Report on exp. MA-522
XRF/XRD microtomography and XRF nanotomography of Ni-containing hydrotalcite layers on FeCrAlY-alloy foams using ESRF-ID22 and ESRF-ID22NI

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1. Introduction

The current and scheduled environmental restrictions on the Sulfur content in fuels, mainly diesel fuels, impose to world refineries the use of increasing amounts of H_2 for the hydrodesulphurization processes. H_2 is industrially produced by steam reforming (StR) of natural gas. StR is a strongly endothermic reaction and operates at about 1173-1273 K; furthermore, since the catalysts are mainly supported on oxides (i.e. insulating materials), even more high temperatures have to be maintained externally to the reactor tubes. These hard conditions have dramatic effects on the tube materials and their lifetime is currently the key-determining factor; unfortunately most of the well know conductive supports (SiC or nitrides) cannot be used in StR processes, since the oxidation conditions employed. To overcome these relevant drawbacks, recently the catalytic partial oxidation (CPO) of natural gas or alcohols have also proposed, since this reaction is weakly exothermic. However, to avoid the total oxidation, CPO has to be performed at ultra-high space velocity (UHSV) values, requiring special catalyst features to avoid high pressure drops. Metallic foams, such as FeCrAlY, because of their very high porosity, thermal stability and conductivity, have shown to be promising supports for catalysts suitable for both StR and CPO processes.

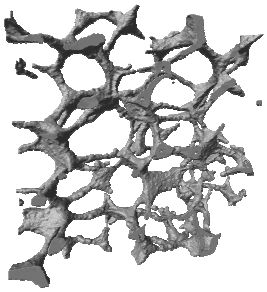


Fig. 1. 3D rendering of a FeCrAlY foam structure

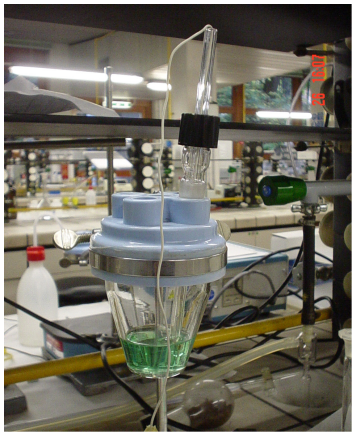


Fig. 2. 3-electrode cell for electrochemical deposition.

Two possible strategies have been proposed for the deposition of the active phase on the surface of the metallic foams:

a) **CP**: a more traditional wash coating of the FeCrAlY pellets, previously calcined at 1173 K, by a 10 wt% dispersion of bohemite in HNO_3, followed by impregnation with a slurry of the hydrotalcite-type (HT) catalyst precursor;

b) **ECD**: an innovative direct electrochemical deposition of the HT catalyst precursor (**Fig. 2**), already successfully used also for the preparation of modified electrodes.

The principal aim of experiment MA-522 was to evaluate the effectiveness of both preparation methods by determining:

1. the effective homogeneity and thickness of the active phase deposited
2. the manner in which interconnecting channels and pores are coated and how the pore morphology affect the properties and the deposition of the active phase
3. The influence of preparation methods and parameters on the final chemico-physical properties and mainly the distribution of the active phase.

To this effect, after suitable sample preparation,
(a) a number of magnified adsorption and holographic phase contrast computed tomography measurements were performed at ID22 and ID19,
(b) combined XRF/XRD microtomography was performed at ID22 using a 2 µm beam;
(c) (sub)µ-XRF imaging (2D mapping) and tomography were done at ID22NI.

2. Experimental method

In Fig. 3 an overview is given of the various steps and treatments comprising the CP and ECD procedures of preparation. It highlights the difference in complexity between both methods.

