

National Energy Technology Laboratory

High Temperature Corrosion of Cr-W Alloys in Simulated Syngas



Ömer Doğan
Sophie Bullard
Bernie Covino
NETL-Albany, Oregon

National Energy Technology Laboratory



Office of Fossil Energy



Objective

- **To determine corrosion behavior of Cr-W alloys in a simulated gasifier atmosphere at 800°C and 1000°C.**



Experimental Procedure

- **Materials**

- Cr samples (C-3a and C-3b)
- Cr - 10 mass % W samples (CW-8a and CW-8b)
- Cr - 30 mass % W samples (CW-10a and CW-10b)
- 310 SS sample
- Alloy 718 sample
- Samples were approximately 0.1 in thick, 0.5 in wide, 0.5 in high. They had a 1/8 in diameter hole for hanging on a rack.



Experimental Procedure

- **Cyclic Corrosion tests**
 - At 800°C and 1000°C
 - In a flowing simulated syngas (500 ml/min) composed of
 - 30%CO
 - 8%CO₂
 - 20%H₂
 - 0.8%H₂S
 - 2%CH₄
 - 40%N₂
 - 0.02%HCl



Corrosion Apparatus



Experimental Procedure

- **One corrosion test cycle consists of**
 - Weighing samples
 - Positioning sample rack in constant temperature zone of the tube of three heat zone furnace and sealing the tube.
 - Starting nitrogen gas flow (500 ml/min) and heating at a rate of 300 K/hour.
 - Once the temperature reaches and stabilizes at test temperature, gas mixture flow (500 ml/min) starts.
 - After the exposure time ends, power to the furnace is turned off and gas mixture flow is stopped. Only nitrogen gas continues to flow.
 - After samples cool down to room temperature, they are taken out of the furnace and weighed.

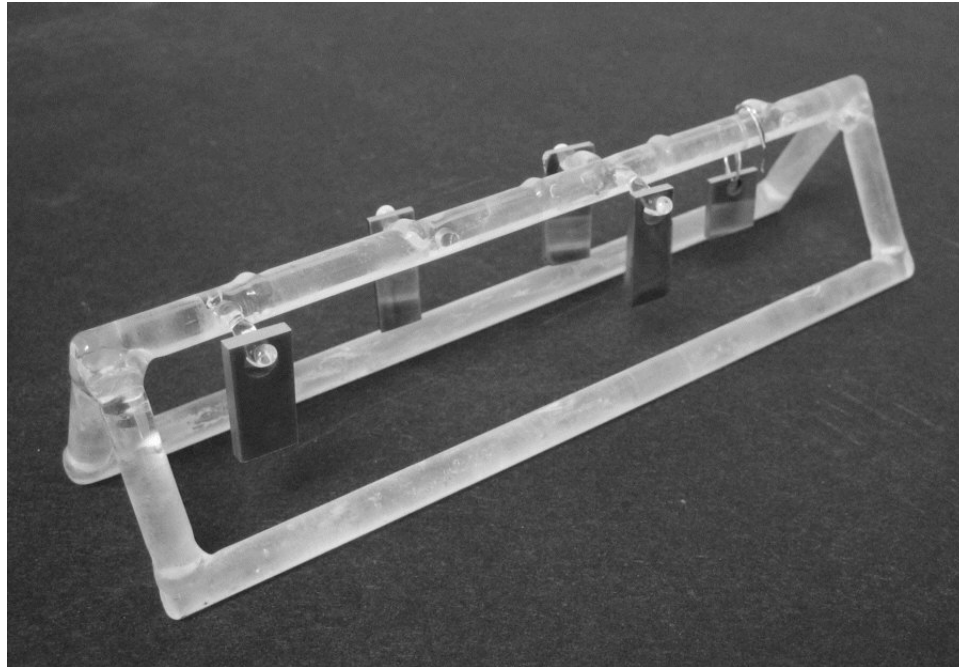


Experimental Procedure

- **Scale characterization**
 - XRD for determination of compounds in surface scale
 - SEM for determination of scale structure
 - SEM-WDX for determination of chemical composition of phases in scale
 - SEM-EDX for determination of chemical composition of phases in scale



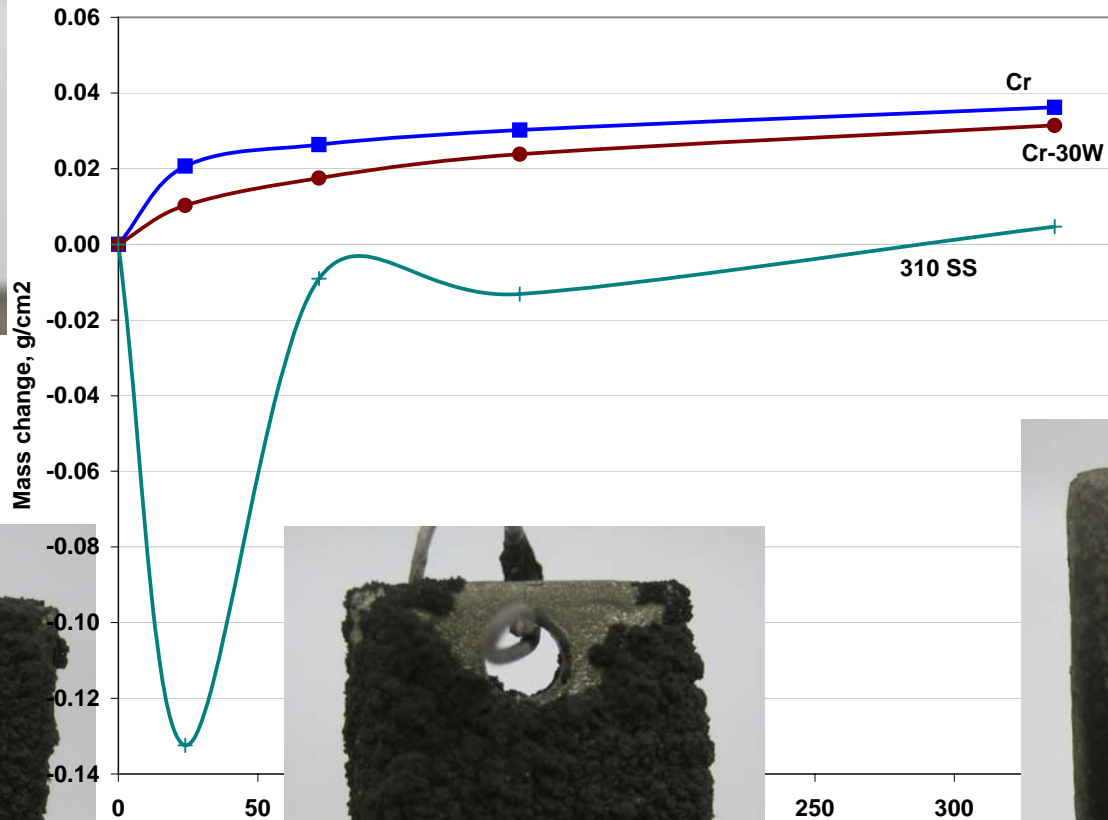
Sample holder



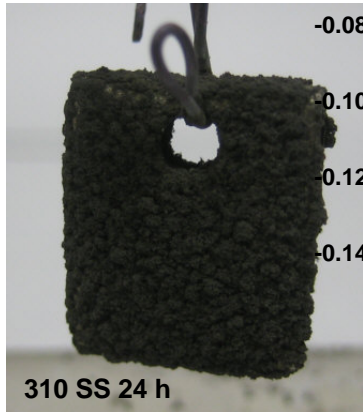
Results of cyclic corrosion test at 800°C



