Effect of Alloy Composition on the Oxidation Behaviour and Cr Vaporization of High-Cr Steels for SOFC Cathode Air Pre-heater

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Introduction
Cathode Air Pre-Heater (CAPH)

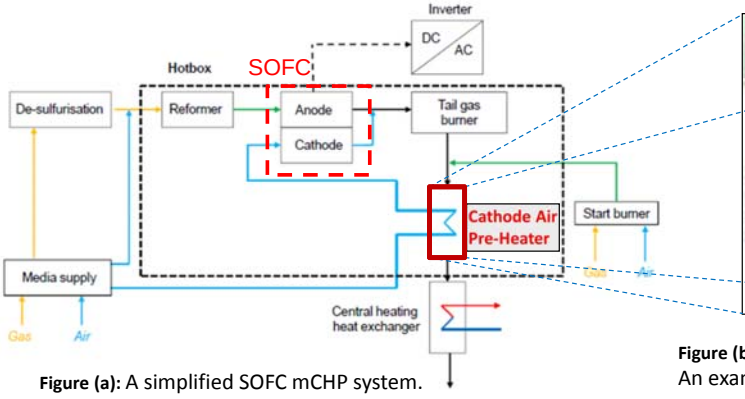


Figure (a): A simplified SOFC mCHP system.

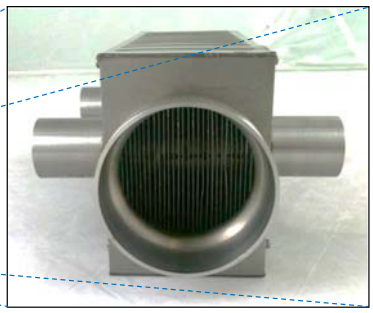
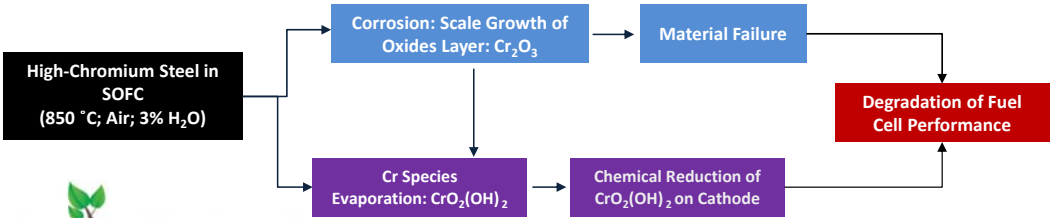


Figure (b):
An example of CAPH from Senior Flexonics, UK.



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Objectives:

- Cost reduction targets will be focused on changing from Inconel to AluChrom;
- Measure the chromium leakage (and high temperature corrosion) of Inconel 625 and AluChrom 318 supplied by VDM Metals;
- Understand the effects of surface aluminisation on the Cr retention capability of SS309.

Material and Methods

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Material: Inconel 625; AluChrom 318; Uncoated SS309; Aluminised SS309 (1 µm Al).

(wt.%)	Fe	Cr	Mn	Al	Ni	Si	Nb	W	Co	others
Inconel 625	5.0	20-23	0.5	0.4	Bal.	0.5	4.15	-	1.0	Ti 0.4; Mo 8-10; P 0.015; S 0.015
AluChrom 318	Bal.	18.8	0.21	3.58	0.24	0.32	0.73	2.02	--	Hf 0.06; Y 0.07; Zr 0.03; Cu 0.03 C 0.01; N 0.01
SS309	Bal.	22-24	2.0	--	12-15	0.75	--	--	--	C 0.2; P 0.045; S 0.03
Aluminised SS309	1 µm aluminium coated was deposited on SS309 surface by PVD technique.									

