Electronic Supplementary Information for "Phase stability, redox-behavior and carbon-tolerance of $Sr_{1-x}(Ti_{0.3}Fe_{0.7-y}Ni_y)O_{3-\delta}$ with exsolved nanoparticles"

1 Purities of the used powders

Cation distribution in wt% respectively impurity-levels for the used starting powders measured by Inductively Coupled Plasma Optical Emission Spectrometry are shown in Table 1. Oxygen was not dissolved during the digestion and is therefore not present in the analysis.

Table 1: Cation distribution (wt%) for the starting powders NiO, $SrCO_3$, Fe_2O_3 and TiO_2.

Element (wt%)	NiO	$SrCO_3$	Fe_2O_3	TiO_2
Fe	0.00416 ± 0.00096	<0.0009	66.12 ± 0.97	<0.009
Ni	71 ± 4	0.0047 ± 0.0018	0.042 ± 0.011	0.0334 ± 0.0006
Mn	<0.0002	<0.0002	0.67 ± 0.03	/
Si	2.78 ± 0.15	<0.007	0.036 ± 0.003	0.006 ± 0.0008
Ti	0.0092 ± 0.0003	<0.0009	0.0098 ± 0.0005	58.1 ± 0.8
Ca	<0.0003	0.0395±0.0011	0.0084 ±0.0004	0.00649 ± 0.00014
Sr	<0.0009	55 ± 2	0.011 ± 0.003	<0,001
Ba	<0.0008	0.856 ± 0.019	<0.0009	/
Al	/	/	/	0.0201 ± 0.0008
K	/	/	/	0.162 ± 0.003
Na	/	/	/	0.0101 ± 0.0005

2 SEM micrographs of aged cross-sections and lichen-like structures

Figure 1 shows SEM micrographs of lichen-like structures formed on the STFN and sSTFN surfaces and grain boundaries after calcination.