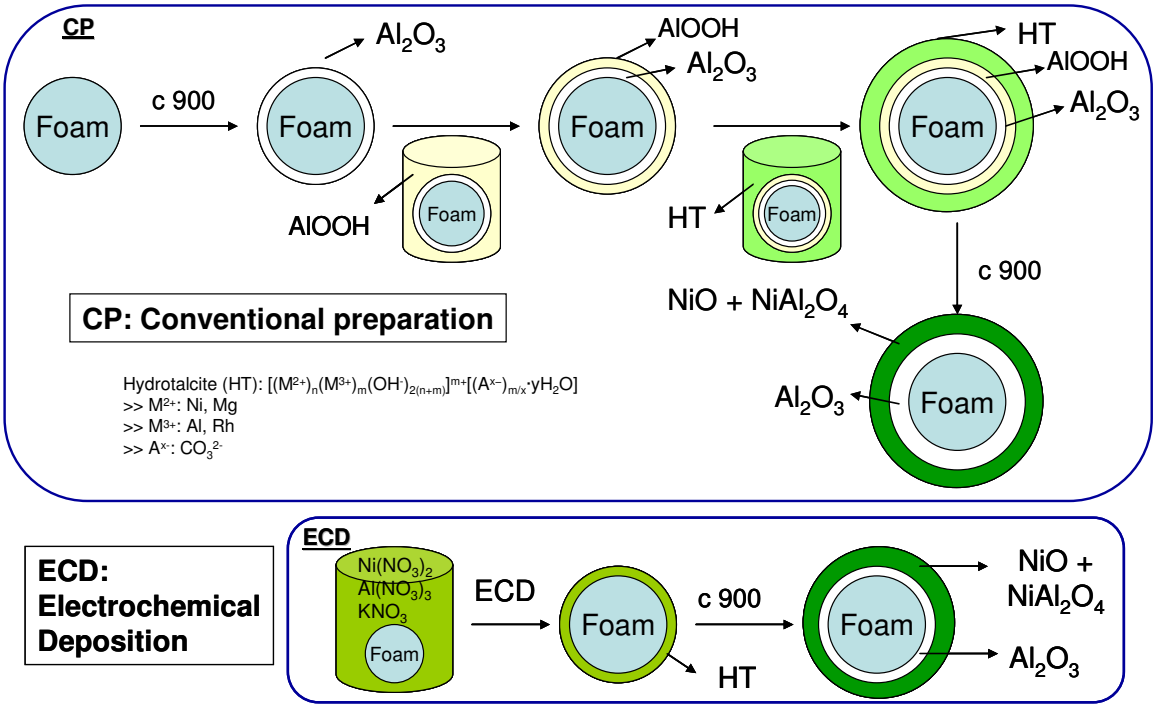
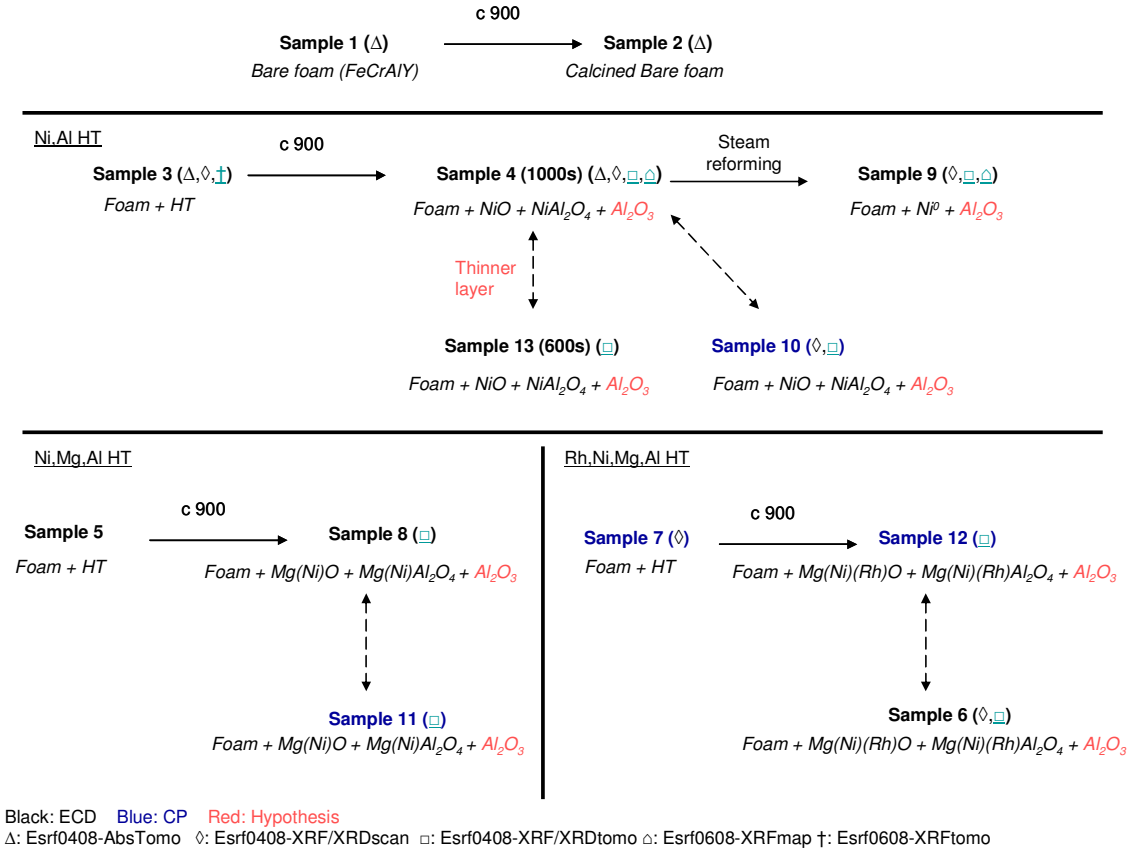


