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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

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

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

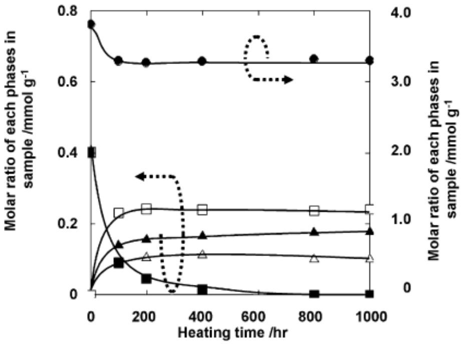
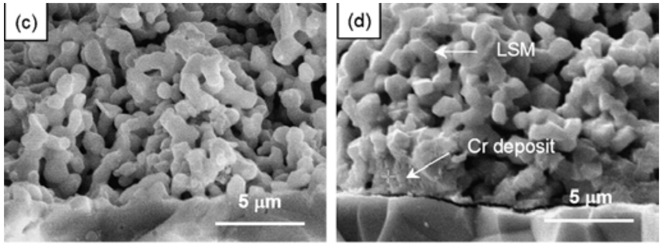
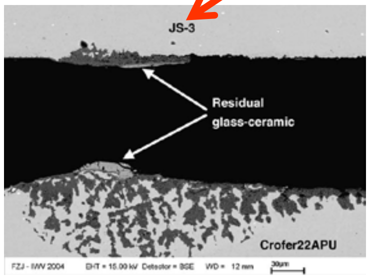


Fig. 4. Molar ratio of phases in LSCF–Cr_2O_3 mixture during heating at 1073 K for 0–1000 h: (●) LSCF, (■) Cr_2O_3, (□) $SrCrO_4$, (▲) $CoCr_2O_4$ spinel, (△) $(Fe,Cr)_2O_3$.



J. Power Sources 162 (2006) 1043–1052



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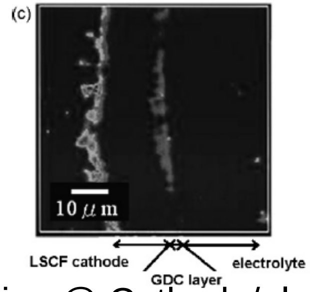


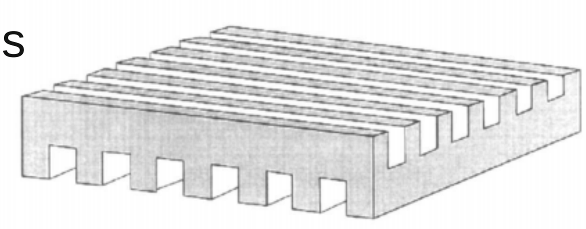
Cr-distribution @ Cathode/electrolyte Interface

Sources of Cr-Species

❑Metallic Interconnects

Ferritic chromia-forming alloys

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



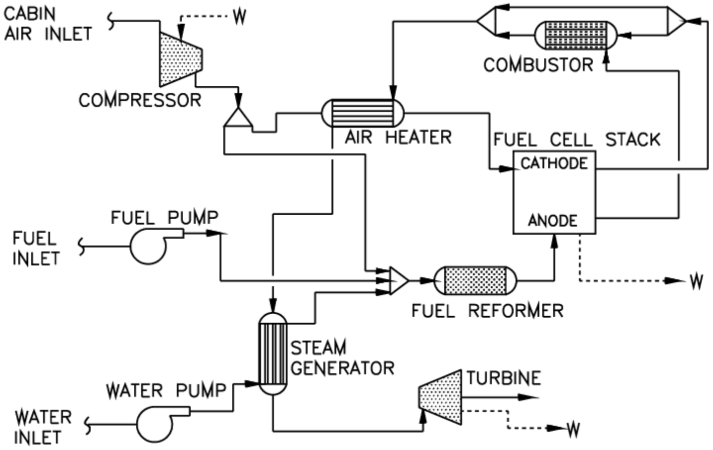
Schematic representation of an interconnect.

❑Balance of Plant components

Nickel- and iron-base austenitic and ferritic alloys

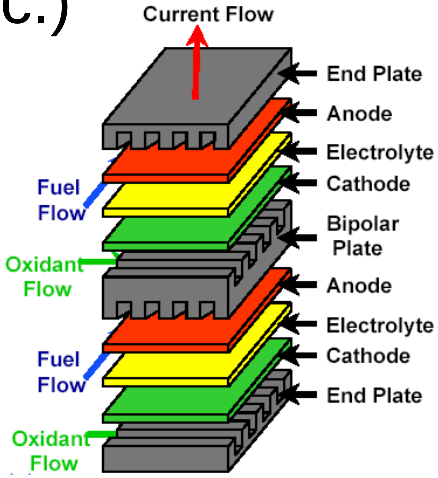
Stack manifold , air delivery tubes and high temperature heat exchangers etc.

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

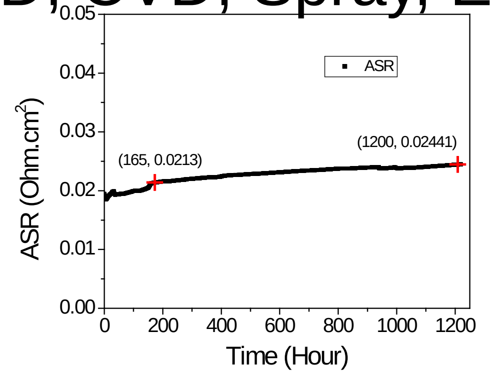


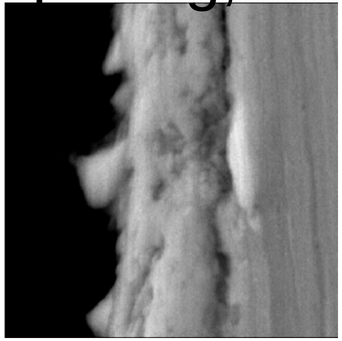
SOFC Interconnect Coatings

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



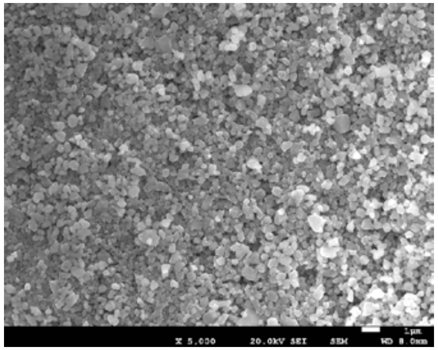
Electro plating Mn-Co

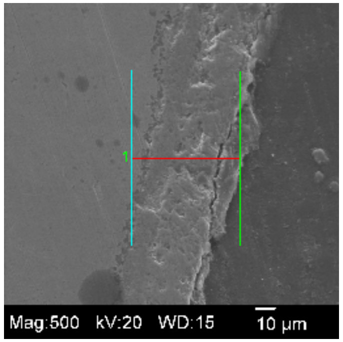




J. Wu, C. Johnson, Y. Jiang, R. Gemmen, **X. Liu***, *Electrochimica Acta (2008) 793-800*

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.

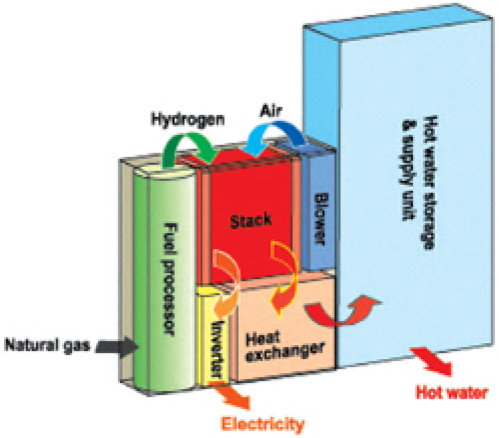
The team has published its research findings in two peer-reviewed journals, and a patent disclosure of the process also has been filed. In addition, team members report exceptionally positive feedback from the report on the coating presented at the 2008 MS&T Conference last October.

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.

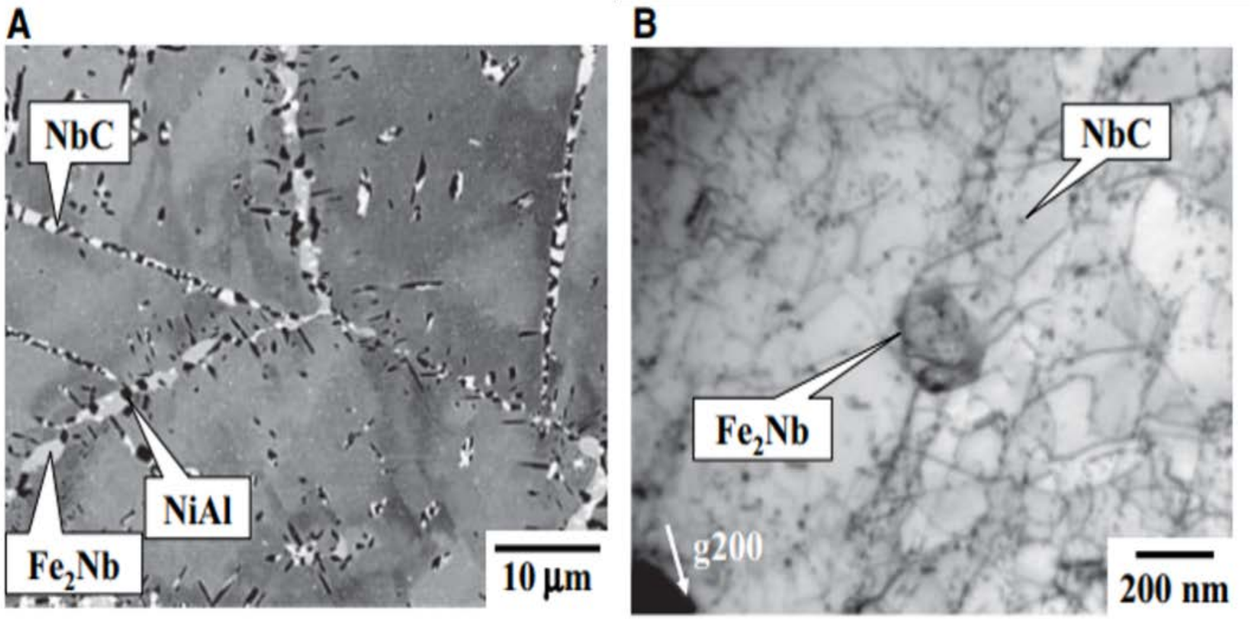
Project Technical Approaches

Developing Cost-Effective Alumina Forming Austenitic Stainless Steels (AFA), to replace Austenitic Stainless Steel 316L and Ni-base Superalloy Inconel 625, for Key **Balance of Plant (BOP) components**, to minimize Cr-Poisoning of SOFC Cathode



