Round-robin results of the quantitative analysis of FeNi nanoparticle compositions

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Introduction

Developments in microscopes, spectrometers, imaging filters, detectors and data processing are leading to the development of new techniques and improvements in quantitative electron microscopy and analysis. In order to determine the accuracy of chemical measurements from nanoscale structures with complex morphologies, we have compared different analytical techniques by applying them to the characterisation of a known object in a "blind" round-robin test.

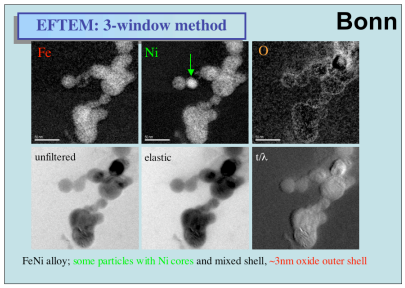
The samples investigated were nanocrystals of FeNi with sizes of between 10 and 120 nm, a range of chemical compositions and thin oxide surface layers. The crystals were prepared using cryogenic evaporation-condensation with known chemical compositions [1].

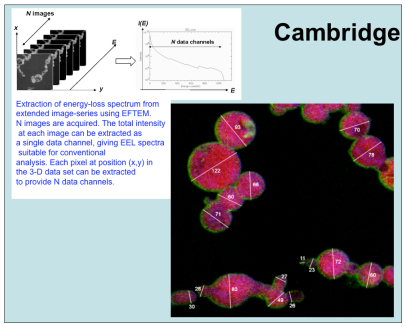
EELS, EFTEM and EDX analyses were performed on the FeNi particles in different laboratories. Different models for scattering cross-sections were used during data analysis, different approaches were used to extract chemical information from the experimental measurements, and near edge fine structures from O, Fe and Ni ionization edges were recorded both from the centres and from the surface layers on the crystals. The results of these experiments were compared and contrasted during the 2004 meeting of the GdR-E QTEM [2].

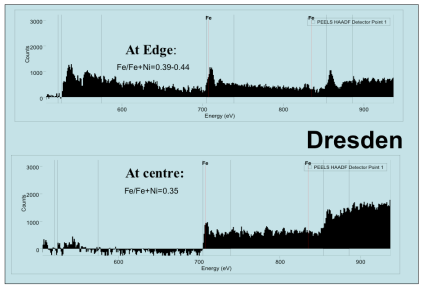
Discussion

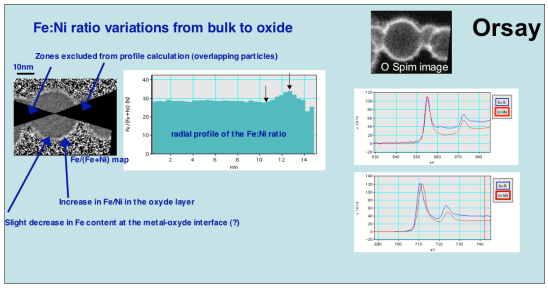
- Cross section: key point ? to be calibrated with well known reference substances ?
- Angle : large panel used
- STEM & TEM elemental images of comparable quality
- Overall results : good agreement

