Local magnetic and electronic properties of surface oxidised Fe particles

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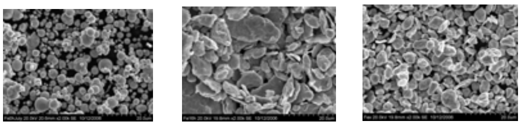
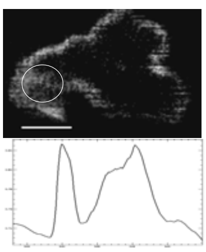
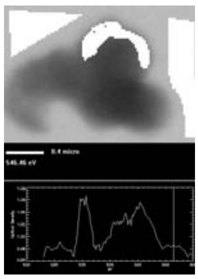


SEM images of the as cast (left), 16h milled (middle) and subsequently vacuum annealed at 300 °C (right) powders. Flat particles obtained with milling regain their round shape upon annealing.



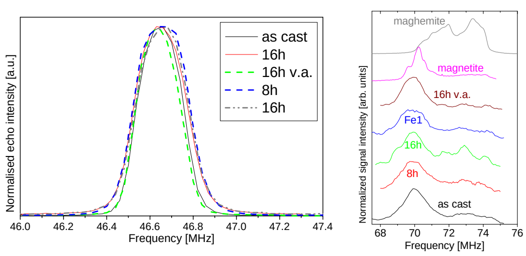
Scanning Transmission X-ray Microscopy results. Top: Oxygen map of a grain of the as cast powder. The oxygen K-edge spectrum (bottom) was integrated over the marked flat area.

The pre-edge peak shape shows that the oxide is magnetite-like.



Top: STXM image of the same grain taken at 546,46 eV. The oxygen K-edge spectrum (bottom) was integrated over the marked area.

The pre-edge peak shape indicates that the oxide is hematite-like



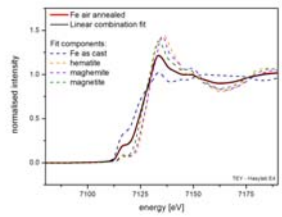
The ^{57}Fe NMR spectra at 4.2K corresponding to the iron core (left) and the oxide shell (right) for various samples.

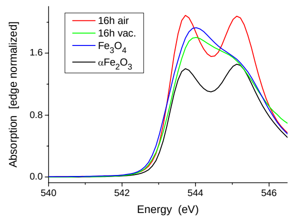
The increase of the linewidth of the metallic iron core with milling reflects the increased strain. Annealing causes a reduction of the linewidth to the initial value which reflects a reduction of strain.

The oxide is mostly magnetite-like with possible small amount of hematite. The Fe hyperfine field is lower than in the bulk oxide, also in the vacuum annealed sample, possibly due to influence of the metallic iron core or strain.

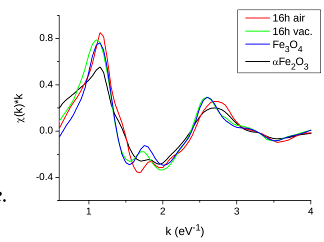
A combined SEM, STXM, XAFS, Moessbauer and NMR study of ball milled Fe powders exhibiting magnetoresistive properties has been carried out in order to determine the morphology and the nature of surface oxides as well as the influence of mechanical treatment (ball milling) and annealing (300 °C vacuum or air) on it.

The Fe K edge XANES spectra in TEY mode of the air annealed powder together with the reference spectra of the as cast powder, magnetite, maghemite and hematite.





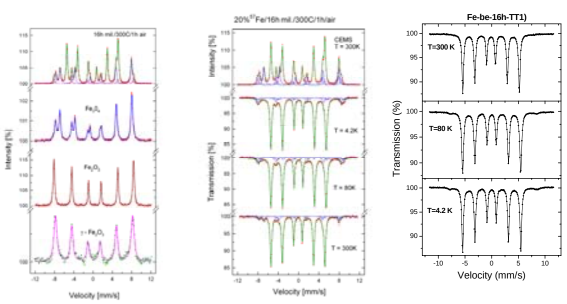
The pre-edge peak in the oxygen K edge XANES spectra of the16h milled 1h air annealed (16h air) sample and the the16h milled 1h vacuum annealed (16h vac.) sample together with the reference spectra of magnetite and hematite.



The EXAFS chi function obtained from the spectra at the oxygen K edge of the16h milled 1hrair annealed (16h air) sample and the the16h milled 1h vacuum annealed (16h vac.) together with the reference spectra of magnetite, and hematite.

The XAFS TEY spectrum at the Fe:K edge, which corresponds to about 300 nm probing depth (similar to CEMS), shows 45% metallic Fe, 42% magnetite and 13% hematite in the layer of such a thickness.

The O:K edge XAFS spectra corresponding to about 5nm probing depth show that the air annealed sample has mostly hematite and the vacuum annealed one – mostly magnetite in the outer oxide layer of such a thickness.



Left: The room temperature CEMS spectra of the air annealed sample 20% ^{57}Fe enriched and the reference oxides. Middle: The CEMS and the temperature transmission MS spectra of the air annealed sample. Right: The temperature transmission MS spectra of the vacuum annealed 20% ^{57}Fe enriched sample. Weak outer lines correspond to the oxide.

The ^{57}Fe CEMS spectra of the air annealed sample show 55% metallic iron, 34% magnetite, 8% hematite and 3% maghemite in the outer layer of 300-500nm, i.e. the CEMS probing depth.

The temperature transmission spectra of the air annealed sampleshow a change in the oxide spectrum between 80 and 300K reflecting the Verwey transition. A lack of the oxide lines in the vacuum annealed sample at RT is related to a low D-W factor or paramagnetism of the thin (about 5nm) oxide layer.

Conclusions:

- ✓**Fe micrometric particles naturally oxidised in a dry atmosphere at ambient temperature have magnetite-like oxide layers of a few nanometer thickness. A hematite-like oxide can form at sharp grain edges.**
- ✓ **Fe hyperfine field is lower than in the bulk oxide possibly due to the influence of the metallic Fe core or strain.**
- ✓**Debye-Waller factor is much lower than in the bulk oxide.**
- ✓**Milling produces flat particles and introduces defects and strain, which are removed with vacuum annealing and a round shape of the particles is re-gained.**
- ✓**Air annealing at 300 °C produces thick magnetite shells with a hematite-like outer layers. A minor contribution of maghemite is found.**

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