Compression Plate in BOP

Microstructure of AFA Alloys

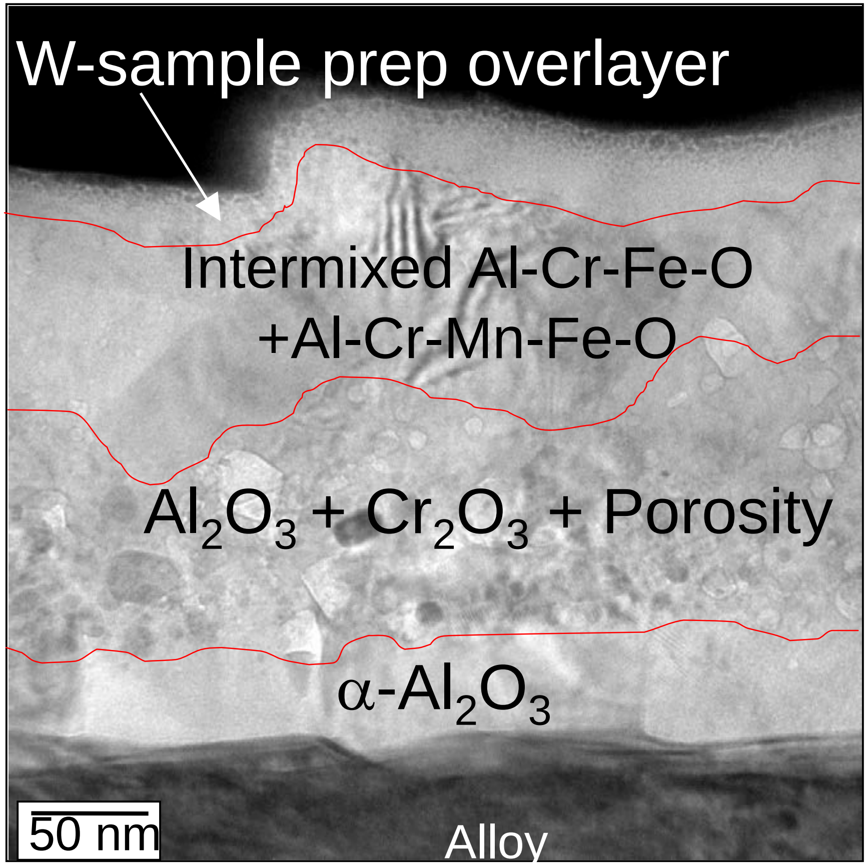


TEM bright-field microstructure of AFA alloy (Fe-20Ni-14Cr-2.5Al-2Mn-2.5Mo-1Nb) after creep testing for 2200 hours at 750° C and 100 MPa

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

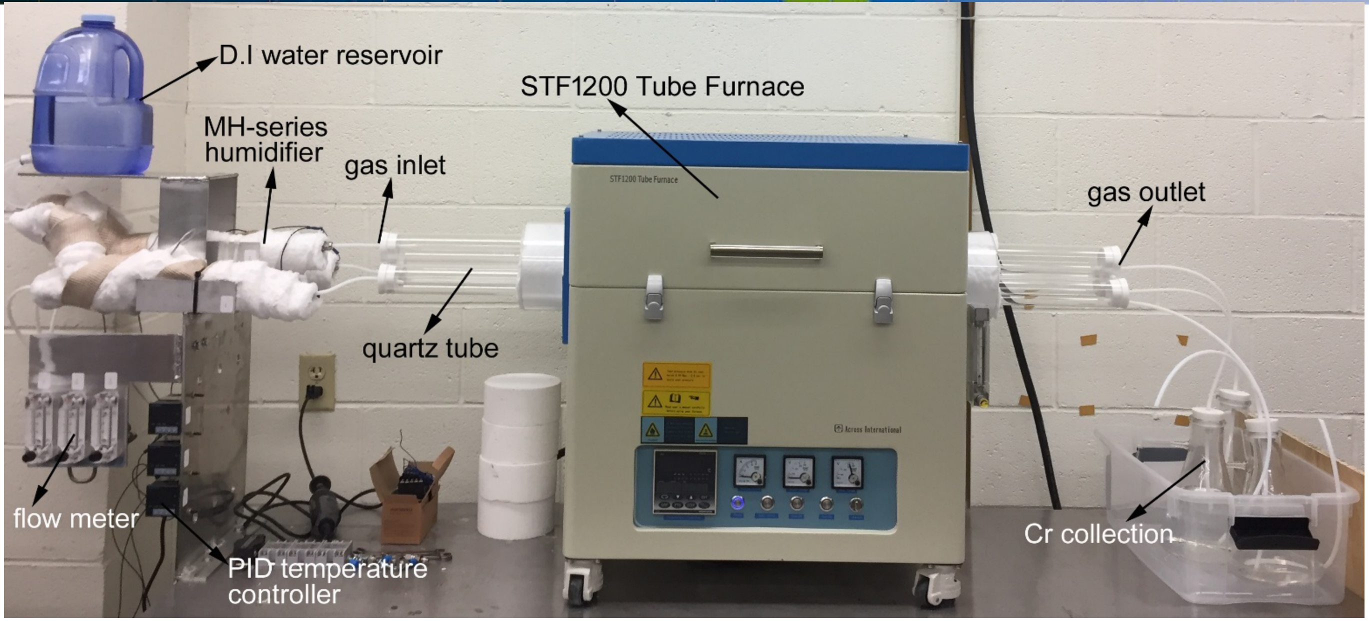
Project Objectives – Phase I

- 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 ^{o}C[*]	√	√	√	√	–	–	√	√
850 ^{o}C	√			√			—	
900 ^{o}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 ^{o}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 ^{o}C	1.09×10^{-11}			*	*	—	2.9×10^{-10}	
900 ^{o}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 Cr-release Testing to understand the kinetics
- 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

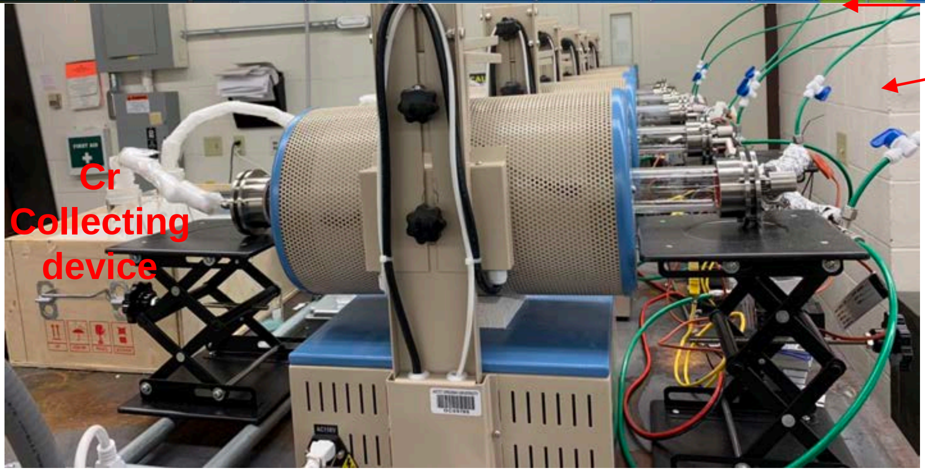
Material Compositions

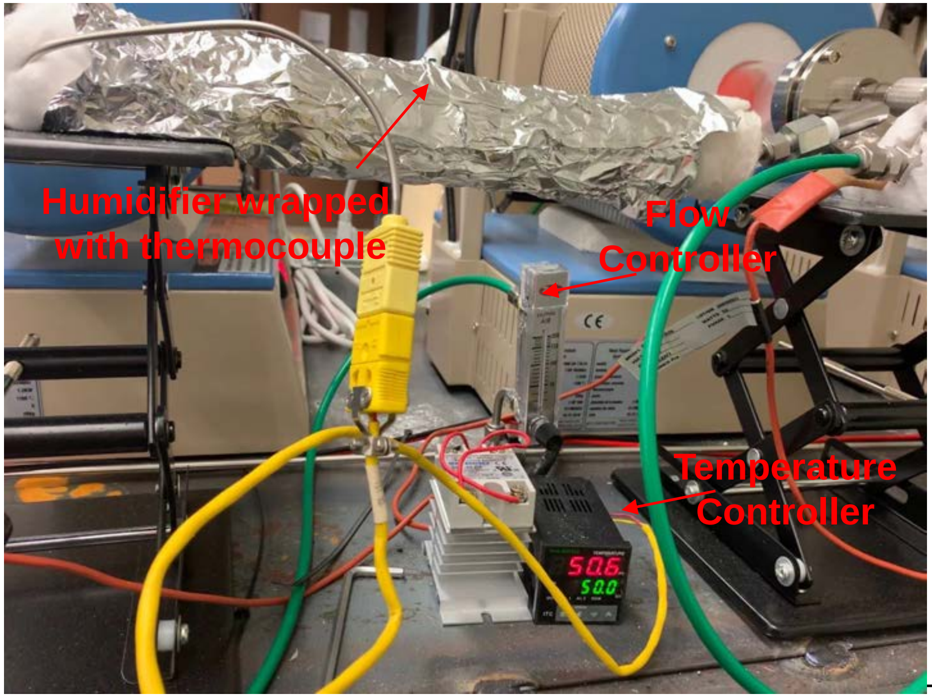
Alloy	Fe	**Ni**	**Cr**	**Al**	**Nb**	Mn	Si	Mo	W	**C**	B	**other**
AFA for ≤ 800°C use												
MOD 2 OCD	51	**25**	**14**	**4**	**1**	2	0.15	2	0	**0.15**	0.01	0.5Cu
OC5	51	**25**	**14**	**3**	**1**	2	0.15	2	1	**0.1**	0.01	0.5Cu
OC4	49	**25**	**14**	**3.5**	**2.5**	2	0.15	2	1	**0.1**	0.01	0.5Cu
AFA 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

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

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}				
	OC4	$<2.25 \times 10^{-12}$	$<3.61 \times 10^{-12}$	$<3.44 \times 10^{-12}$	$<3.83 \times 10^{-12}$	$<3.67 \times 10^{-12}$	$<3.73 \times 10^{-12}$				
	OC5	2.8×10^{-12}	$<3.17 \times 10^{-12}$	$<3.04 \times 10^{-12}$	$<2.98 \times 10^{-12}$	$<3.15 \times 10^{-12}$	$<3.05 \times 10^{-12}$				
	MOD	4.31×10^{-12}	$<3.31 \times 10^{-12}$	$<3.23 \times 10^{-12}$	$<2.84 \times 10^{-12}$	$<3.17 \times 10^{-12}$	$<3.23 \times 10^{-12}$				
	OC11	6.37×10^{-12}	$<8.38 \times 10^{-12}$	$<3.66 \times 10^{-12}$	$<3.24 \times 10^{-12}$	$<2.95 \times 10^{-12}$	$<3.15 \times 10^{-12}$				
	OC11-LZ	4.14×10^{-12}	$<3.15 \times 10^{-12}$	$<3.53 \times 10^{-12}$	$<3.24 \times 10^{-12}$	$<3.40 \times 10^{-12}$	$<3.35 \times 10^{-12}$				
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}		
	OC11	1.29×10^{-11}	$<7.6 \times 10^{-12}$	$<7.9 \times 10^{-12}$	$<7.38 \times 10^{-12}$	$<7.56 \times 10^{-12}$	$<7.67 \times 10^{-12}$	$<7.53 \times 10^{-12}$	$<7.79 \times 10^{-12}$		
	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}		