- ***Experiment:***
  - ➢ High Temperature Oxidation Test (long-term exposure): **Normal Tubular Glassware**
  - ➢ Quantification of Cr Evaporation (short-term Cr quantification): **Denuder Technique**
- ***Test Condition:***
  - ➢ 850 ˚C; 6.0 L/min Air Flow; 3 vol% H_2O

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Denuder Technique for Cr Quantification

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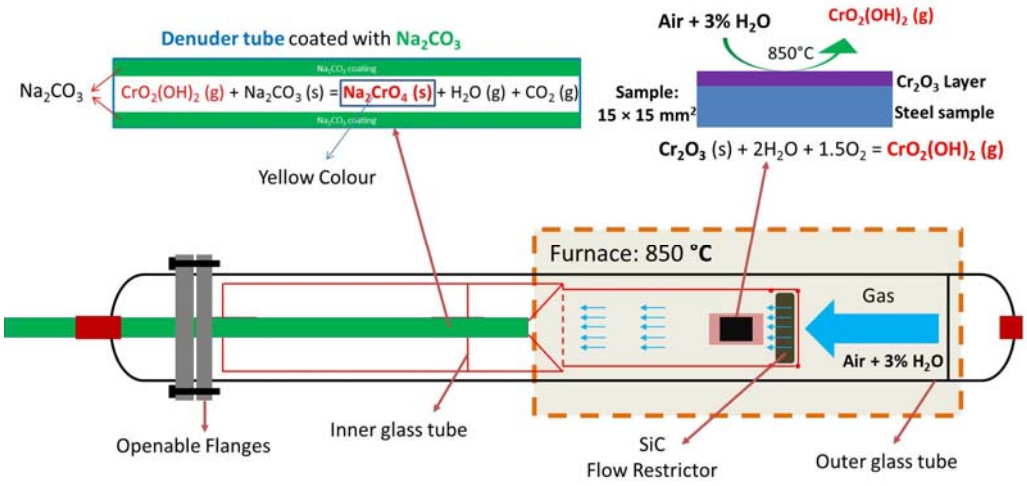
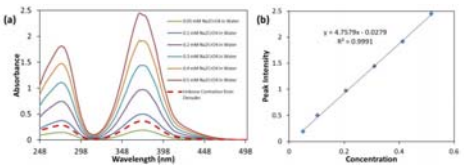
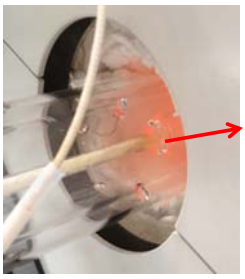




- Na_2CO_3 coating in denuder tube is washed off with DI water and quantified using UV-vis spectrophotometer;
- pure Cr_2O_3 pellets are used as Cr volatile source to confirm accuracy of denuder setup under SOFC conditions;
- efficiency of the denuder setup for Cr volatiles collection is confirmed to be around 98%.



When Cr species is collected, the denuder tube will turn yellow.

Reference:
J. Froitzheim, H. Ravash, E. Larsson, L.G. Johansson, J.E. Svensson, *J Electrochemical Society* 157 (2010) B1295.