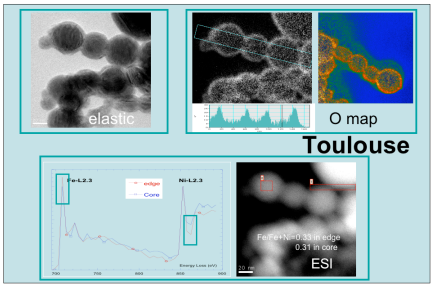
	Cambridge	Bonn with Lausanne	Bonn	Orsay	Dresden	Dresden	Toulouse
Instrument Gun Voltage	**CM**300 FEG **297kV**	**CM**300UT, FEG **297kV**	**CM**300UT, FEG **297kV**	**VG** STEM, 100kV, FEG **100 kV**	**Tecnai** F30 ST FEG (TEM/STEM) **300kV**	**Tecnai** F30 ST FEG (TEM/STEM) **300kV**	**Tecnai** F20 UT FEG Cs-corrected **200 kV**
PEELS or filter	2k GIF2000	1k GIF	1k GIF	PEELS	Gatan GIF 200	Gatan GIF 200	GIF Tridiem 2k
Angles	α = rather big β =5.2 mrad	α = 2 mrad, β = 14 mrad	α = 1 mrad, β = 5 mrad	α = 7.5 mrad, β = 22 mrad	α = 1.5 mrad, β = 25 mrad	α = 5 mrad β = 7.3 mrad	alpha =2.7 mrad beta = 30 mrad
Method	**ESI**	EFTEM	EELS	Image-spectrum 128x100 pixel (0.5 nm)	EFTEM	EELS	Image spectroscopy
n° of Window window size and position	**50 windows (20 eV) or 100 windows (10 eV)** **Pre-edge** 20-60eV/20eV steps. **Post-edge** 20-120eV/20eV steps at least 5eV after energy-loss edge	**3 windows** **Post edge** **50eV** from onset of L3 edge	**Pre-edge** 25 eV **Post-edge** **50 eV** from onset of L3 edge	**Post edge** **140eV** from the edge onset	**3 windows** **Pre-edge** 30 eV **Post edge** **30 eV** (from 718 & 865, with (some) white lines)		**75 windows of 5 eV** **Pre-edge** **30 eV** **Post edge** **45 eV** (from the edge onset)
Exposure time	1500 s (50 windows) or 2700s (100 windows)			50ms/pixel, **640s** total acquisition time	30sec exposure each 3mm entrance aperture		10s/Imagex75 images, total acquisition time **750s**, 5 mm entrance
Cross-sections	**Hartree-Slater**, (Hydrogenic and Hydrogenic with white lines were used for cross-sections calculations)	**Hartree-Slater** from onset of L3 edge,	**Hartree-Slater** O = 508 b Fe = 865 b Ni = 516 b σ_{Ni}/σ_{Fe} **= 0.59**	**Hartree-Slater** O = 2820 b Fe = 5100 b Ni = 3245 b σ_{Ni}/σ_{Fe} **= 0.63** with 4/3 correction for sNi from exp. measurement on a ref. NiO powder.	**Hartree-Slater** O = 230 b Fe = 500 b Ni = 280 b σ_{Ni}/σ_{Fe} **= 0.56**		**Hartree-Slater** O = 1027 b Fe = 1702 b Ni = 1028 b σ_{Ni}/σ_{Fe} **= 0.60**
Particle diameter	10-120 nm particles for 3 different samples over 6 regions	20 nm		25 nm	100 nm 50 nm 10 nm	100 nm 50 nm 10 nm	30 nm
probe size	N.A.			Probe size: 0.5 to 0.7 nm. pixel size: 0.39nm		Probe size: 0.5 to 0.7 nm.	
Results	**Fe/Fe+Ni = 0.33 ± 0.03** average of 48 calculations from 6 particles and 2 regions	Existence of some Ni –rich cores in 20 nm small particles	**Fe/Fe+Ni = 0.37 ± 0.05** (0.34 ± 0.05 with hydrogenic cross section without WL correction, **0.29 ± 0.04** for Hydrogenic cross section with WL correction from ELP3.0)	**Fe/Fe+Ni = 0.29**	Large : **Fe/Fe+Ni = 0.33-0.35** Medium : **Fe/Fe+N i= 0.32-0.34** Small : **Fe/Fe+Ni = 0.28**	Large particle: **Fe/Fe+N i= 0.35** Medium Particle: **Fe/Fe+Ni = 0.34** Small particle: **Fe/Fe+Ni = 0.34**	**Fe/Fe+Ni = 0.31**
Layer oxide	3 nm	2-3 nm				Core of particle: **Fe/Fe+Ni = 0.35** edge of particle: **Fe/Fe+Ni = 0.39 -0.44**	3 nm
Complementary EDX results		**Zeiss LEO922A 200kV, probe size 5 nm Fe/Fe+Ni = 0.31 ± 0.02** For particle larger than 80 nm Fe/Fe+Ni went up 0.54 in their center			**STEM-EDX** FEG HT 300 kV, spot9 , Fe/(Fe+Ni) ratio ESVision(TIA) EDAXGenesis calc (Zalu./Mott) Large particle: 0.26 0.31 0.29 Medium particle : 0.26 0.32 0.295 Small particle: 0.25 0.295 0.27		











[1] Cécilie Duhamel, Yannick Champion, Marcel Tencé and Michael Walls, Journal of Alloys and Compounds 393 (2005) 204-210
Synthesis of controlled-chemistry ultrafine FexNi1-x ferromagnetic powders
[2] European Research Group on Quantitative Electron Microscopy funded by the CNRS