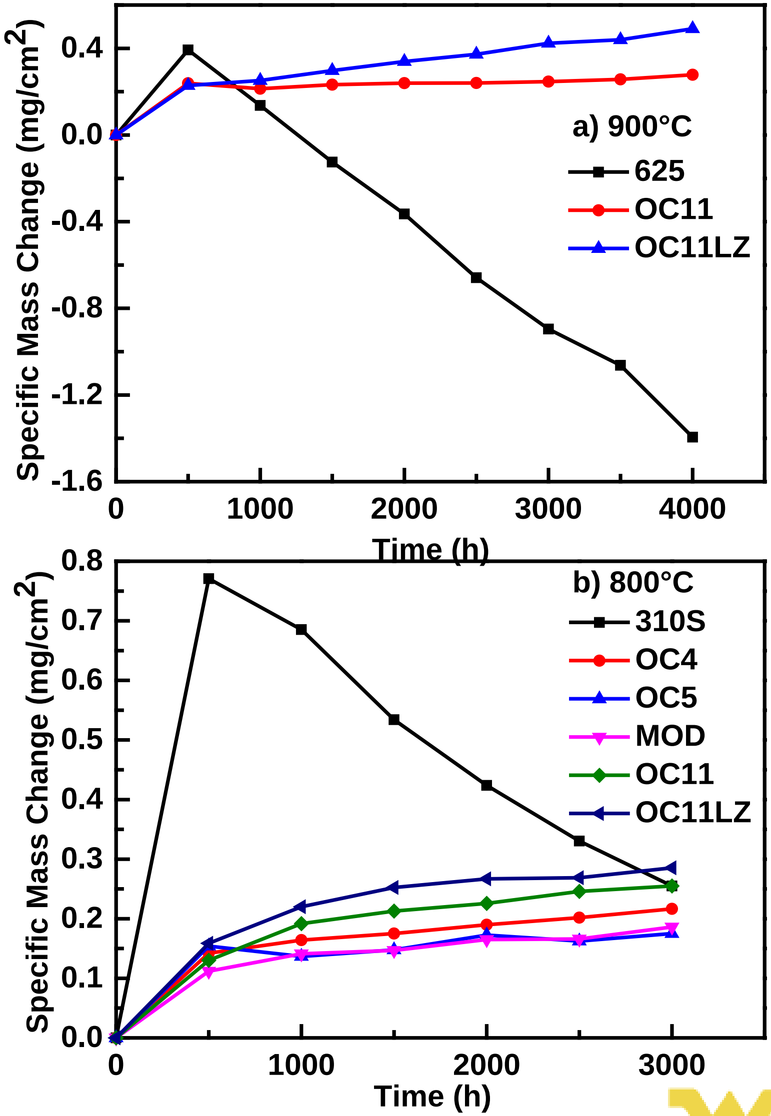
Oxidation Kinetics Analysis

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

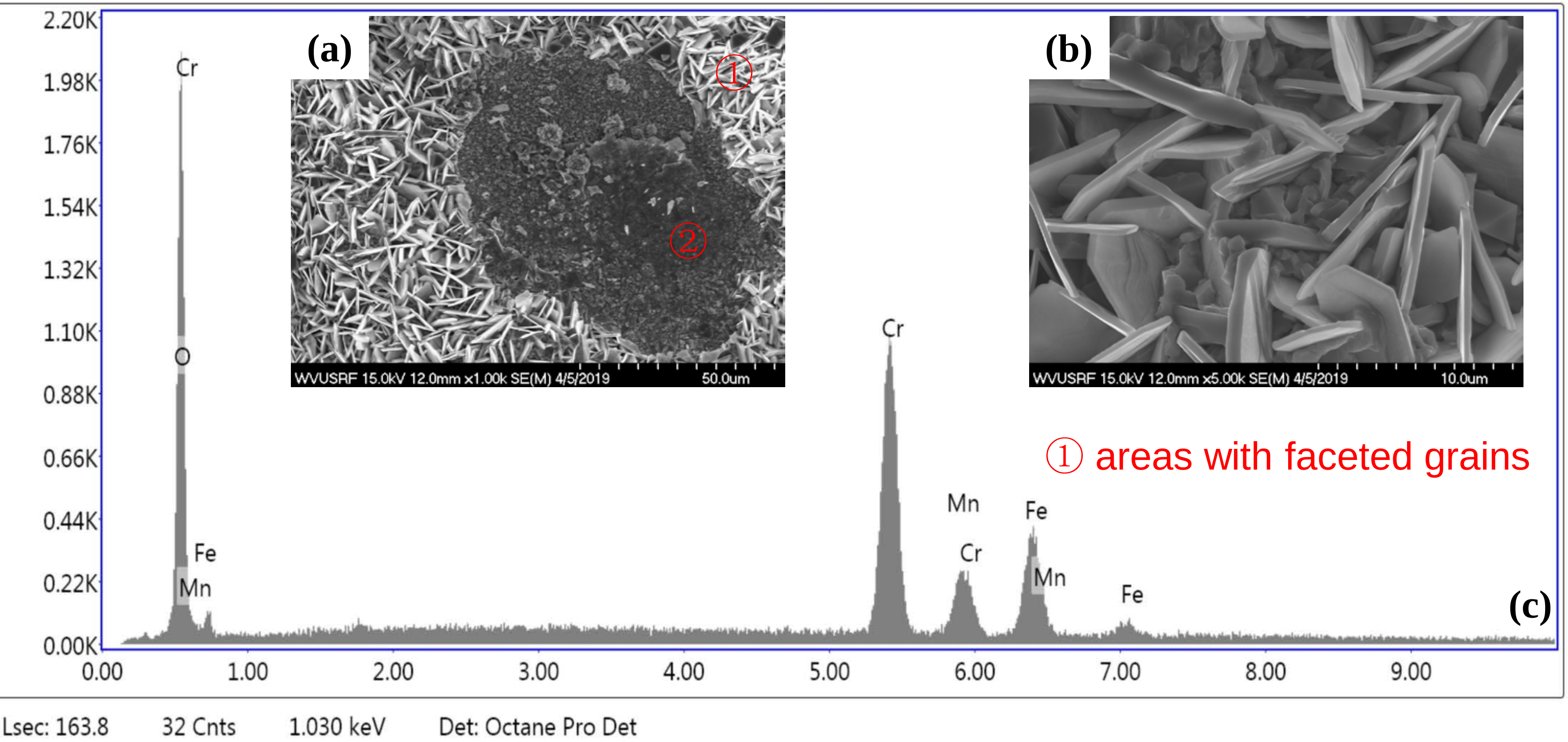
- At 900^{o}C, the OC11 and OC11LZ AFA alloys exhibited significantly lower Cr evaporation rate than 625. 625 suffered from spallation and mass loss which resulted in higher Cr evaporation rate.

- 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.



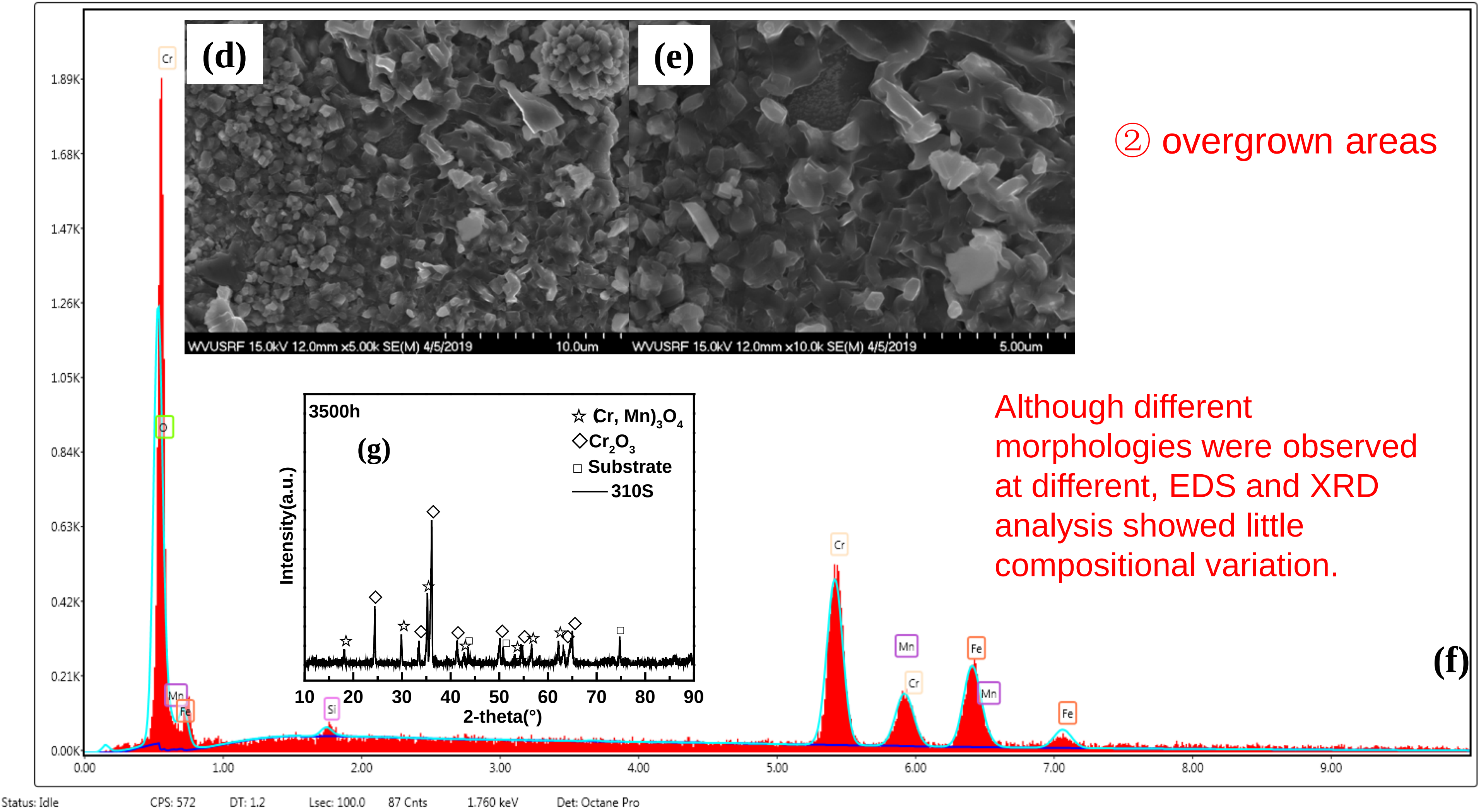
310S in 10% H_2O at 800 ºC for 3500 hours



① areas with faceted grains

(a) Microstructural analysis of 310s tested in 10% H_2O at 800 ºC for 3500 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 ºC for 3500 hours

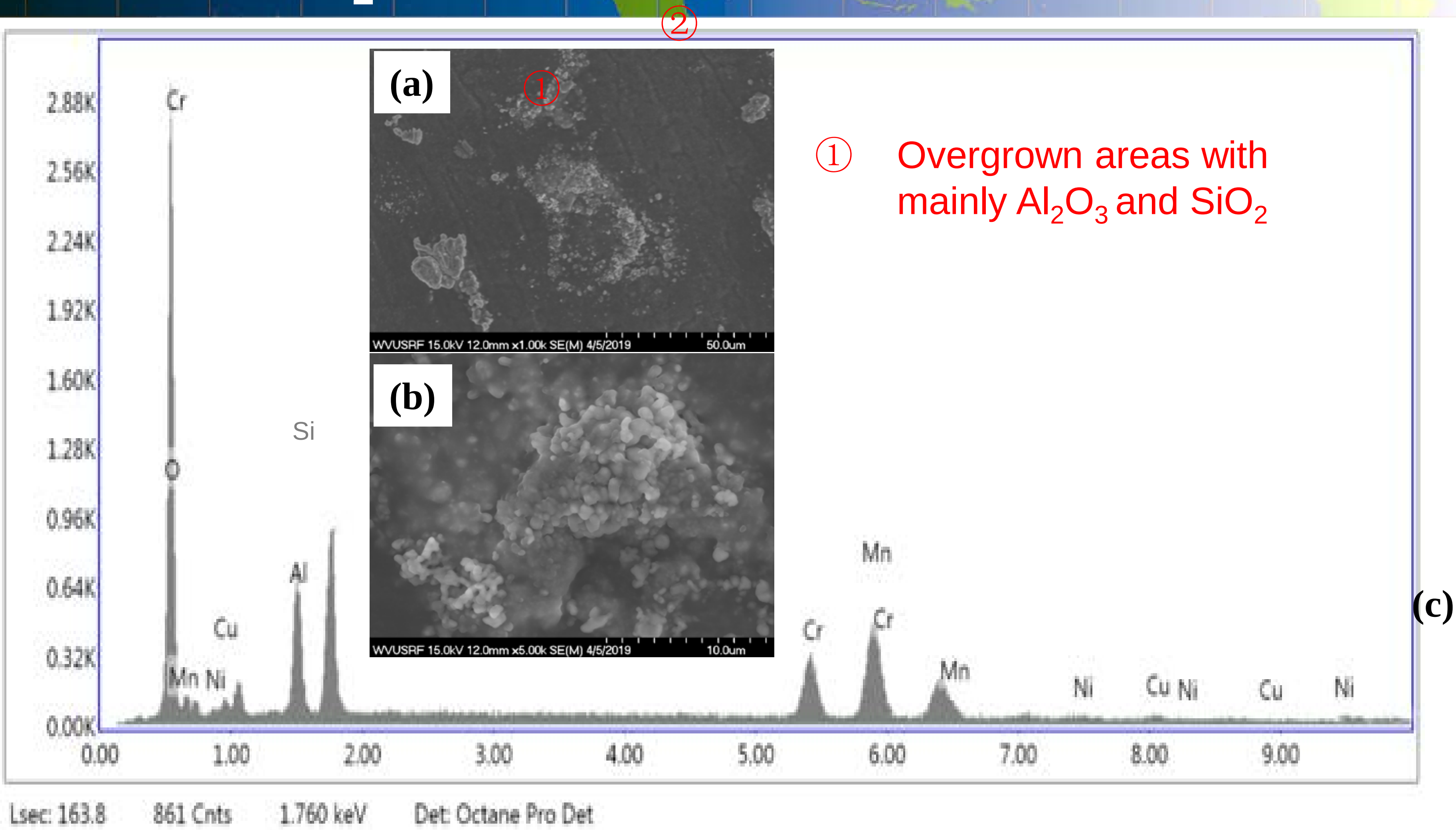


② overgrown areas

Although different morphologies were observed at different, EDS and XRD analysis showed little compositional variation.