Cr 72 h



Cr-30W 336 h



310 SS 24 h



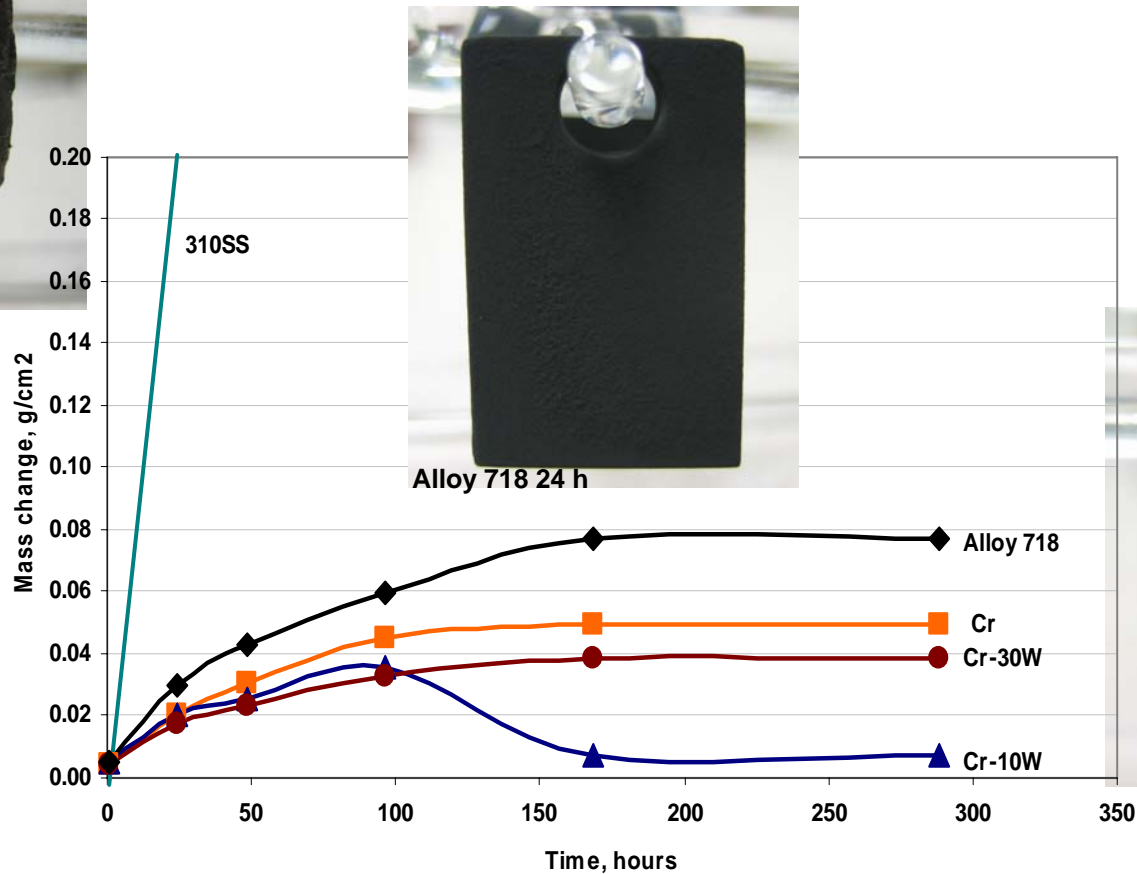
310 SS 144 h



310 SS 336 h

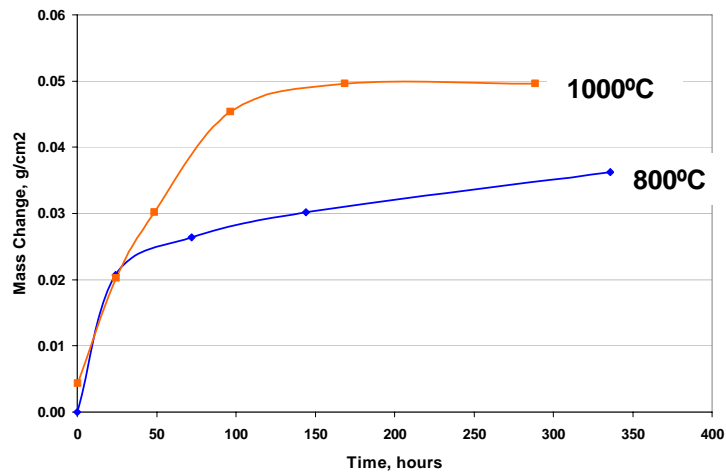


Results of cyclic corrosion test at 1000°C

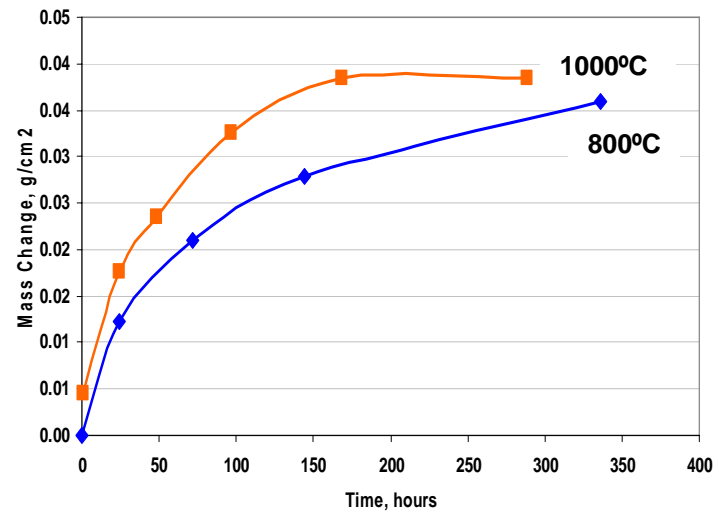


Corrosion in Syngas

Cr

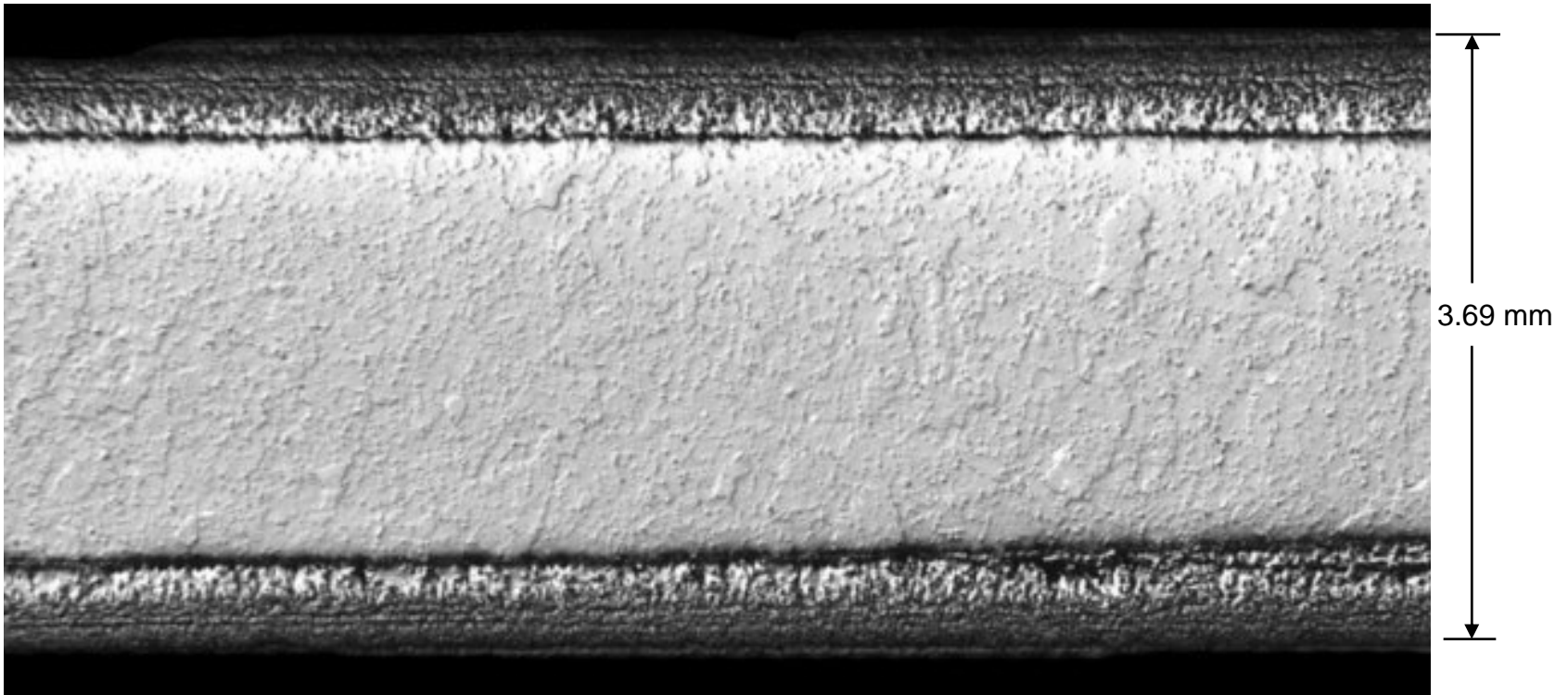


Cr-30W

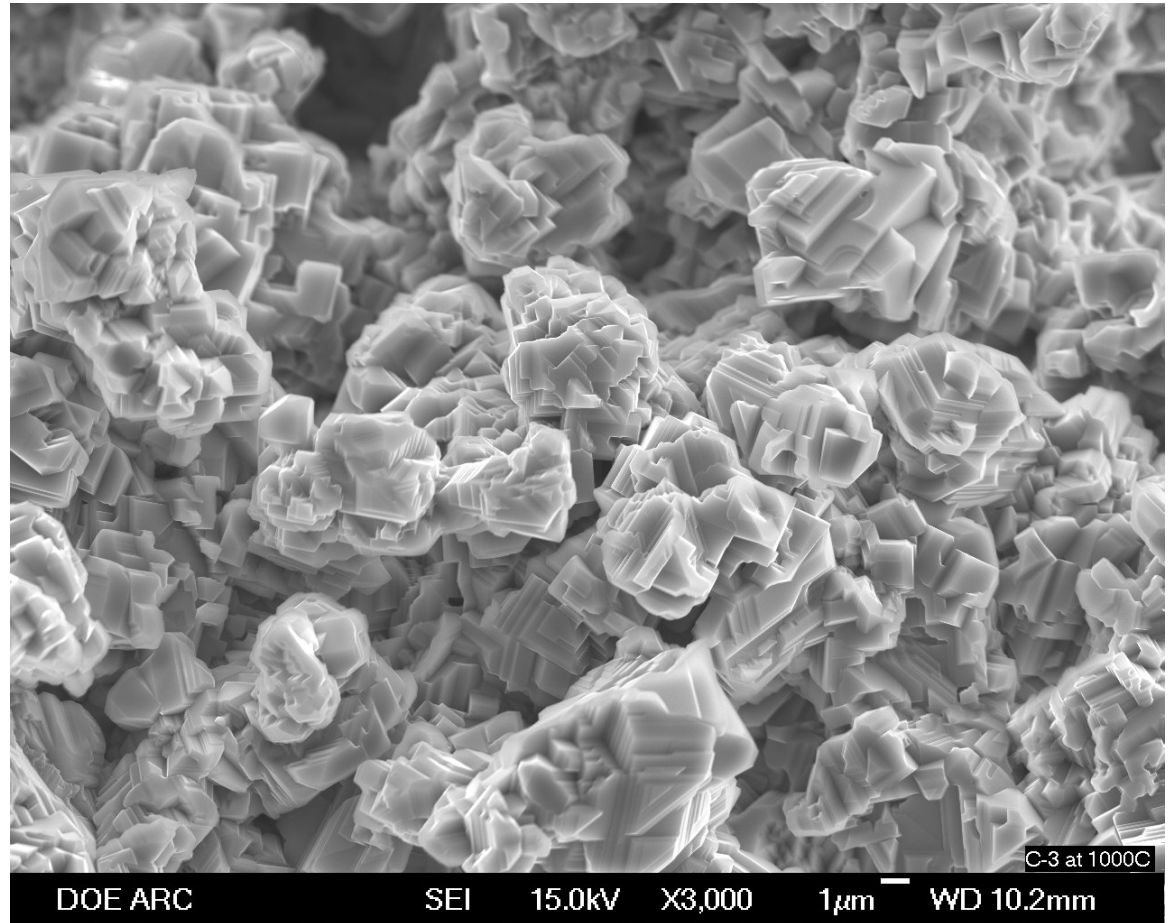


After corrosion test for 288 hours at 1000°C

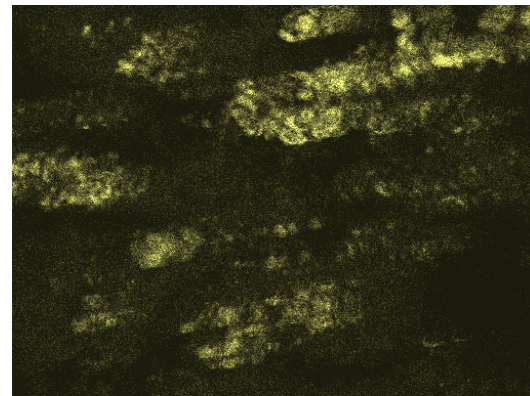
