XRPD and TEM as tools to determine crystallite size of nanocrystalline iron

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Introduction

Nanocrystalline iron and its compounds became of high interest lately due to their numerous applications e.g. as magnetic devices in medicine or EMI shielding and filtering [1-3].

A method commonly used to determine structural properties of these materials, such as crystallite size, is X-ray diffraction (XRD). However, analysis of the data with different approaches [4-6] might lead to ambiguous results. For this reason, the use of different analytical techniques is required to confirm the XRD analysis. Here, we have chosen electron microscopy (EM). It needs to be pointed out, that this method might be misleading as well. The EM images show particles that tend to be agglomerates of multiple crystallites when XRD focuses on separate crystallites with continuous lattice.

Sample
- Commercial iron
- 99.5%
- 25 nm particle size

Reaction chamber
Anton Paar XRK 900

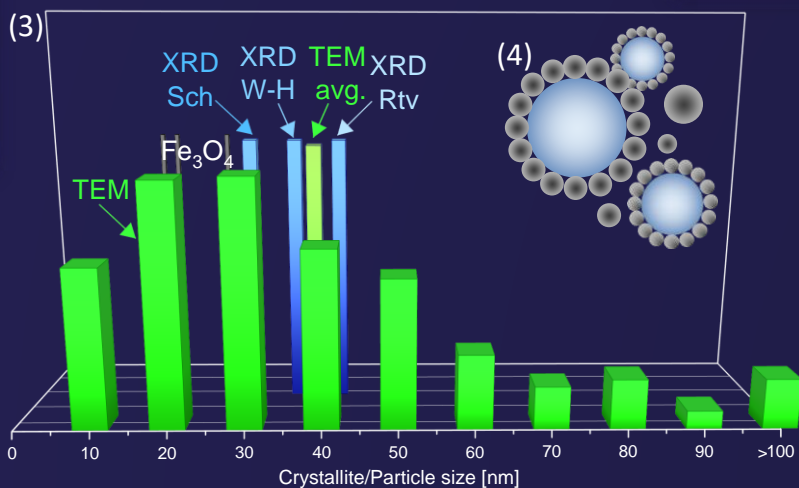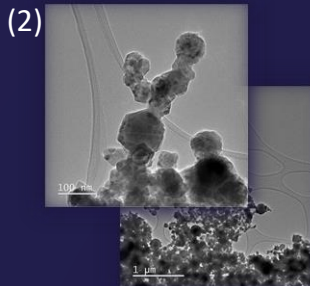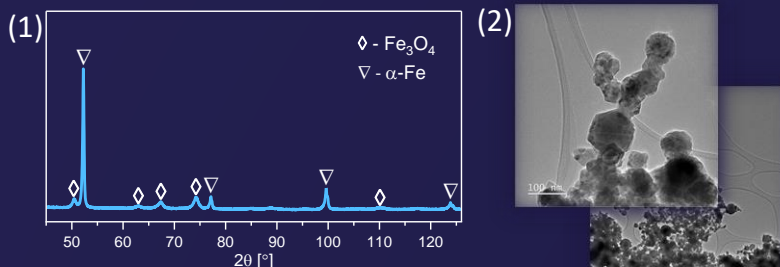**Diffractometer**
- Philips X'Pert Pro MPD
- Co Kα radiation
- PIXcel^{1D} detector
- 0.02°2θ step

TEM
- Tecnai F30
- 200 kV

Results

The samples of nanocrystalline iron were analysed as a model for the comparison of different approaches to determining particle/crystallite size. The mean crystallite size (MCS) of the α-Fe phase was calculated from XRD data (1) using Scherrer (Sch), Williamson-Hall (W-H) and Rietveld (Rtv) methods. The results were 30 nm, 36 nm and 42 nm respectively. It is noteworthy, that a major part of the sample (60 wt.%) consisted of magnetite phase (Fe_3O_4), with MCS of ca. 9 nm (Sch), 8 nm (W-H) and 16 nm (Rtv). However, considering the numbers of particles of each phase (calculated from MCS and wt.%) the resulting mean crystallite size of both phases together would be ca. 9 nm (Sch), 8 nm (W-H) and 17 nm (Rtv).

The mean particle diameter measured from TEM images (e.g. 2) was 39 nm.

(1) ◇ - Fe_3O_4 ▽ - α-Fe

2θ [°]

(3)

XRD Sch   XRD W-H   TEM avg.   XRD Rtv

Fe_3O_4

TEM

Crystallite/Particle size [nm]

Conclusions

When both metallic and oxide phases are considered as distinguishable particles in TEM images and the average values from TEM and XRD are calculated the same way (by number), the results do not match at all (grey lines on 3).