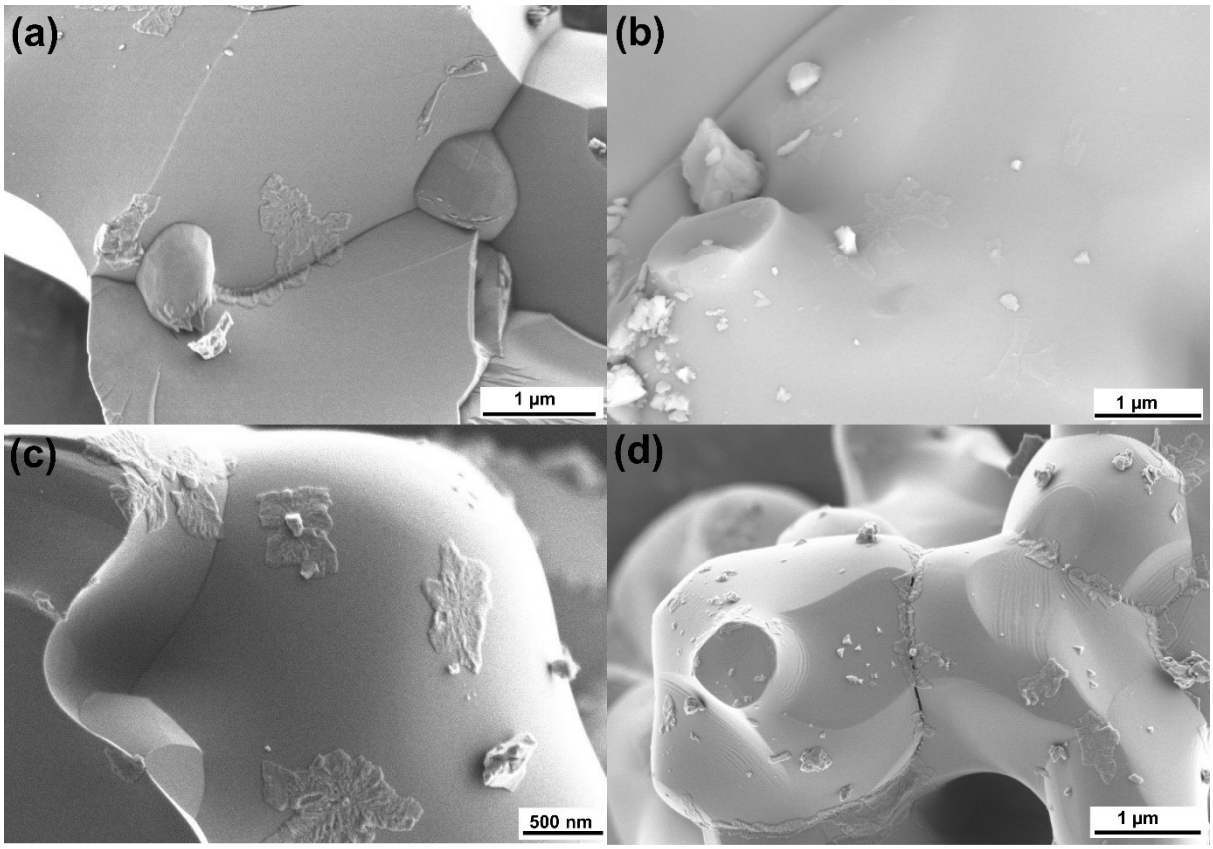


Figure 1: SEM micrographs of lichen-like structures on the surface and at the grain boundaries of (a-c) STFN and (d) sSTFN. (a,c,d) show secondary electron