Fig. 3. Sequence of preparation steps constituting the CP and ECD preparation methods.

Samples were obtained executing one, several or all steps of one of the procedures.

The scheme in Fig. 4 indicates which type of measurements were performed on each sample.



Black: ECD Blue: CP Red: Hypothesis
Δ: Esrf0408-AbsTomo ◊: Esrf0408-XRF/XRDscan □: Esrf0408-XRF/XRDtomo ⌂: Esrf0608-XRFmap †: Esrf0608-XRFtomo

Fig. 4. Overview of different samples investigated using different methods during the april and june 2008 sessions of exp. MA-522.

3. Results

3.1 Absorption tomography

After initial attempts to visualise the heavy-metals (Ni, Rh) rich layers at the surface of the coated metal foams by using the absorption tomography station at ID22 failed, higher resolution tomographic recordings were performed at ID19.

Basically the better quality of results obtained at ID19 respect to ID22 is due to the higher spatial resolution (0.28 μm vs. 0.7 μm) and the different energy used in the experiments (27 keV vs. 18 keV).

The reconstructed images reveal that:

(a) FeCrAlY foams are hollow and they are connected with the external environment. Therefore the (Ni, Rh) layer could be coated not only on the external surface of the support, but also on the internal one (see Fig. 5).

(b) the layer originated from the calcination process (constituted by alumina) is homogenously distributed on the surface with an average thickness of about 1.4 μm. Empty spaces between the foam and the alumina layer are present.

(c) the layer deposited by ECD seems to be inhomogeneously distributed and quite irregular in thickness, ranging from few to 30 microns.

