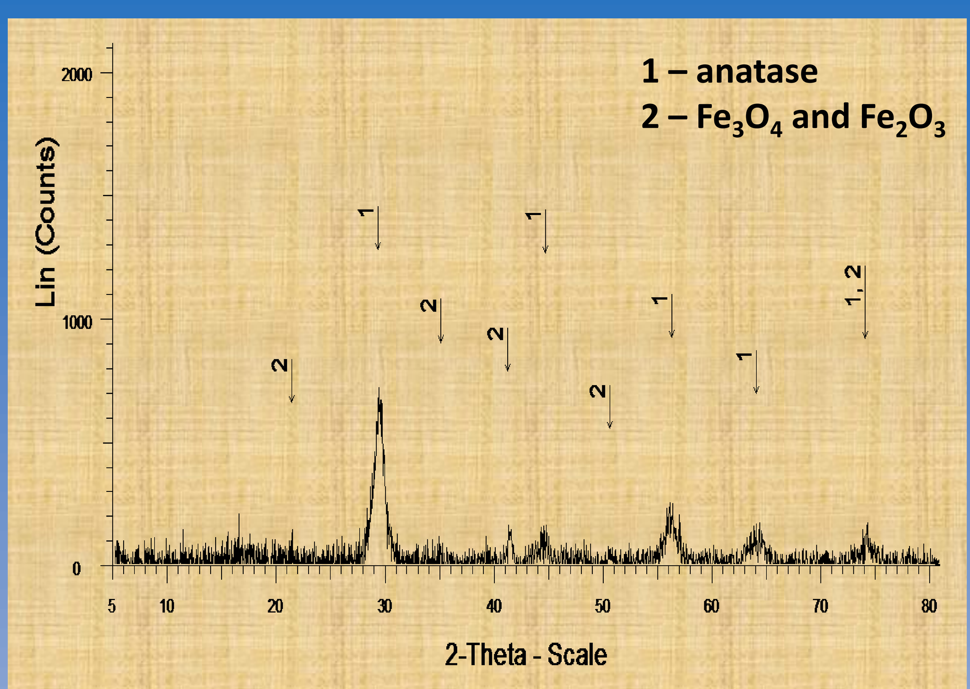
- **SEM (Scanning Electron Microscopy)** – PHILIPS XL-30 with spectrometer EDAX
- **XRPD (X-Ray Powder Diffraction)** – CoKα irradiation (λ = 0.1789 nm), Bragg-Brentano geometry, 2θ range 5 ÷ 80°, and 0.02° step
- **VSM (Vibrating Sample Magnetometer)**
  - **thermomagnetic curve (TMC)** – from RT up to 924 K in an external magnetic field of 16 kA/m, temperature increase of 5 K/min and Ar atmosphere to prevent oxidation
  - **hysteresis loop** – up to magnetic field ±1600 kA/m with the step of 1.6 kA/m
  - **Henkel plot** – $\delta M(H) = 2\frac{IRM(H)}{IRM(\infty)} - \frac{DCD(H)}{DCD(\infty)} - 1 = 2IRM\_norm(H) - DCD\_norm(H) - 1$
  - **irreversible susceptibility** – $\chi_{irr}(H) = \frac{d(M_{irr}(H))}{dH}$, $M_{irr}(H) = \frac{1}{2}(1 - DCD\_norm(H))$
  - **reversible susceptibility** – $\chi_{rev}(H) = \frac{d(M_{rev}(H))}{dH}$, $M_{rev}(H) = DCD\_norm(H) - \frac{hys\_pos(H)}{IRM(\infty)}$