micrographs. (b) shows a backscattered electron micrograph.

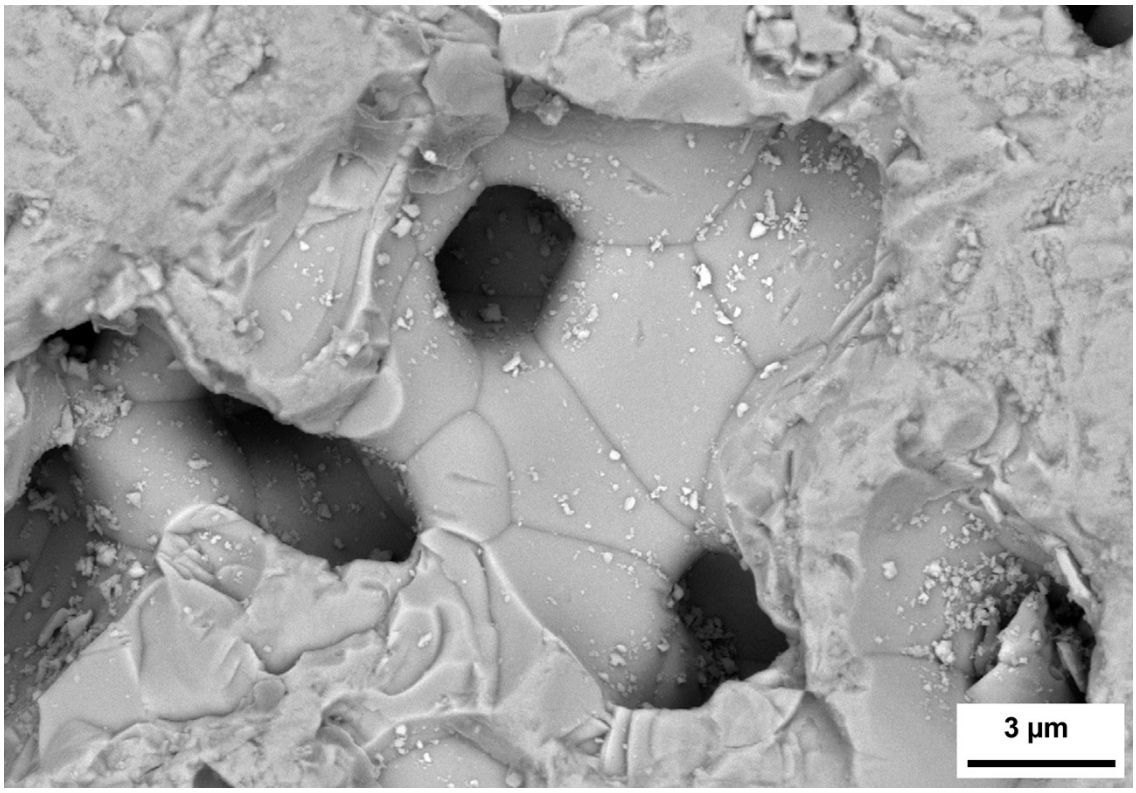


Figure 2: Cross-section of STF reduced at 710°C in 100 % H_2 after carbon degradation experiments.