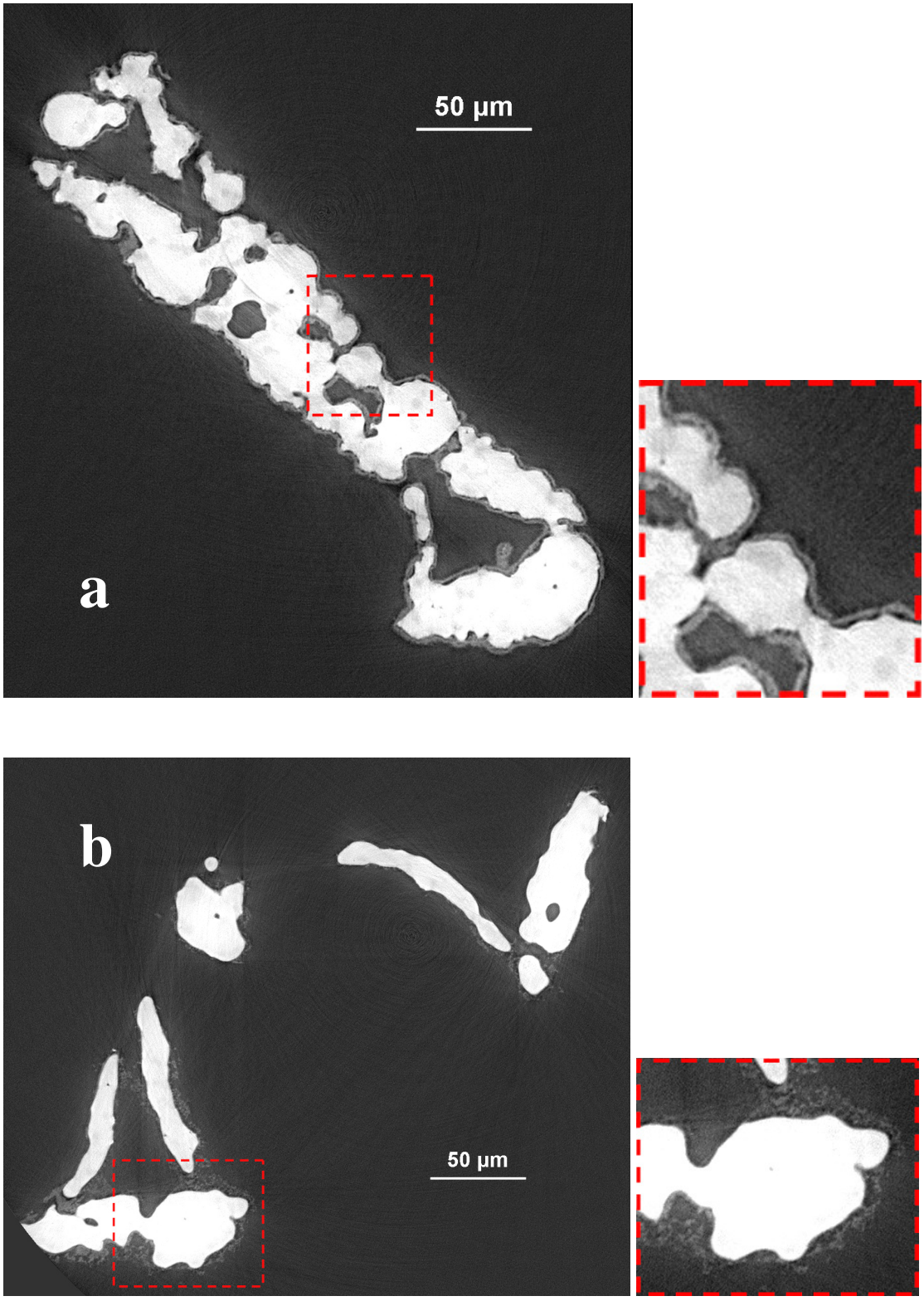


Fig. 5 Absorption tomogram of (a) sample #2 (invidual strut of untreated calcined foam) on which alumina layer is formed; (b) sample #3 (ECD deposited layer on foam).

3.2 XRF/XRD tomography

Combined scanning microbeam tomography was performed at ID22 using two XRF detectors perpendicular to the primary beam and a fast FreLON XRD camera in transmission to record diffraction patterns. An energy of 25 keV was employed for sample excitation. The experimental arrangement is schematically shown in Fig. 6.

