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MINIMIZING CR-EVAPORATION FROM BALANCE OF PLANT COMPONENTS BY UTILIZING COST-EFFECTIVE ALUMINA-FORMING AUSTENITIC STEELS

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Background - SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Strontium segregation related issues

$$2Sr_{La}^{'} + V_{O,LSCF}^{\bullet\bullet} + 2O_O^x \leftrightarrow 2SrO(s)$$

- Chemical reaction with YSZ electrolyte.

$$La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \qquad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)$$

- **Poisoning of the cathode** (e.g. by CO_2, **chromium species** etc.)

$$SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \qquad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$$

$$2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g)$$

Cr_2O_3 Related Degradations

- Cr poisoning of SOFC Cathode

$$Cr_2O_3(s) + 1.5O_2(g) = 2CrO_3(g)$$

$$Cr_2O_3(s) + 1.5O_2(g) + 2H_2O(g) = 2CrO_2(OH)_2(g)$$

- Reactions with other components

$$2Cr_2O_3(s) + 4BaO(s) + 3O_2(g) = 4BaCrO_4(s)$$

$$CrO_2(OH)_2(g) + BaO(s) = BaCrO_4(s) + H_2O(g)$$

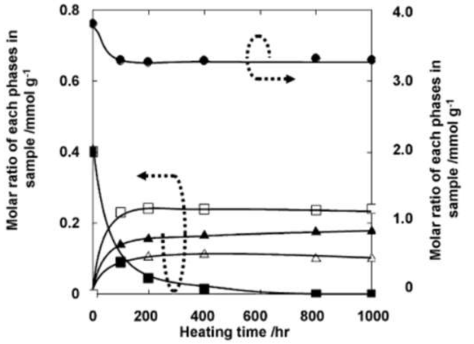
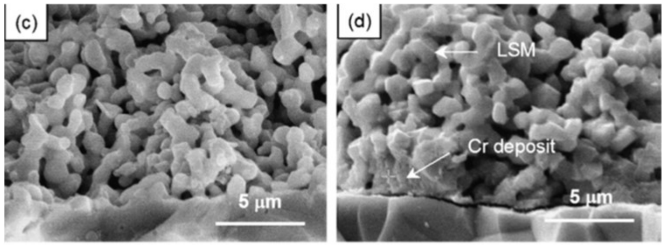
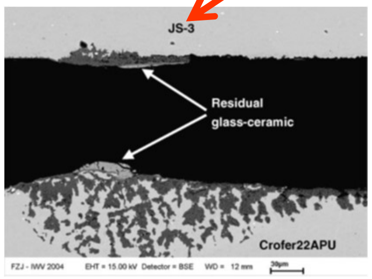


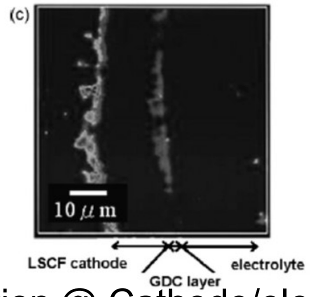
Fig. 4. Molar ratio of phases in LSCF–Cr_2O_3 mixture during heating at 1073 K for 0–1000 h: (●) LSCF, (■) Cr_2O_3, (□) $SrCrO_4$, (▲) $CoCr_2O_4$ spinel, (△) $(Fe,Cr)_2O_3$.



J. Power Sources 162 (2006) 1043–1052



J. Power Sources 152 (2005) 156–167



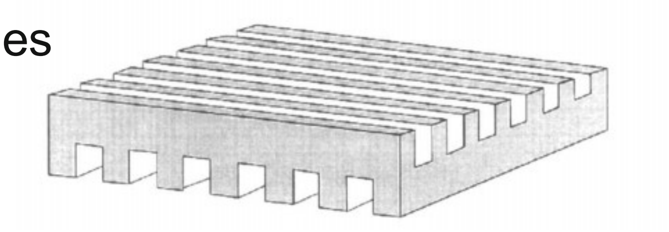
Cr-distribution @ Cathode/electrolyte Interface

Sources of Cr-Species

❑Metallic Interconnects

Ferritic chromia-forming alloys

- Suitable thermal expansion coefficients
- Capable of forming electronically conducting oxides



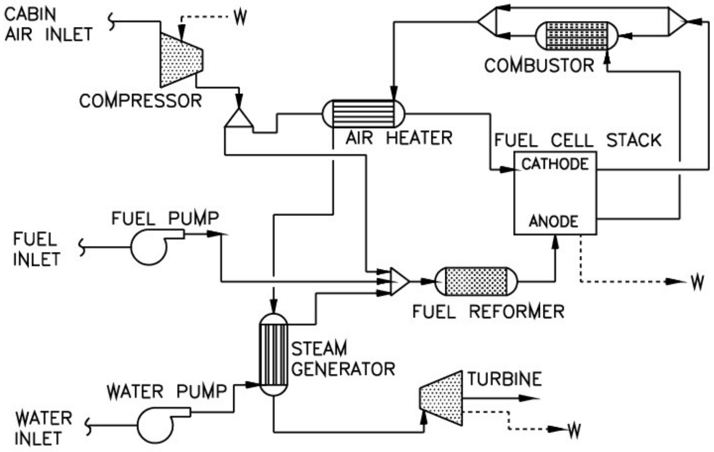
Schematic representation of an interconnect.

❑Balance of Plant components

Nickel- and iron-base Austenitic and Ferritic alloys

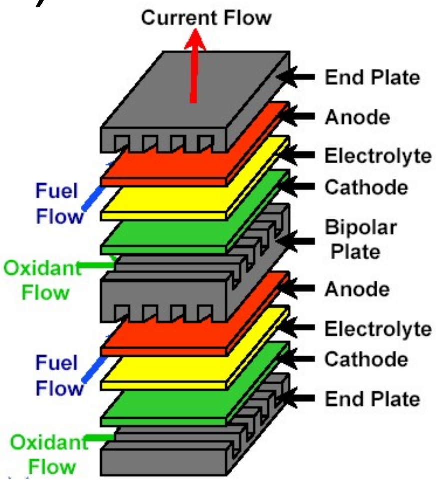
Stack manifold, air delivery tubes and high temperature heat exchangers etc.

- High temperature strength
- Long-term creep resistance
- Corrosion resistance
- Cost
- **Chromium Release**

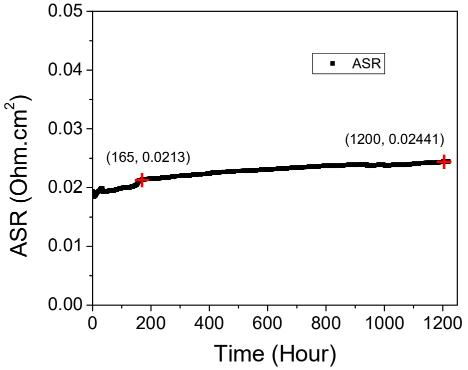


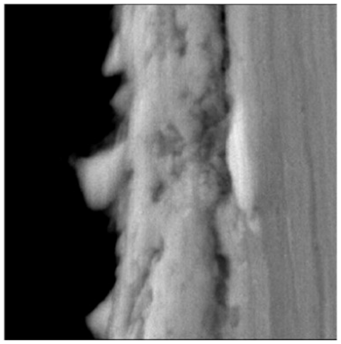
SOFC Interconnect Coatings

- Various Spinel Coatings (Mn-Co, Mn-Cu, etc.)
    - Electronic Conducting
    - Oxygen Insulating
- PVD, CVD, Spray, Electroplating, EPD



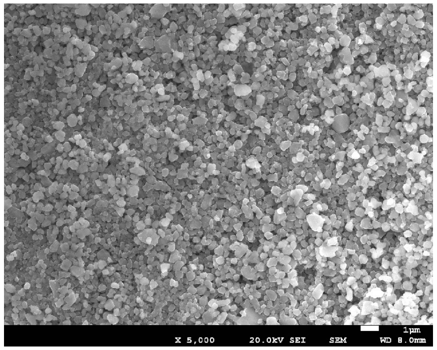
Electro plating Mn-Co

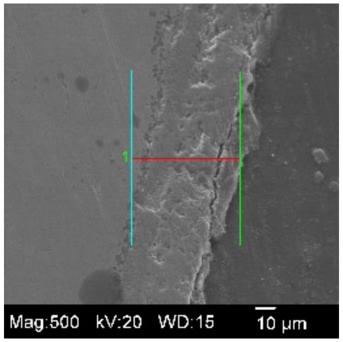




J. Wu, C. Johnson, Y. Jiang, R. Gemmen, **X. Liu***, *Electrochimica Acta (2008) 793-800*

EPD Mn-Co spinel





Hui Zhang, Zhaolin Zhan, **Xingbo Liu**, *JPS 196 (2011) 8041-8047*

Coating impedes degradation of SOFCs

Researchers at West Virginia University have put their heads together with scientists from the Department of Energy's National Energy Technology Laboratory. The result of this collaboration has been the development of a new manganese-cobalt coating for solid oxide fuel cell interconnects.

The new process uses an electroplating technique that reportedly does not harm the environment, and offers significant advantages in terms of cost and ease of operations over other coating methods, the researchers say. Extensive on-cell testing has demonstrated considerable improvement of SOFC degradation compared to uncoated interconnects, the researchers contend.

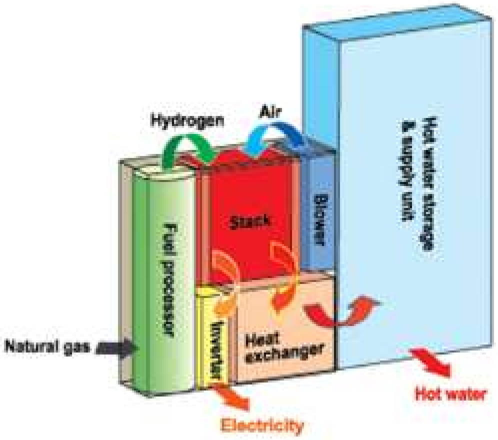
The team has published its research findings in two peer-reviewed journals, and a patent disclosure of the process also has been filed. In addition, team members report exceptionally positive feedback from the report on the coating presented at the 2008 MS&T Conference last October.

Recent results during on-cell testing showed considerable improvement of SOFC degradation with this coating method as compared with uncoated interconnects. Further improvements are anticipated as optimized plating variables are identified. (Visit: http://netl.doe.gov) ■

Junwei Wu, a Ph.D. student at West Virginia University, demonstrates environmentally friendly electroplating for SOFC interconnects.

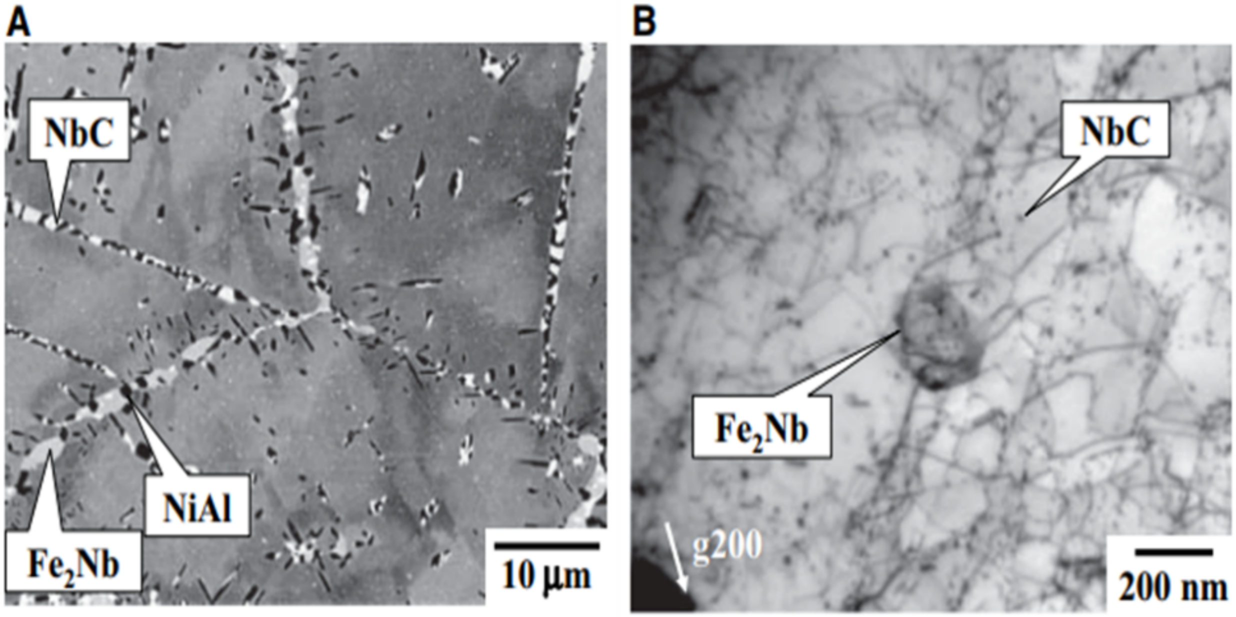
Project Technical Approaches

Developing Cost-Effective Alumina Forming Austenitic Stainless Steels (AFA), to replace Austenitic Stainless Steel and Ni-base Superalloy, for Key **Balance of Plant (BOP) components**, to minimize Cr-Poisoning of SOFC Cathode



Compression Plate in BOP

Microstructure of AFA Alloys

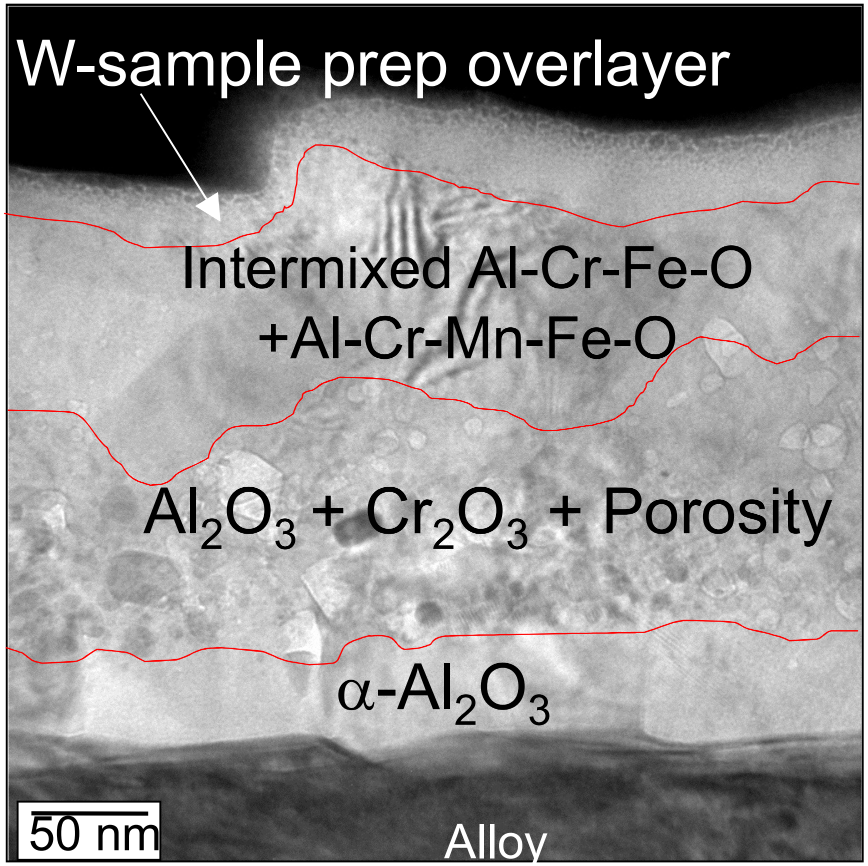


TEM bright-field microstructure of AFA alloy (Fe-20Ni-14Cr-2.5Al-2Mn-2.5Mo-1Nb) after creep testing for 2200 hours at 750°C and 100 MPa