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

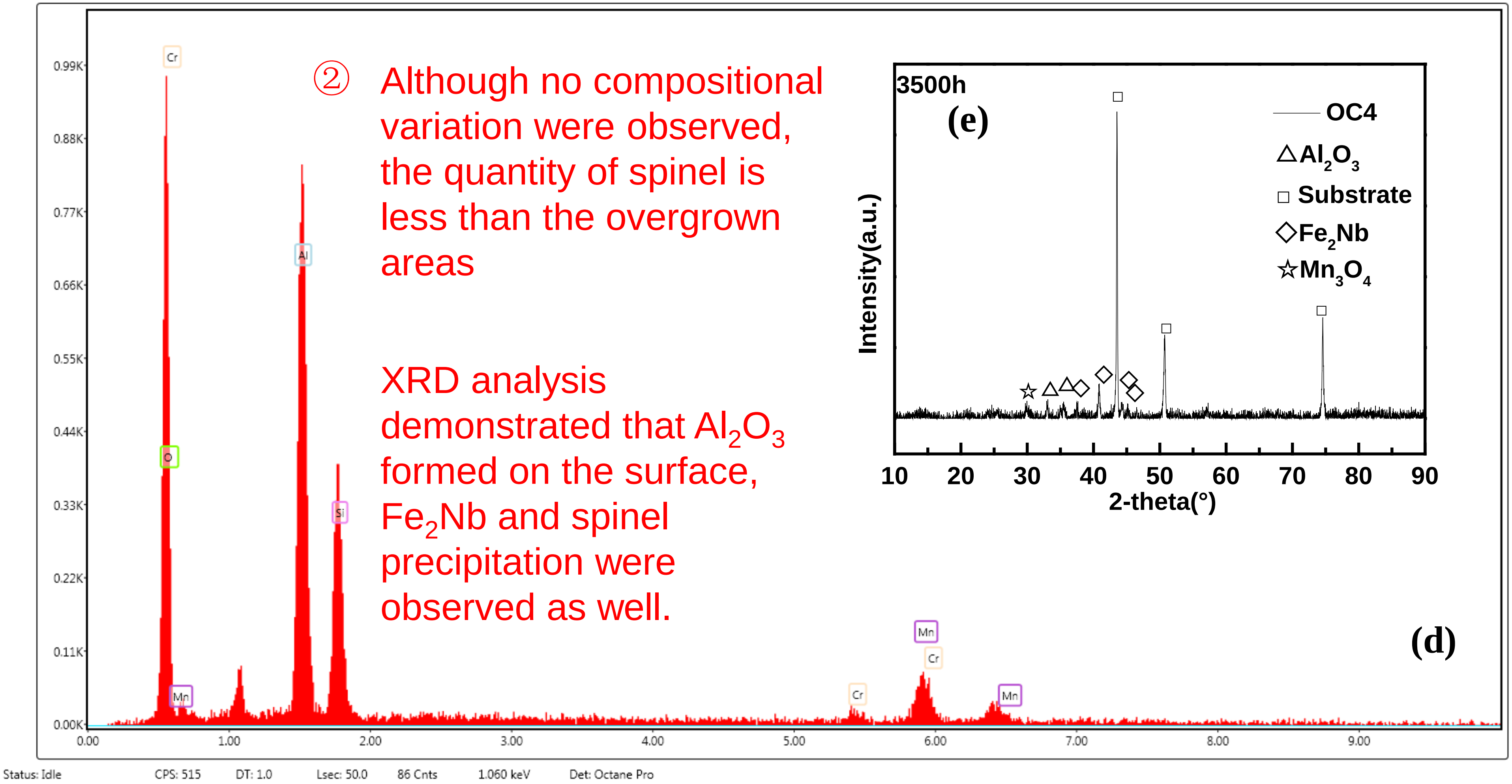
OC4 in 10% H_2O at 800 °C for 3500 hours



① Overgrown areas with mainly Al_2O_3 and SiO_2

(a) Microstructural analysis of **OC4** tested in 10% H_2O at 800 °C for 3500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b).

OC4 in 10% H_2O at 800 ºC for 3500 hours

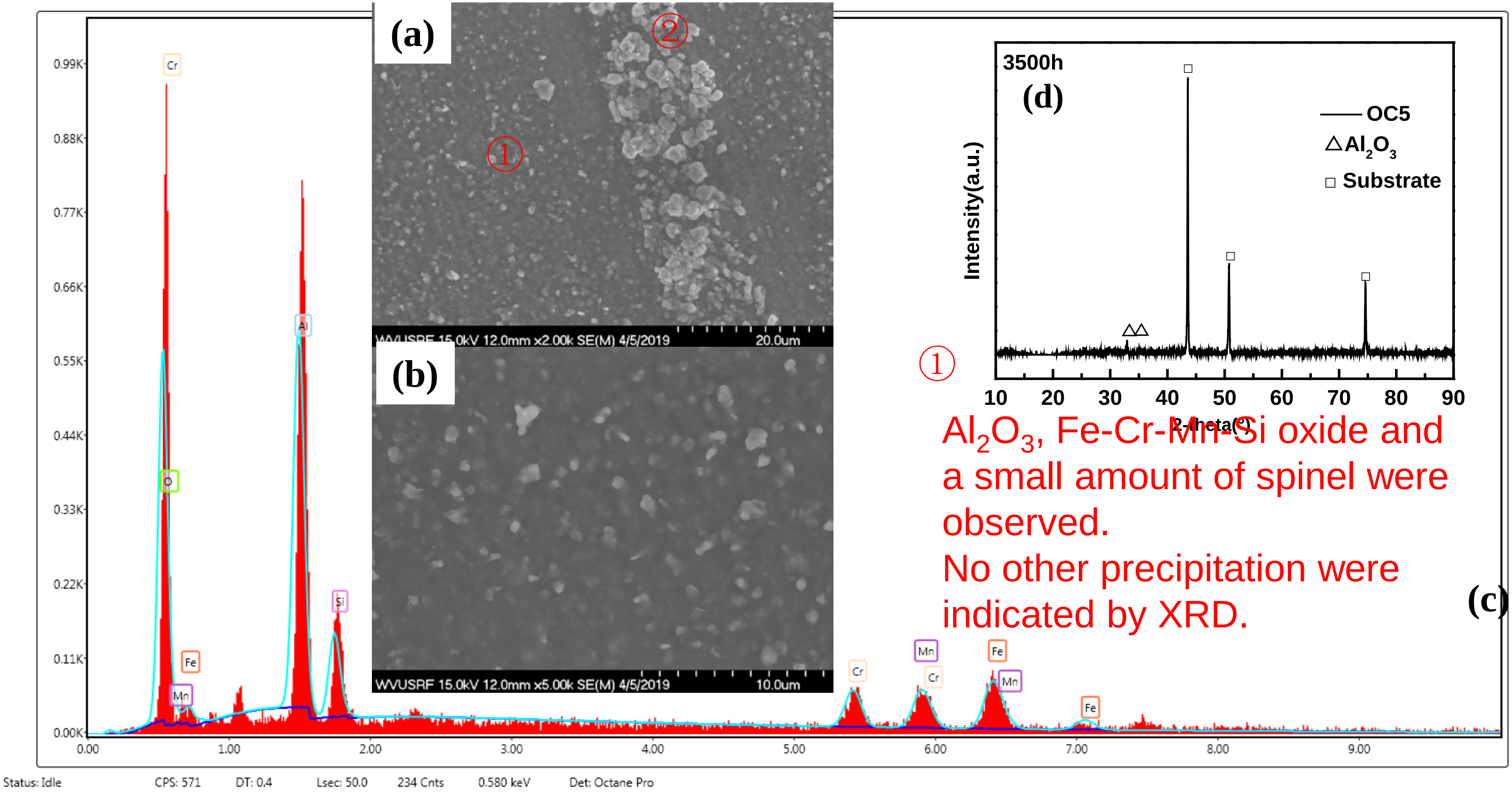


② Although no compositional variation were observed, the quantity of spinel is less than the overgrown areas

XRD analysis demonstrated that Al_2O_3 formed on the surface, Fe_2Nb and spinel precipitation were observed as well.

(d) is the corresponding EDS spectrum of area ②, (f) is the XRD analysis.