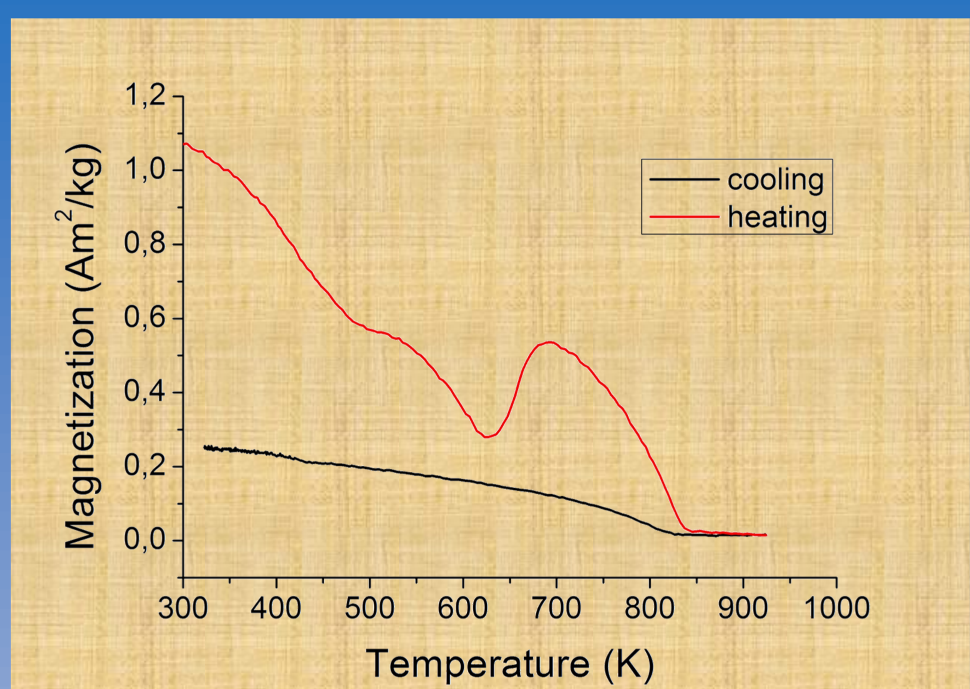
IRM (Isothermal ReManence) curve, *DCD* (DC Demagnetization) curve

Results and discussions

XRPD and SEM

- XRPD diffraction pattern confirmed the presence of anatase and Fe_3O_4
- detailed analysis indicates the minor representation of γ-Fe_2O_3 and α-Fe_2O_3
- particles of anatase lower than 10 µm
- different shape of anatase particles in non-magnetic (SEM figure a)) and magnetic (SEM figure b)) form
- particles of iron oxides present on the surface of anatase particles
- size of iron oxide particles lower than 1 µm