Uniform nanodispersions NbC carbides (~10 nm in diameter) were observed throughout the microstructure, with extensive dislocation pinning, indicating that these were the source of the excellent creep rupture resistance

AFA Form Transient Al-Rich Oxide Overlying Inner, Columnar a-Al_2O_3

TEM of HTUPS 4 After 1000 h at 800°C in Air + 10% Water Vapor



- α-Al_2O_3 the source of the excellent oxidation resistance
- Occasional transient nodules 0.5-5 μm thick, some Nb-oxide also detected

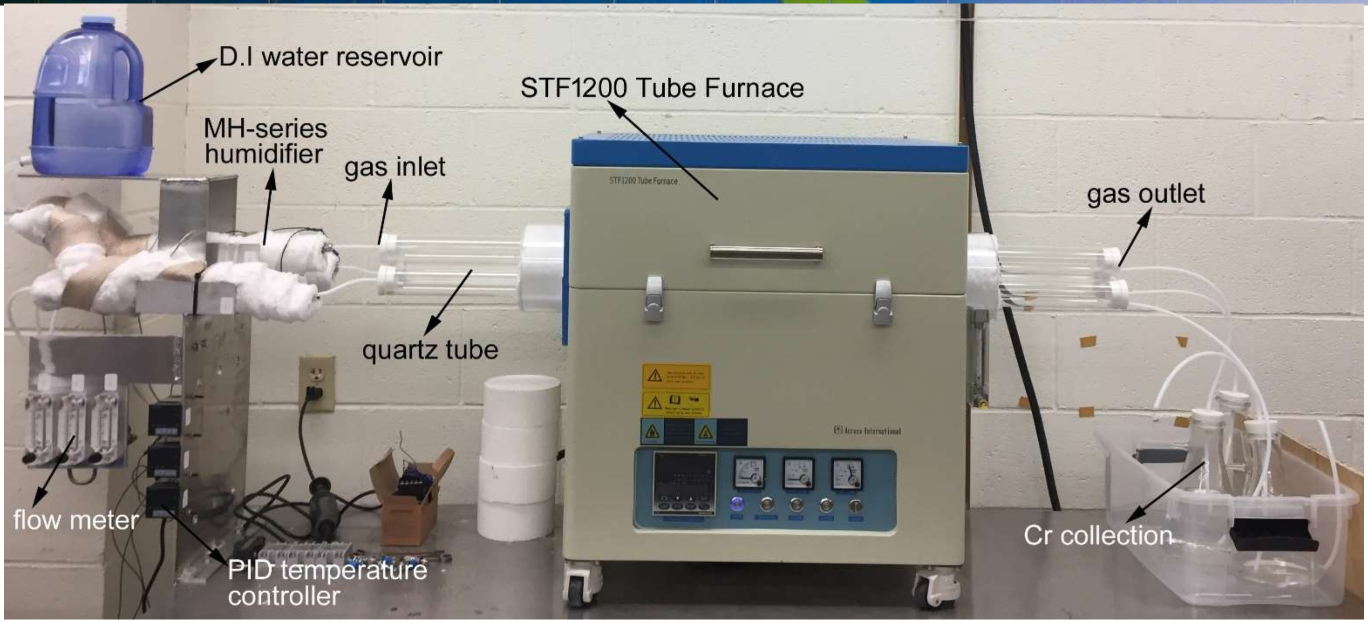
Project Objectives – Phase I

- Develop and utilize cost-effective alumina forming austenitic steels (AFAs) for balance of plant (BOP) components and pipes in solid oxide fuel cell (SOFC) systems to minimize the Cr-poisoning and improve system stability;

- Systematically investigate the influence of the operation condition, i.e., temperature and moisture, on the oxidation and Cr-release from the AFA steels, and their effects on the degradation of SOFC performance

- Prepare for Phase II of the project, in which we will manufacture and test the related BOP components in industrial SOFC systems

Experimental Set up and Test Matrix



Sample size: 25 mm×20 mm×1 mm, polished up to 800 grit before use.

Fresh sample test:10% H_2O, 500 hours								
Sample	**OC4**	**OC5**	**OCF**	**310S**	**New 35 Ni**	**OC-11**	**MOD 2 OC-D**	**Alloy 625**
700 °C*	√	√	√	√	–	–	√	√
850 °C	√			√			—	
900 °C	√	—	√	√	√	√	—	√

*Note: at 700°C, the Cr release was below the detection limit for the AFA alloys and Ni-base alloy 625 control.

Conclusions – Phase I

- The 6 evaluated AFA alloy variations exhibited superior oxidation resistance to benchmark chromia-forming alloys at 800-1000°C in the simulated SOFC BOP environment of air + 10% H_2O.

- Significantly reduced Cr release rates were observed in 500 hour testing from 700-900°C; with, for example, a nearly 30x Cr release rate reduction for AFA alloy OC4 at 850°C compared to benchmark Cr_2O_3-forming 310S stainless steel.

Sample	OC4	OC5	OCF	New 35 Ni	OC-11	MOD 2 OC-D	310S	Alloy 625
700 °C	$<2.34 \times 10^{-12}$	$<2.14 \times 10^{-12}$	$<2.16 \times 10^{-12}$	—	—	$<2.14 \times 10^{-12}$	2.75×10^{-12}	$<2.20 \times 10^{-12}$
850 °C	1.09×10^{-11}			*	*	—	2.9×10^{-10}	
900 °C	4.72×10^{-11}	—	5.87×10^{-11}	4.62×10^{-11}	1.81×10^{-11}	—	3.81×10^{-10}	7.36×10^{-11}

Project Objective - Phase II

- Optimization and down-select of 2 grades of AFA alloys for SOFC BOP testing :
  - 1 grade for ≤ 800°C operation
  - 1 more highly-alloyed grade for 850-950°C operation.
- Long-Term Properties: Cr-release, Oxidation, HT mechanical properties
- On-cell testing to understand the degradation of cells as function of Cr
- Working with Industrial Partners (Bloom Energy & Fuel Cell Energy) on manufacturing and testing AFA components in industrial environments

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Materials Design

Multiple AFA Grades Under Study for Balance of Cost, Processability, Cr-Evaporation, and Oxidation

- Two temperature regimes of interest: 700-800° C and 900-950° C
  - -temperature targets vary with component and SOFC manufacturer

- Upper-temperature oxidation limit for AFA composition dependent
  - -≤ 850° C: Fe-25Ni-14Cr-(3-3.5)Al-(1-2.5)Nb-(0.1-0.2C) *base
  - -900-1000° C: Fe-(25-35)Ni-(15-18)Cr-4Al-(1-2.5)Nb-(0.1-0.2C) *base ± Hf, Y, Zr

- Cost and ease of processing varies with alloy content
  - -higher Ni, Nb, and Hf, Y, Zr increases cost
  - -Zr lower cost than Hf, easier processing

*Minor additions of Mn, Si, Mo, W, B, etc. also used in some AFA compositions

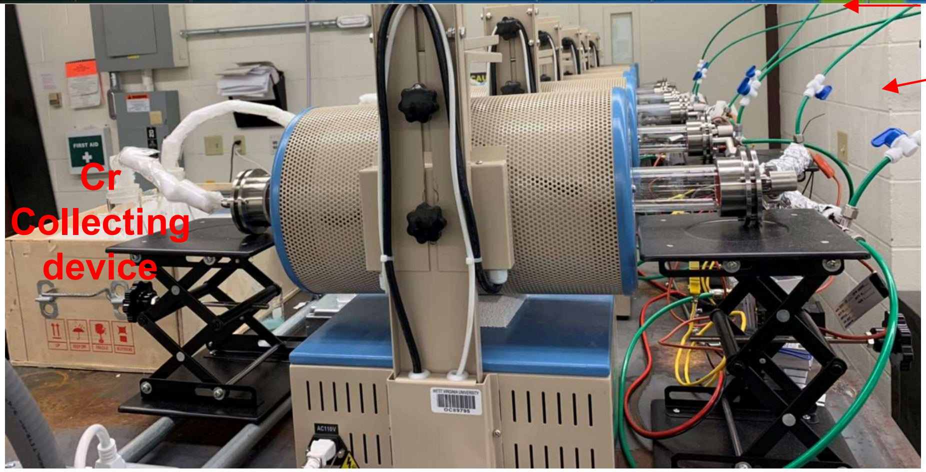
Material Compositions

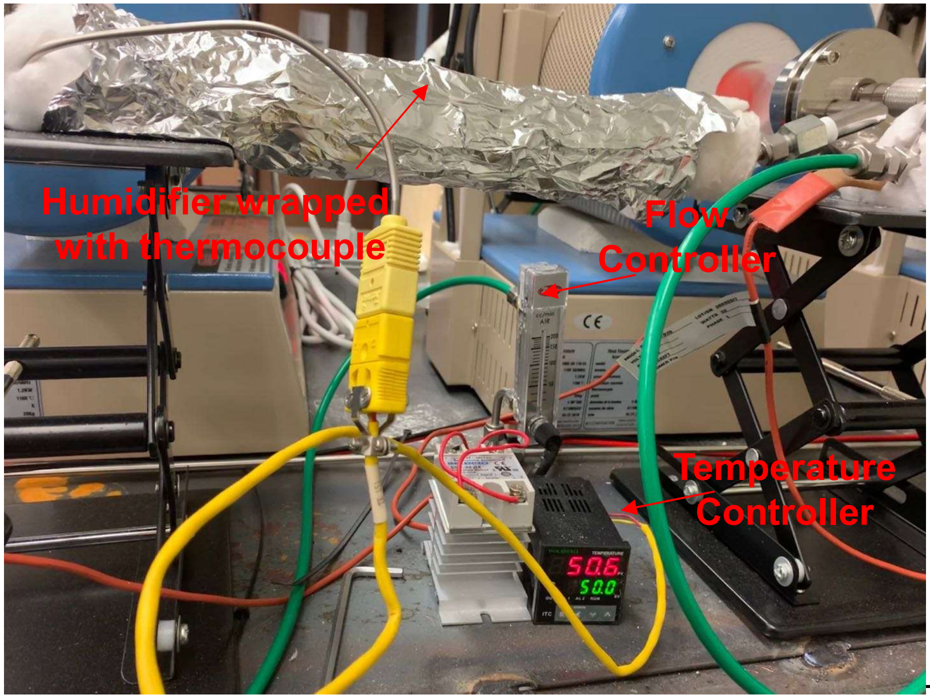
Alloy	Fe	**Ni**	**Cr**	**Al**	**Nb**	Mn	Si	Mo	W	**C**	B	**other**
AFA for ≤ 800°C use												
MOD 2 OCD	51	**25**	**14**	**4**	**1**	2	0.15	2	0	**0.15**	0.01	0.5Cu
OC5	51	**25**	**14**	**3**	**1**	2	0.15	2	1	**0.1**	0.01	0.5Cu
OC4	49	**25**	**14**	**3.5**	**2.5**	2	0.15	2	1	**0.1**	0.01	0.5Cu
AFA for ≥ 850°C use												
OCF	49	**25**	**14**	**4**	**2.5**	2	0.15	2	1	**0.2**	0.01	0.5Cu
OC11	49	**25**	**15**	**4**	**2.5**	2	0.15	2	0	**0.1**	0.01	0.5Cu **Hf, Y**
35Ni	39	**35**	**18**	**3.5**	**1**	2	0.15	0	0	**0.15**	0.01	0.5Cu **Hf, Y**
Benchmark commercial Cr_2O_3-forming alloys												
310S	53	20	25	0	0	2	0.75	0.75	0	0.08	0	0.5Cu
625	5	61	22	0.2	3	0.4	0.25	8		0.04	0	0.2Ti

🟨 Rare element additive; 🟪 Benchmark samples;

- *Alloy compositions confirmed by bulk chemical analysis.*

Long-term Cr-release Characterization

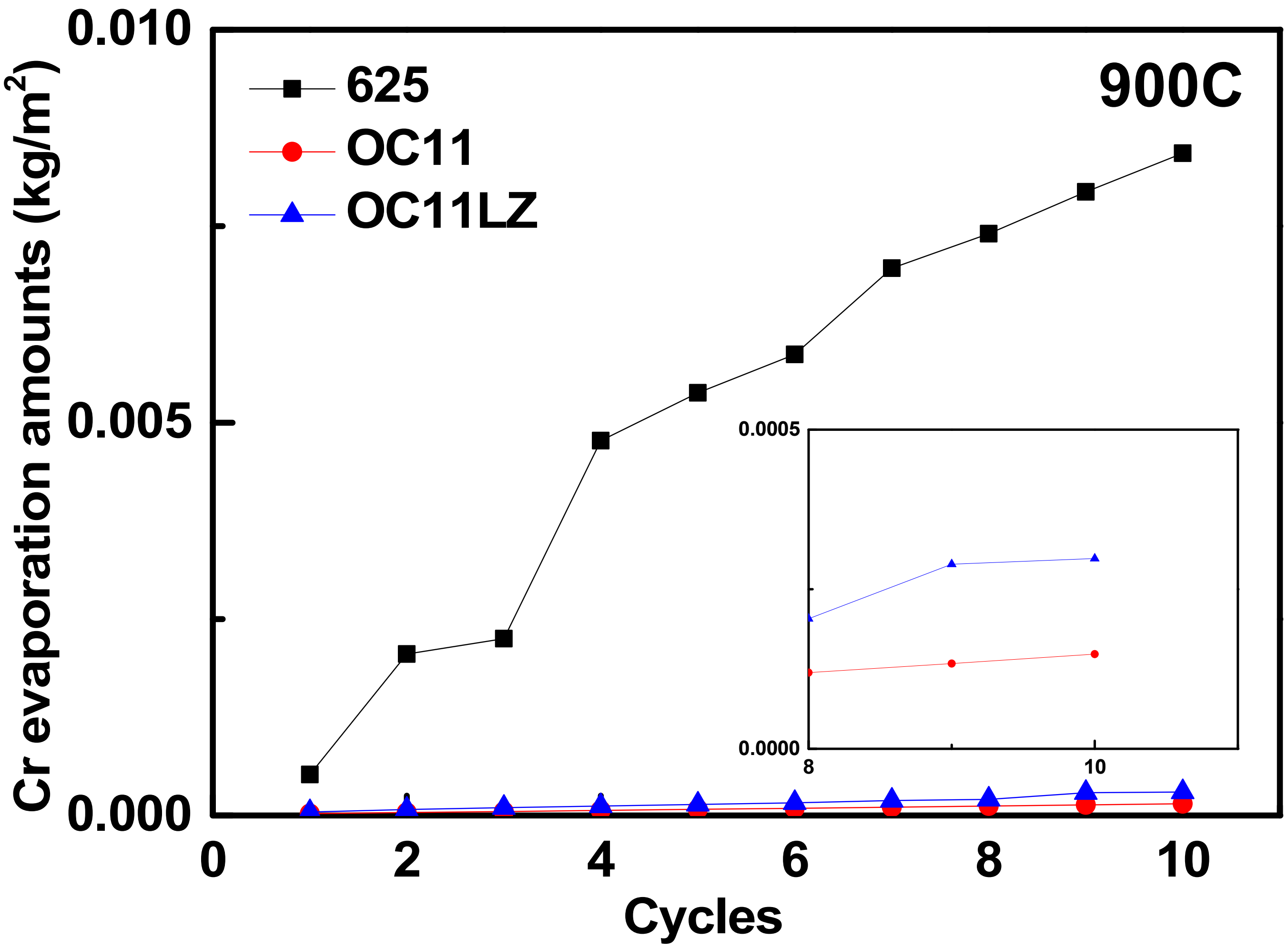




High Throughput – Six separate tube furnaces are constructed to measure Cr evaporation rates for several samples in the meantime for 5000h(10 cycles) long-term operation.