OC5 in 10% H_2O at 800 ºC for 3500 hours

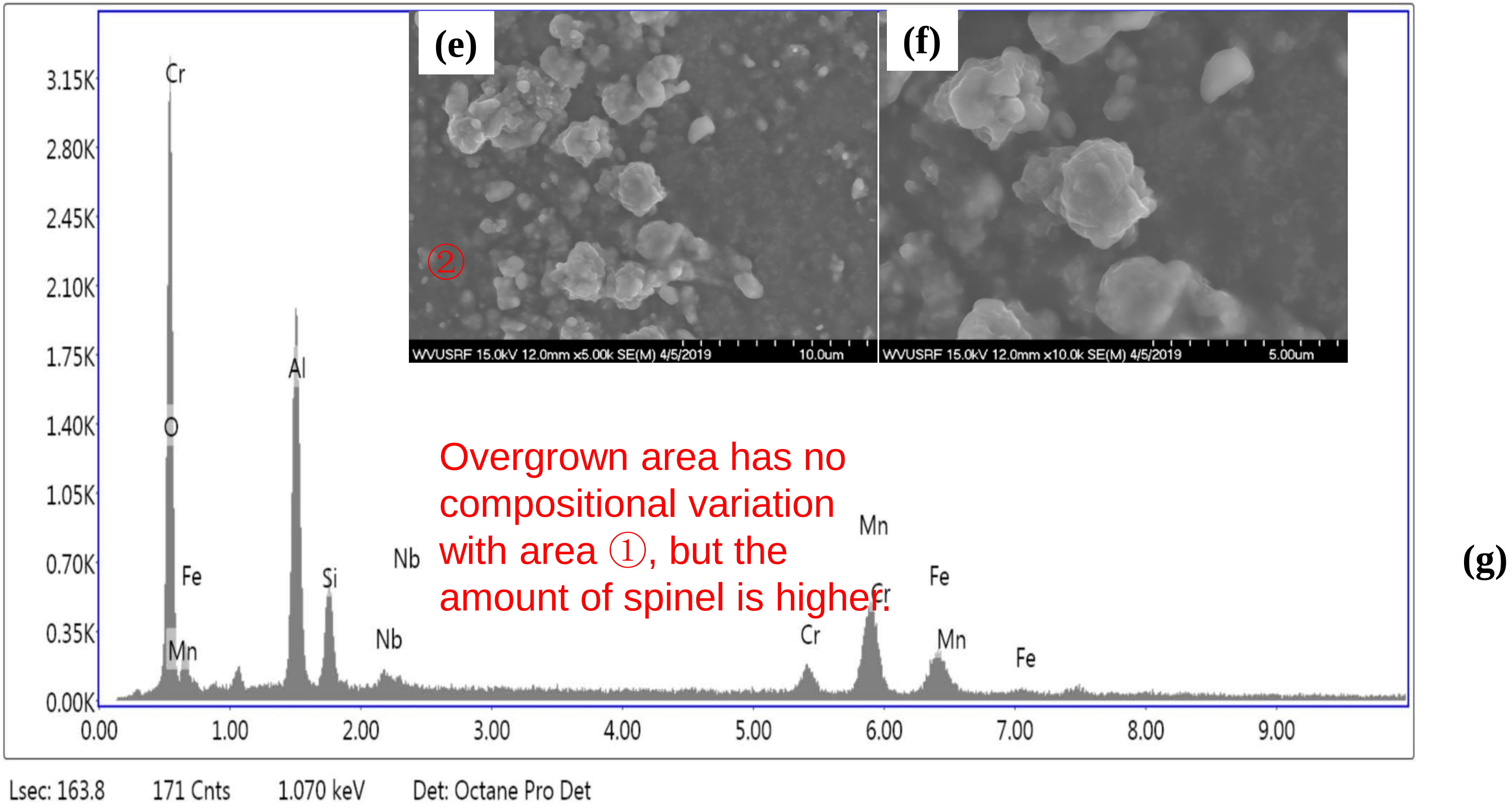


Al$_2$O$_3$, Fe-Cr-Mn-Si oxide and a small amount of spinel were observed.

No other precipitation were indicated by XRD.

(a) Microstructural analysis of **OC5** tested in 10% H_2O at 800 ºC for 3500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis.

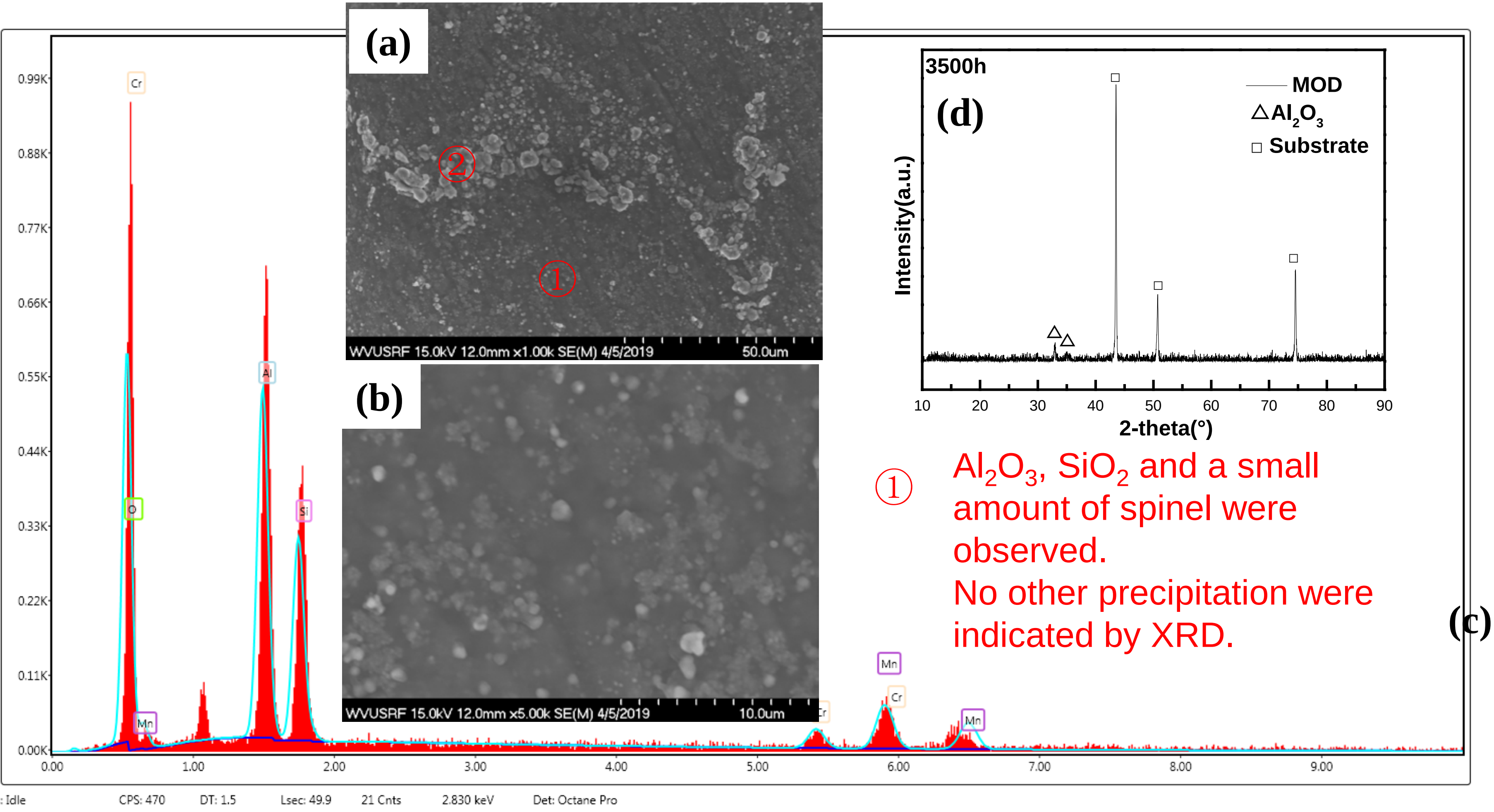
OC5 in 10% H_2O at 800 °C for 3500 hours



Overgrown area has no compositional variation with area ①, but the amount of spinel is higher.

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

MOD in 10% H_2O at 800 °C for 3500 hours



① Al_2O_3, SiO_2 and a small amount of spinel were observed.
No other precipitation were indicated by XRD.

(a) Microstructural analysis of **MOD** tested in 10% H_2O at 800 °C for 3500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis.

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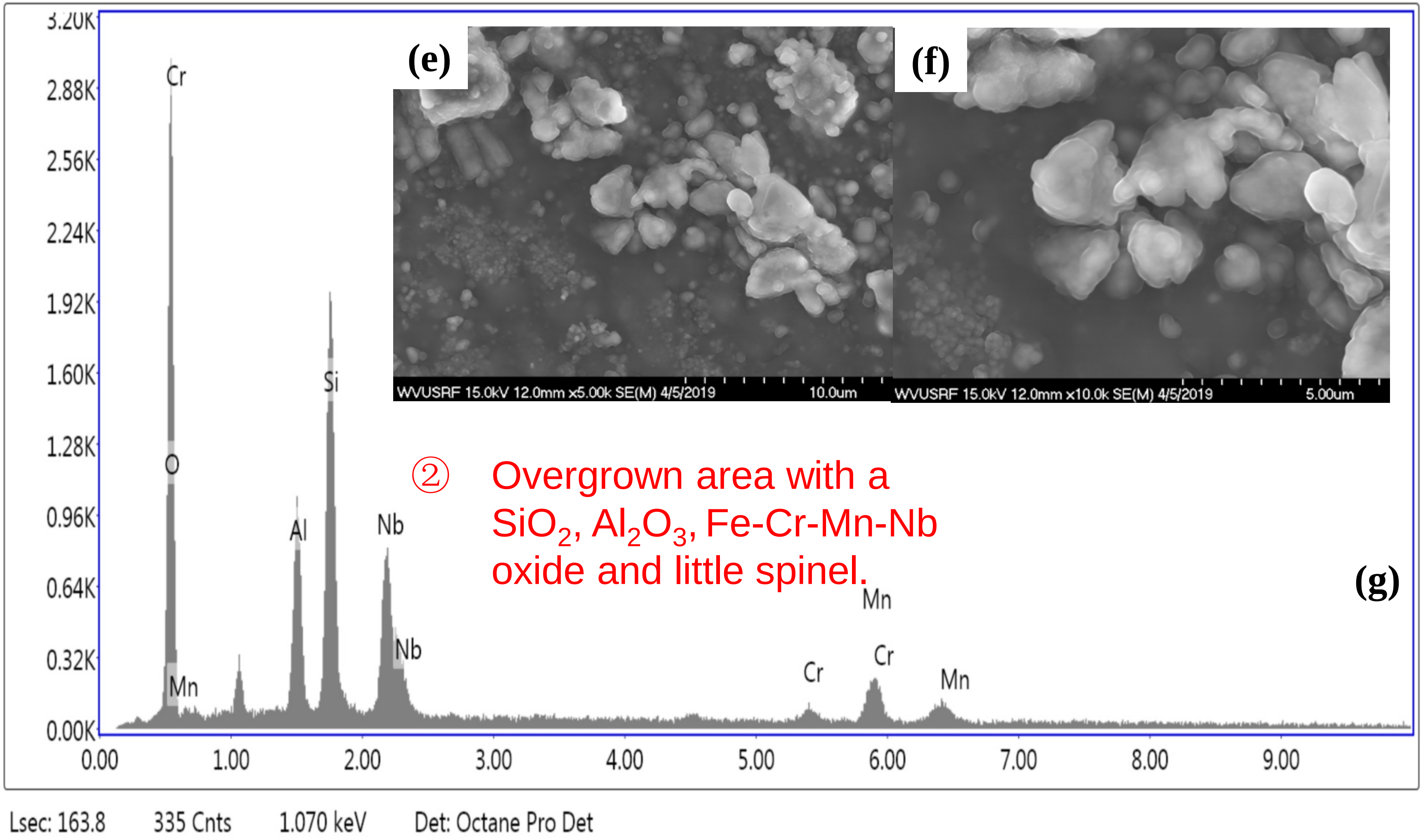
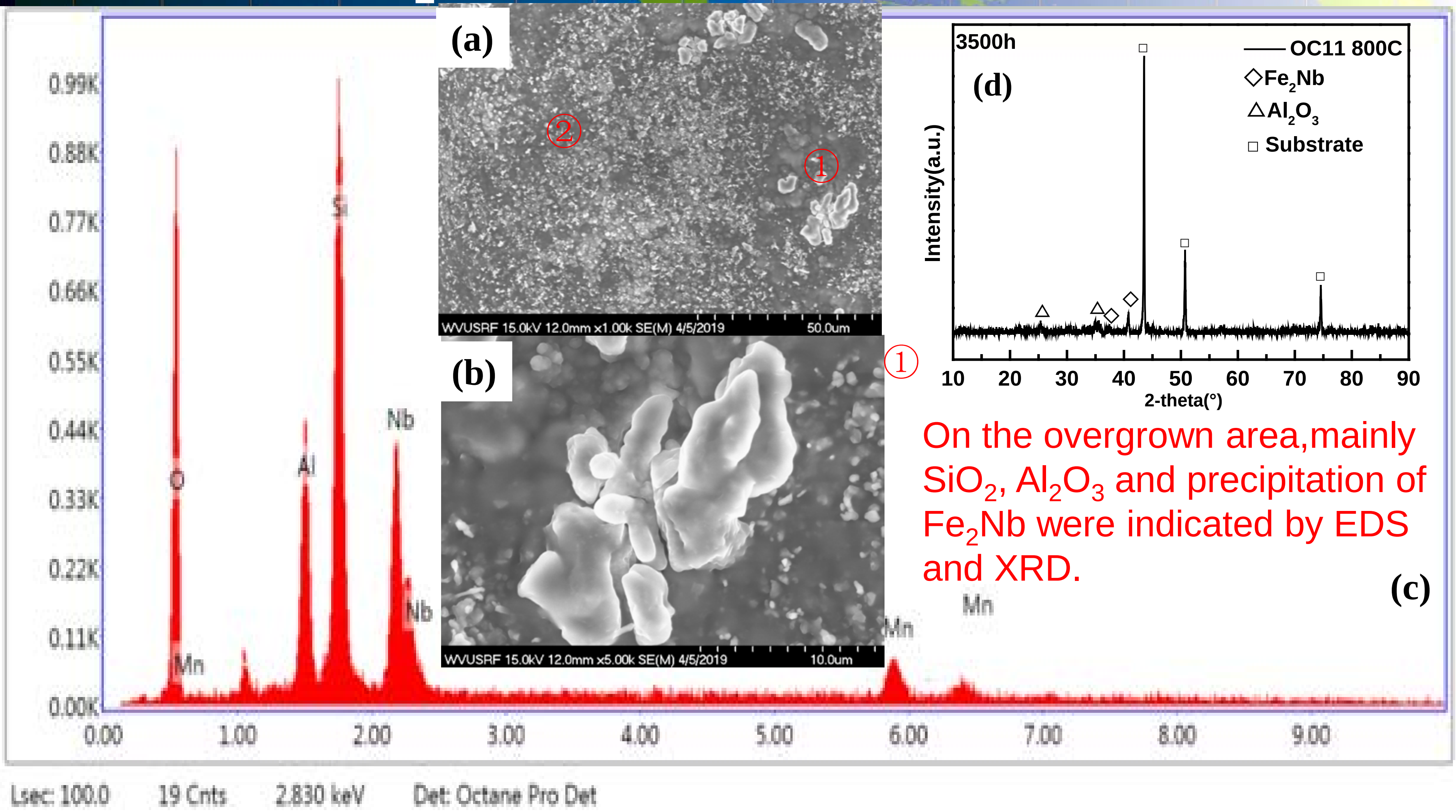
MOD in 10% H_2O at 800 °C for 3500 hours