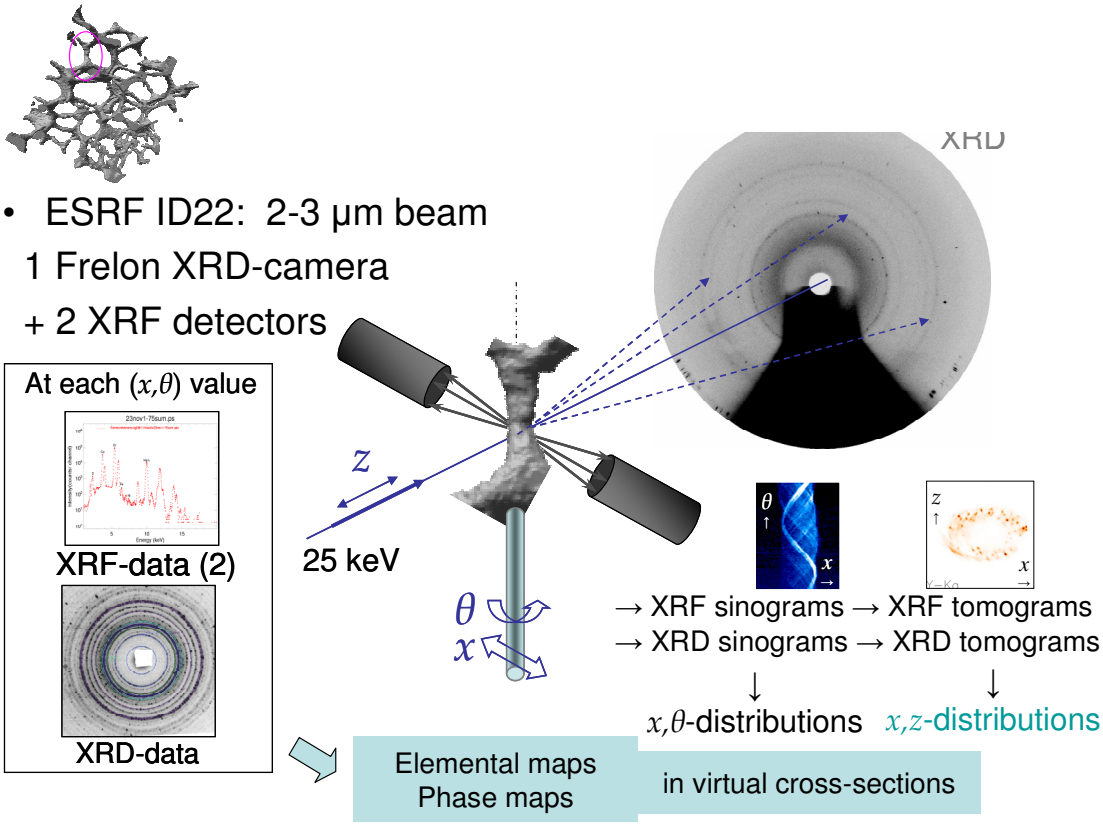


Fig. 6. Experimental scheme employed at ID22 for executing the combined XRF/XRD microtomography experiments.

As an example, Fig. 7 and 8 show elemental (XRF) and phase (XRD) sinograms derived from analysis of a strut of sample #4 (calcined version of ECD deposited foam). By combining the elemental tomograms obtained from the reconstruction of the XRF-intensity sinograms, uncorrected for self-absorption, with the phase tomographs, obtained by reconstruction of the XRD-phase intensity sinograms, information on the shape and approximate thickness of the various layers on top of the metal foam could be obtained. The Ni is deposited in thin crystalline layer of non-uniform thickness that has a Ni-spinel and a NiO structure.

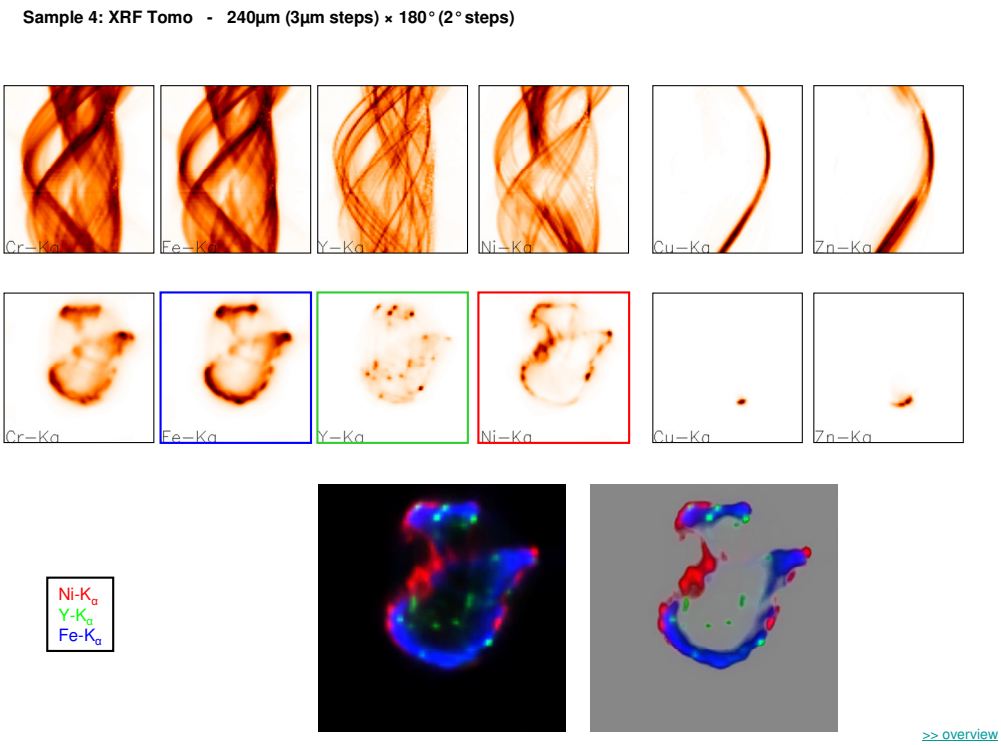


Fig. 7. XRF tomography results obtained from by analysing a strut of sample #4 (see Fig. 8 for corresponding XRF tomograms). Note the significant self-absorption of the lower-energy fluorescence radiation (Cr-K, Fe-K) in the CrFeAlY-matrix, preventing information from the inner parts of the foam struts to be obtained via the XRF signals.