A cross-section of a STF pellet reduced at 710 °C after carbon degradation experiments is shown in Figure 2. No cracks are observable.

Figure 3 shows backscattered electron micrographs of cross-sections of STFN and sSTFN pellets reduced at 900 °C. The micrographs indicate bulk exsolution and spots where the number of nanoparticles increase.

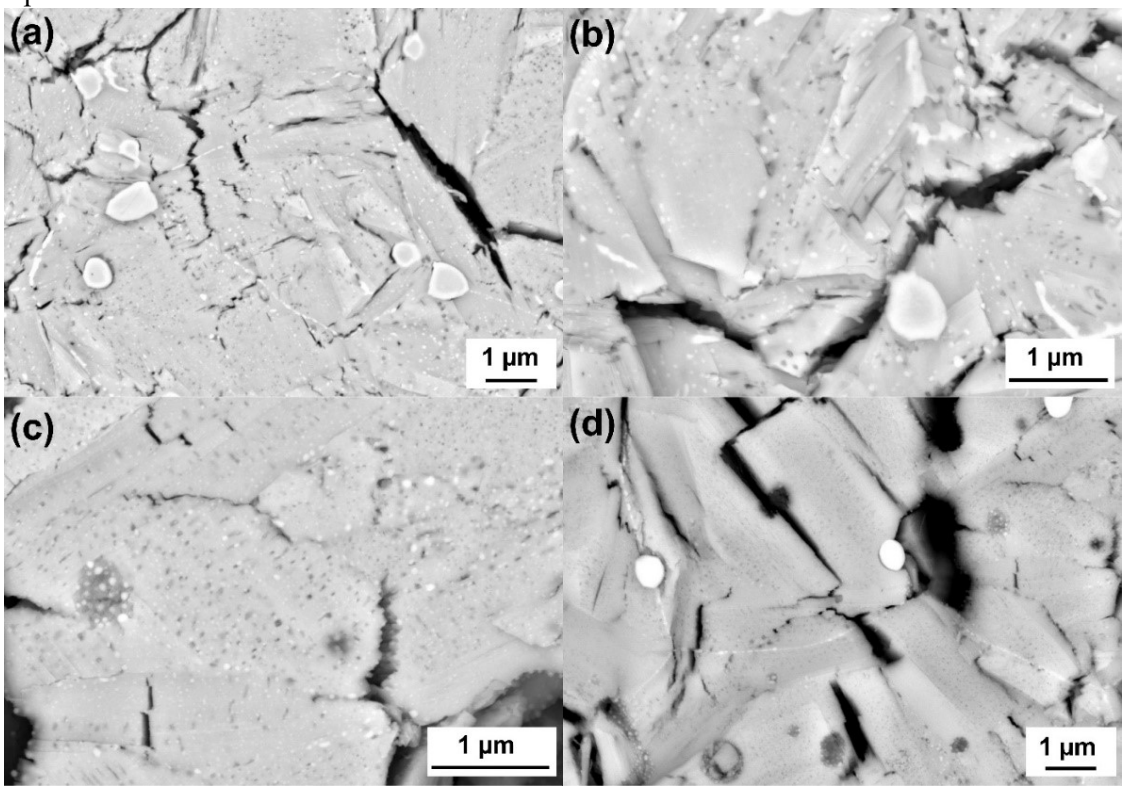
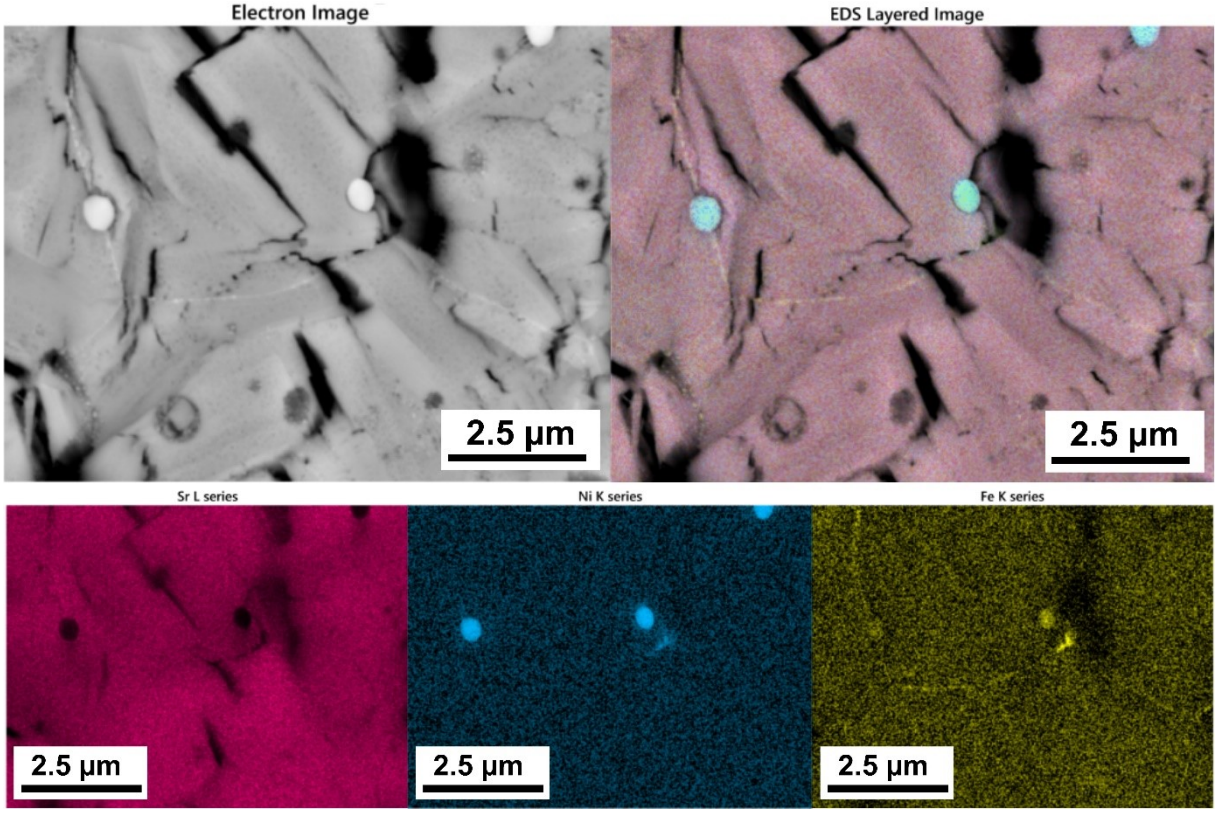