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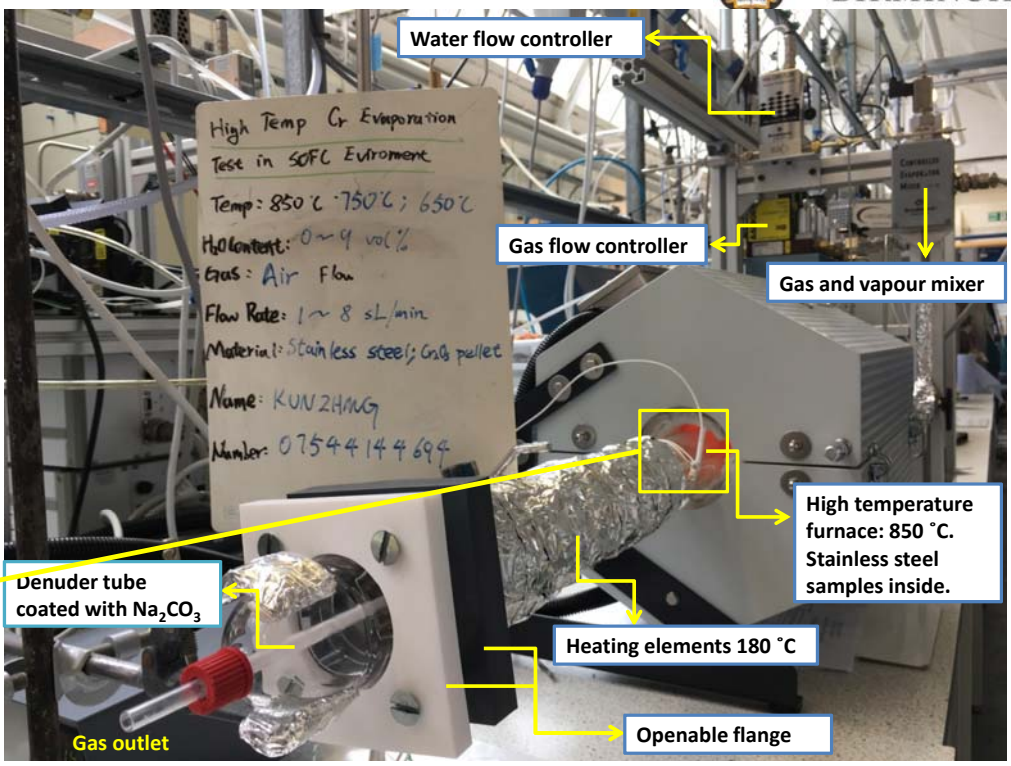
Denuder Technique for Cr Quantification – Laboratory Setup



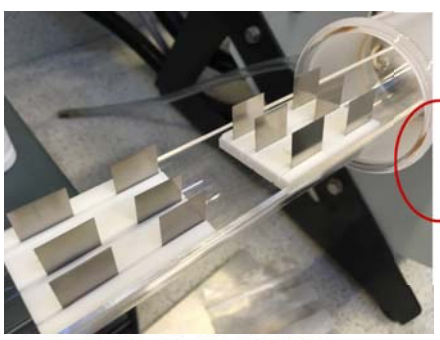
High Temperature Oxidation Test

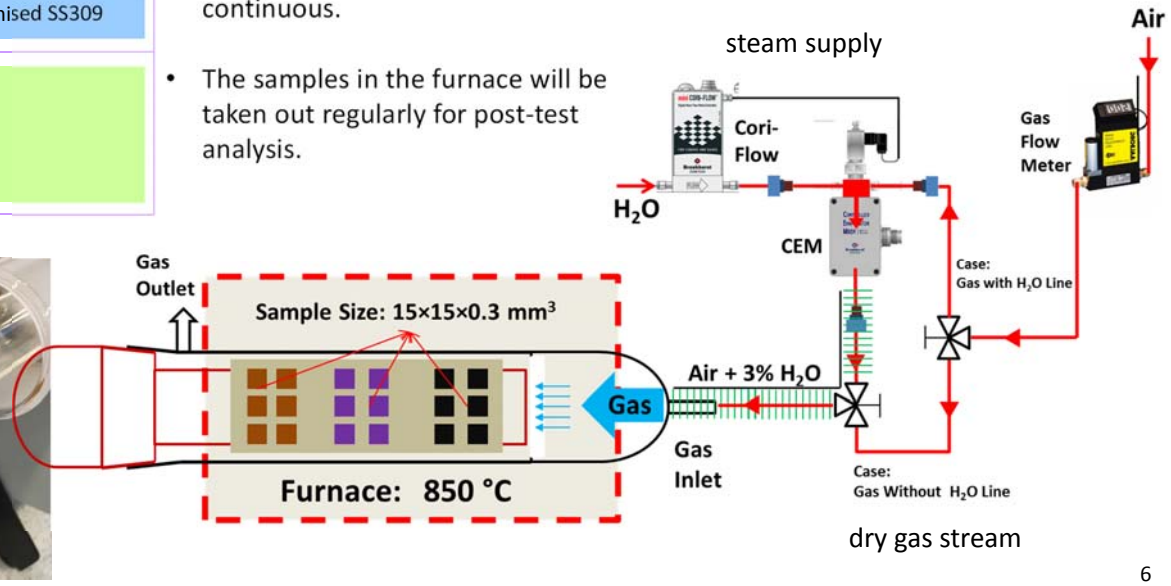
Test Condition:
Temp: 850 ˚C;
Gas: Air + 3% H_2O;
Flow rate: 6.0 L/min;
Time: 2,000 hours