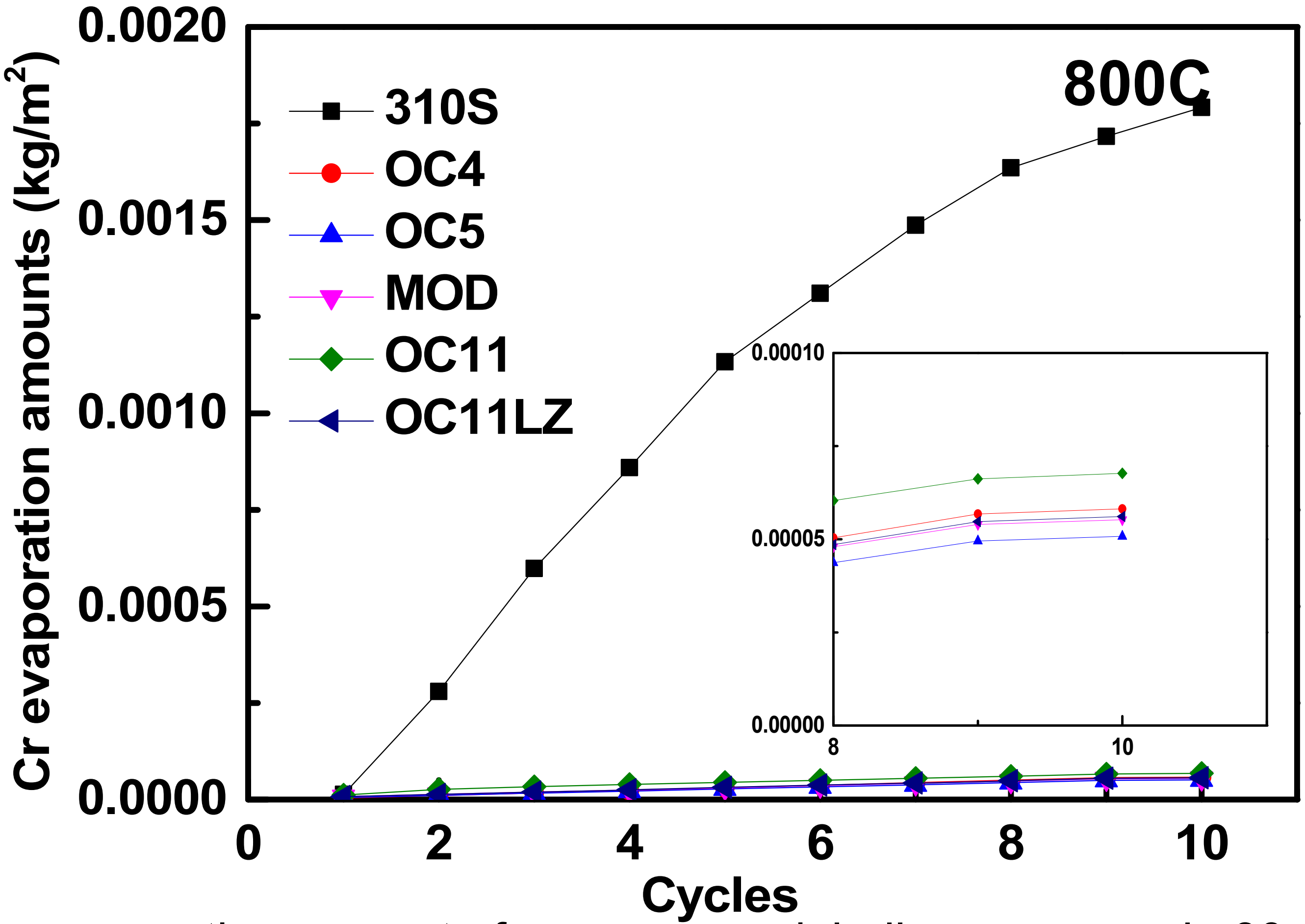
All samples were taken out for weighing, SEM and XRD characterization after every cycle(500h)

Cr Release Kinetics of Alloys



5000 hours (10 cycle) Cr release measurements in air + 10% H_2O

Cr Release Kinetics of Alloys



- Cr evaporation amounts from commercial alloy were nearly 30 times higher than AFA alloys after 5000h test.
- Cr evaporation amounts increased with temperature.

5000 hours (10 cycle) Cr release measurements in air + 10% H_2O

Cr Release Kinetics of Alloys

Cycle		1	2	3	4	5	6	7	8	9	10
800 °C	310S	7.45×10^{-12}	1.48×10^{-10}	1.77×10^{-10}	1.45×10^{-10}	1.52×10^{-10}	9.85×10^{-11}	9.79×10^{-11}	8.28×10^{-11}	4.5×10^{-11}	4.18×10^{-11}
	OC4	$<2.25 \times 10^{-12}$	$<3.61 \times 10^{-12}$	$<3.44 \times 10^{-12}$	$<3.83 \times 10^{-12}$	$<3.67 \times 10^{-12}$	$<3.73 \times 10^{-12}$	$<3.73 \times 10^{-12}$	$<3.73 \times 10^{-12}$	$<3.56 \times 10^{-12}$	$<7.66 \times 10^{-13}$
	OC5	2.8×10^{-12}	$<3.17 \times 10^{-12}$	$<3.04 \times 10^{-12}$	$<2.98 \times 10^{-12}$	$<3.15 \times 10^{-12}$	$<3.05 \times 10^{-12}$	$<3.00 \times 10^{-12}$	$<3.09 \times 10^{-12}$	$<3.23 \times 10^{-12}$	$<7.02 \times 10^{-13}$
	MOD	4.31×10^{-12}	$<3.31 \times 10^{-12}$	$<3.23 \times 10^{-12}$	$<2.84 \times 10^{-12}$	$<3.17 \times 10^{-12}$	$<3.23 \times 10^{-12}$	$<3.32 \times 10^{-12}$	$<3.25 \times 10^{-12}$	$<3.33 \times 10^{-12}$	$<6.97 \times 10^{-13}$
	OC11	6.37×10^{-12}	$<8.38 \times 10^{-12}$	$<3.66 \times 10^{-12}$	$<3.24 \times 10^{-12}$	$<2.95 \times 10^{-12}$	$<3.15 \times 10^{-12}$	$<2.76 \times 10^{-12}$	$<3.04 \times 10^{-12}$	$<3.24 \times 10^{-12}$	$<8.23 \times 10^{-13}$
	OC11-LZ	4.14×10^{-12}	$<3.15 \times 10^{-12}$	$<3.53 \times 10^{-12}$	$<3.24 \times 10^{-12}$	$<3.40 \times 10^{-12}$	$<3.35 \times 10^{-12}$	$<2.92 \times 10^{-12}$	$<3.25 \times 10^{-12}$	$<3.43 \times 10^{-12}$	$<7.66 \times 10^{-13}$
900 °C	625	2.89×10^{-10}	8.52×10^{-10}	1.09×10^{-10}	1.4×10^{-9}	3.38×10^{-10}	2.72×10^{-10}	6.09×10^{-10}	2.44×10^{-10}	2.96×10^{-10}	2.74×10^{-10}
	OC11	1.29×10^{-11}	$<7.6 \times 10^{-12}$	$<7.9 \times 10^{-12}$	$<7.38 \times 10^{-12}$	$<7.56 \times 10^{-12}$	$<7.67 \times 10^{-12}$	$<7.53 \times 10^{-12}$	$<7.79 \times 10^{-12}$	$<7.90 \times 10^{-12}$	$<8.16 \times 10^{-12}$
	OC11-LZ	2.51×10^{-11}	1.74×10^{-11}	1.35×10^{-11}	1.04×10^{-11}	$<1.14 \times 10^{-11}$	$<1.09 \times 10^{-11}$	1.74×10^{-11}	7.09×10^{-12}	4.75×10^{-11}	$<4.93 \times 10^{-12}$

5000 hours (10 cycle) Cr release measurements in air + 10% H_2O*(Unit:* $kg/(m^2 \cdot s)$*).*

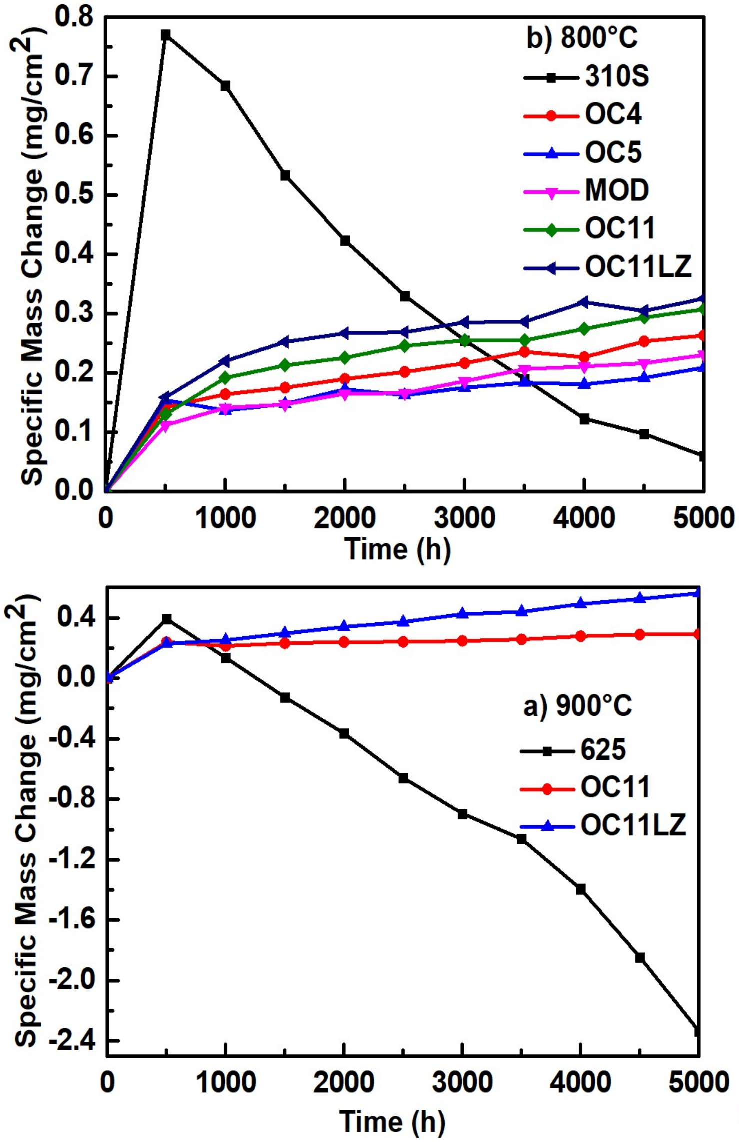
Oxidation Kinetics Analysis

- Lower Cr evaporation rate and oxidation rates od AFA alloys than 310S and 625 at 800^{o}C and 900^{o}C , respectively.

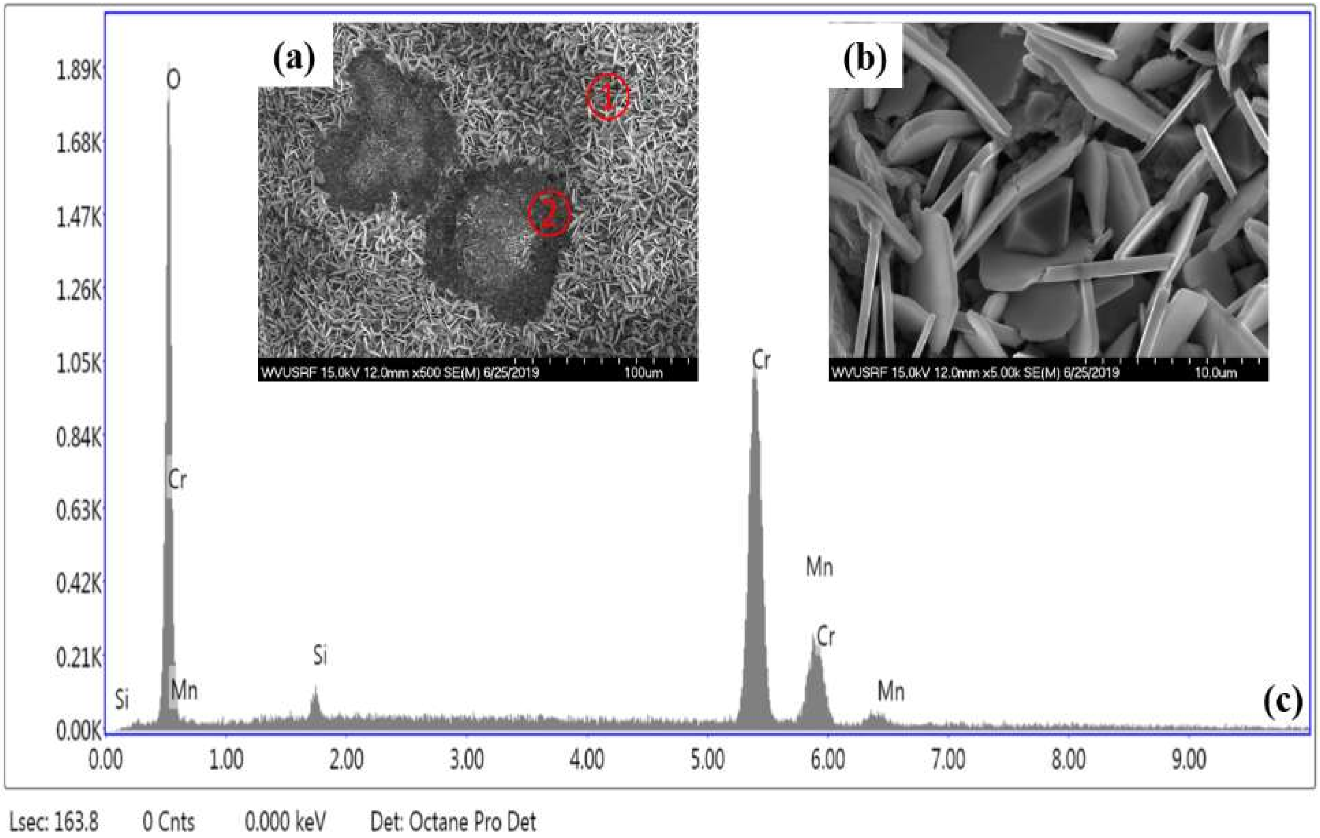
- At 900^{o}C, the OC11 and OC11LZ AFA alloys exhibited significantly lower Cr evaporation rate than 625. 625 suffered from spallation and mass loss which resulted in higher Cr evaporation rate.

- At 800^{o}C, the 310S exhibited the highest Cr evaporation rate than AFA alloys which exhibited low rates of oxidation and Cr evaporation rate which is ascribed to the protective alumina scale formation.

- AFA alloys exhibited significantly greater oxidation resistance than the Cr-forming 310 and 625 alloys in air + H_2O environments can be of great importance for the application in BoP components in SOFC stacks.