② Overgrown area with a SiO_2, Al_2O_3, Fe-Cr-Mn-Nb oxide and little spinel.

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

OC11 in 10% H_2O at 800 ºC for 3500 hours



On the overgrown area, mainly SiO_2, Al_2O_3 and precipitation of Fe_2Nb were indicated by EDS and XRD.

(a) Microstructural analysis of **OC11** tested in 10% H_2O at 800 ºC for 3500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis.

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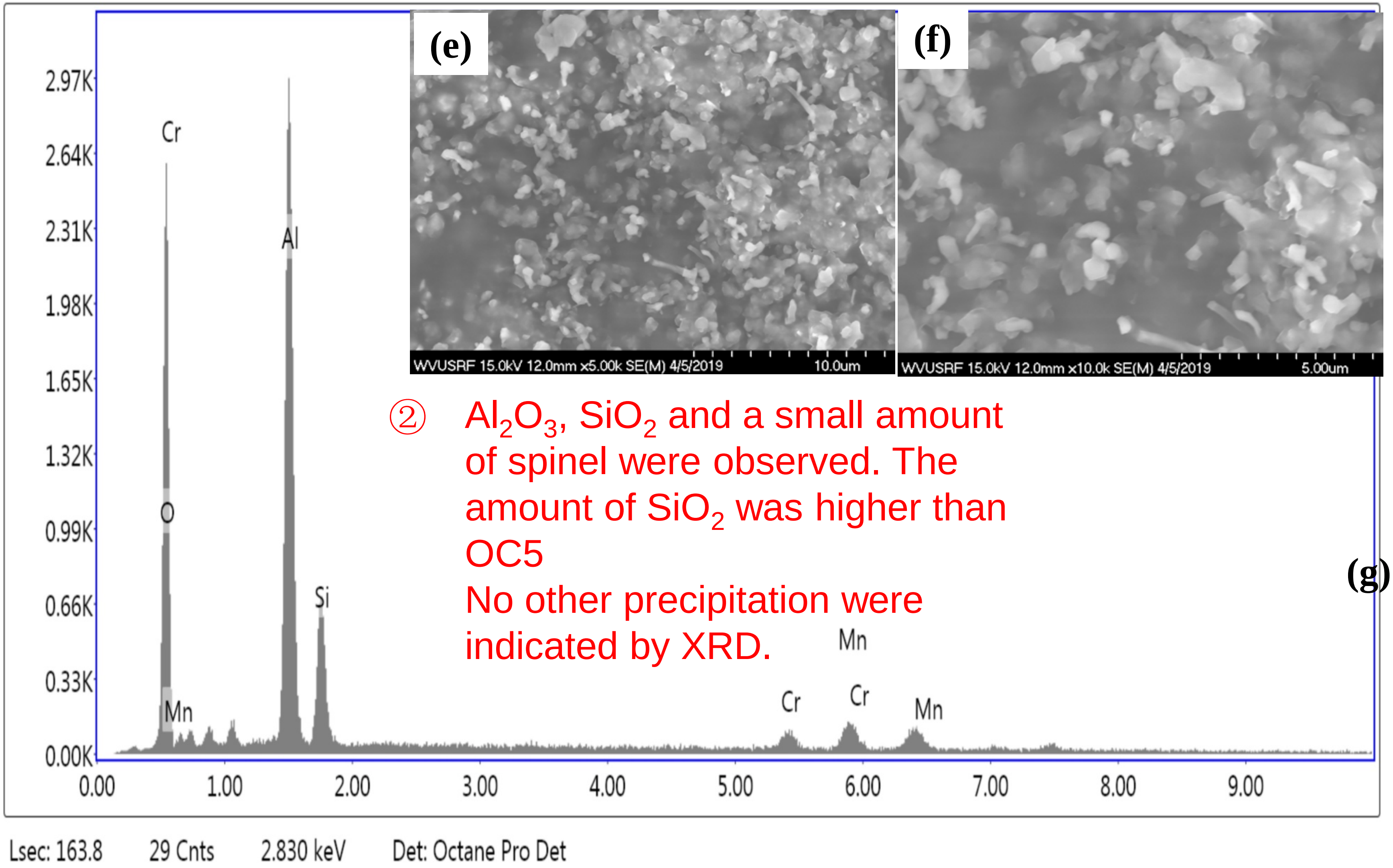
OC11 in 10% H_2O at 800 °C for 3500 hours

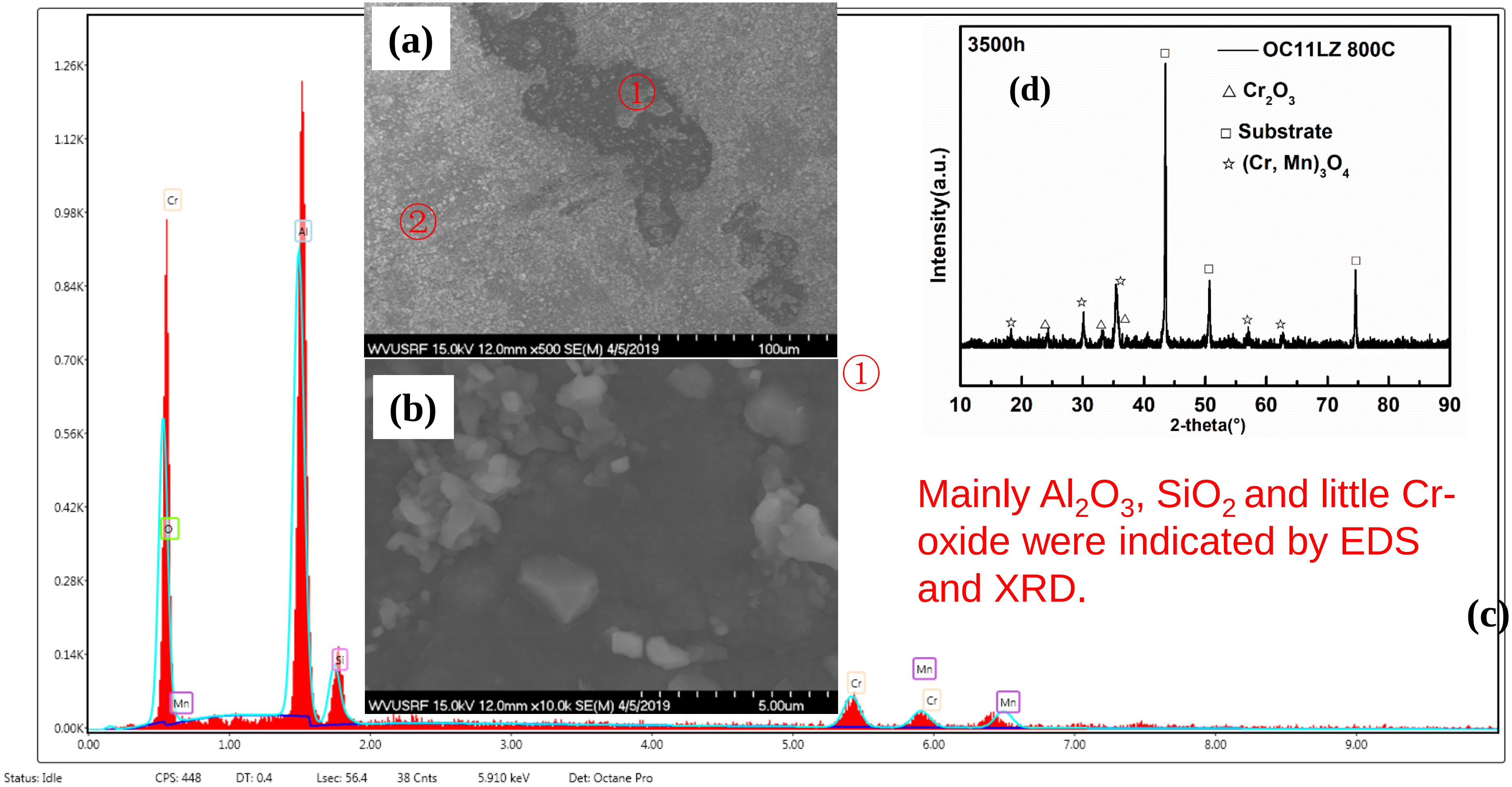


② Al_2O_3, SiO_2 and a small amount of spinel were observed. The amount of SiO_2 was higher than OC5

No other precipitation were indicated by XRD.