Materials:
- Inconel 625;
- AluChrom 318
- SS309
- Aluminised SS309

Post-analysis:
weighing; surface SEM/EDX;
cross-section SEM/EDX; surface XRD.

- For HT oxidation tests, all different kinds of samples are exposed in one furnace (as shown below).
- HT oxidation test is not continuous.
- The samples in the furnace will be taken out regularly for post-test analysis.





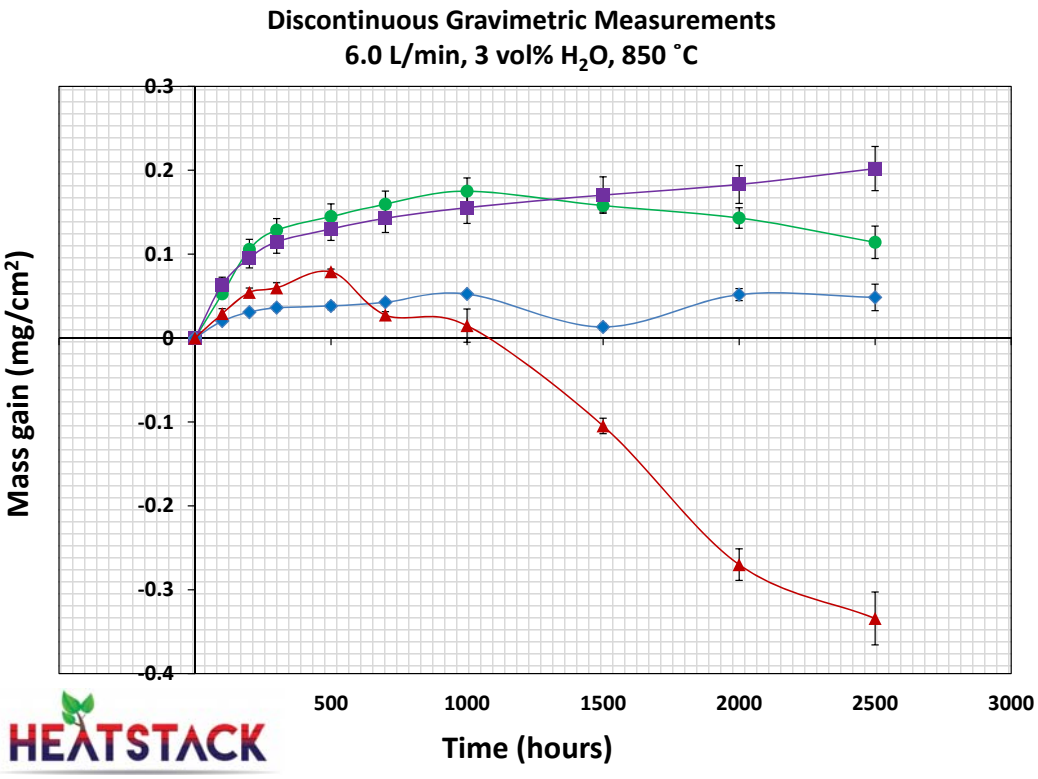
Mass Measurement & Cr Evaporation

Material: Inconel 625; AluChrom 318; Uncoated SS309; Aluminised SS309.

Test Conditions: 850 °C; 6.0 L/min Airflow; 3 vol% H_2O.

Equipment: Normal tubular glassware for high temperature corrosion test; Denuder Technique for evaporated Cr collection.