Figure 3: Backscattered electron micrographs of cross-sections of (a,b) STFN and (c,d) sSTFN reduced at 900°C in Ar/ 50 % H_2.


Electron Image
EDS Layered Image
2.5 µm
2.5 µm
Sr L series
Ni K series
Fe K series
2.5 µm
2.5 µm
2.5 µm

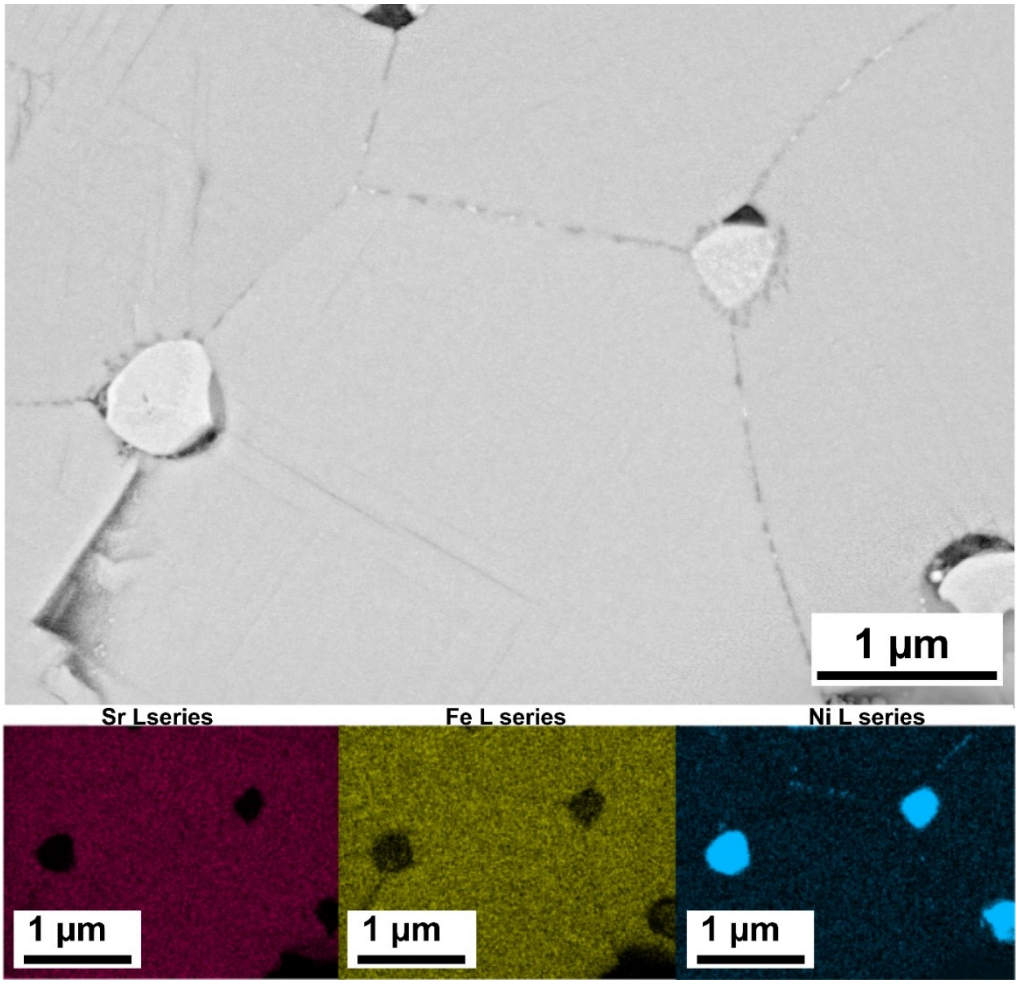


Figure 5: EDS analysis of a cross-section of sSTFN reduced at 710 °C in 100 % H_2.

Figure 4: EDS analysis of a cross-section of sSTFN reduced at 900°C in Ar/ 50 % H_2.