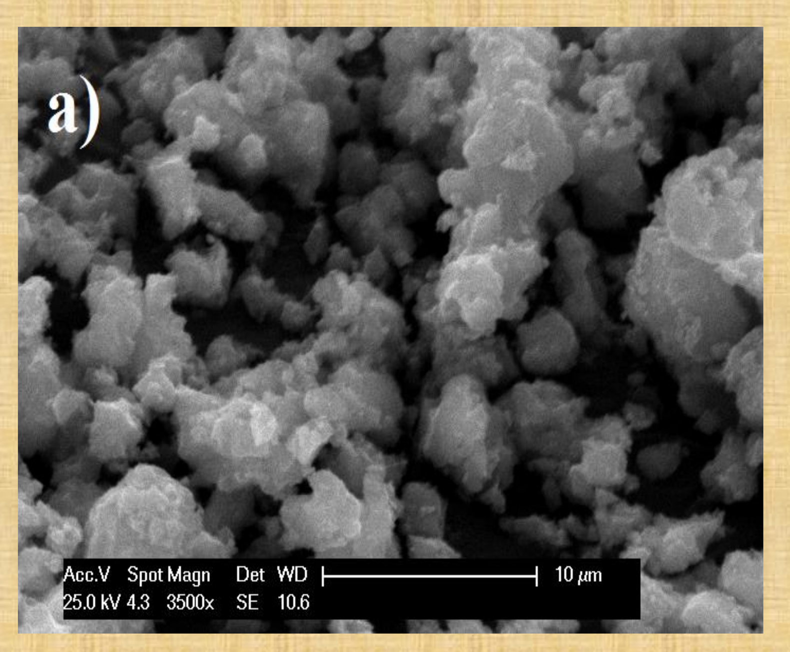


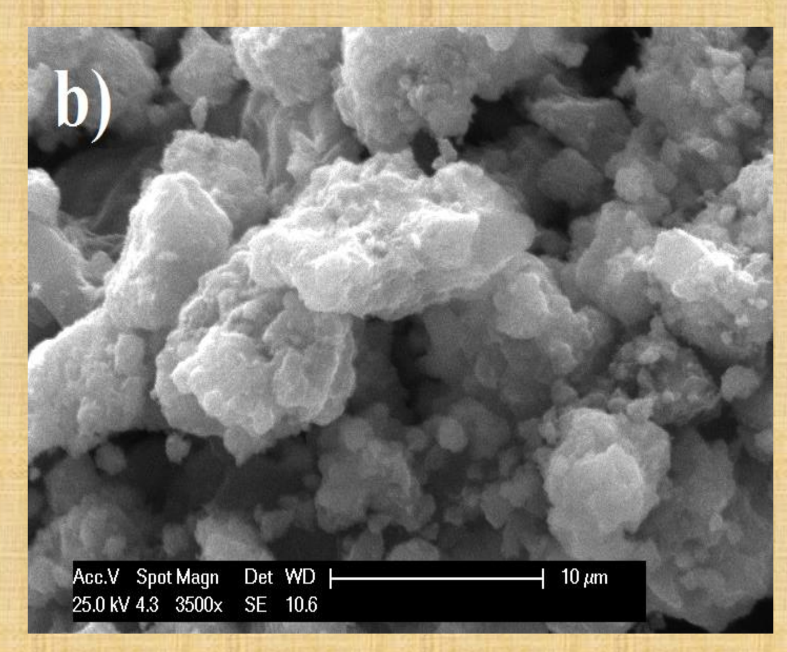


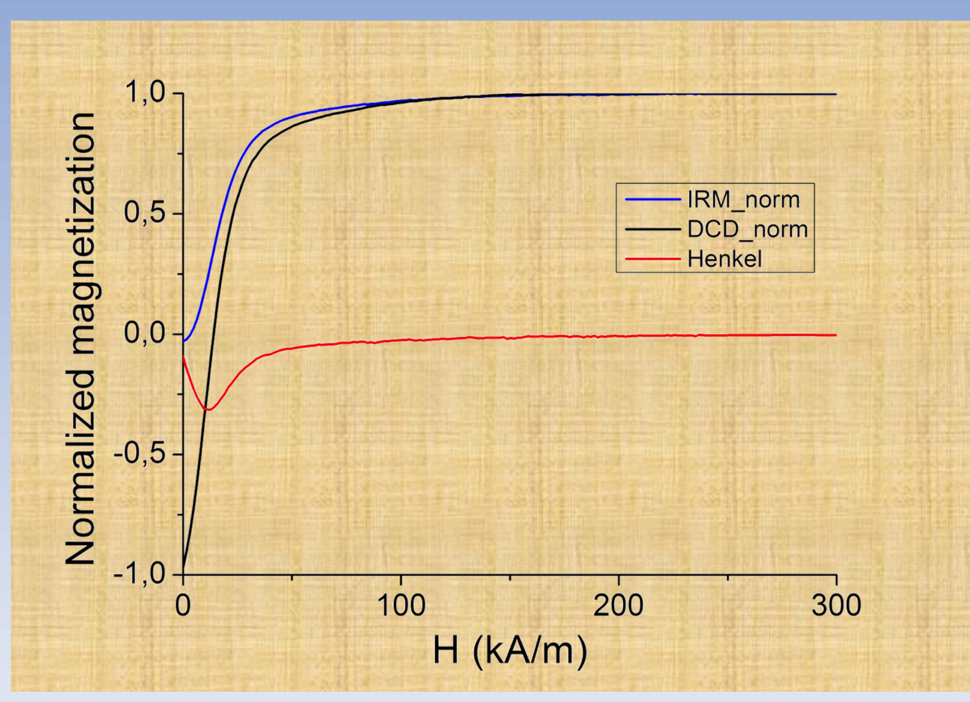
Magnetization and TMC curve

- magnetic parameters before and after the TMC summarized in Table 2
- return to ferromagnetic state and magnetic hardening after the TMC
- three phase transitions detected during heating
- at 480 K the transition of magnetite particles to maghemite is observed
- the second peak about 620-630 K indicates probably transformation of maghemite to hematite
- transition to a paramagnetic state at about 820-850 K