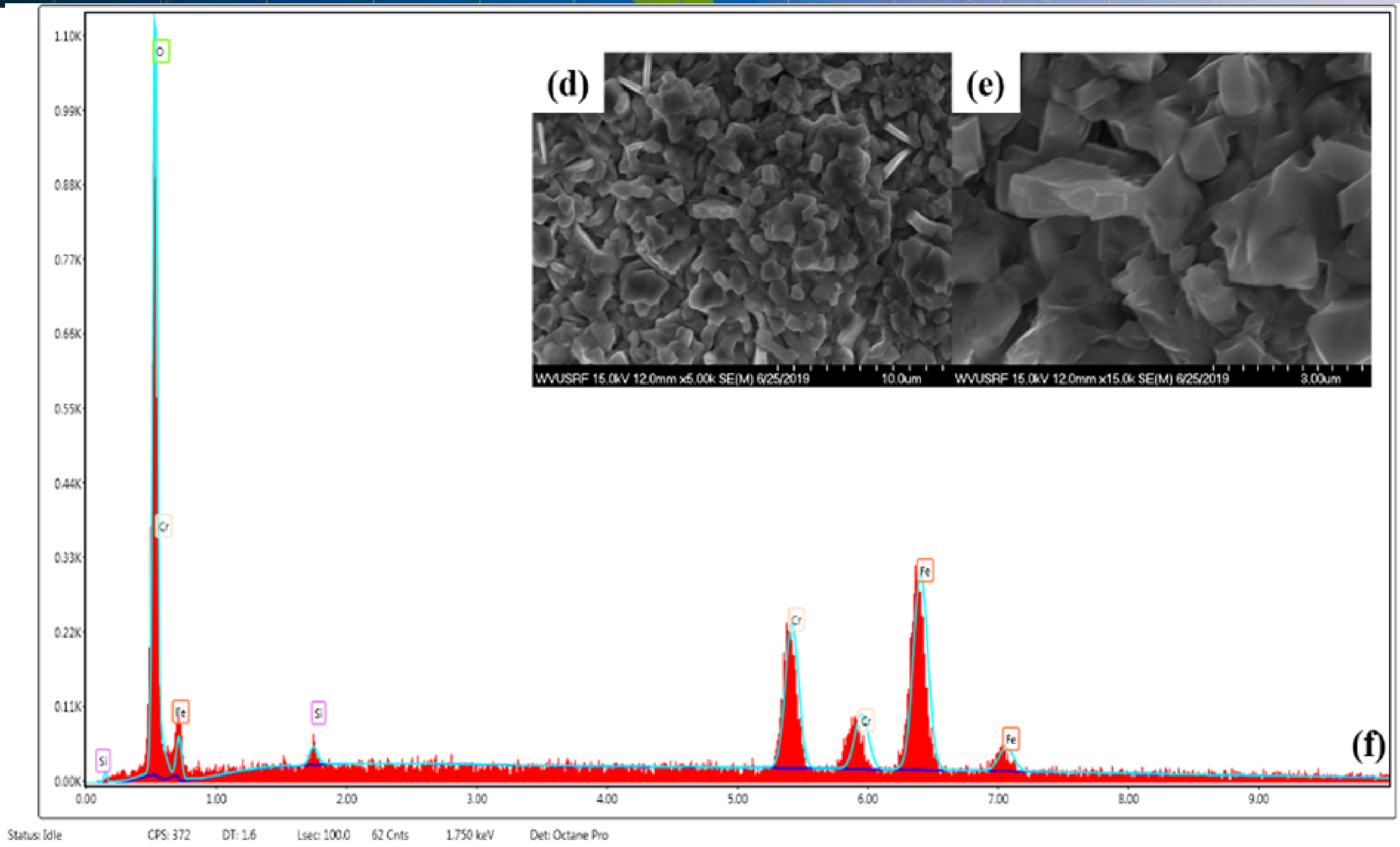


310S in 10% H_2O at 800 °C for 5000 hours



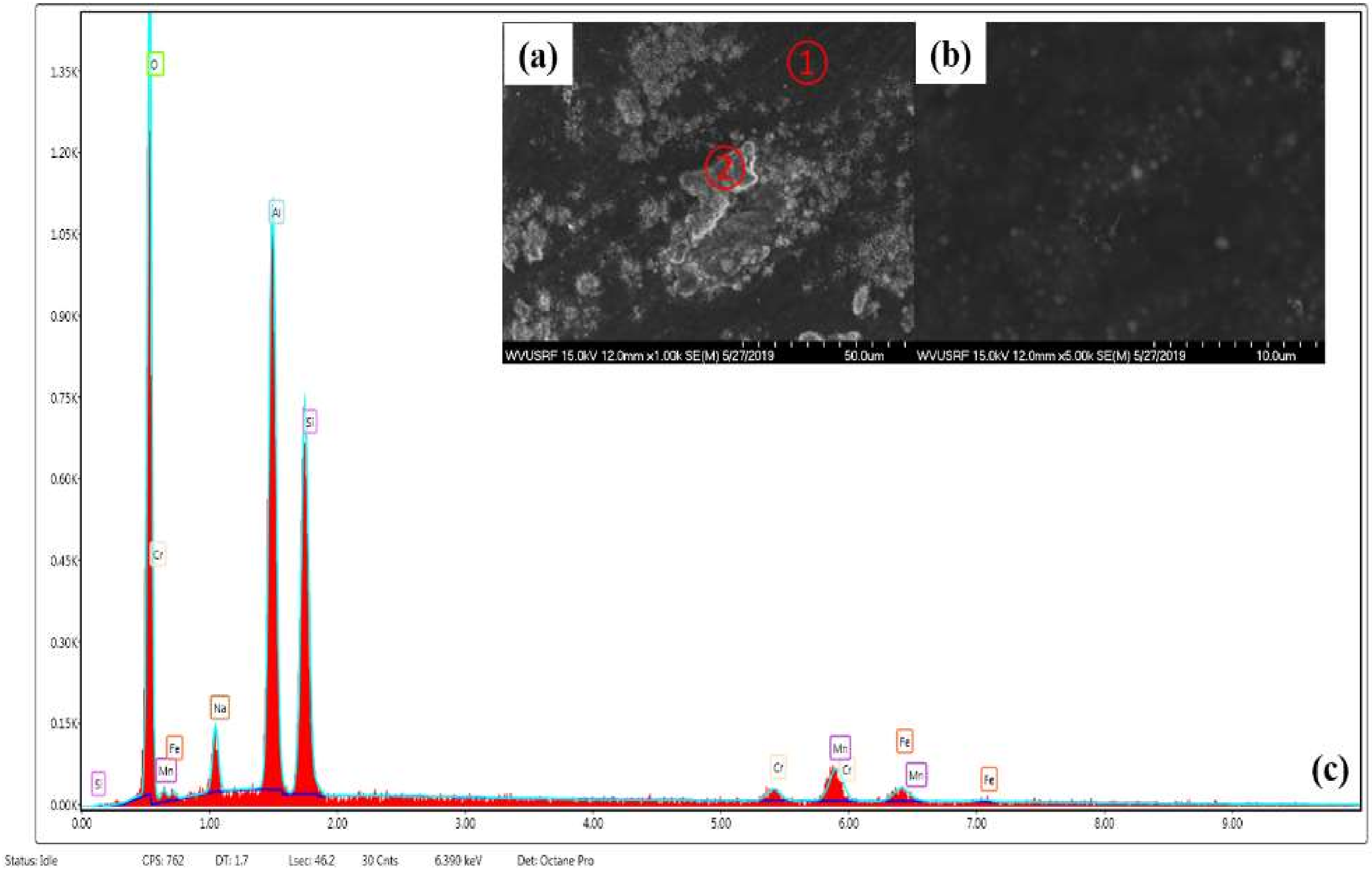
(a) Microstructural analysis of 310S tested in 10% H_2O at 800 °C for 5000 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b)

310S in 10% H_2O at 800 °C for 5000 hours



(d,e) are the high-magnification images of area ②, (f) is the corresponding EDS spectrum of (e)

OC4 in 10% H_2O at 800 °C for 4500 hours



(a) Microstructural analysis of **OC4** tested in 10% H_2O at 800 °C for 4500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b).

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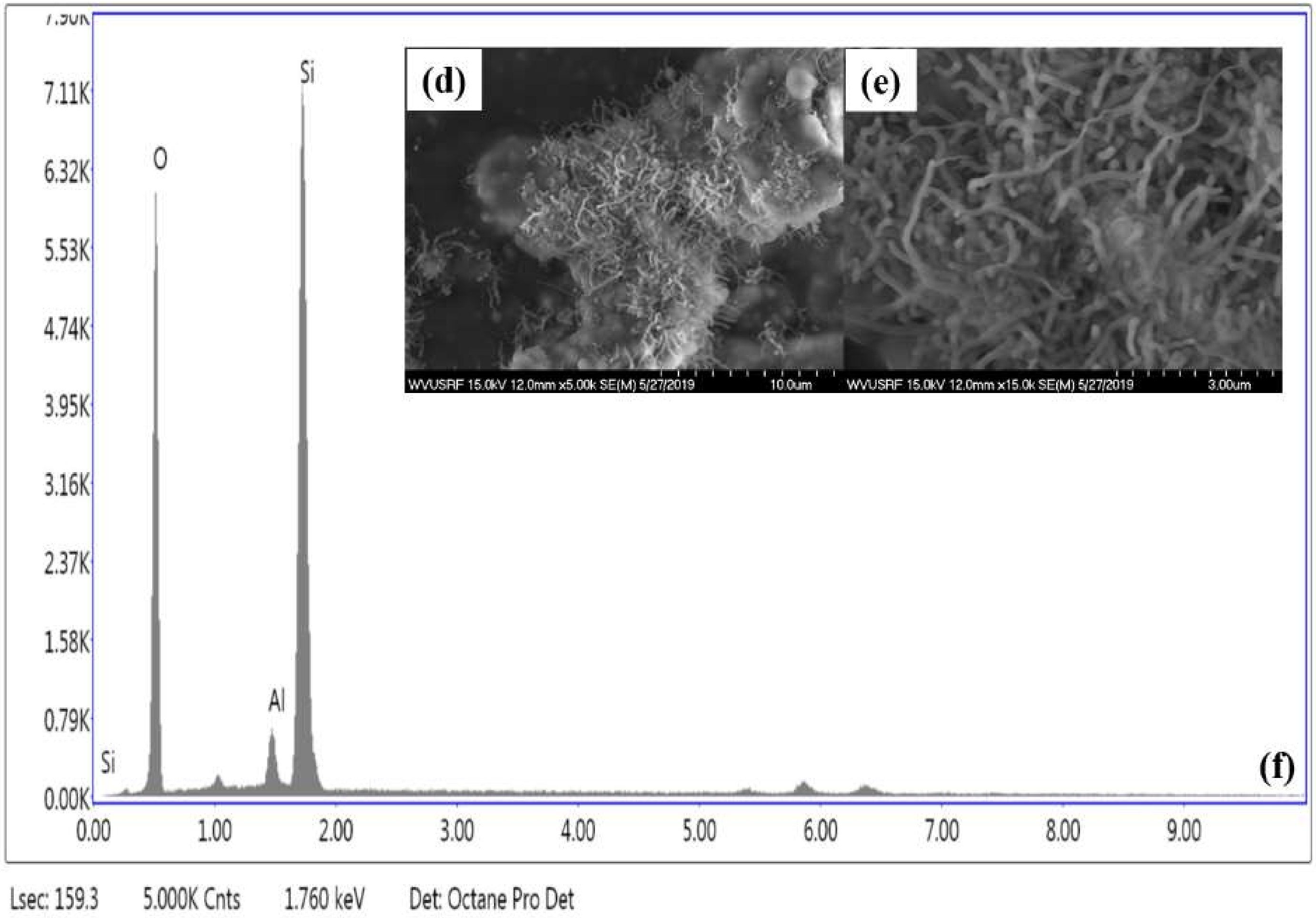
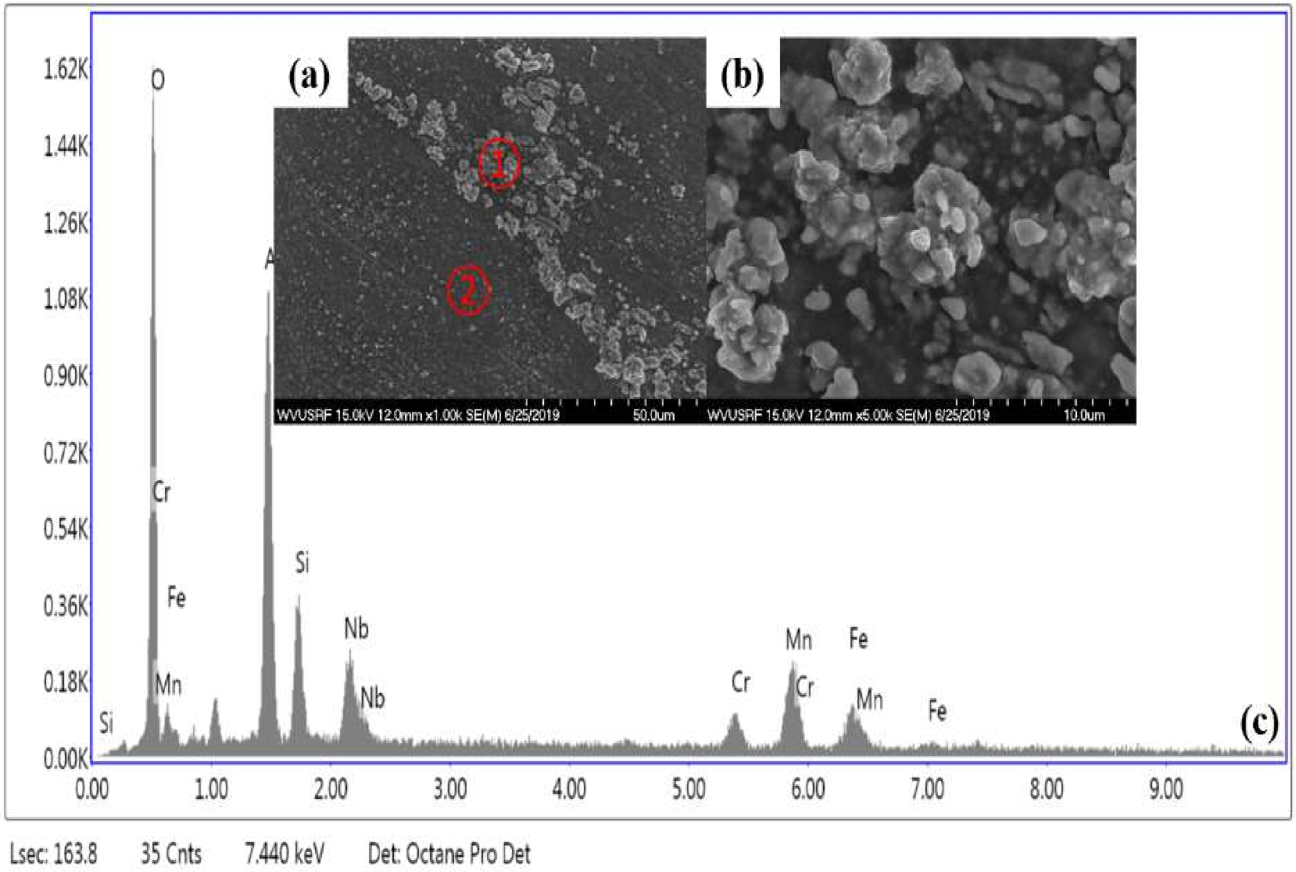
OC4 in 10% H_2O at 800 °C for 4500 hours