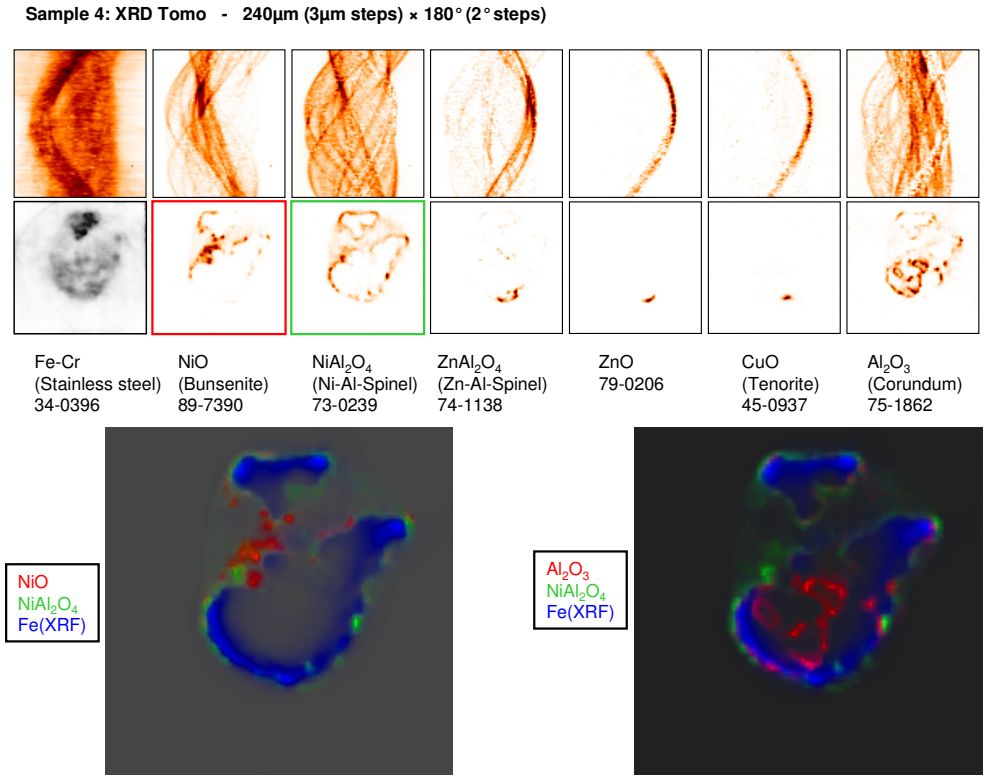


Fig. 8. XRD tomography results obtained from by analysing a strut of sample #4 (see Fig. 7 for corresponding XRF tomograms). In the XRD tomograms, no significant self-absorption is noticeable.

Sample	Type	<FWHM>	1s	stdFWHM	1s	n
13	ECD(600s)	5,73	0,07	1,70	0,19	27
6	ECD(+Mg+Rh)	5,74	0,15	1,9	0,7	25
8	ECD(+Mg)	6,0	0,1	2,3	0,6	34
4	ECD	7,0	0,1	2,11	0,27	27
9a	ECD(used)	7,95	0,13	2,0	0,3	22
9b	ECD(used)	8,1	0,1	1,86	0,15	19
11	CP(+Mg)	8,4	0,2	3,0	1,2	33
10	CP	10,66	0,19	5,4	1,8	27
12	CP(+Mg+Rh)	10,89	0,19	5,5	1,7	36

By considering multiple cross-sections through the XRD tomograms and fitting gaussian profiles to the latter, statistically valid estimates of the thickness of the spinel Ni/Rh-containing layers could be obtained. In Table 1, the obtained thicknesses of the superficial spinel layer as compared for the various treatments/samples. These indicate that the CP method gives rise to statistically significant thicker layers (8-10 µm thickness) than the ECD method (5-8 µm).

3.3 XRF nanotomography

Since the experimentally determined layer thicknesses may be broadened by the use of an primary X-ray beam of ca 2-3 µm and by the use of the tomographic imaging method, a smaller series of samples were analysed by means of a 130x170 nm^2 X-ray beam available at ID22NI at an energy of 18 keV.