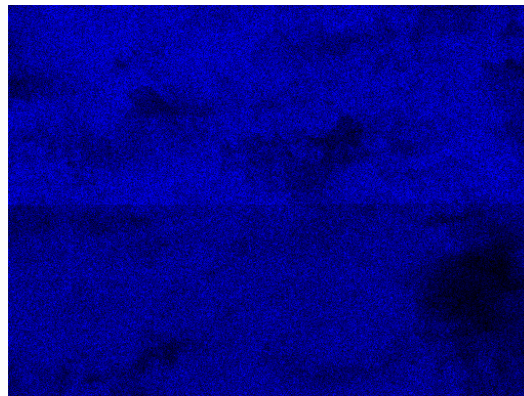
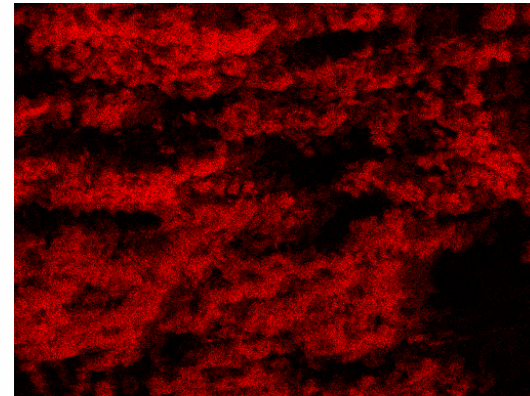
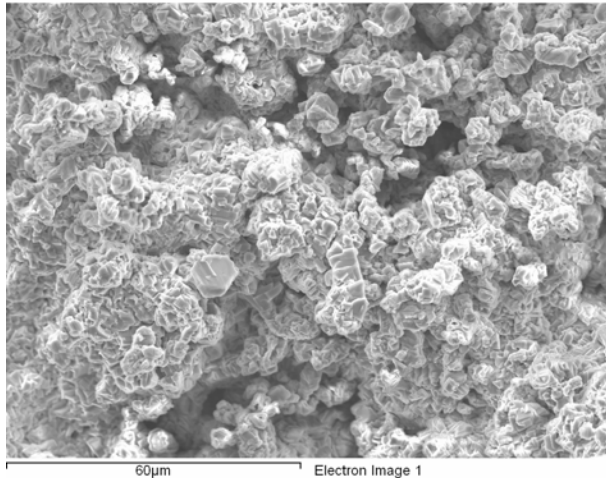
Cr Specimen



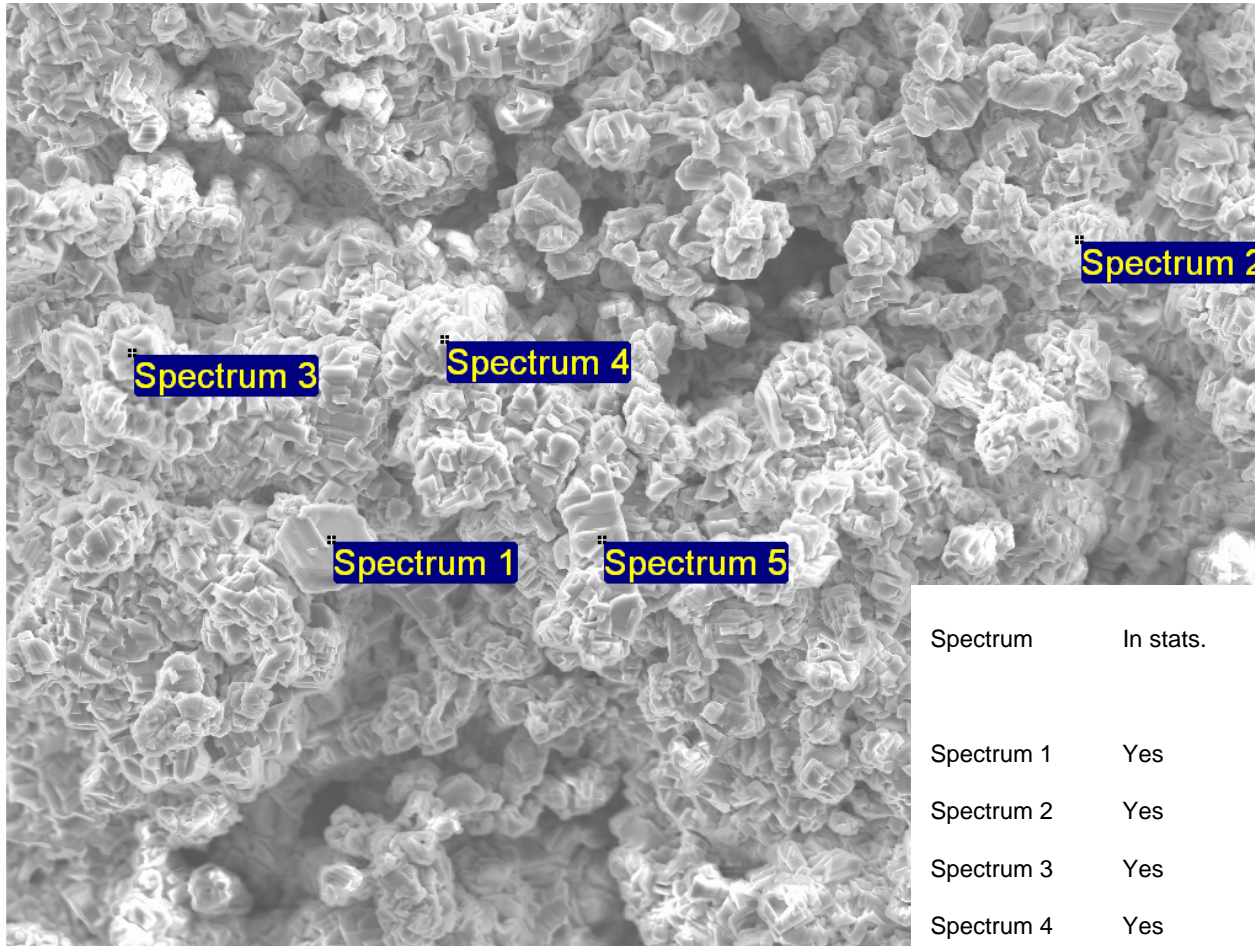
Top Surface of Scale on the Cr Specimen After Corrosion Test at 1000°C for 288 hours



Top Surface of Scale on the Cr Specimen After Corrosion Test at 1000°C for 288 hours



Top Surface of Scale on the Cr Specimen After Corrosion Test at 1000°C for 288 hours