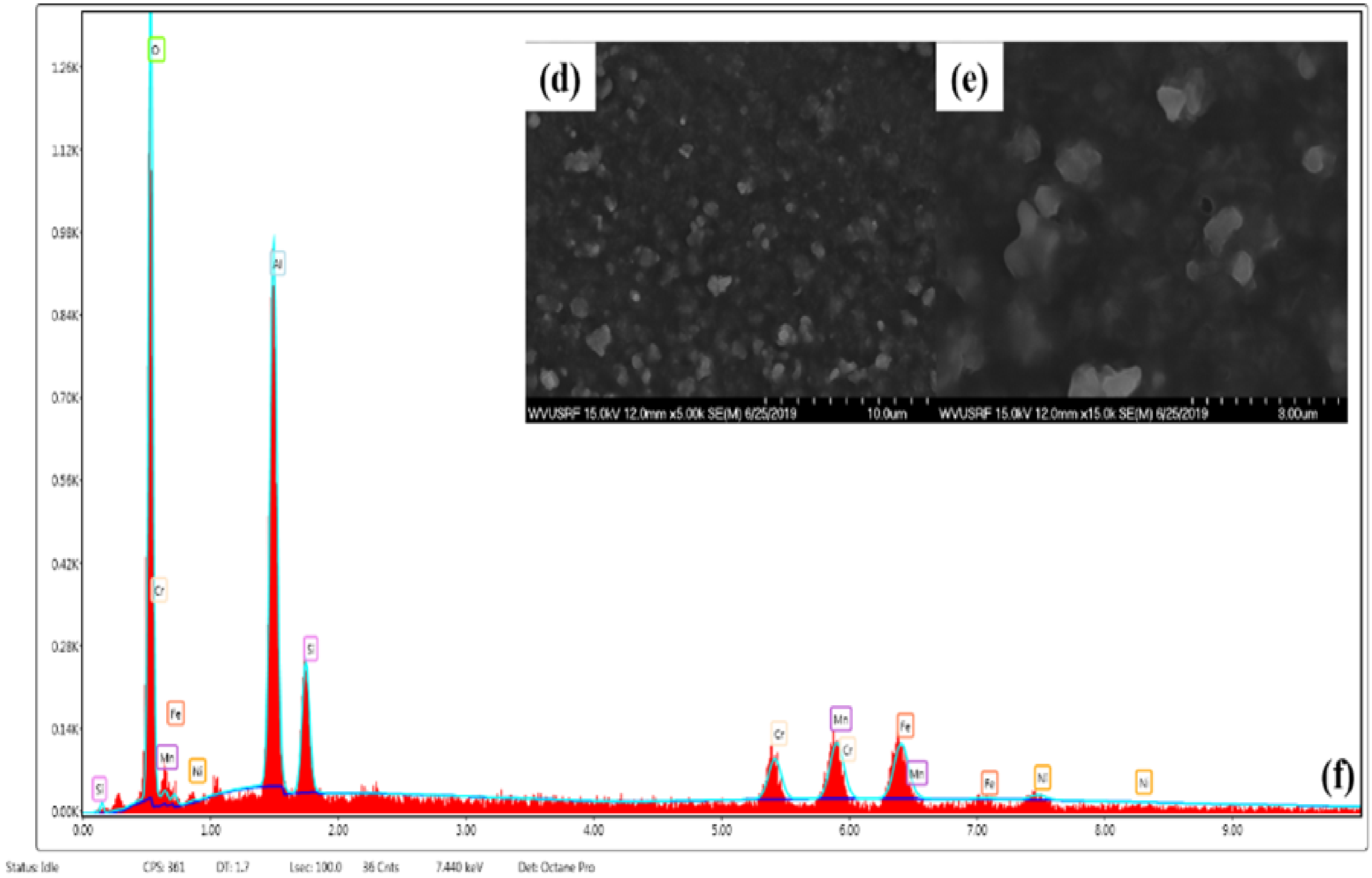
(d) is the corresponding EDS spectrum of area ②, (f) is the corresponding EDS spectrum of (e)

OC5 in 10% H_2O at 800 °C for 5000 hours



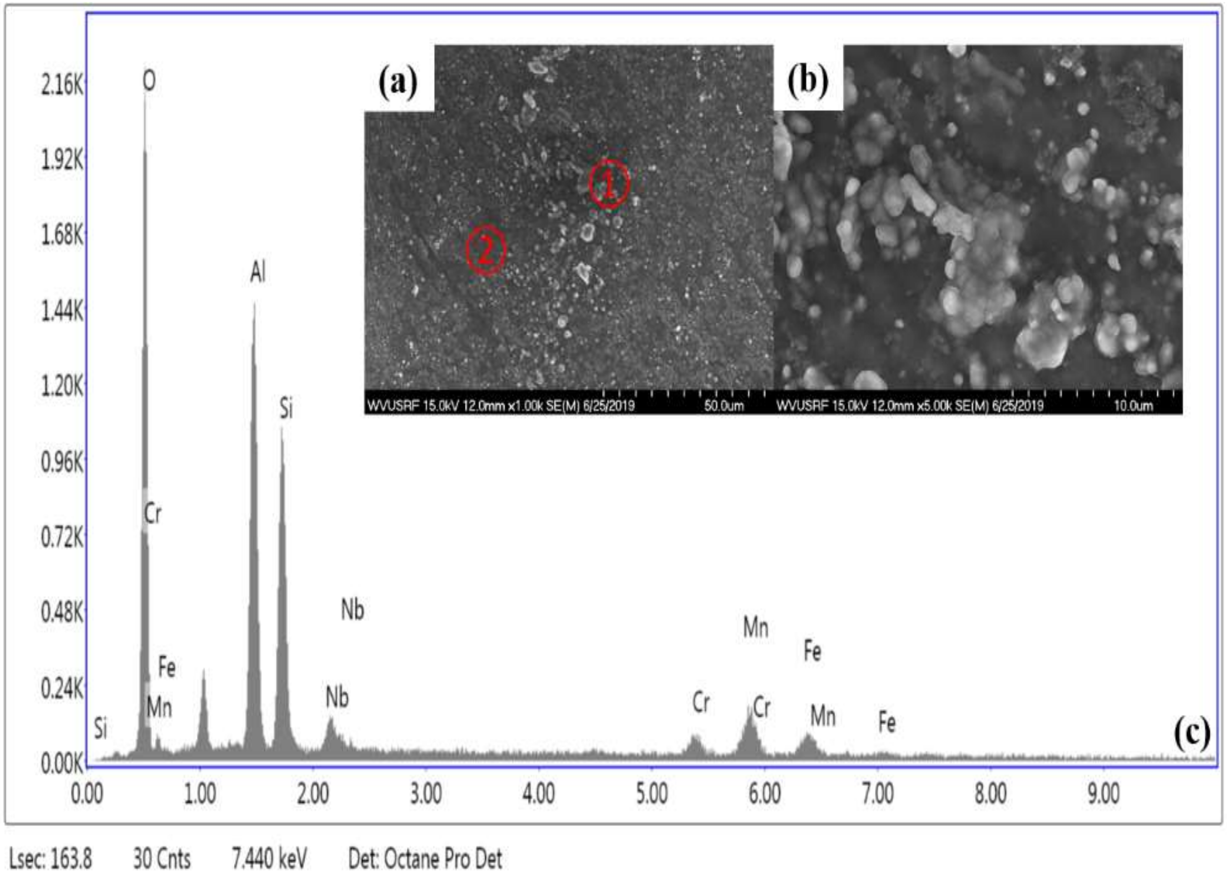
(a) Microstructural analysis of OC5 tested in 10% H_2O at 800 °C for 5000 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b)

OC5 in 10% H_2O at 800 °C for 5000 hours



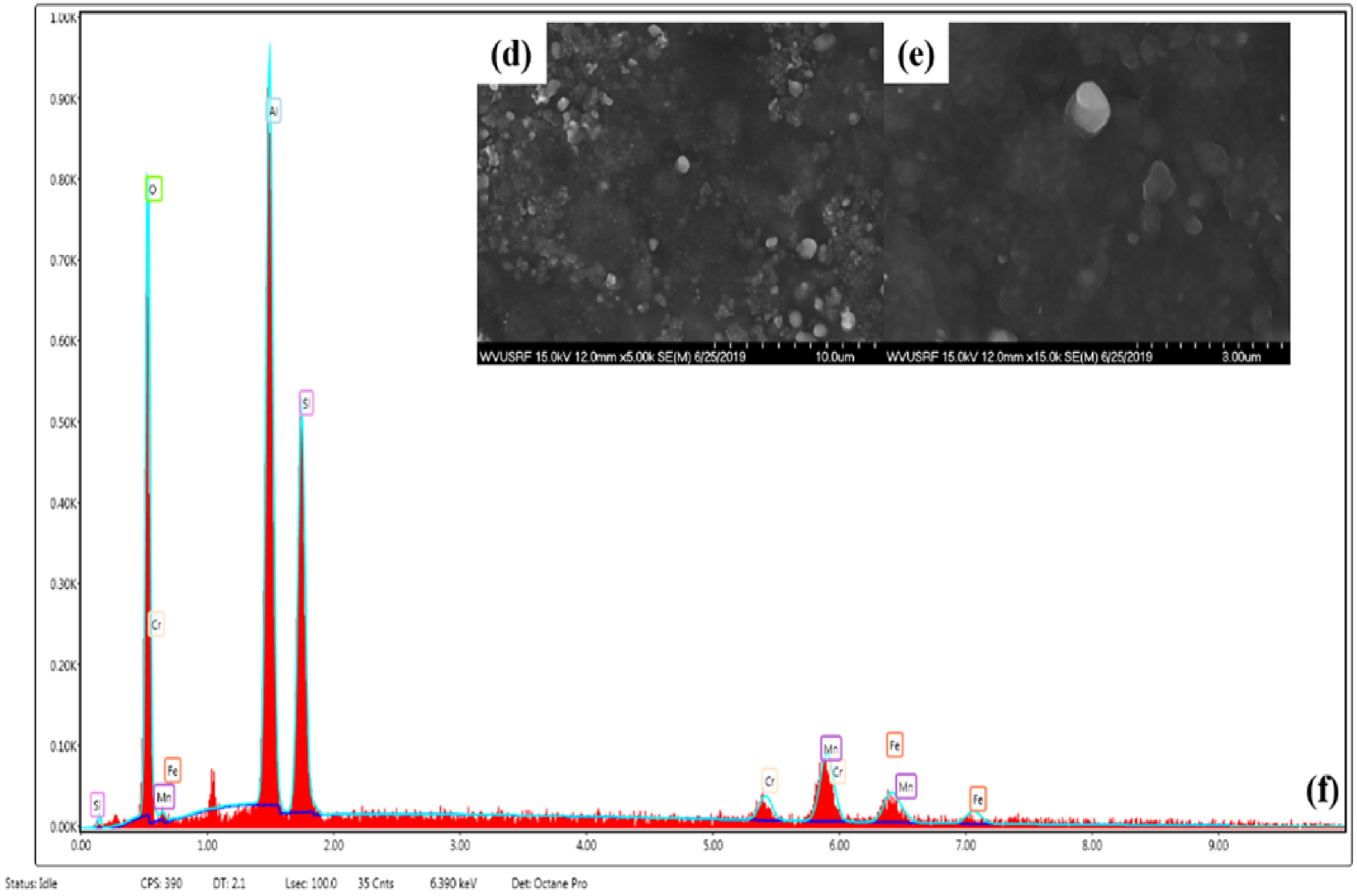
(d,e) are the high-magnification images of area ②, (f) is the corresponding EDS spectrum of (e).

MOD in 10% H_2O at 800 °C for 5000 hours



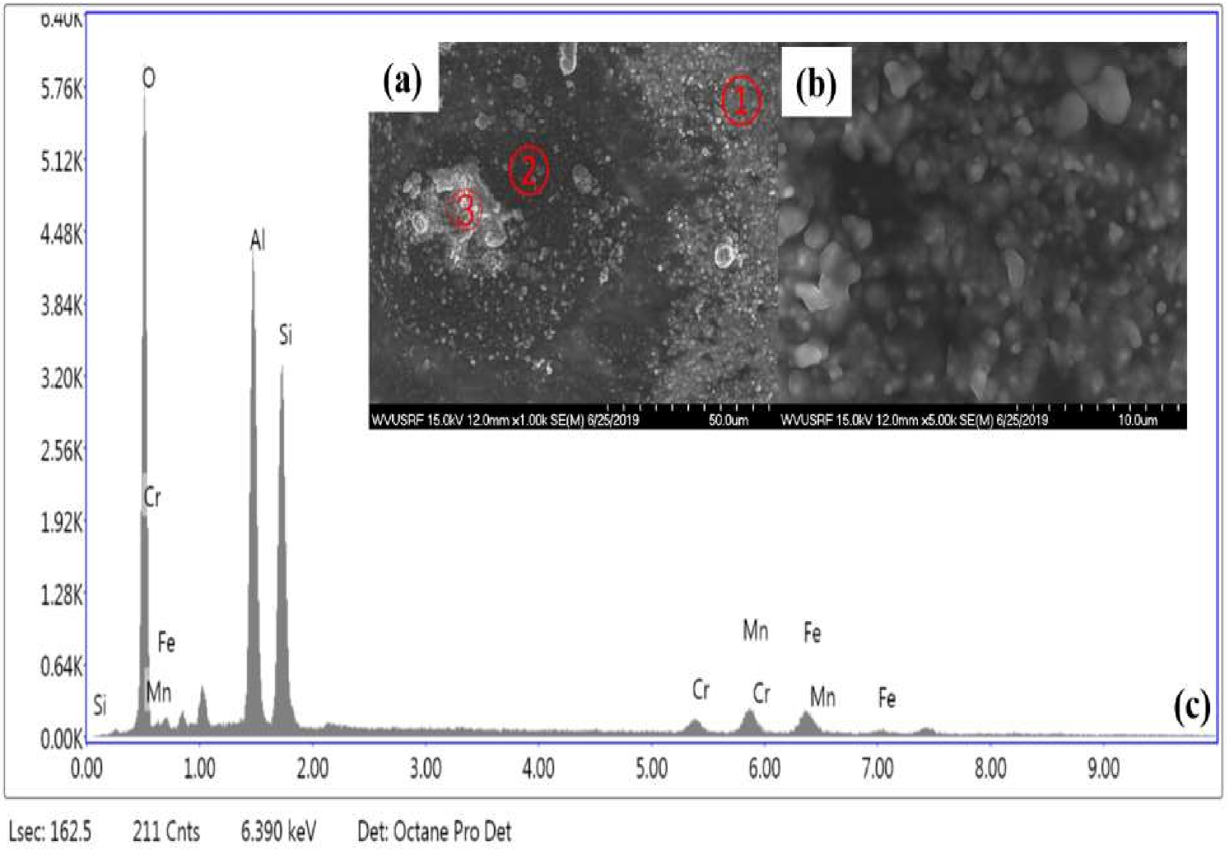
(a) Microstructural analysis of MOD tested in 10% H_2O at 800 °C for 5000 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b)

MOD in 10% H_2O at 800 °C for 5000 hours



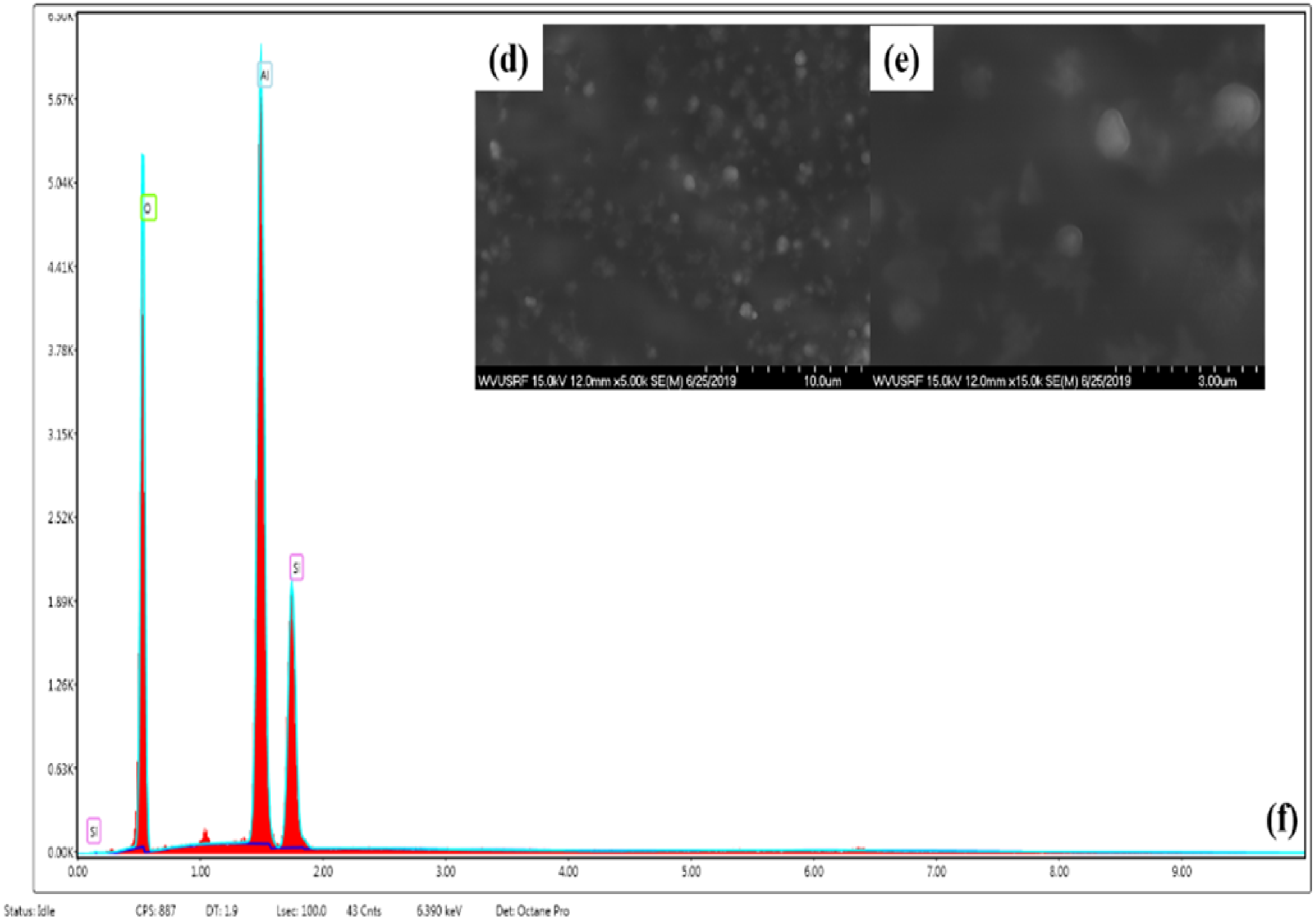
(d,e) are the high-magnification images of area ②, (f) is the corresponding EDS spectrum of (e).