However, during sample preparation, the pyrophoric metallic particles are covered with a thin layer of oxide for protection. Thus, the more legitimate (hypothetical) model of such a system would be that metallic particles are covered with a polycrystalline layer or multiple small crystallites of oxide (4). The oxidating potential seems only enough to transform the outer layer of large particles and the smallest particles in the system. In that case, the TEM images would show core-shell particles slightly larger than metallic counterparts before passivation and small particles of oxide. Effectively, the measured mean particle size would be raised due to the passivation layer and reduced by omitting the particles too small to be measured. The measured by TEM value might also be erroneous due to the high agglomeration of ferromagnetic material leading to poor statistics (340 measurable particles).

Considering above, the TEM results match closely with MCS for α-Fe phase calculated with the Rietveld and Williamson-Hall methods, both of which use full pattern approach. The Scherrer method proved to be more inaccurate. It is also mathematically simplest and most prone to errors due to basing on a single reflection and basing on a shape coefficient K that does not work well for mixed-shape particles.

TEM analysis also confirmed the log-normal distribution of particle size in metallic (and oxide) nanoparticles.

Bibliography

[1] U. Rajaji, et al., Sensors and Actuators B: Chemical, 2019, 291, 120-129.
[2] K. Wu, et al., ACS Omega, 2020, 5, 11756-11767.
[3] H. Gargama, et al., J. Alloys Compd., 2016, 654, 209-215.
[4] P. Scherrer, Nachr. Ges. Wiss. Göttingen, 1918, 2, 96-100.
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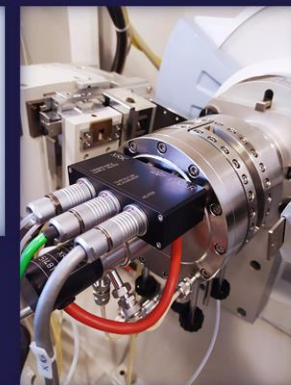
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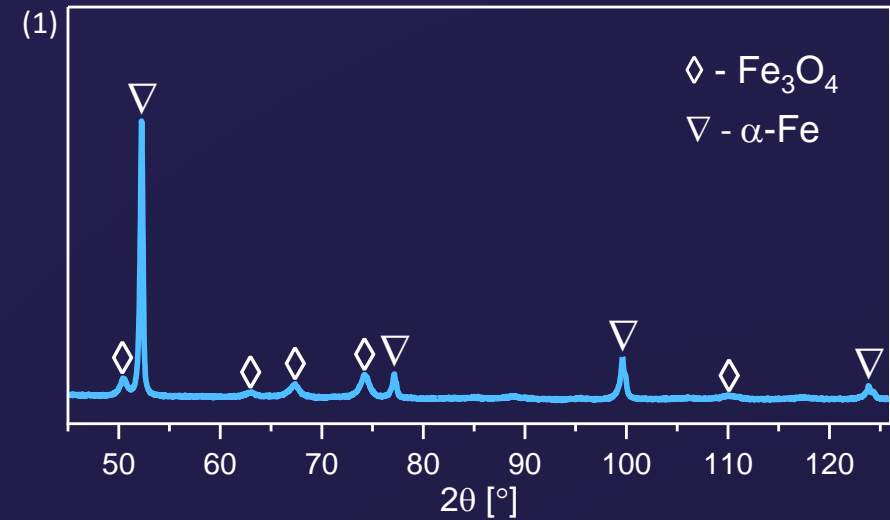# XRPD and TEM as tools to determine crystallite size of nanocrystalline iron