Both direct 2D scanning of cross-sectioned samples and tomographic scanning on original struts (no sample preparation) was performed. An example of the former is shown in Fig. 9 and of the latter results in Fig. 10. In sample #4, a thin layer of Ni-rich material (Ni,Al hydrotalcite) can be discerned on the outer surface of the potassium-rich layer that coats the metal foam. The observed thickness of the Ni-layer is between 0.5 and 1 µm.

4. Conclusions

On the instrumental level, the results obtained both at ID22 and ID22NI appear to be very promising for the future, as:
(a) the XRF/XRD tomographic data acquisition mode at ID22 appears to be working very well and yields mutually consistent results
(b) the sub-microscopic XRF tomography at ID22NI also yields artefact-free datasets in which features/layers below 1 µm can be visualized.

For the first time, we succeeded in the structural and detailed chemical characterization of the solid supported on the FeCrAlloy foam, not possible with conventional laboratory techniques such as PXRD. The effectiveness of the novel ECD method in the preparation of catalytic systems with different compositions in comparison to the CP method was evaluated.

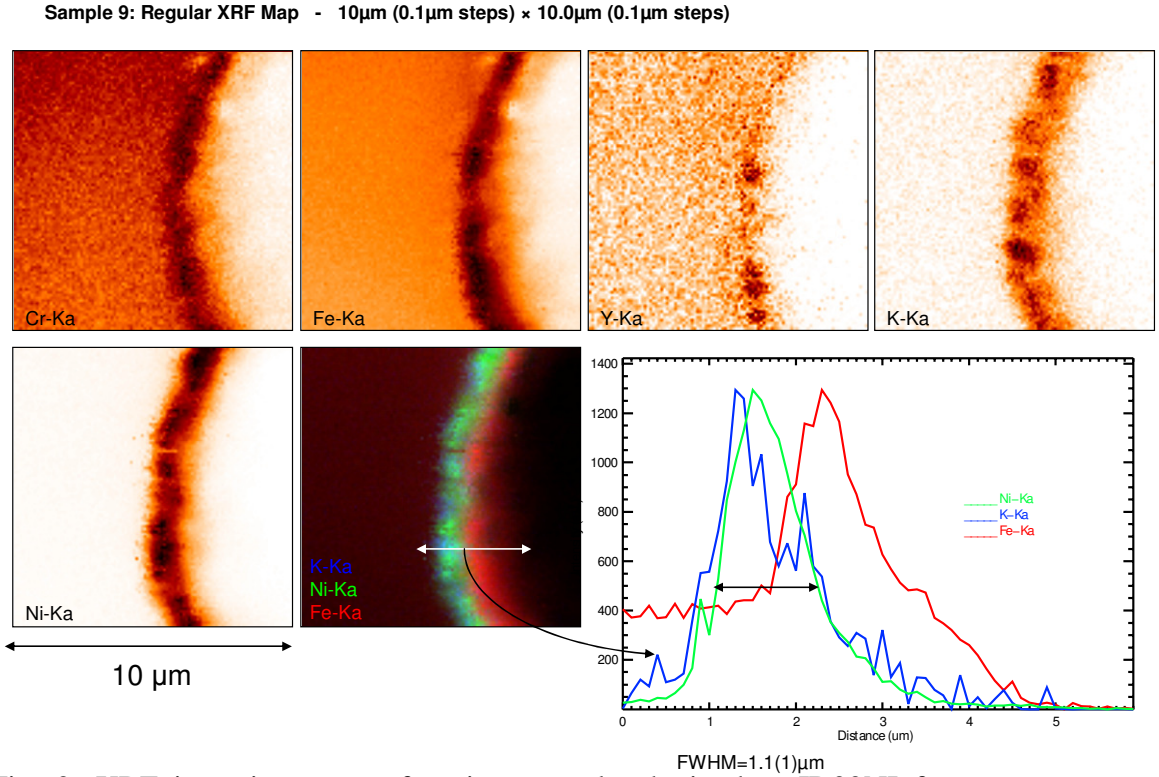


Fig. 9. XRF intensity maps of various metals obtained at ID22NI from a cross-sectioned piece of sample #9.