before magnetic modification / **after magnetic modification**





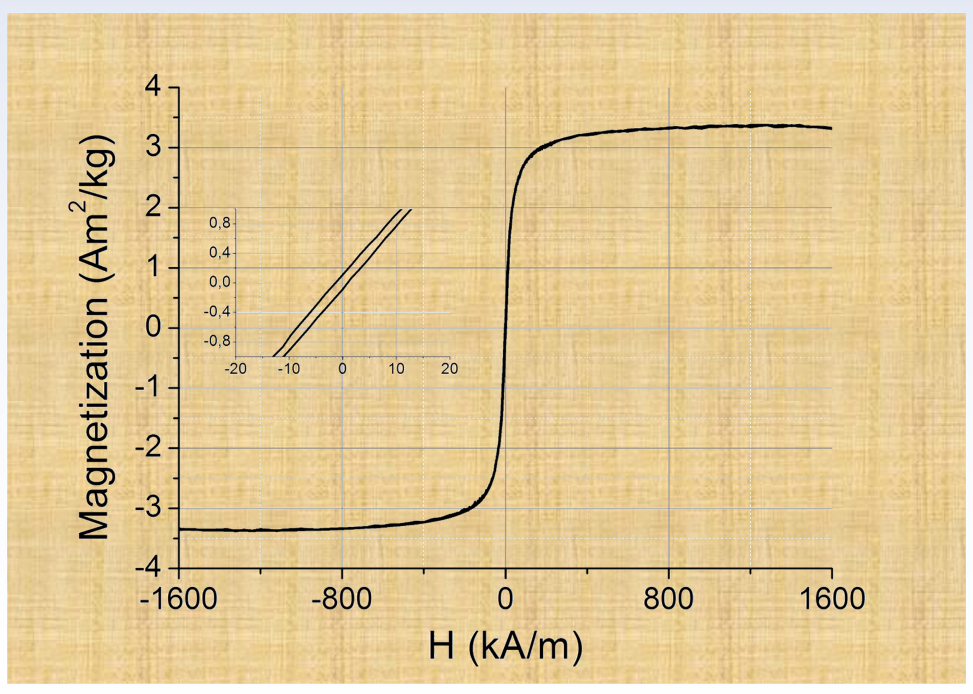


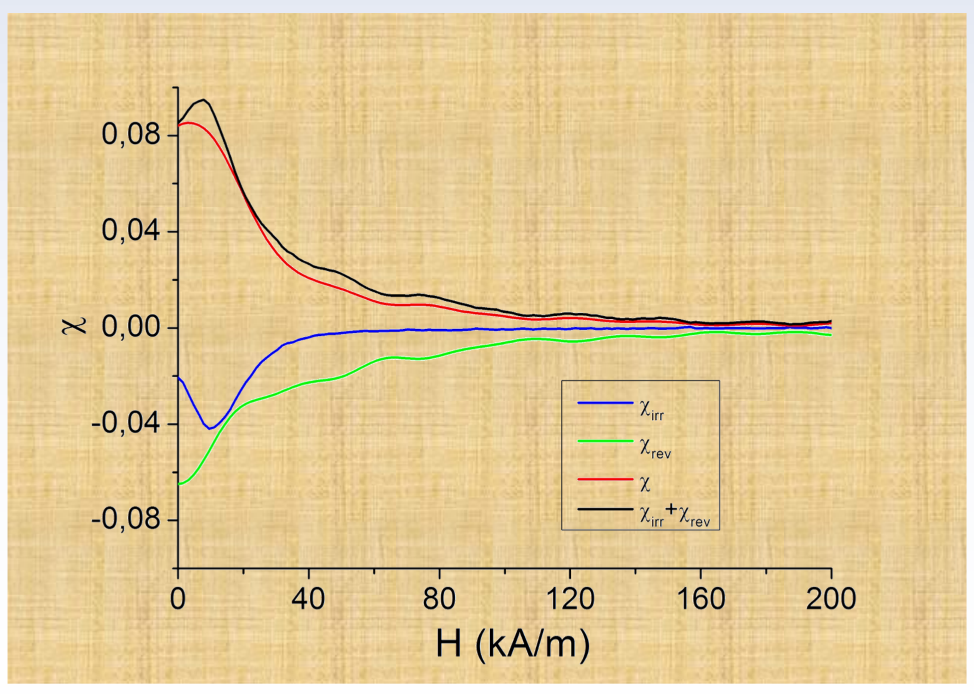
Henkel plot

- changes in *DCD* curve faster than that in *IRM* curve
- prevailing negative (dipolar) interactions, $\delta M(H) < 0$, and demagnetization is stimulated in the sample
- intensity of Henkel plot peak and magnetic field at which the peak is observed give the values -0.32 and 12 kA/m
- at higher magnetic fields (above 12 kA/m) the decrease of $\delta M(H)$ intensity with increasing *H* is observed

	H_c	M_s	M_r	T_c
	kA/m	Am^2/kg	Am^2/kg	K
I	1.11	3.38	0.10	cca 850
II	10.77	0.74	0.14	

Table 2: Magnetic parameters obtained from the magnetization curve prior (I – left figure) and after (II) the thermomagnetic treatment (RT→924 K→RT). H_c – coercive field; M_s – saturation magnetization; M_r – remanent magnetization; T_c – Curie temperature.





Magnetic susceptibility

- SFD curve – $\kappa_{irr}(H)$ – blue line – exhibits typical one-peak behavior
- obtained value of nucleation field H_n is about 8 kA/m
- reversible part of susceptibility – $\kappa_{rev}(H)$ – green line – has the highest value close to zero magnetic field
- two approaches for total susceptibility: (i) sum of $\kappa_{irr}(H)$ and $\kappa_{rev}(H)$ – black line and (ii) derivative of the magnetization curve – red line
- low reversible effects are responsible for similar results of both approaches

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