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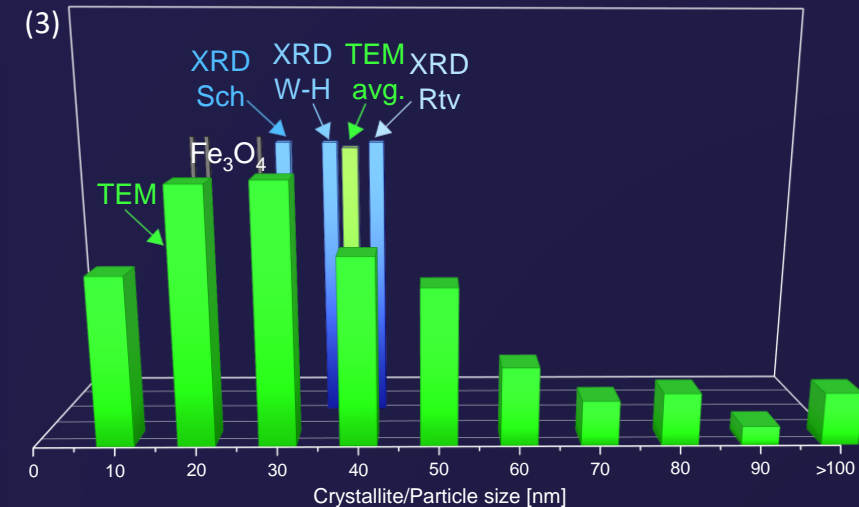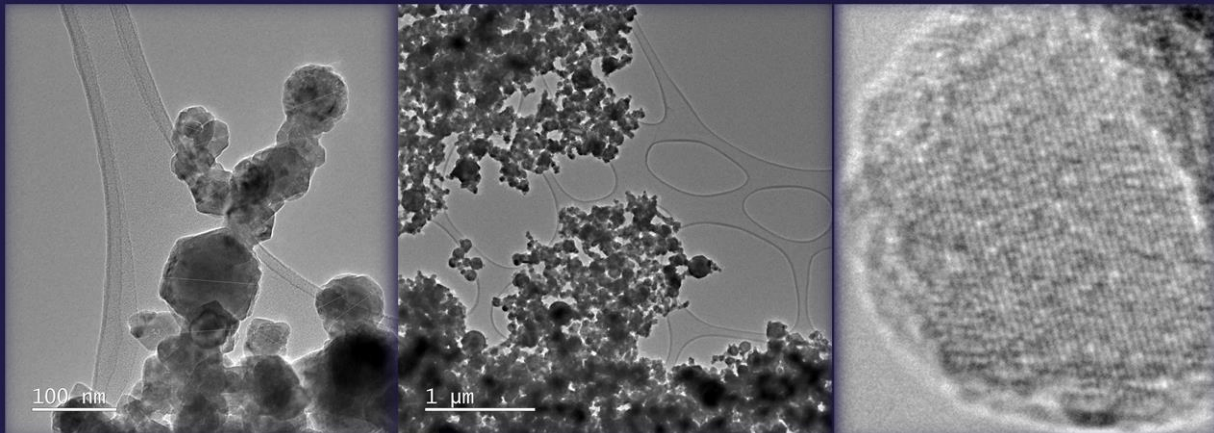*Contact Author E-mail Address: aleksander.albrecht@zut.edu.pl*

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(1) $\diamond$ - Fe_3O_4 ∇ - α-Fe

(2) >60 images

(3)

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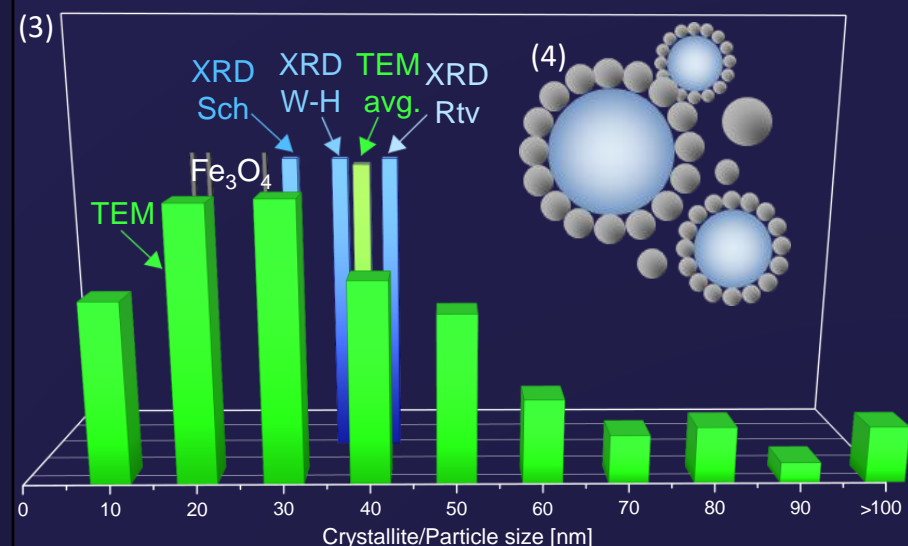*Contact Author E-mail Address: aleksander.albrecht@zut.edu.pl*

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In the future, the Warren-Averbach approach from XRD combined with quasi in situ TEM might be the better solution to precisely determine crystallite size and its distribution.

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