OC11 in 10% H_2O at 800 °C for 5000 hours



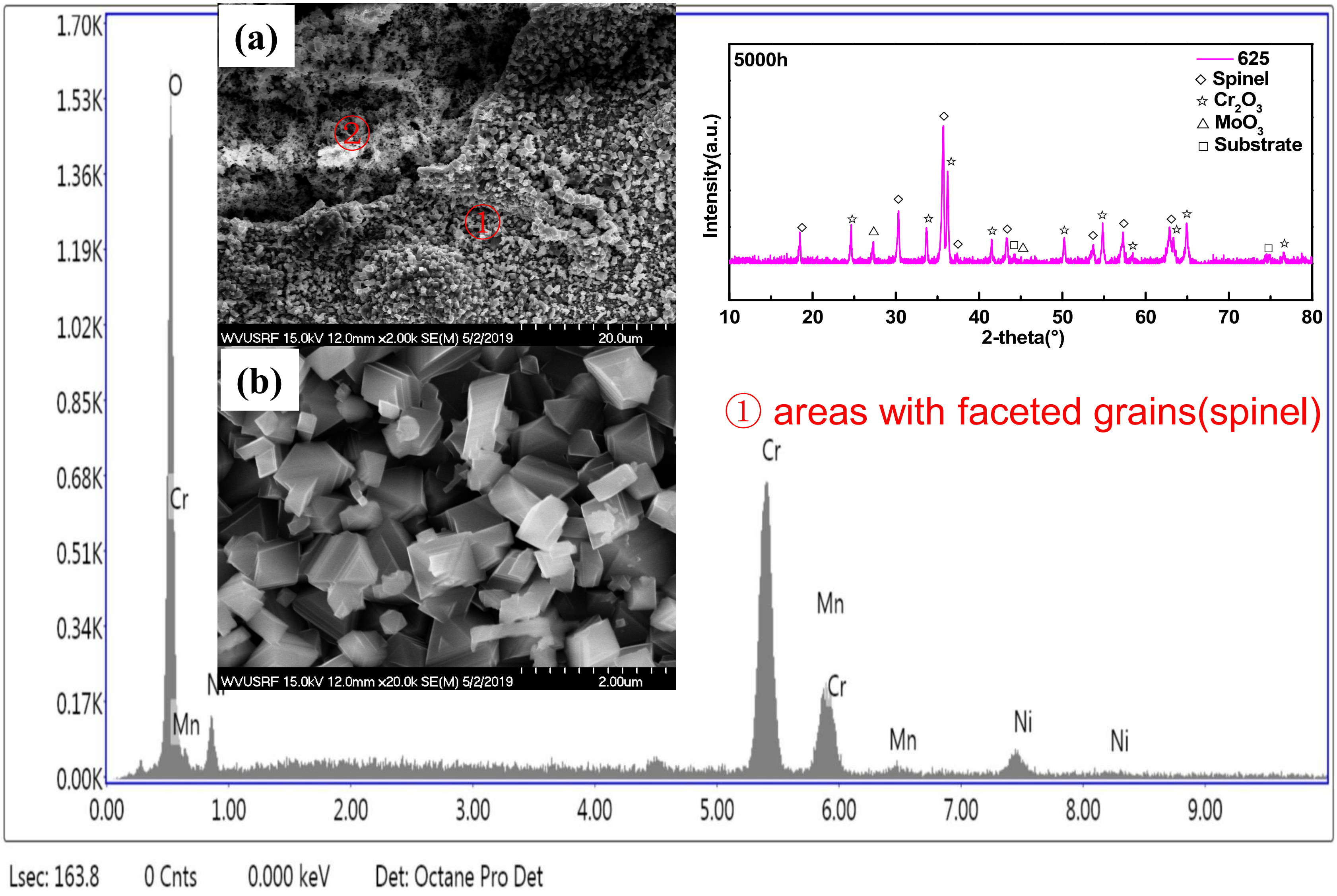
(a) Microstructural analysis of OC11 tested in 10% H_2O at 800 °C for 5000 hours, (b) the high-magnification image of area ①, (c) the corresponding EDS spectrum of (b)

OC11 in 10% H_2O at 800 °C for 5000 hours



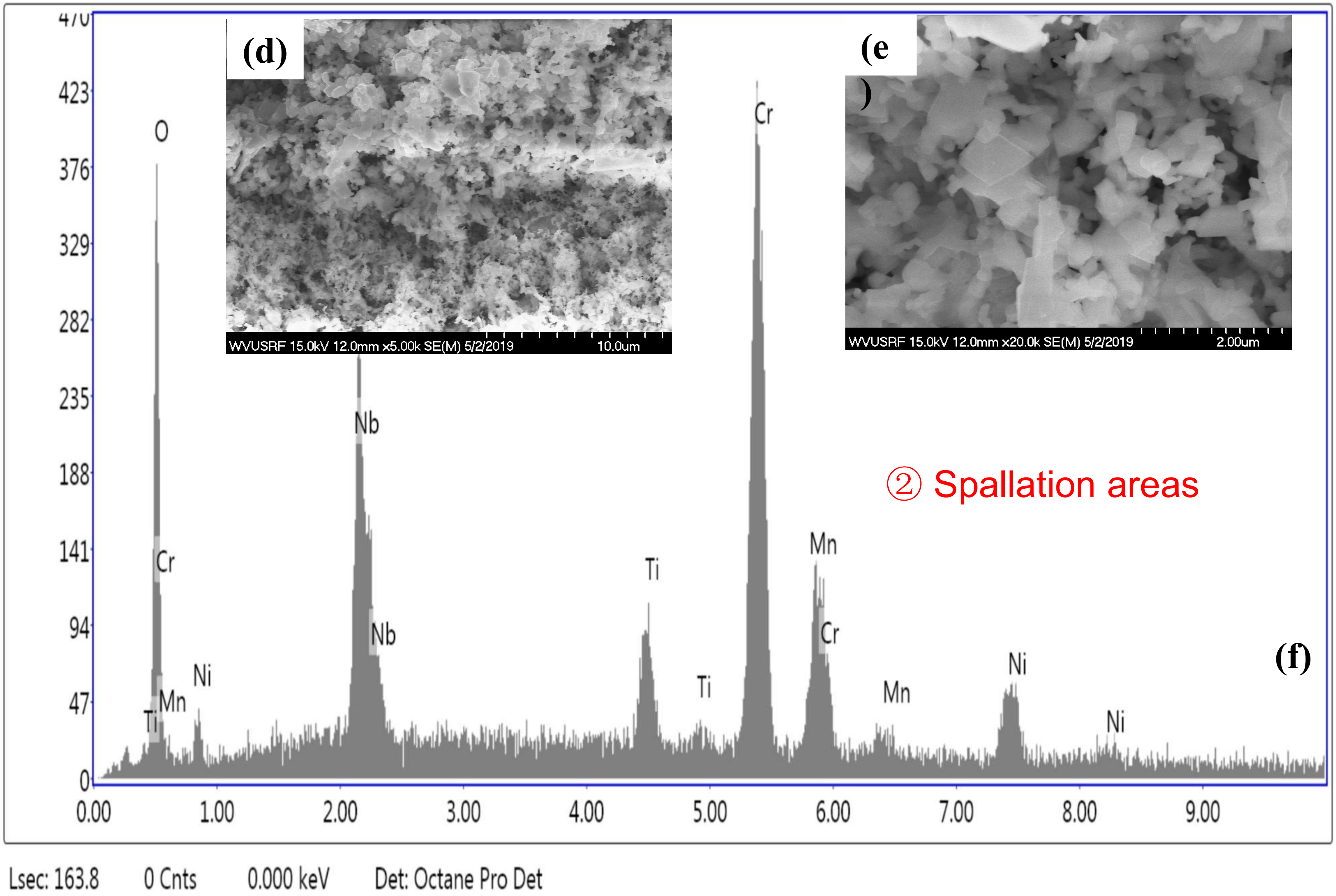
(d,e) the high-magnification images of area ②, (f) the corresponding EDS spectrum of (e),

Alloy 625 in 10% H_2O at 900°C for 5000 hours



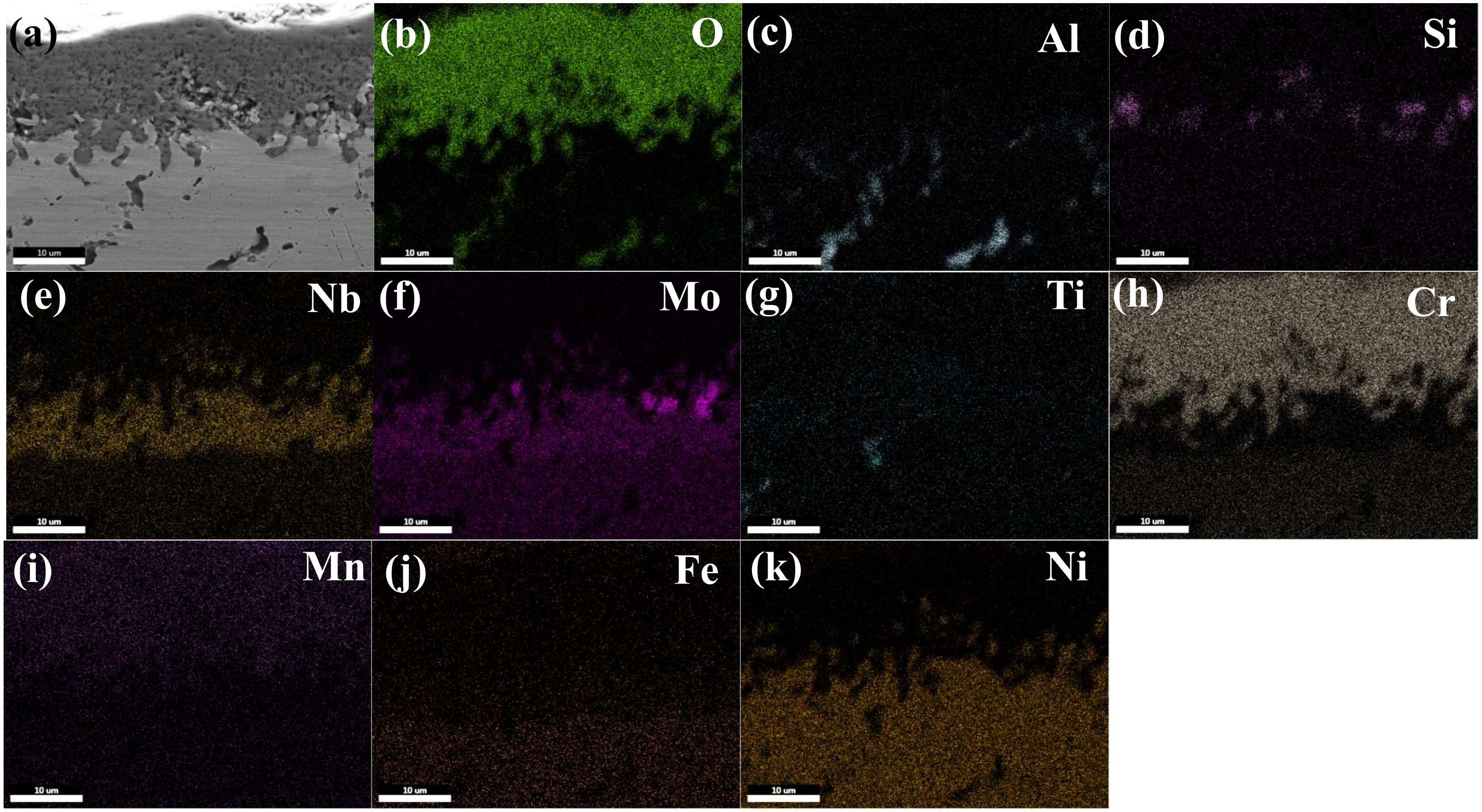
① areas with faceted grains(spinel)