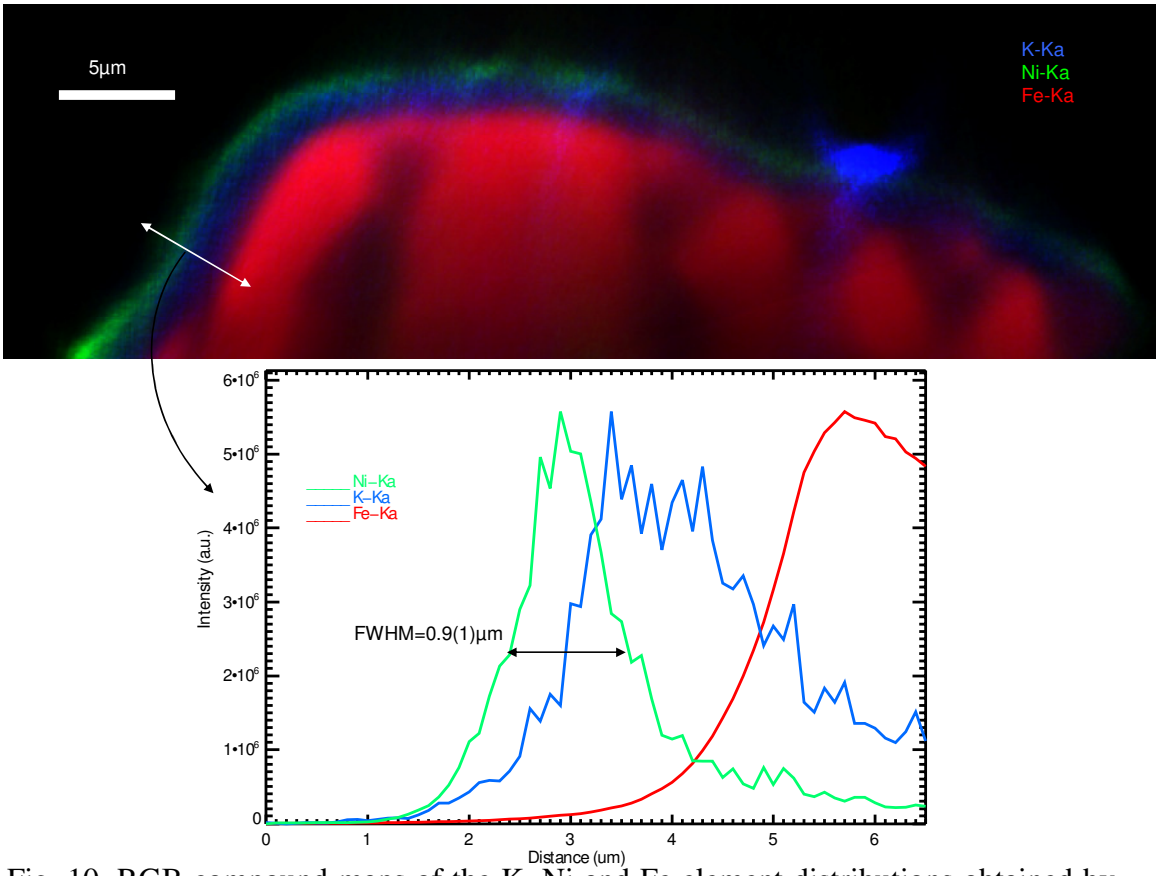


Fig. 10. RGB compound maps of the K, Ni and Fe element distributions obtained by submicroscopic XRF tomography from an original (no sample preparation) strut of sample #3.

Crystallographic phases present in catalysts prepared by ECD and CP were similar, spinel and oxide. Since the phases obtained by calcination depended on the composition of the hydrotalcite compound deposited by ECD and CP, these results indicated that the deposition by ECD was successful. The distribution of the species and the film thickness was strongly dependent on the synthesis method. A thinner layer was obtained by ECD; however, it should be pointed that with ECD the distribution of the spinel and oxide phase was not homogeneous. The segregation α-Al_2O_3 from the foam was also confirmed. This phase can act as binder between the catalyst and the metallic support improving the adhesion of the deposited catalyst. The characterization of a sample after catalytic tests, sample 9, showed that metallic nickel was homogeneously distributed all over the surface of the foam, furthermore the presence of a (as yet unidentified) potassium-containing phase was elucidated. In summary, our findings indicate that by means of the ECD method, a one step synthesis method, it is possible to deposit extremely thin and fairly uniform superficial layers of Ni-containing hydrotalcite, allowing in this manner to employ the catalytically active metal in the most efficient manner. These results were in agreement with the improved catalytic performances of sample 4 in comparison with a conventional pelletized catalyst, even though the amount of active phase was considerable reduced.