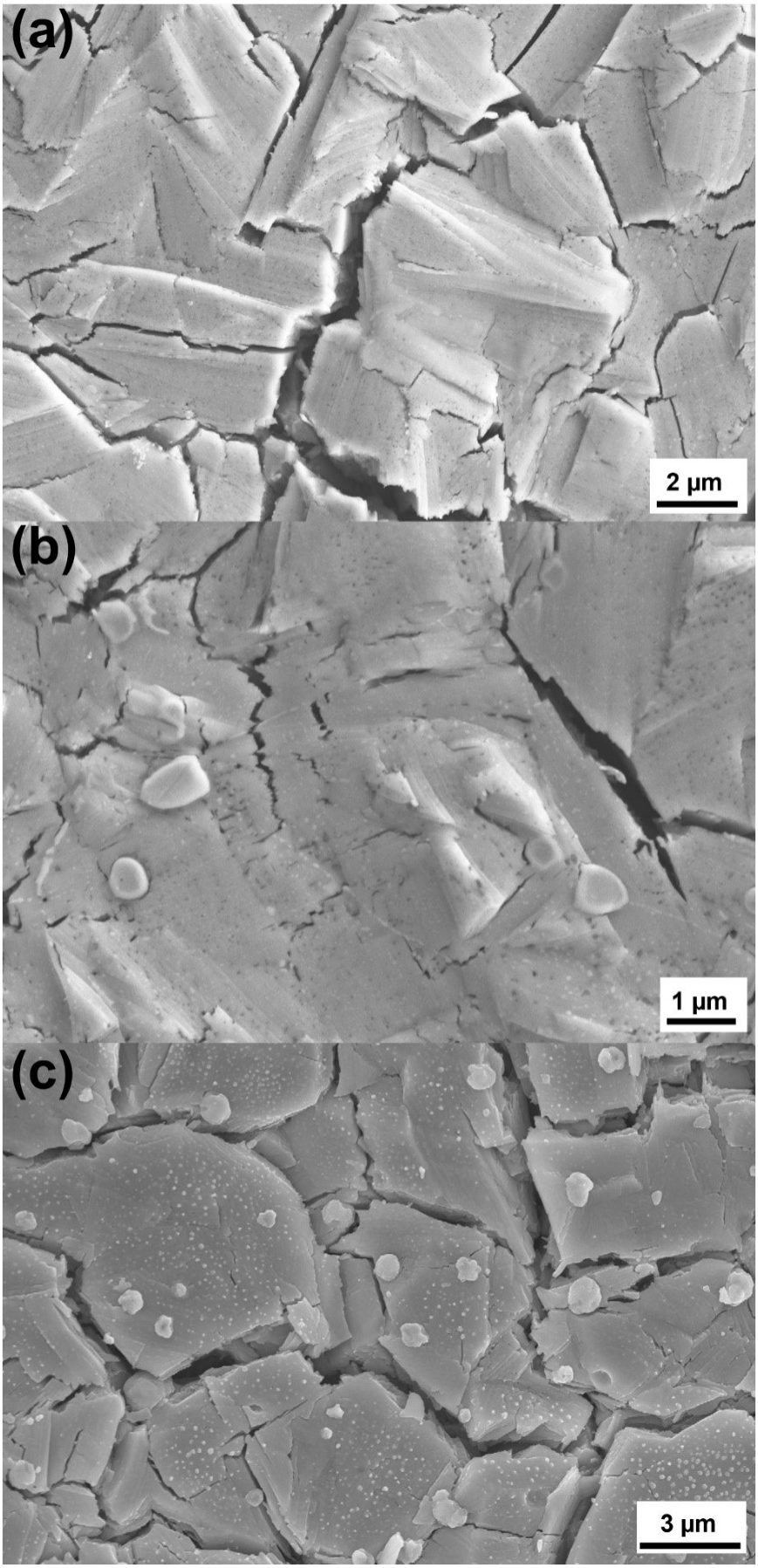


Figure 6: Secondary electron micrographs of polished and aged cross-sections of (a) STF and (b,c) STFN reduced at 900 °C in Ar/ 50 % H_2.

Figure 4 shows an EDS analysis of a cross-section of sSTFN reduced at 900°C. Again, bulk exsolution is visible. Figure 5 shows an EDS analysis of a cross-section of a sSTFN pellet reduced at 710 °C. Ni nucleates at the grain boundaries.

The topography (respectively secondary electron micrographs) of polished and aged cross-sections of STF and STFN are shown in Figure 6. The cross-sections were in contact with water during the preparation process and stored in ambient air before SEM analyses.

3 Redox and exsolution stability by analysis of the phase distribution

The exact values of the calculated relative phase distributions of STF, STFN and sSTFN after reduction at temperatures of 710-900 °C in Ar/ 50 % H_2 and reoxidation at 900 °C in ambient air are given in the Table 2.

Table 2: Relative phase distribution of STF, STFN and sSTFN reduced at temperatures of 710-900 °C in 50 % Ar/ 50 % H_2 for 8 h and reoxidized at 900 °C in air for 8 h.

	Material		Reduction temperatures (°C)						
			710	740	780	820	860	900	Re-oxidized (900 °C)
Relative phase distribution (%)	STF	STF	100	100	97	96	37	60	97
		SF-RP	0	0	0	0	44	34	0
		ST-RP	/	/	/	/	/	/	/
		Fe	0	0	3	4	19	6	0
		SF-P	/	/	/	/	/	/	3
	STFN	STFN	100	100	27	13	6	26	96
		SF-RP	0	0	63	75	41	20	0
		ST-RP	0	0	0	0	40	44	0
		NiFe	0	0	10	12	13	10	0
		$NiFeO_x$	/	/	/	/	/	/	4
	sSTFN	sSTFN	98	98	42	14	6	14	97
		SF-RP	0	0	50	73	35	29	0
		ST-RP	0	0	0	0	43	46	0
		NiFe	2	2	8	13	16	11	0
		$NiFeO_x$	/	/	/	/	/	/	3

4 EDS analysis of a post-mortem sample

Figure 7 shows EDS point analysis of the cross-section of a STFN pellet reduced at 710 °C in 100 % H_2 after carbon degradation experiments. Spectrum 1 is taken at the surface of the pellet which was in contact with the Ni-mesh of the tube reactor during carbon degradation experiments. Spectrum 2 is taken of a grain which is likely a leftover Ni(O) precursor particle.