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

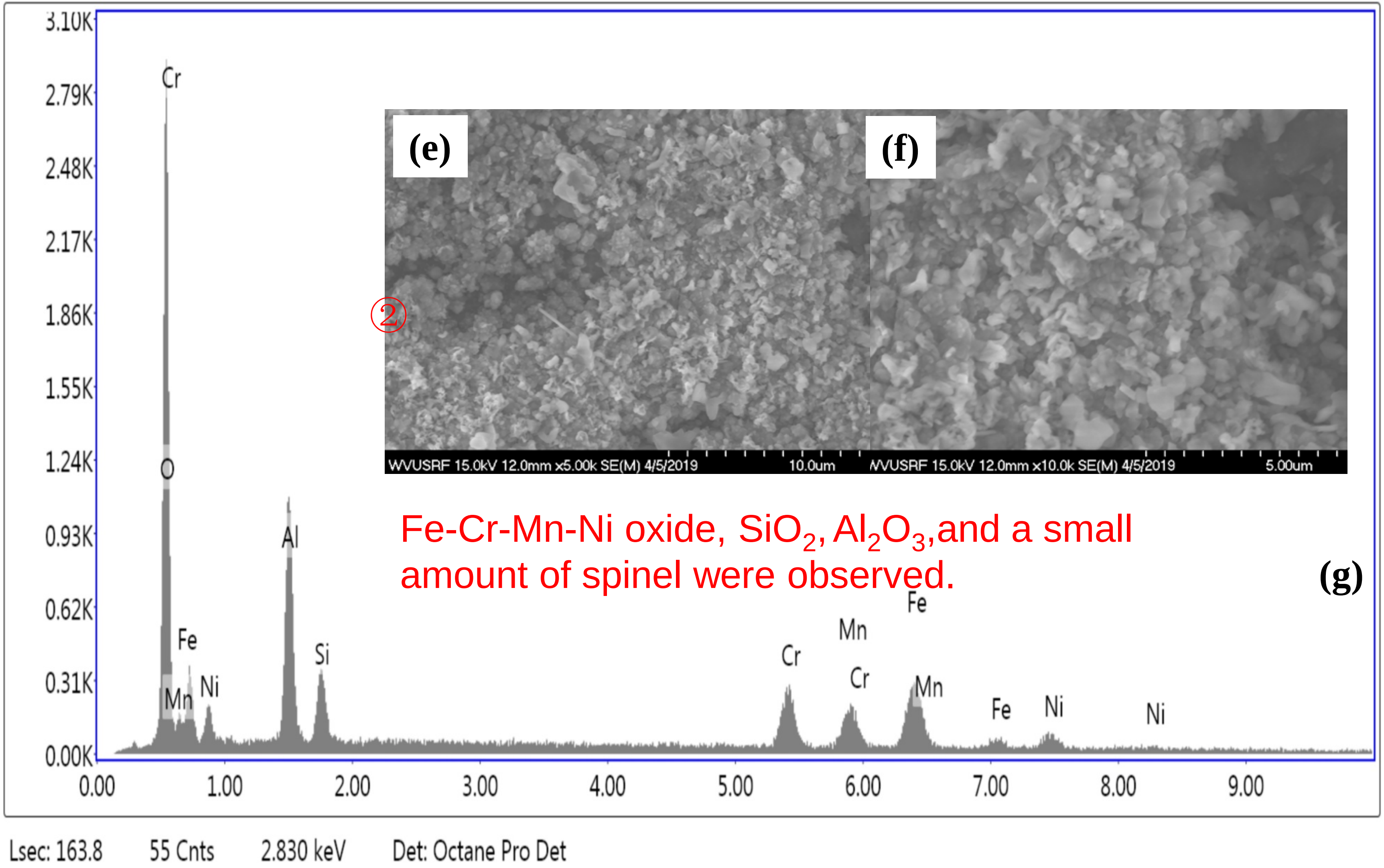
OC11-LZ in 10% H_2O at 800°C for 3500 hours



Mainly Al_2O_3, SiO_2 and little Cr-oxide were indicated by EDS and XRD.

(a) Microstructural analysis of **OC11LZ** tested in 10% H_2O at 800 °C for 3500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis.

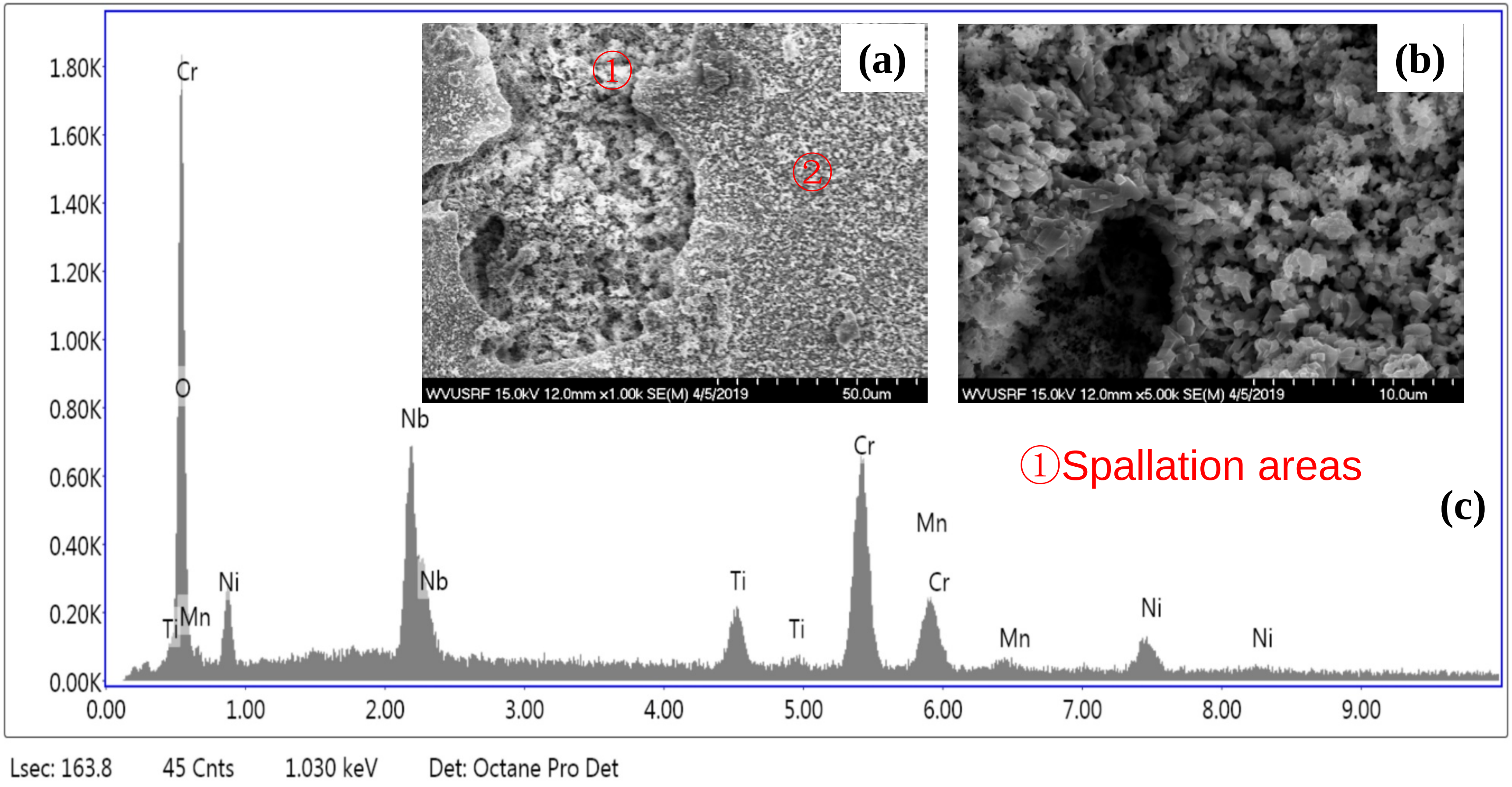
OC11-LZ in 10% H_2O at 800°C for 3500 hours



Fe-Cr-Mn-Ni oxide, SiO_2, Al_2O_3,and a small amount of spinel were observed.

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

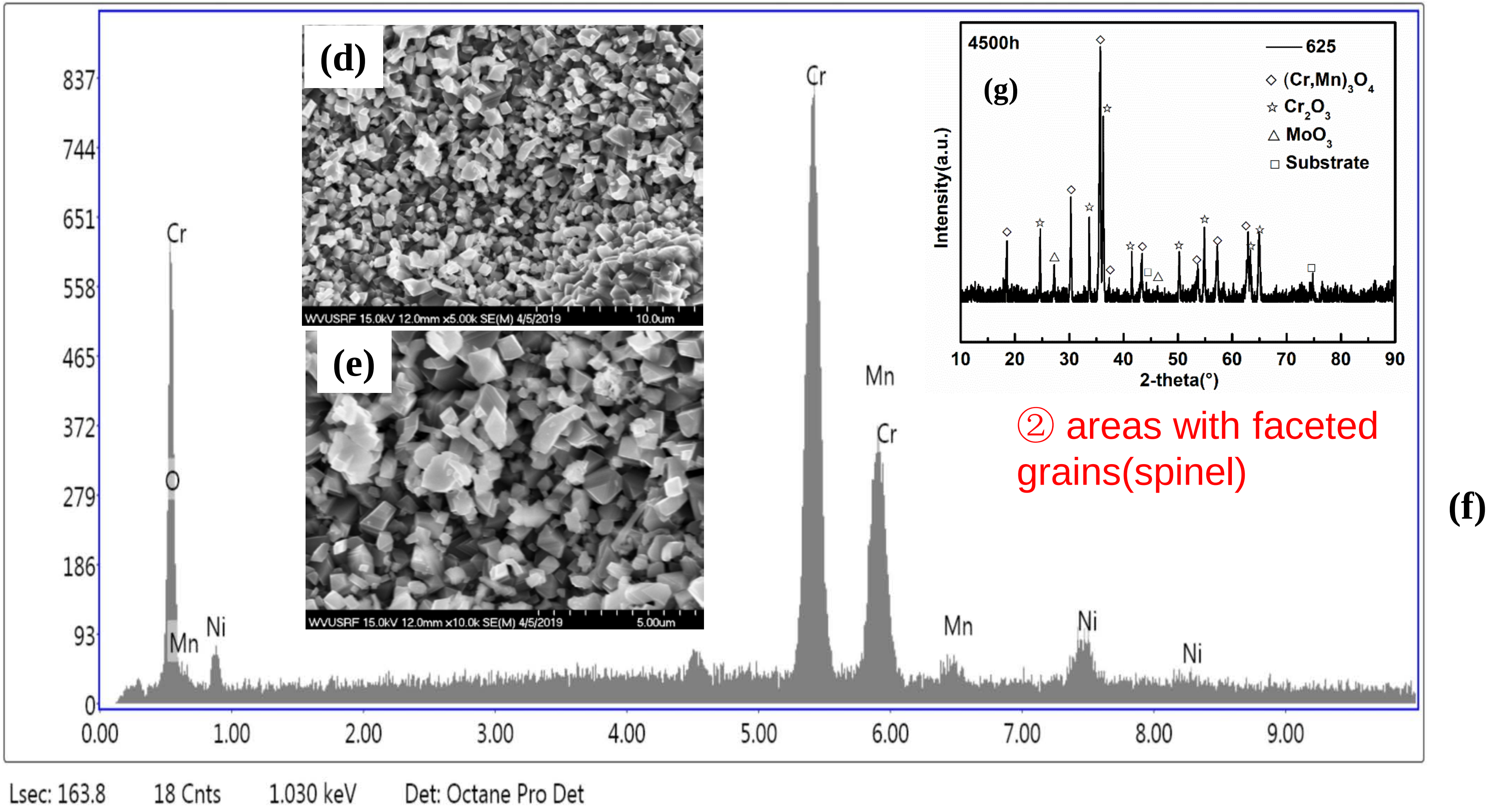
Alloy 625 in 10% H_2O at 900ºC for 4500 hours



①Spallation areas

(a) Microstructural analysis of 625 tested in 10% H_2O at 900 ºC for 4500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b) .