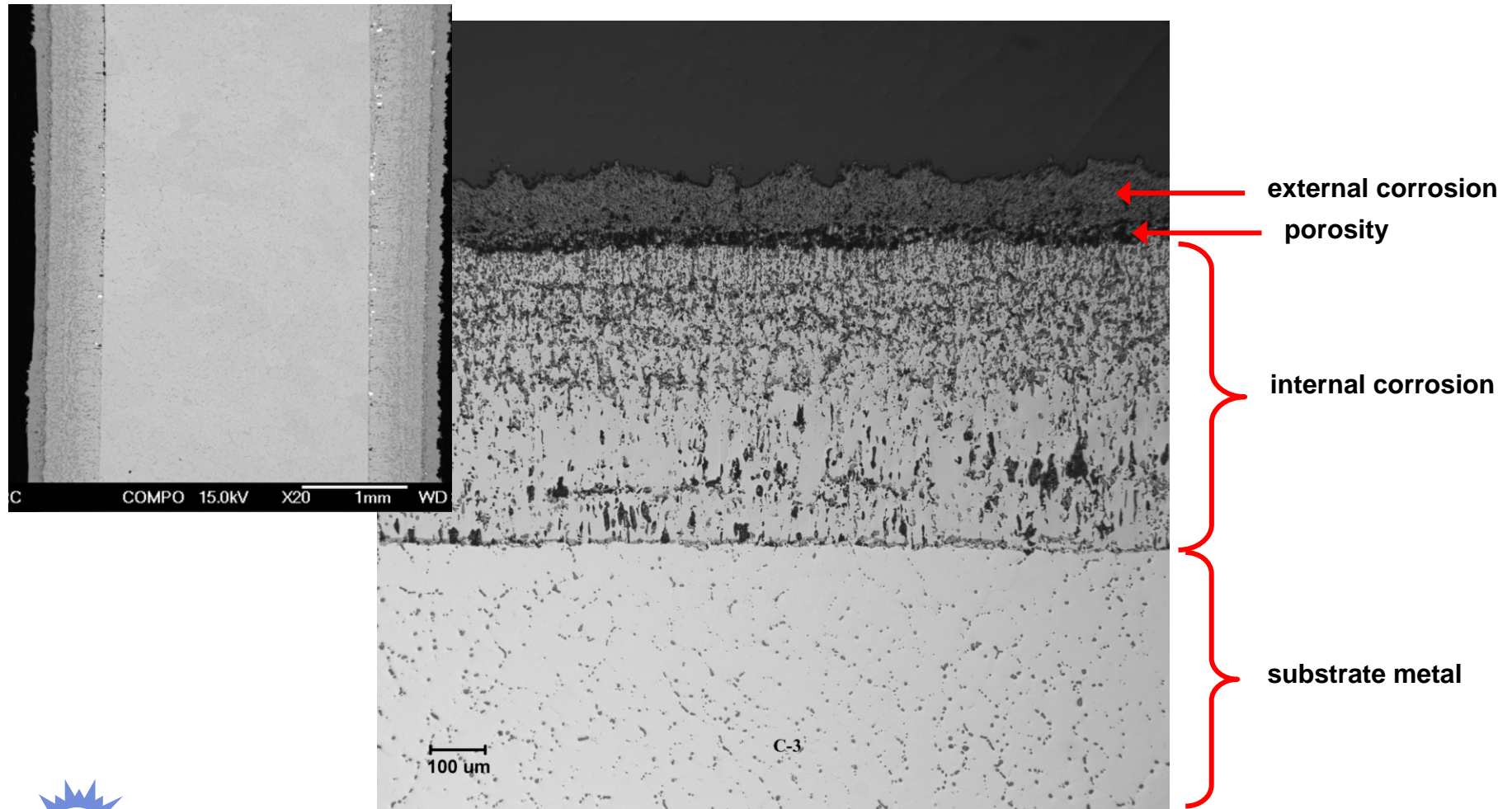


60µm

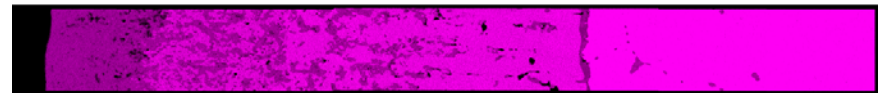
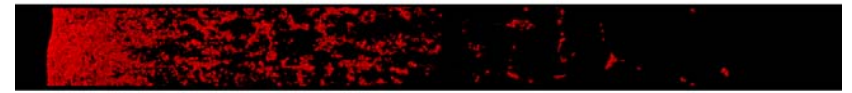
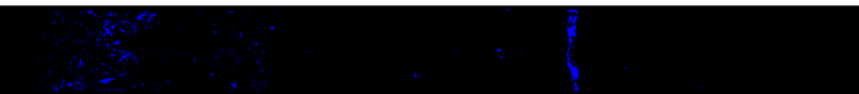
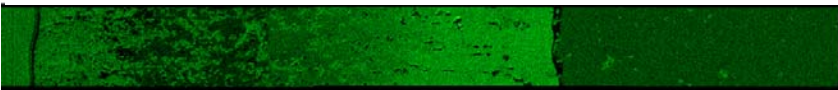
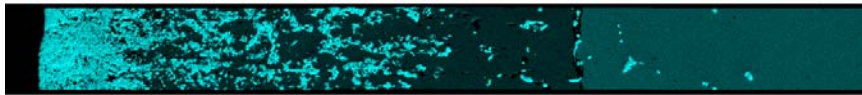
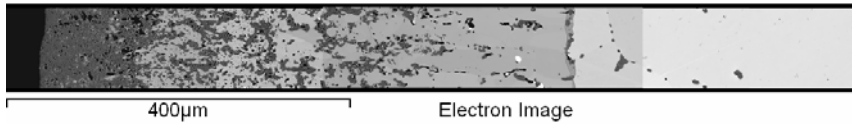
Electron Image 1

Spectrum	In stats.	O	S	Cr
Spectrum 1	Yes	40.13	20.83	39.04
Spectrum 2	Yes	52.72	1.65	45.62
Spectrum 3	Yes	64.12	4.62	31.26
Spectrum 4	Yes	48.46	0.25	51.28
Spectrum 5	Yes	51.29	1.01	47.70

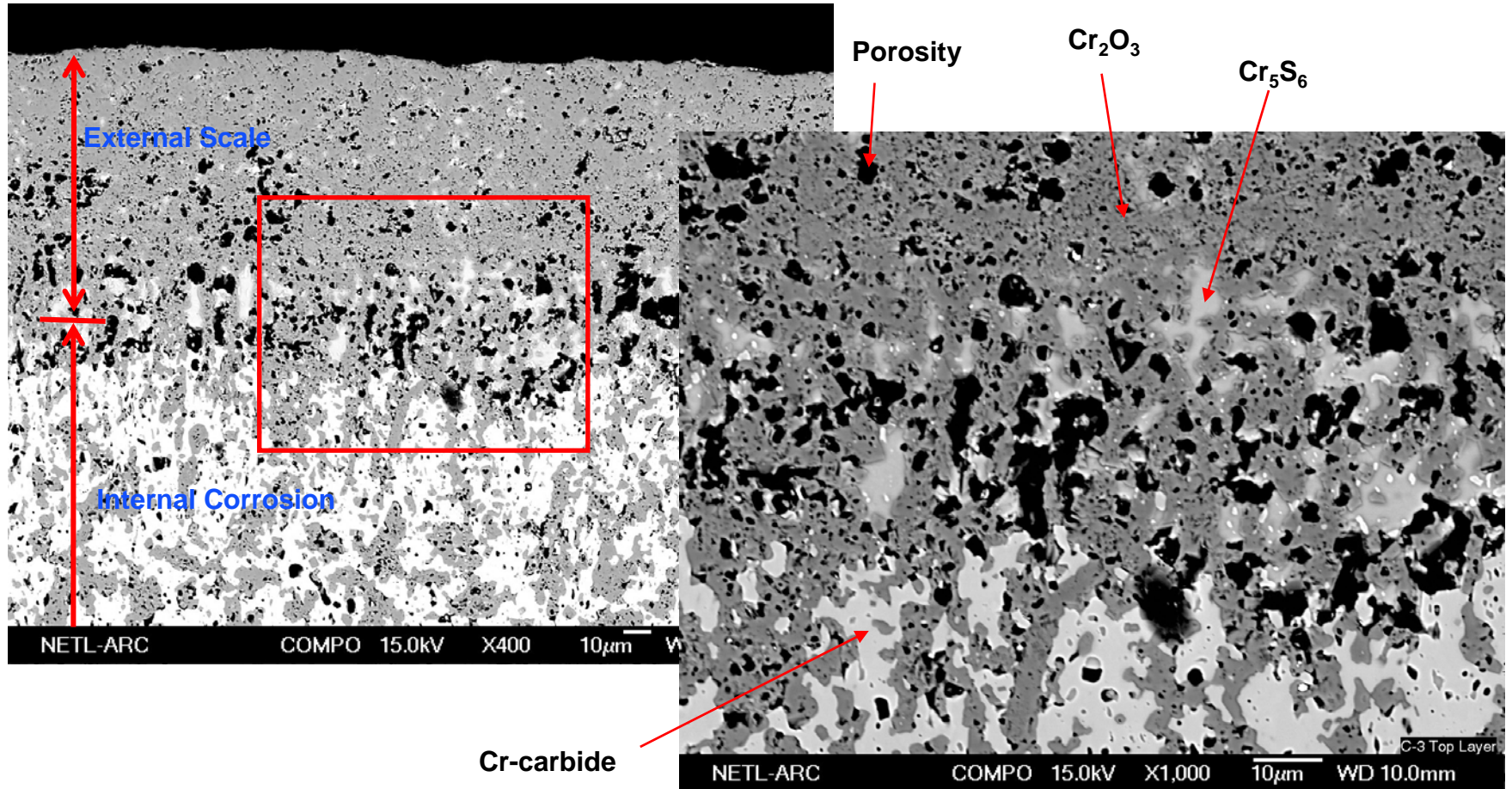
Cross Section of Corrosion Zone on the Cr Specimen After Exposure to Syngas at 1000°C for 288 hours



Cross Section of Corrosion Zone on the Cr Specimen After Exposure to Syngas at 1000°C for 288 hours