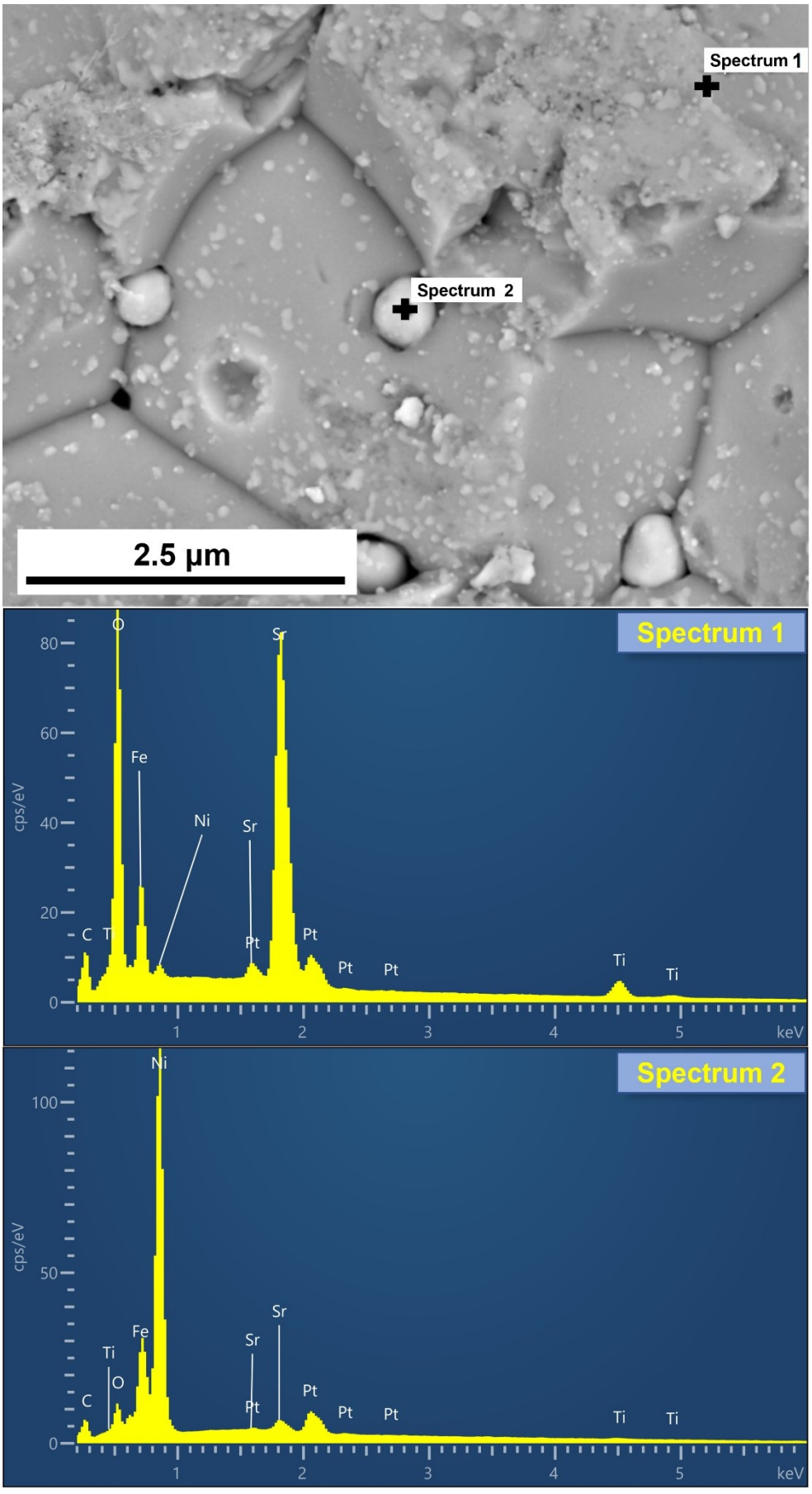


Figure 7: Surface EDS point analysis (U = 8kV) of a STFN pellet reduced in-situ at 710 °C in 100 % H_2 after carbon degradation experiments.