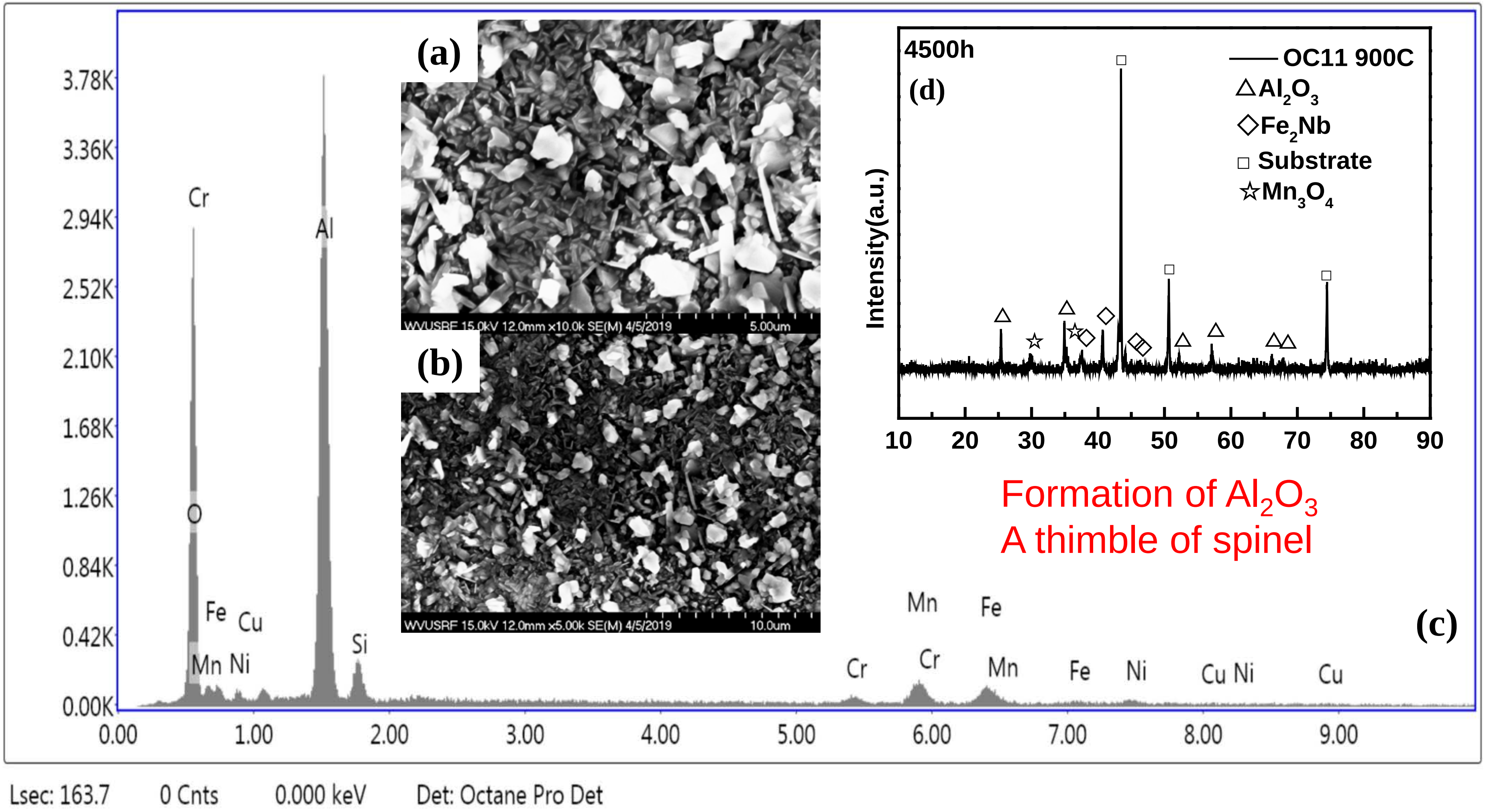
Alloy 625 in 10% H_2O at 900ºC for 4500 hours



② areas with faceted grains(spinel)

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

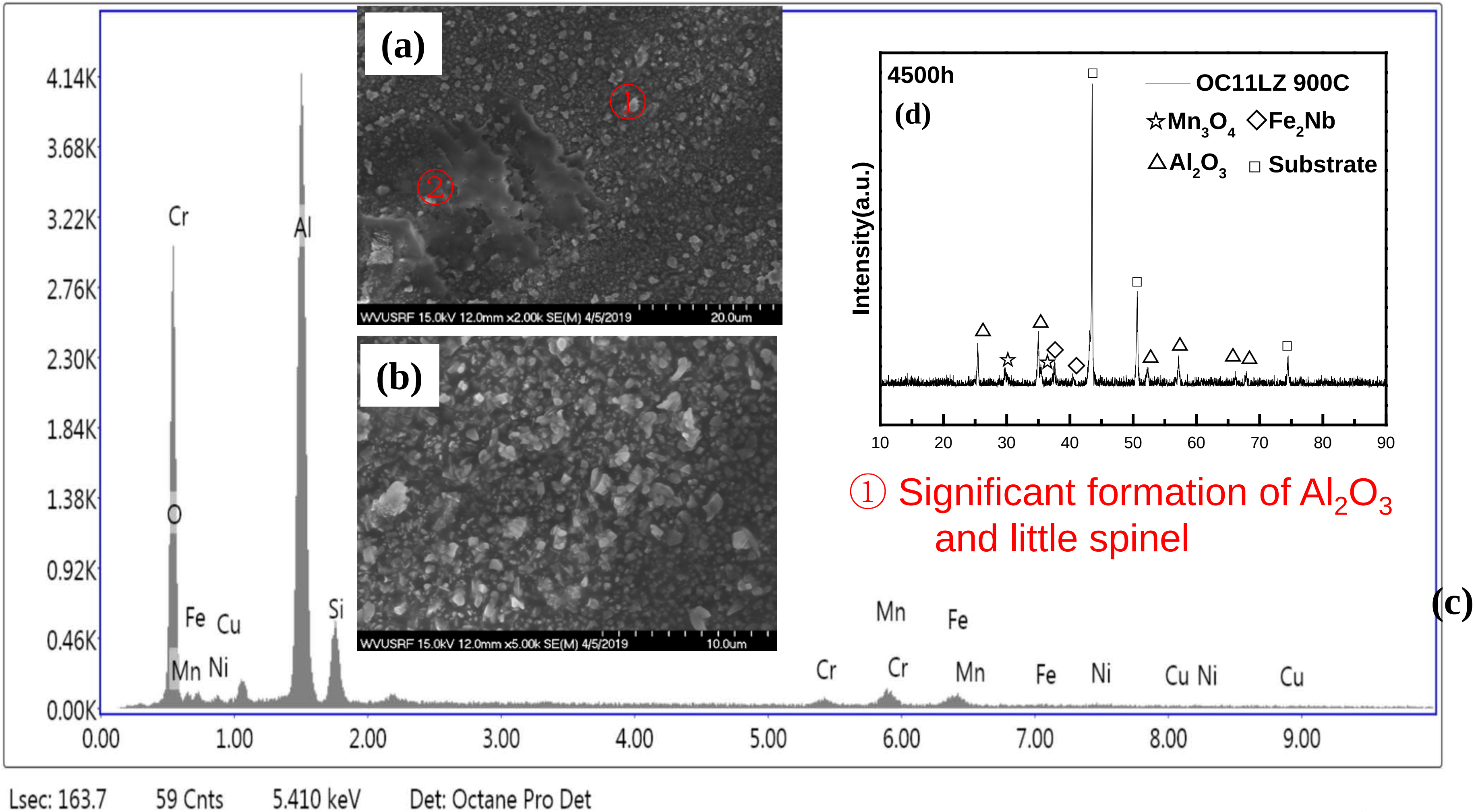
OC11 in 10% H_2O at 900 ºC for 4500 hours.



Formation of Al_2O_3
A thimble of spinel

(a) Microstructural analysis of OC11 tested in 10% H_2O at 900 ºC for 4500 hours, (b) is the high-magnification image of (a), (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis .

OC11-LZ in 10% H_2O at 900ºC for 4500 hours



① Significant formation of Al_2O_3 and little spinel

(a) Microstructural analysis of **OC11LZ** tested in 10% H_2O at 900 ºC for 4500 hours, (b) is the high-magnification image of area ①, (c) is the corresponding EDS spectrum of (b), (d) is the XRD analysis.

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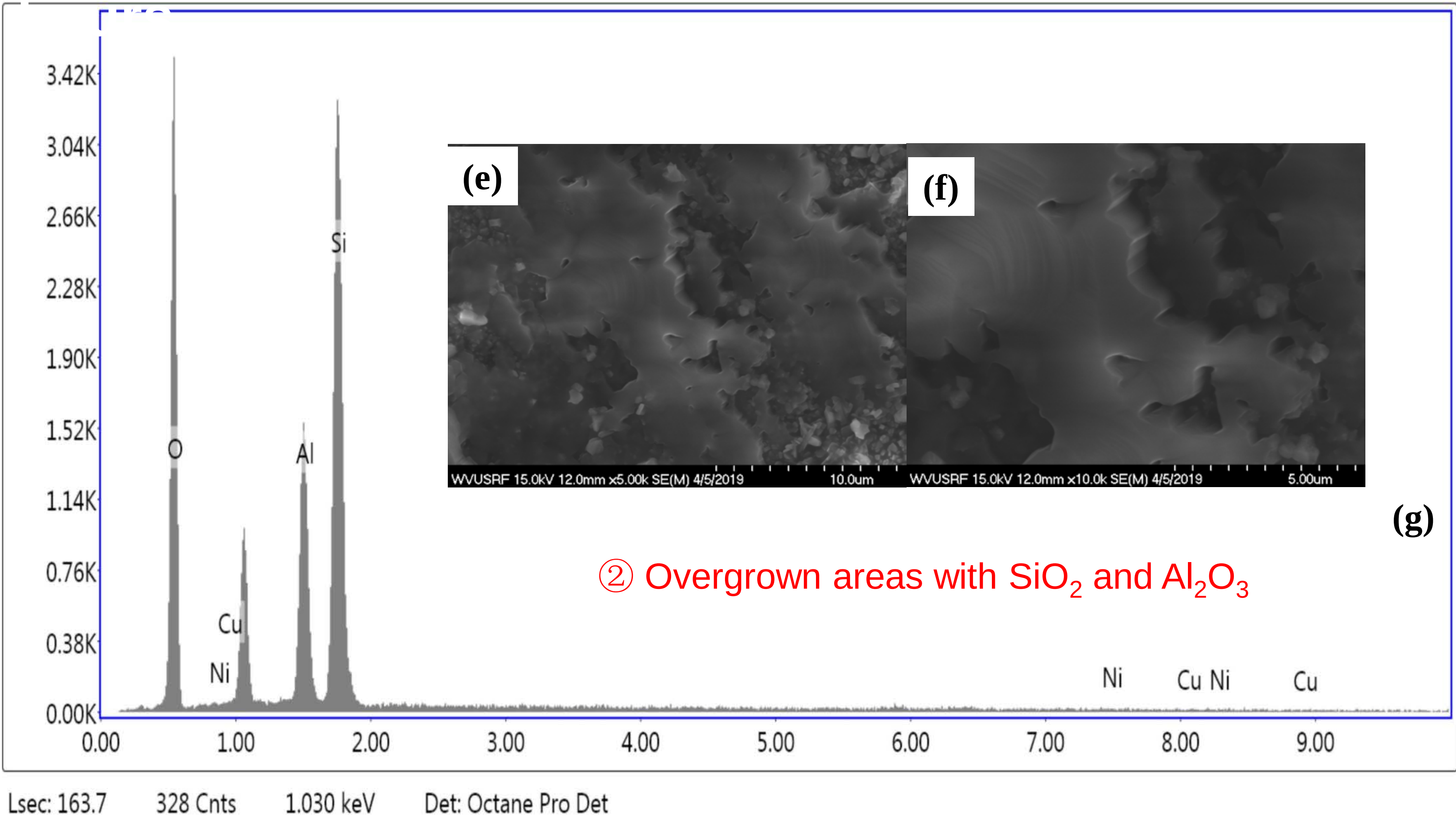
OC11-LZ in 10% H_2O at 900°C for 4500 hours



② Overgrown areas with SiO_2 and Al_2O_3

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

Progress To Date

- 5000h (10 cycles) long-term operation was carried out on AFA alloys and commercial allys. Five kinds of AFA alloys demonstrated higher oxidation resistance and lower Cr evaporation rate than benchmark Cr_2O_3-forming alloys 310S and 625 at 800 and 900 °C, respectively. Significantly reduced Cr evaporation rates observed on AFA alloys was attributed to the Al_2O_3 formation on the alloys.

- OC11 and OC5 exhibited the highest oxidation resistance and lowest Cr evaporation rate at 900 °C and 800 °C, respectively. The reason is due to the less precipitation formed on the alloy surface.

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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