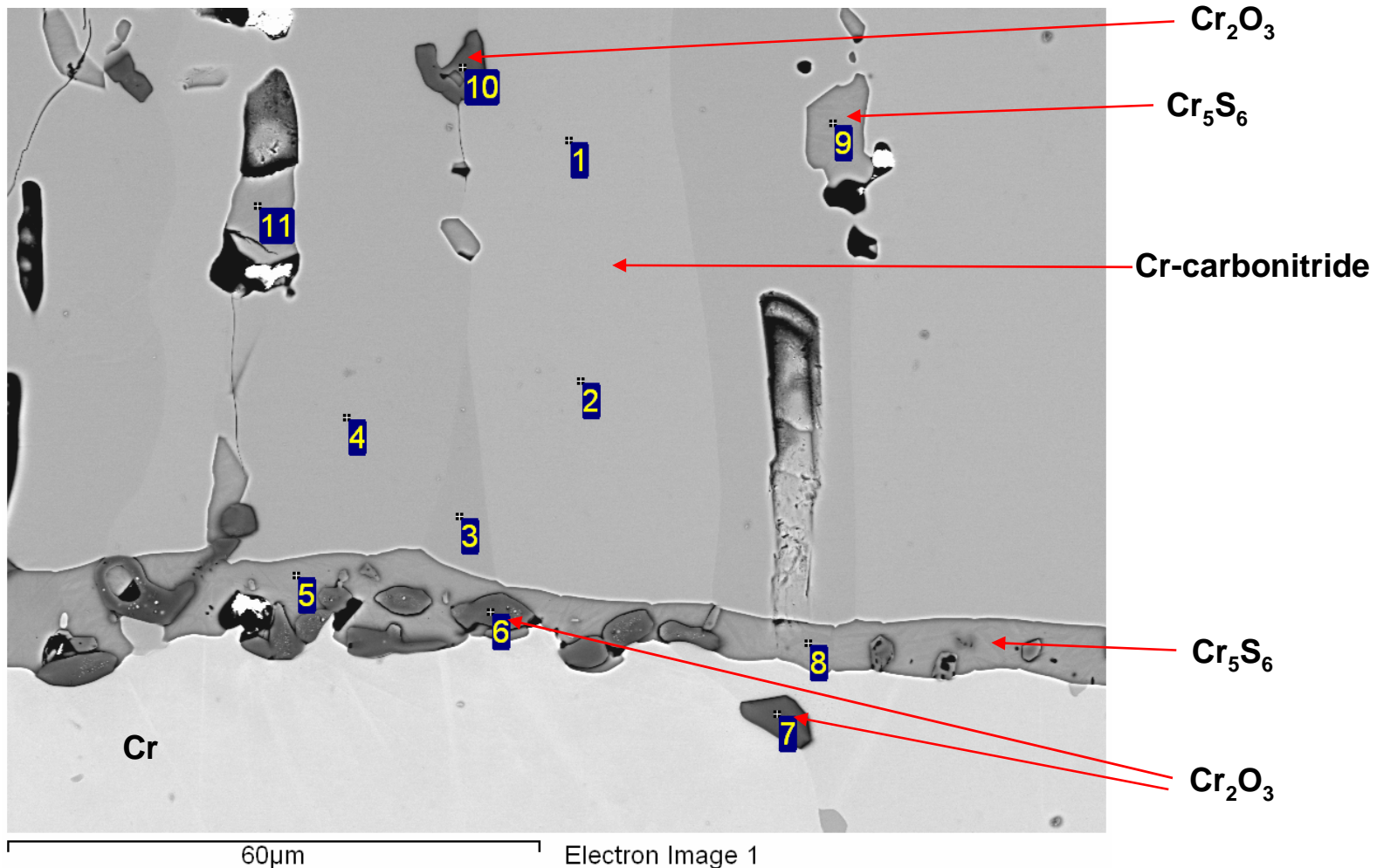


Cross Section of Corrosion Zone on the Cr Specimen After Exposure to Syngas at 1000°C for 288 hours



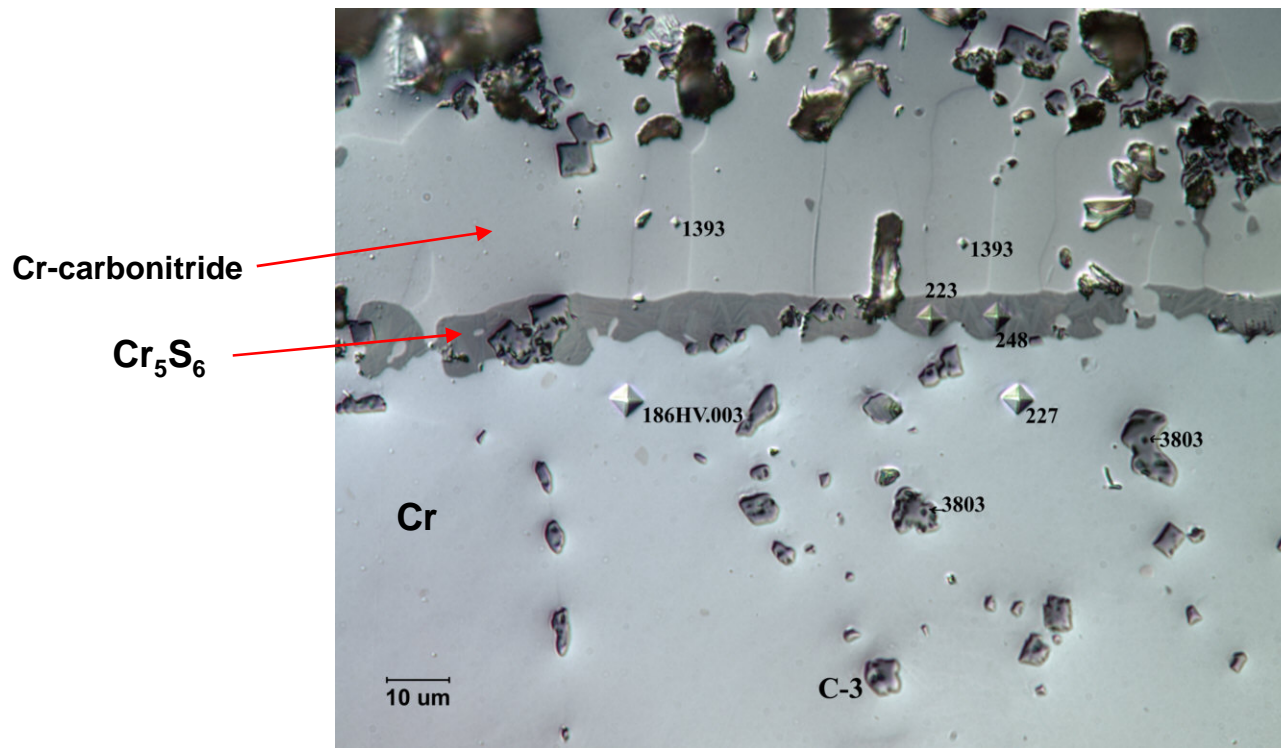
Cross Section of Corrosion Zone on the Cr Specimen After Exposure to Syngas at 1000°C for 288 hours

Near Substrate Metal



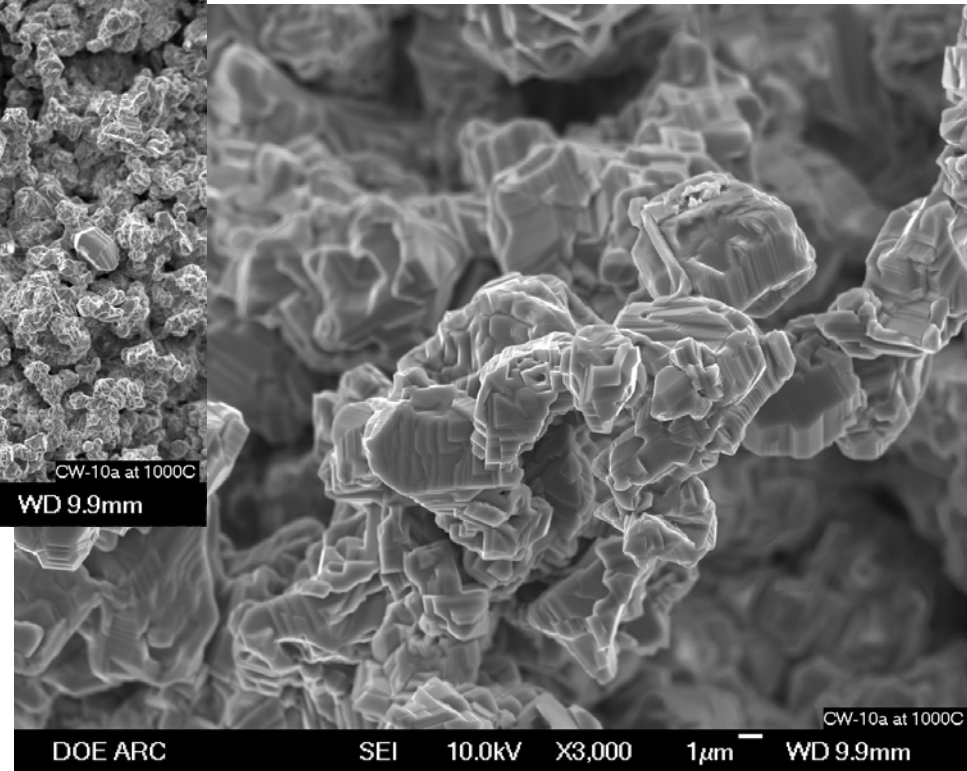
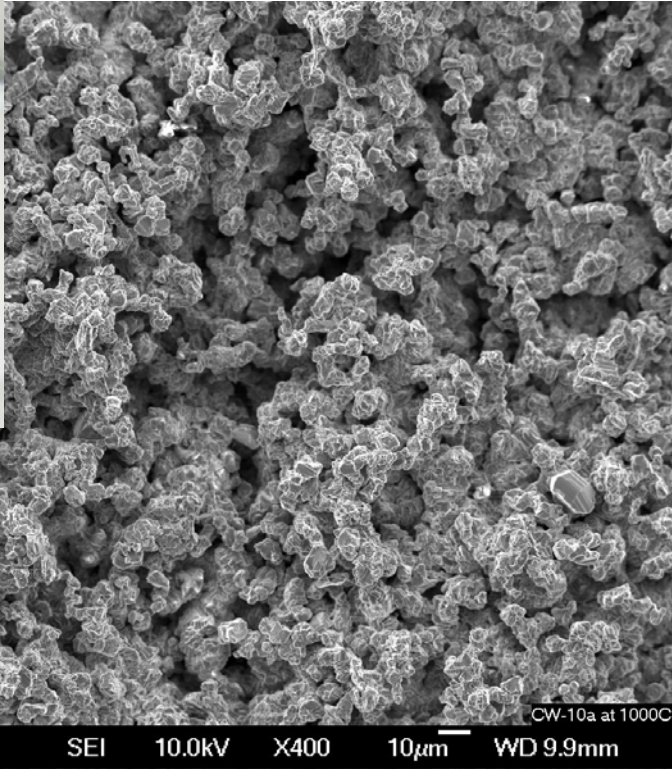
Cross Section of Corrosion Zone on the Cr Specimen After Exposure to Syngas at 1000°C for 288 hours