Alloy 625 in 10% H_2O at 900°C for 5000 hours



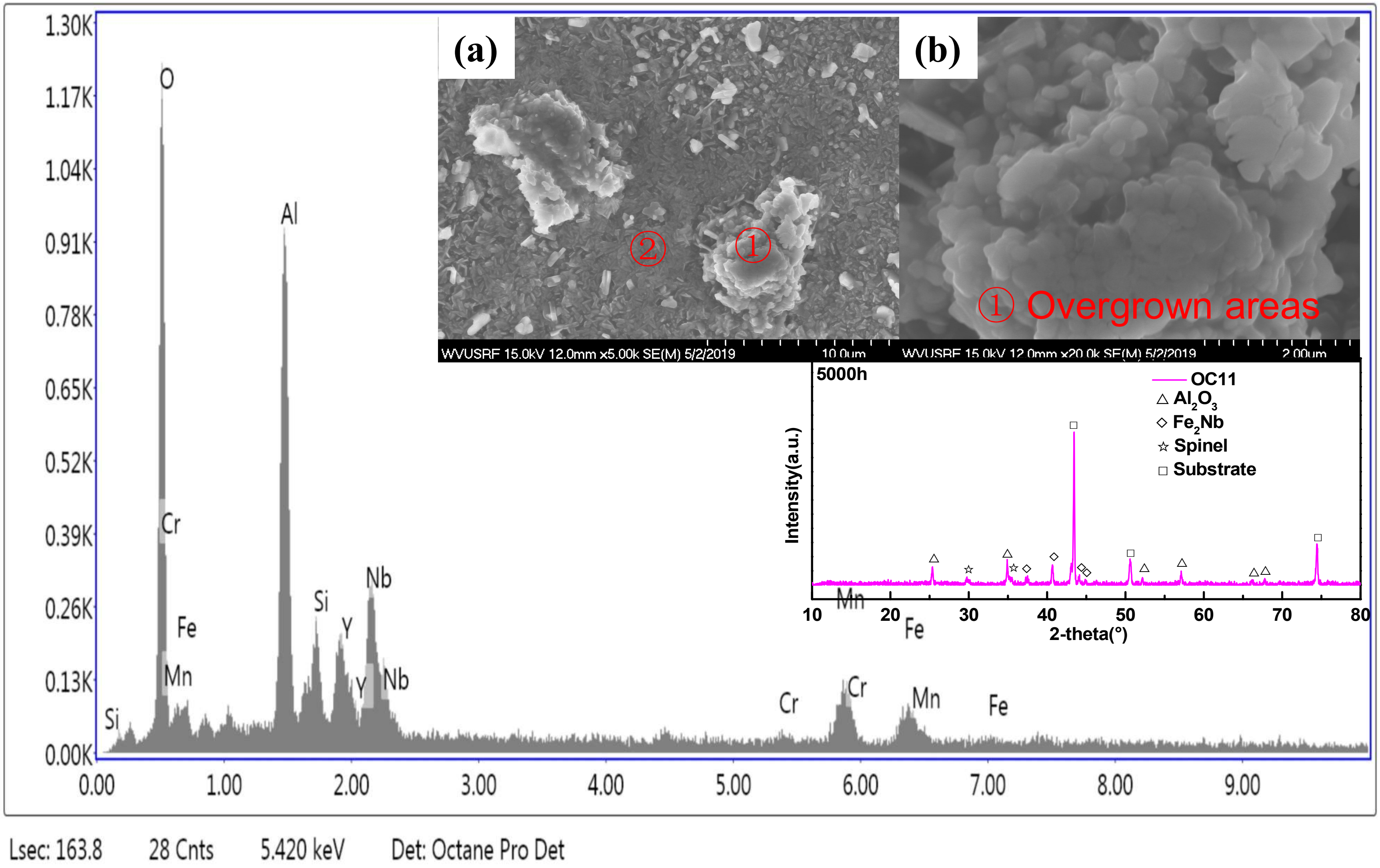
② Spallation areas

Alloy 625 in 10% H_2O at 900°C for 5000 hours

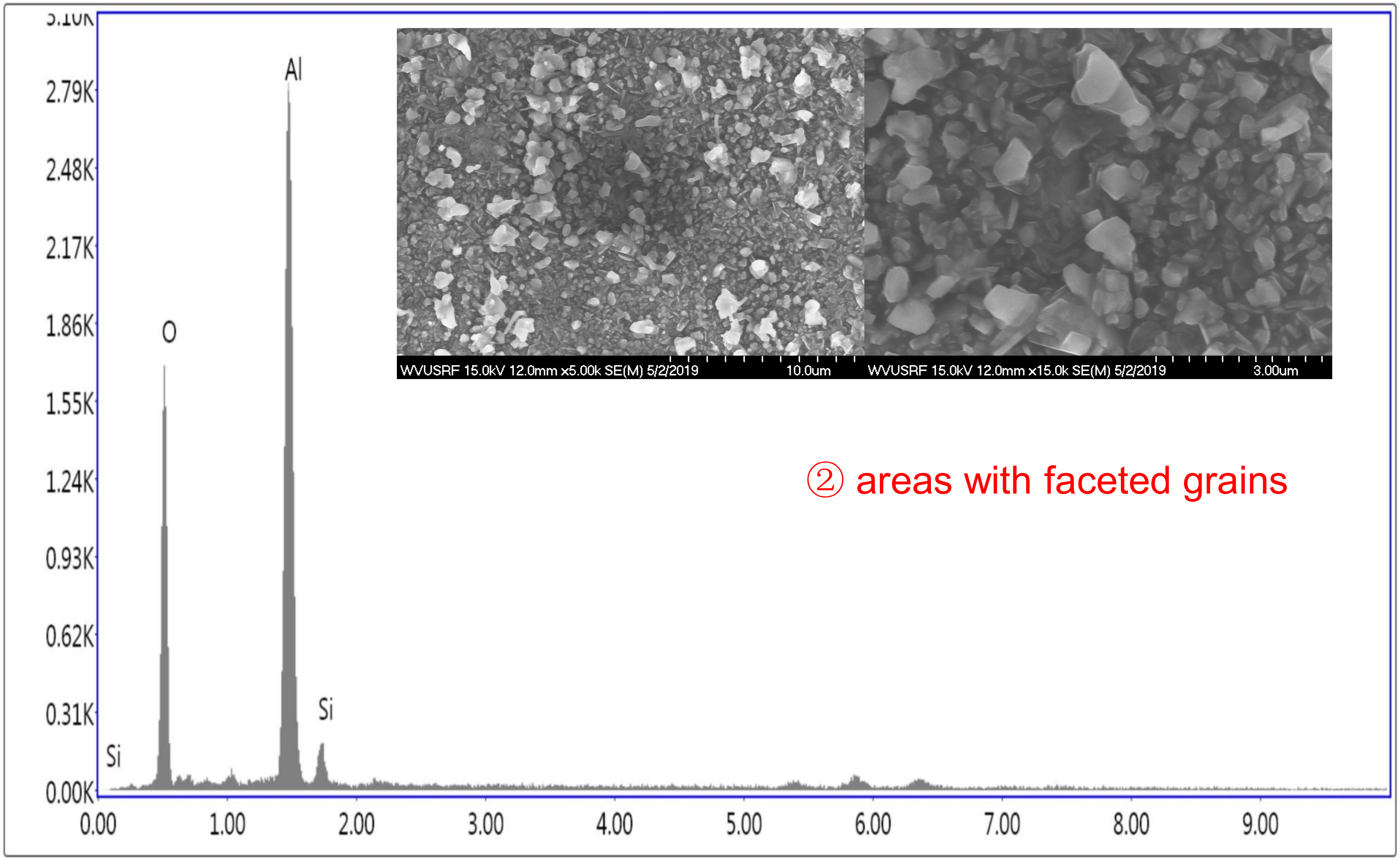


- Thickness of the scale is about 20 microns which consisted of two layers
- The outer layer consists mainly of Cr and Mn, also with a few Fe and Al, and the inner scale shows especially high content of Si.

OC11 in 10% H_2O at 900 ºC for 5000 hours.



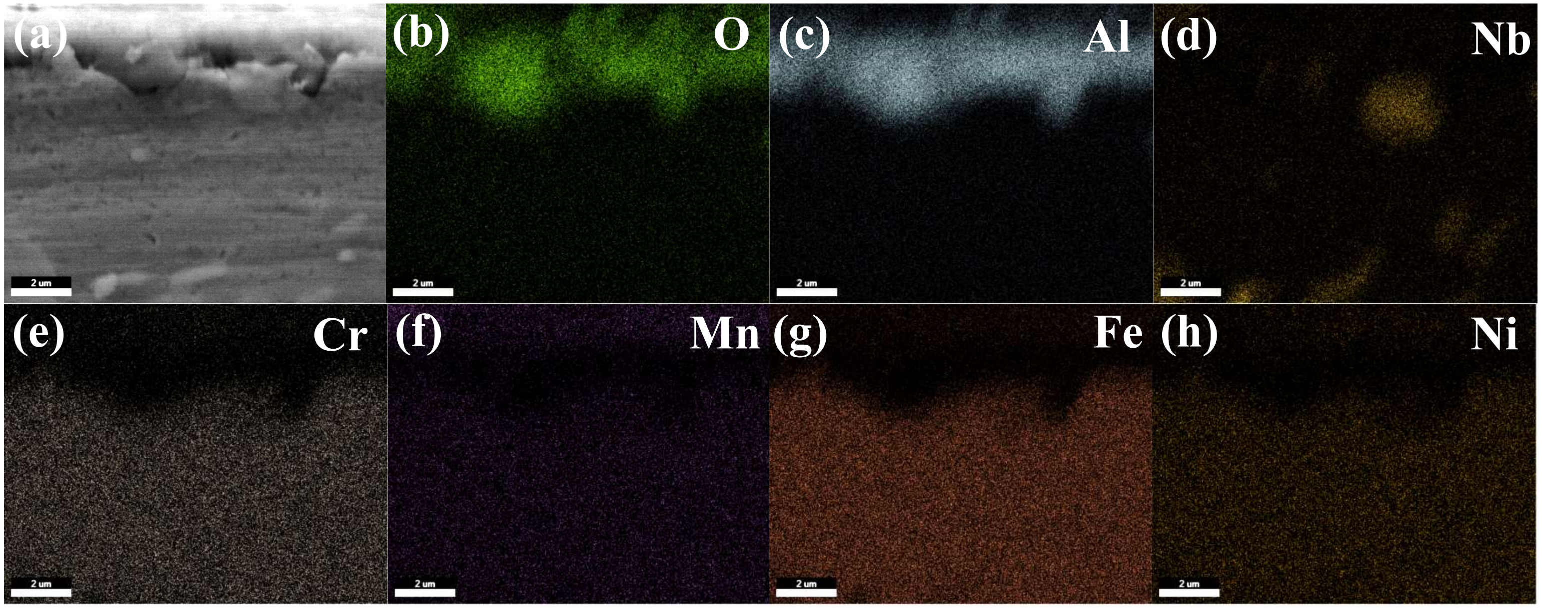
OC11 in 10% H_2O at 900 ºC for 5000 hours.



② areas with faceted grains

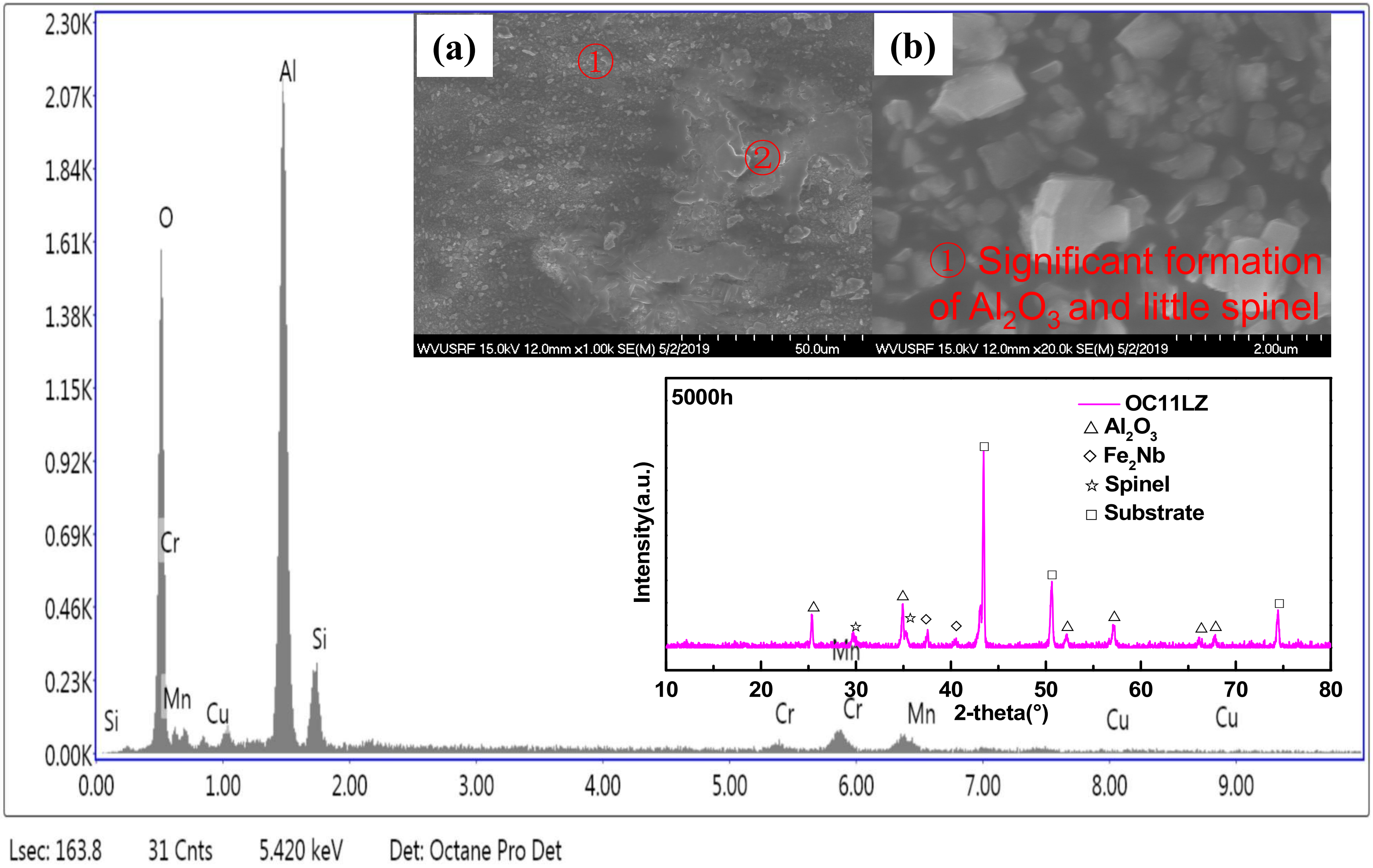
Lsec: 163.8 0 Cnts 0.000 keV Det: Octane Pro Det

OC11 in 10% H_2O at 900 °C for 5000 hours.



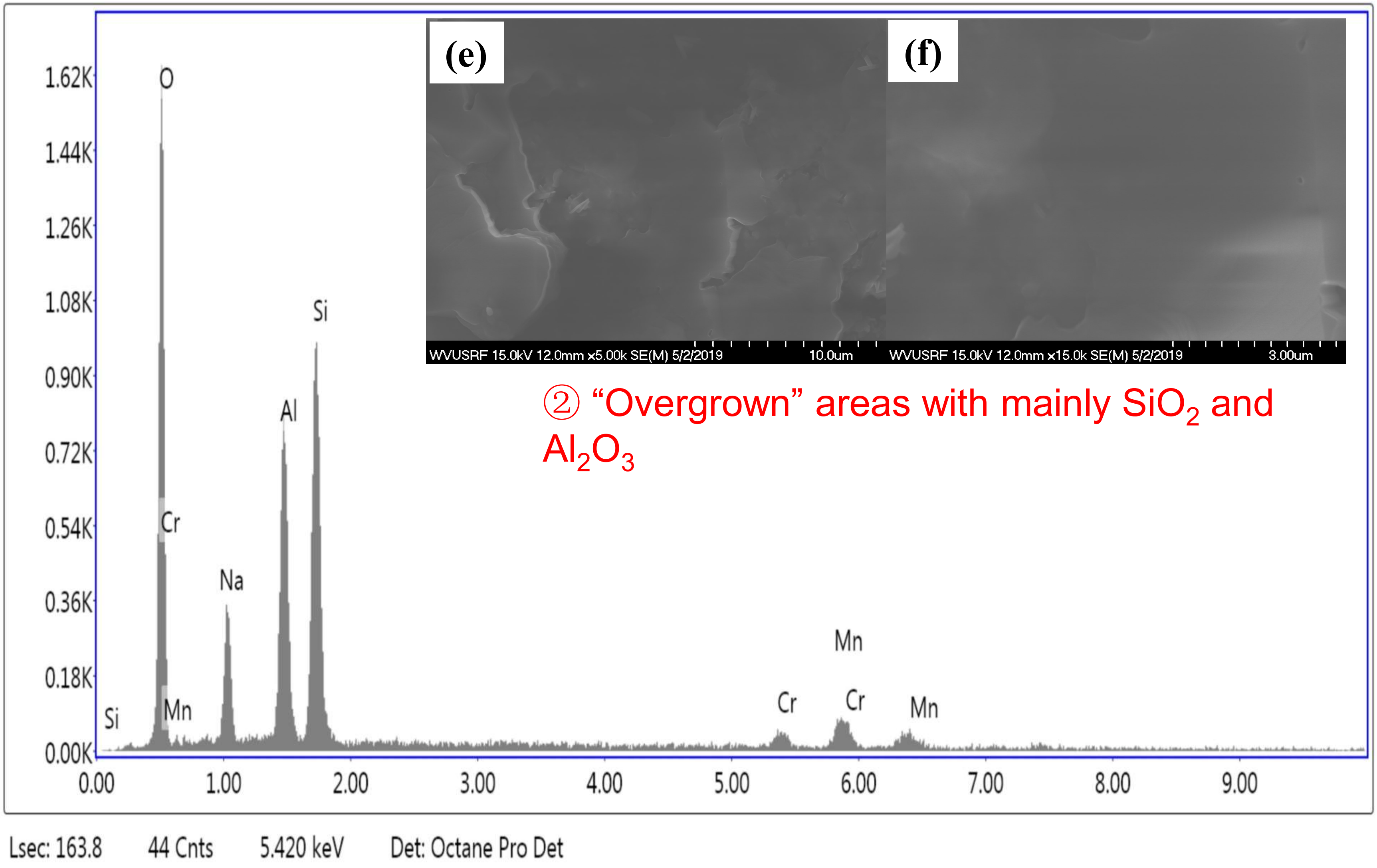
- A dense and continuous Al_2O_3 layer (~3 μm)can be formed.
- The outer Fe-Mn-Cr-Al-Ni rich oxide and inner Al_2O_3 layer are well arranged and distinguished.