Near Substrate Metal

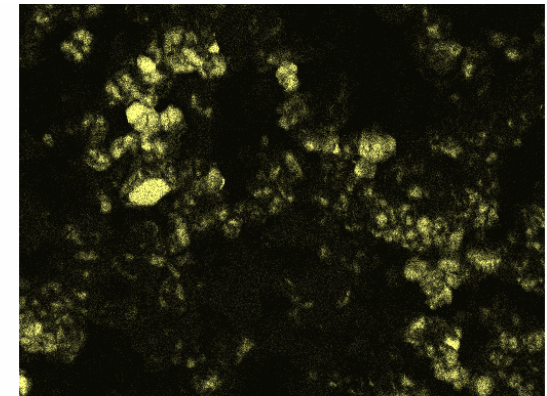
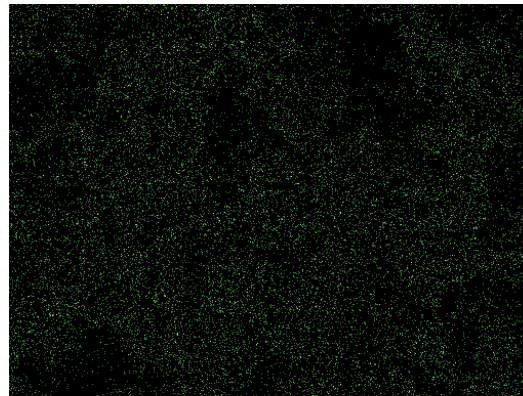
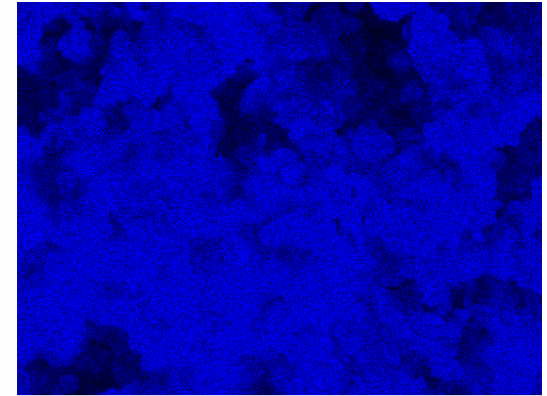
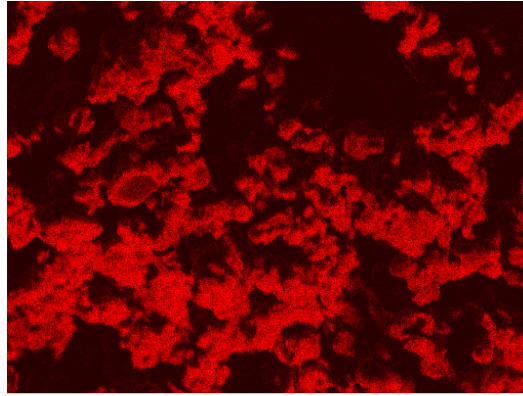
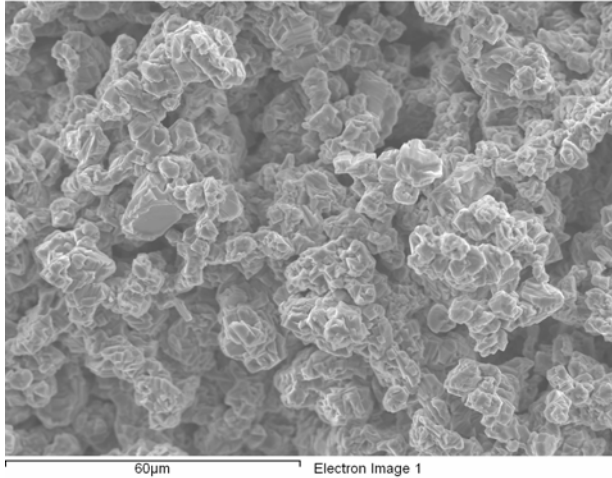


Vickers Hardness (Load = 3 grams)

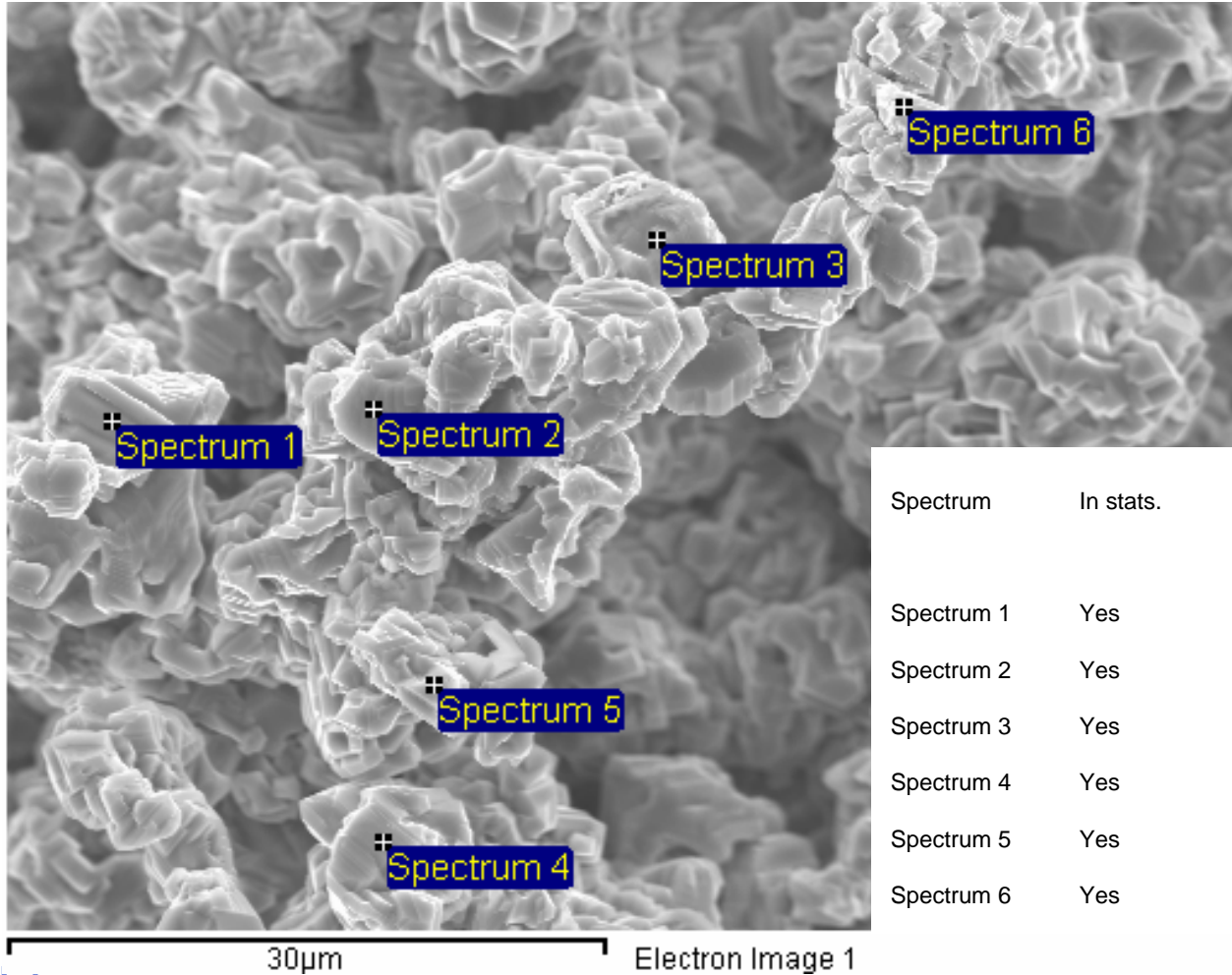
Top Surface of Scale on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours



Top Surface of Scale on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours

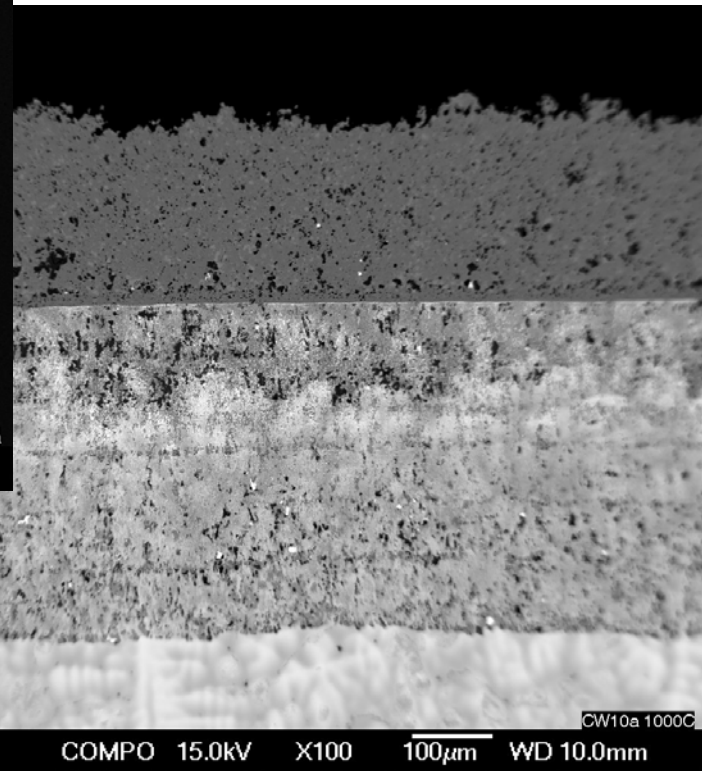
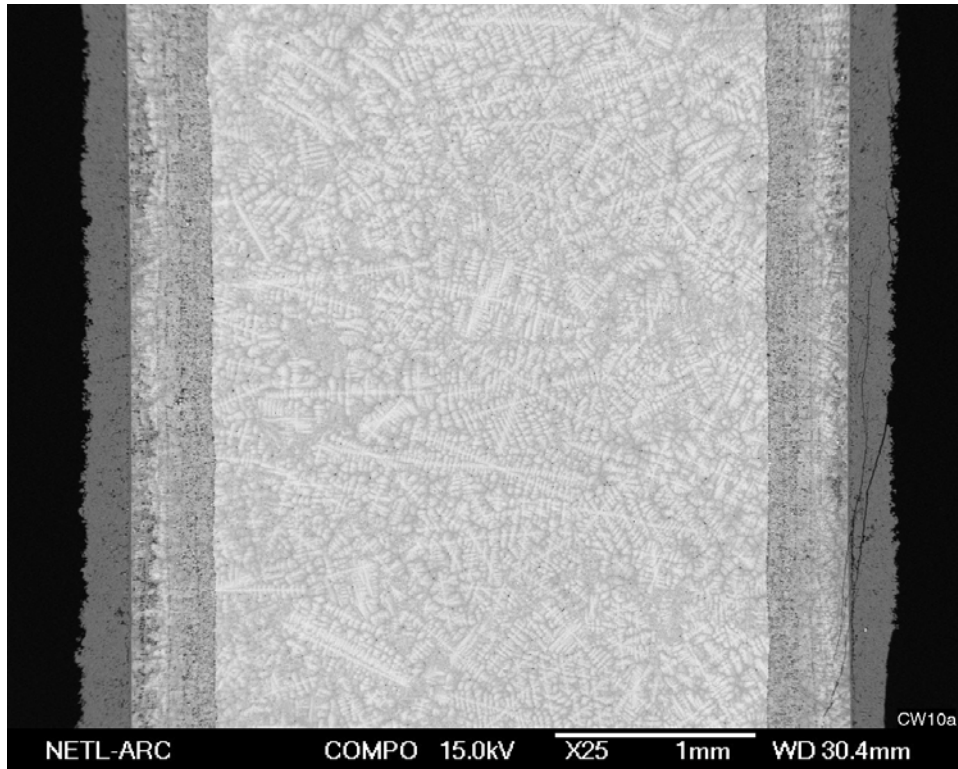


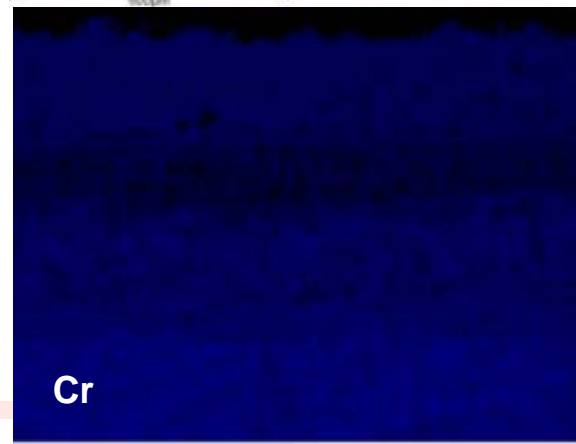
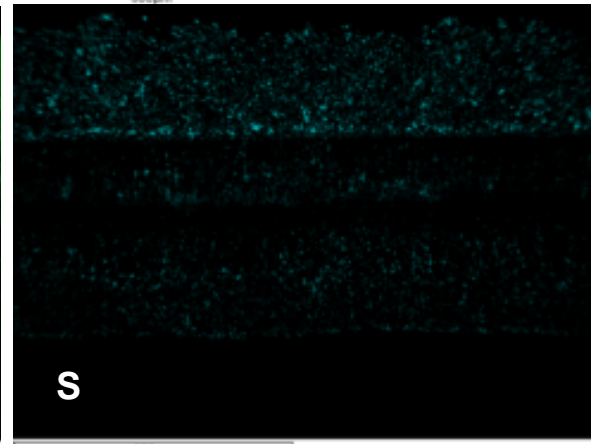
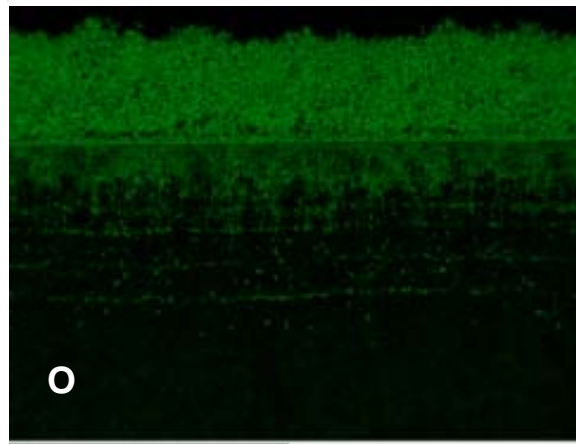
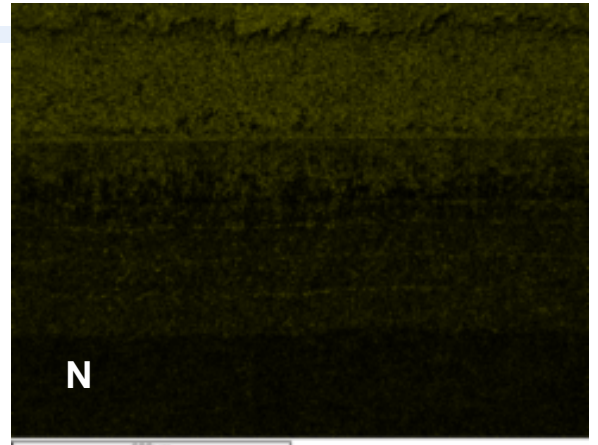
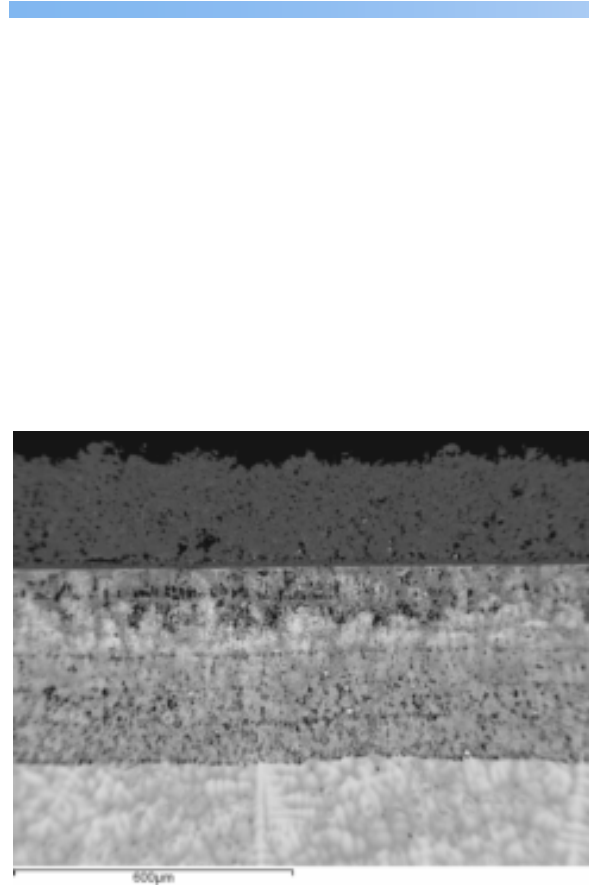
Top Surface of Scale on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours



Spectrum	In stats.	O	S	Cr
Spectrum 1	Yes	51.62	15.69	32.69
Spectrum 2	Yes	41.42	26.12	32.46
Spectrum 3	Yes	43.51	23.34	33.15
Spectrum 4	Yes	50.28	11.04	38.68
Spectrum 5	Yes	64.04	1.66	34.29
Spectrum 6	Yes	65.40	1.91	32.70

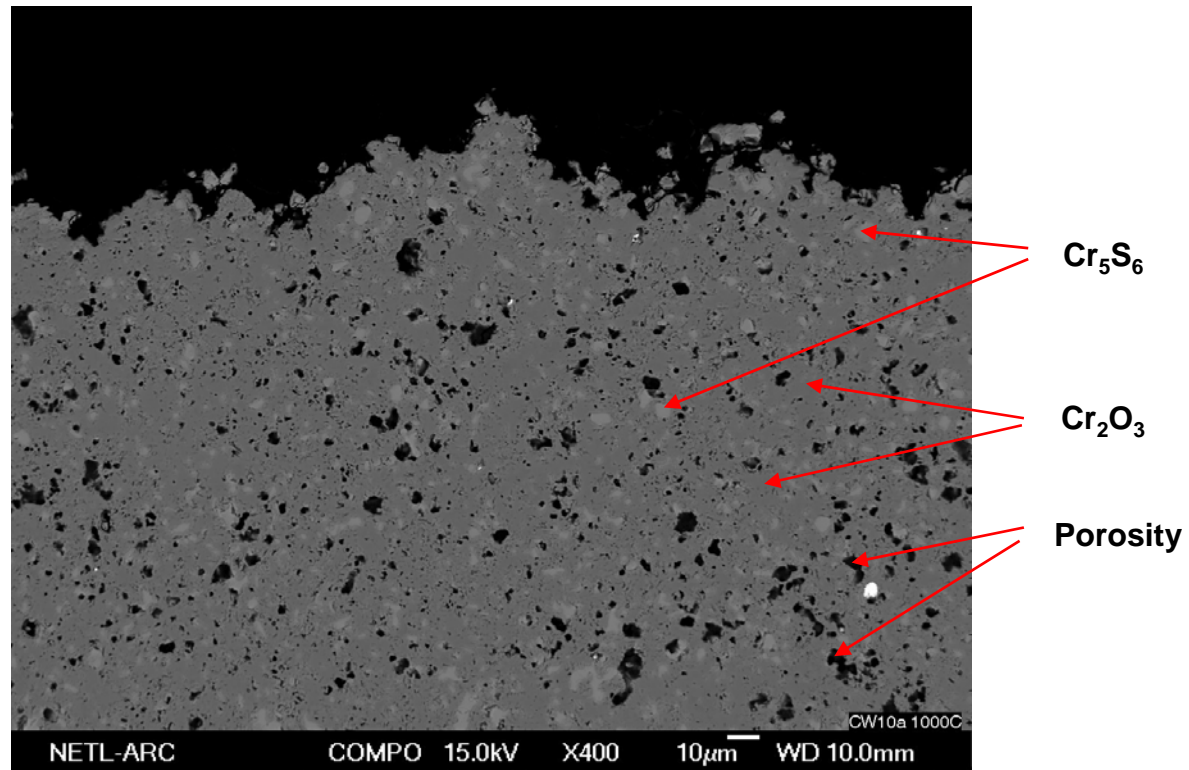
Cross Section of Corrosion Zone on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours



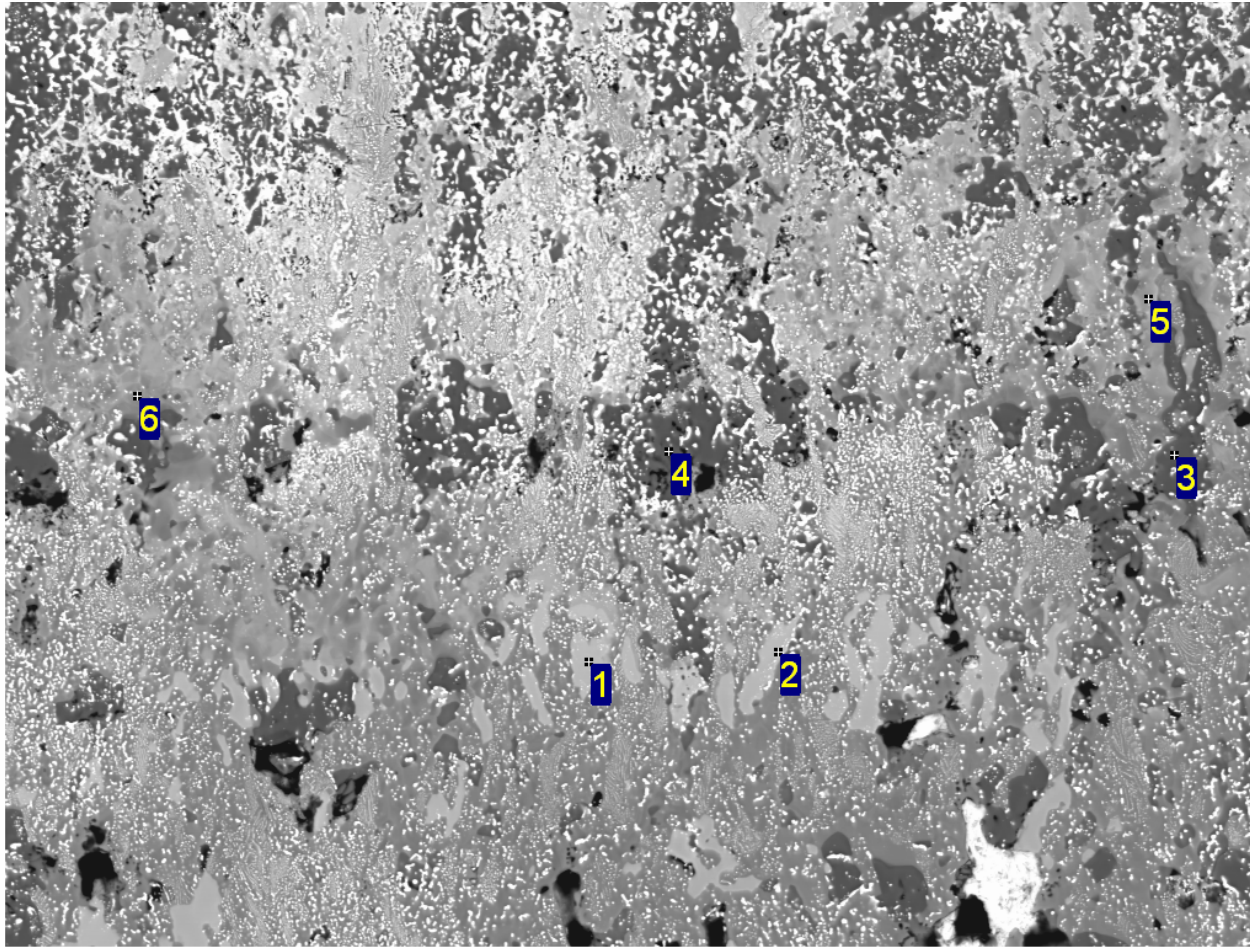


Cross Section of Corrosion Zone on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours

External Corrosion Scale



Cross Section of Corrosion Zone on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours



60μm

Electron Image 1

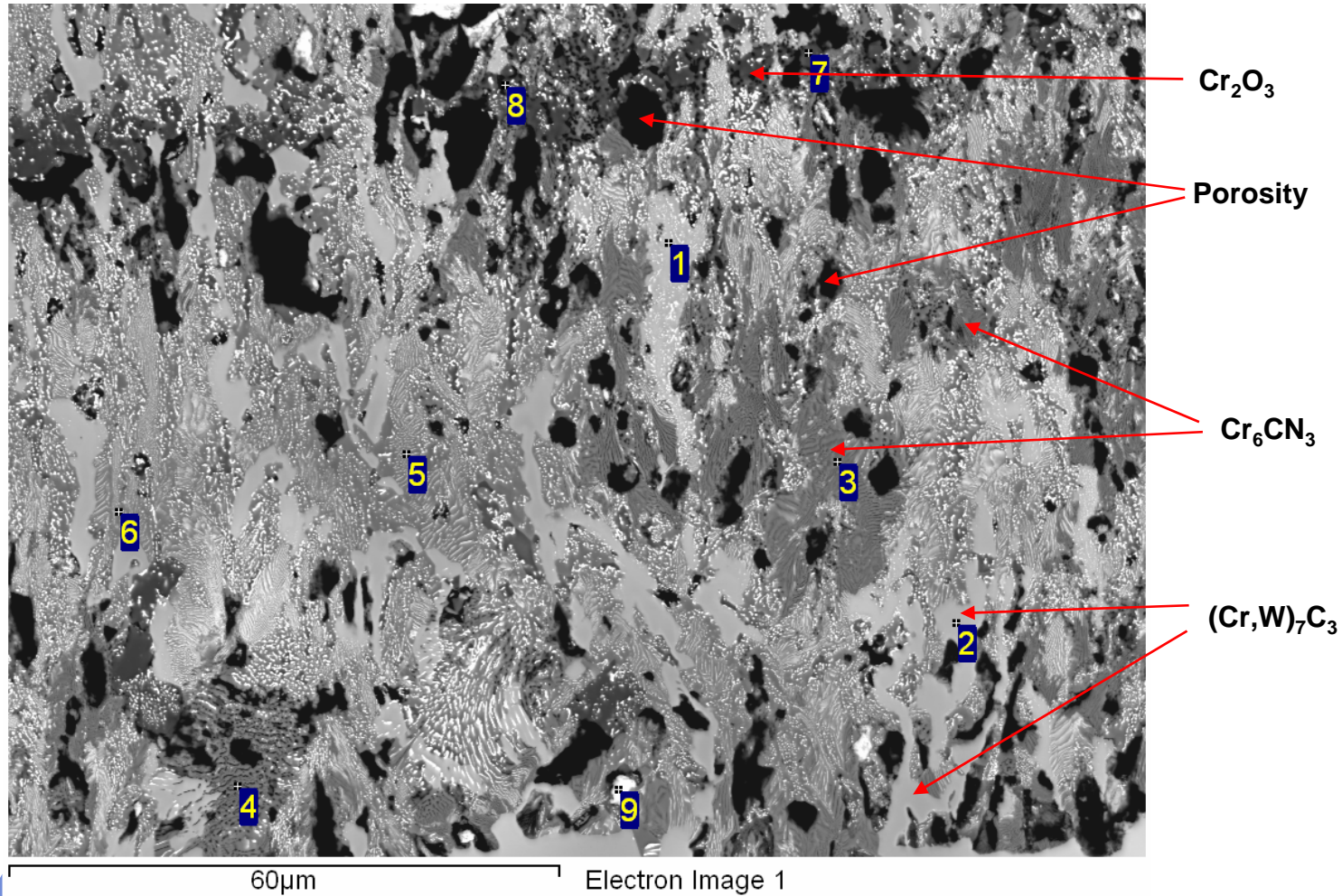
Below external scale

1, 2 : $(\text{Cr,W})_7\text{C}_3$

3, 4 : Cr_2O_3

5, 6 : $(\text{Cr,W})_6\text{C}_3\text{N}$

Cross Section of Corrosion Zone on the Cr-30W Specimen After Exposure to Syngas at 1000°C for 288 hours



Summary

- **Cr-W alloys were tested for corrosion resistance in a simulated syngas mixture at 800°C and 1000°C.**
- **Corrosion rates of Cr and Cr-30W alloys were lower than both Alloy 718 and 310 SS.**
- **Stable external corrosion scale composed of Cr_2O_3 and Cr_5S_6 was formed during exposure.**
- **Below the external scale, internal corrosion resulted in compounds such as Cr-carbides, Cr-carbonitrides, Cr_2O_3 , Cr_5S_6 near the surface.**