OC11-LZ in 10% H_2O at 900°C for 5000 hours



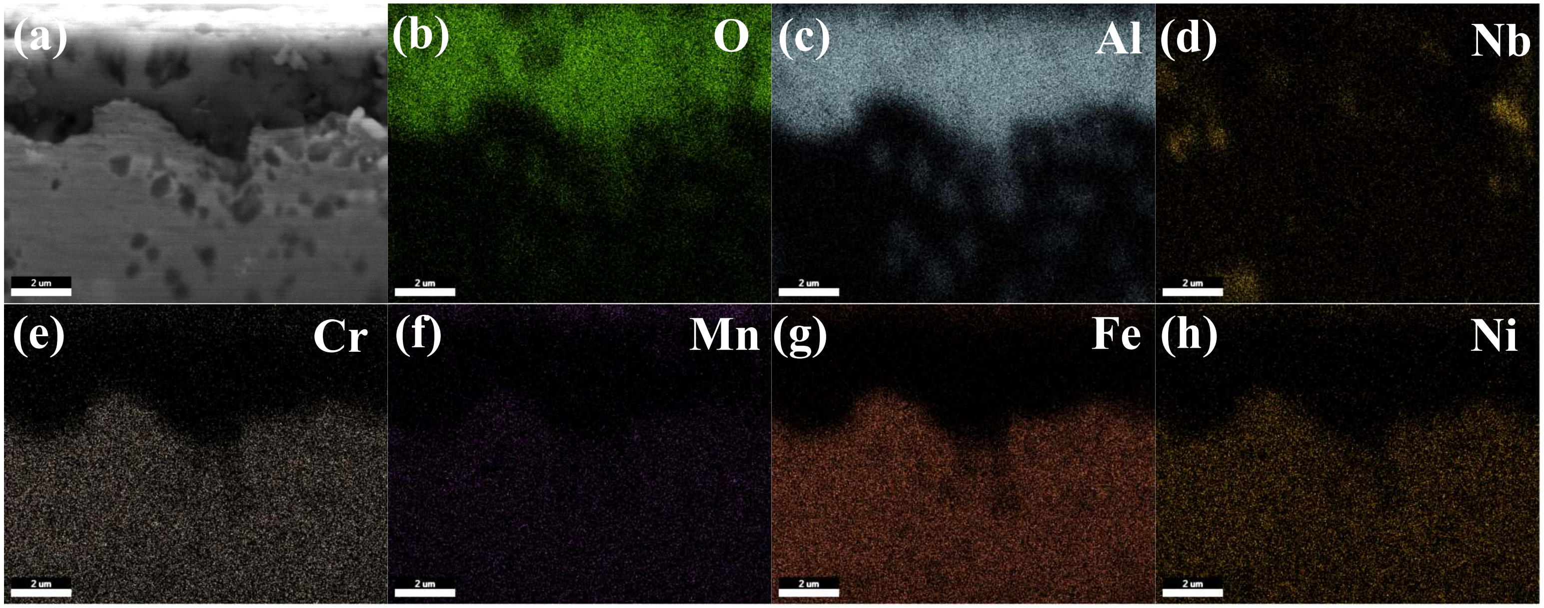
① Significant formation of Al_2O_3 and little spinel

OC11-LZ in 10% H_2O at 900°C for 5000 hours



② “Overgrown” areas with mainly SiO_2 and Al_2O_3

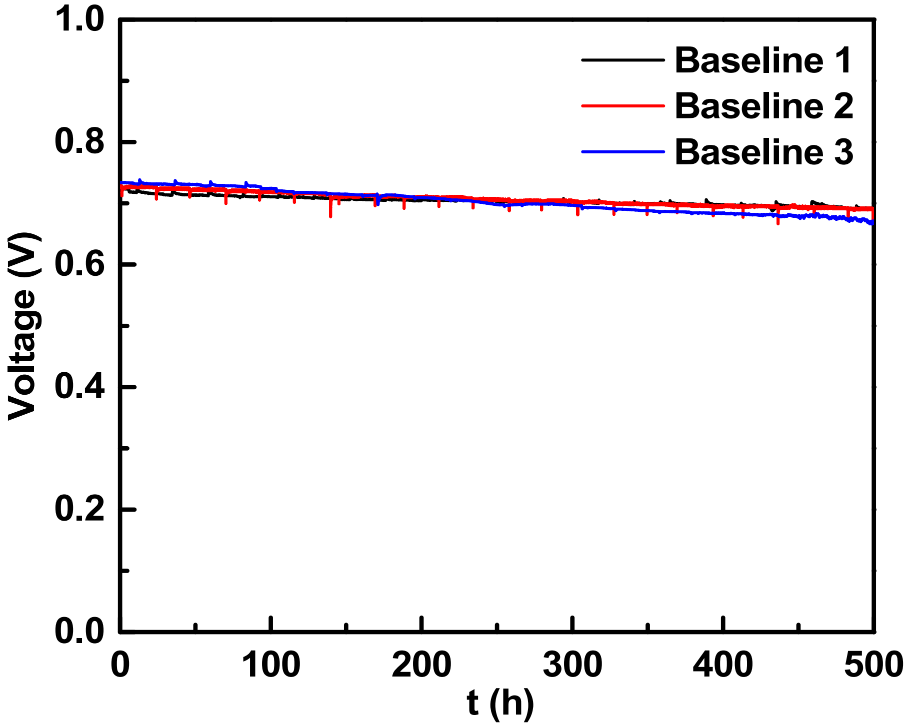
OC11-LZ in 10% H_2O at 900°C for 5000 hours



- For OC11LZ alloy, the continuum alumina layer (3-5 μm)can also be formed.
- The outer layer consists mainly of Fe-Mn-Cr-Al-Ni rich oxide and an inner Al_2O_3 layer.

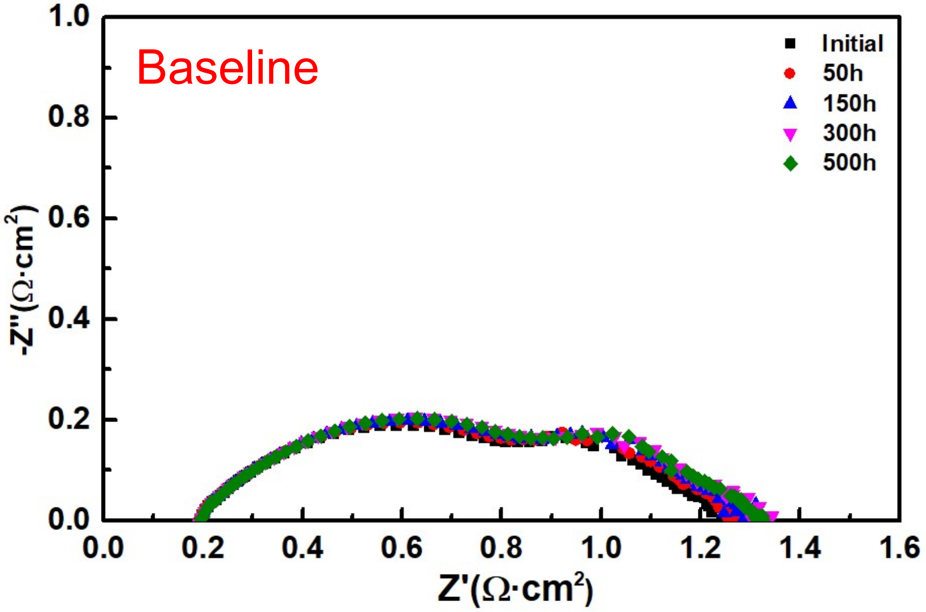
Cell Degradation due to Cr-poisoning

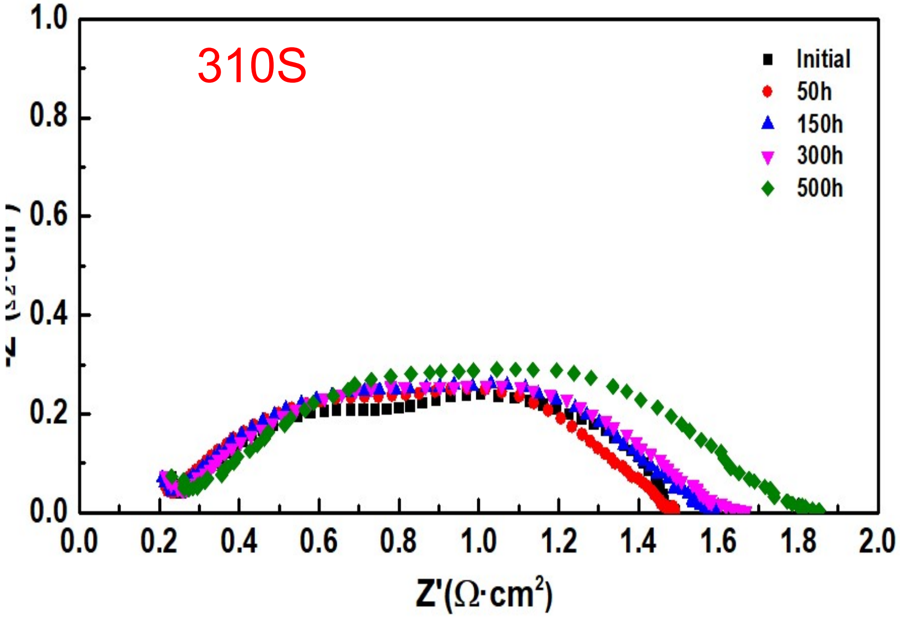
Baseline

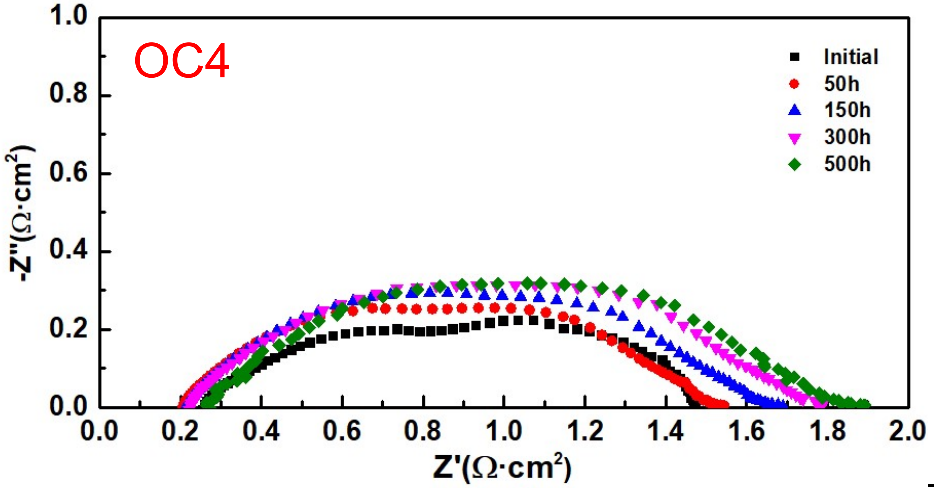


The repeatability of the cell is good, and the degradation rate is 5.08%±1.61%/500h

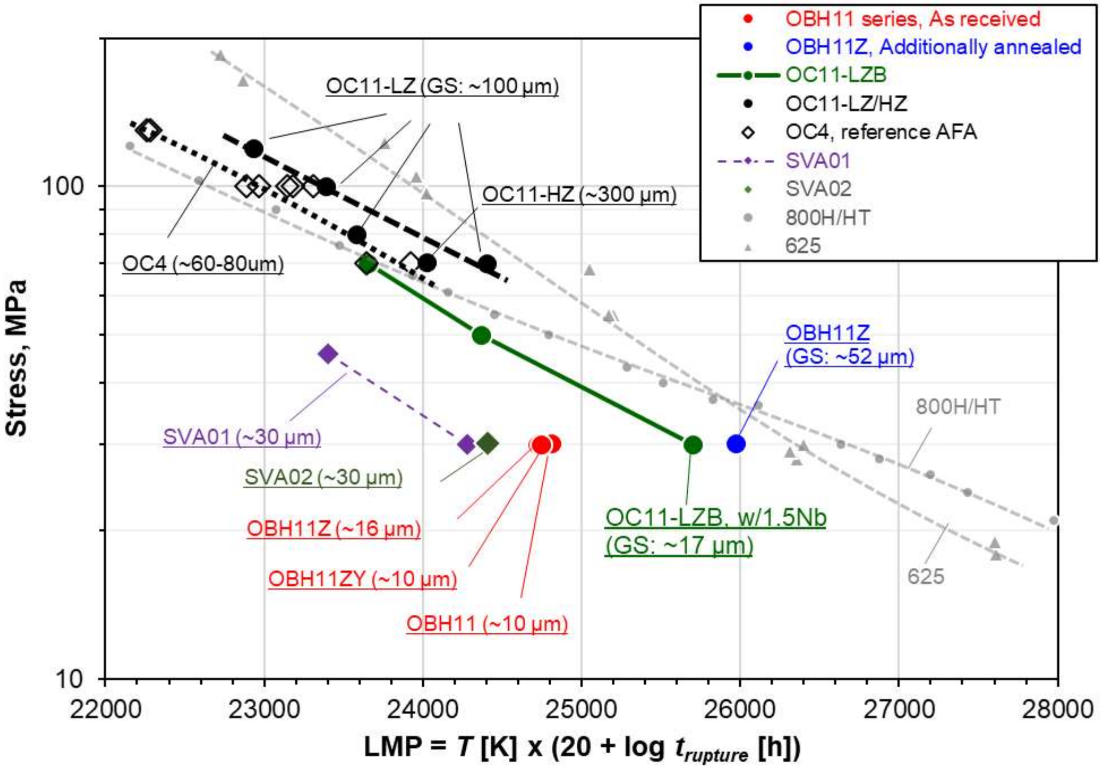
Cell Degradation due to Cr-poisoning







Creep Properties of AFA Alloys



- ➢ The creep-rupture performance is sensitive to the grain size.
- ➢ The coarser grains the better creep performance.

Manufacturing of BOP Components with AFA


[redacted]

(a) Coil No.1


[redacted]

(b) Coil No.2

- 300 mm wide sheets and foils of four thicknesses were fully processed

Summary To-date

- Cr evaporation amounts from commercial alloy were nearly 30 times higher than AFA alloys after 5000h test.
- AFA alloys exhibited higher oxidation resistance than commercial alloys, and the continuous alumina layer formed on surface of AFA alloys still bonded well to the substrate after 5000h test.
- The degradation rate of the cells tested with OC4 is lower than that tested with commercial alloys, and the EIS and DRT analysis indicated that most of the degradation was attributed to the cathodes.
- The creep-rupture performance in the OC11 composition range under these conditions is sensitive to the grain size, and the coarser grains the better creep performance.
- 600 Kg each heats were fully processed using production machinery to make 300 mm wide sheets and foils of four thicknesses 1.5, 1.0, 0.5 and 0.2mm. Of which the most important issue was edge cracking.

Ongoing and Future Work

Industrial Development

- Alloy Manufacturing
- Processing, Welding, etc.
- Components Manufacturing, Testing
- Post Mortem Analysis

Lab-scale Research

- Long-term Cr-evaporation tests to investigate the oxidation kinetics and the Cr evaporation rate;
- Investigation on Cr-poisoning of SOFC cathode in associate with BOP materials.

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