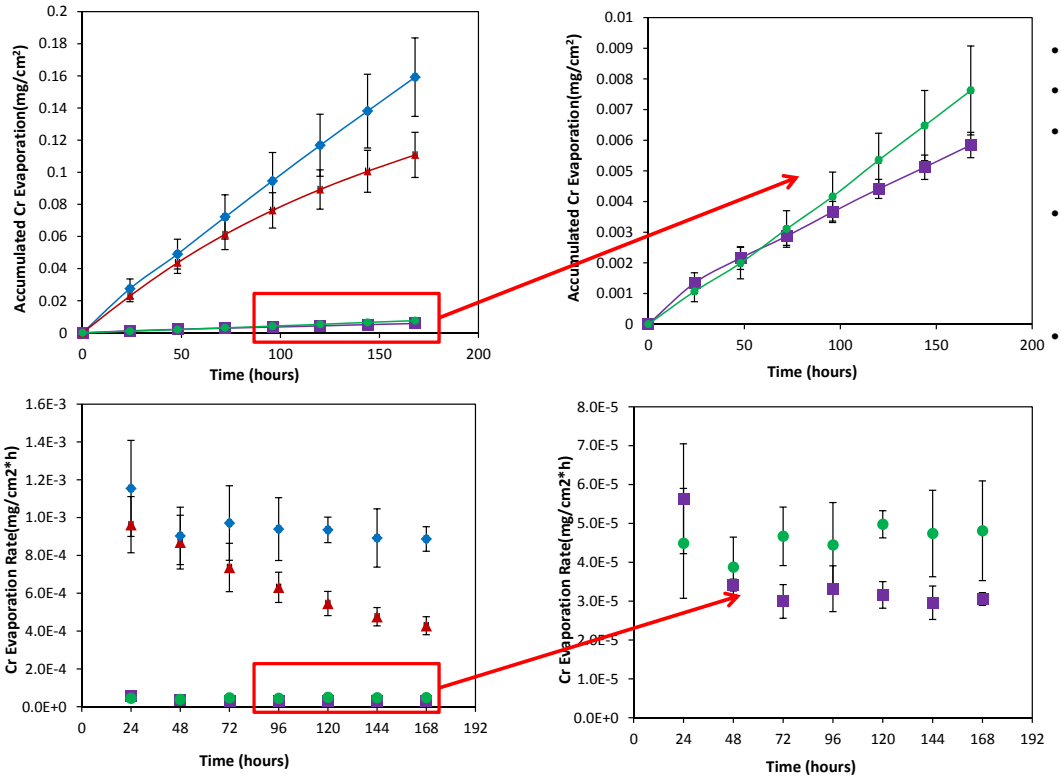
Mass Gain Measurements (High temperature oxidation test)



1. mass gain of AluChrom 318 increases even beyond 2,500 hours, which means aluminium oxide keeps growing on the surface.
2. mass gain of aluminised 309 decreases after 1,000 hours, which means the aluminium oxide spalls from the surface.
3. Inconel 625 has a relatively lower mass gain indicating that the Cr evaporation is very high.

Inconel 625 · SS309 · Aluminised SS309 · AluChrom 318

Continuous Cr Evaporation Measurements



- 3 repeats for all samples;
- Error obtained for every sample;
- Results from Denuder testing are reliable and repeatable;
- Aluminisation for SS309 could effectively prevent Cr evaporation, but not in the long term (with the method used here).
- The results shows that AluChrom 318 has the lowest amount of Cr evaporation among all these materials.

Inconel 625 SS309 Aluminised SS309 AluChrom 318

Microstructure Analysis - SEM & EDX

Material: Inconel 625; AluChrom 318; Uncoated SS309; Aluminised SS309.

Exposure time: 0 hours; 100 hours; 500 hours; 1000 hours.

Include: Surface SEM images; Cross section SEM

Surface elemental concentration;

EDX line scan; EDX mapping;

X-ray diffraction

SEM/EDX: Inconel 625

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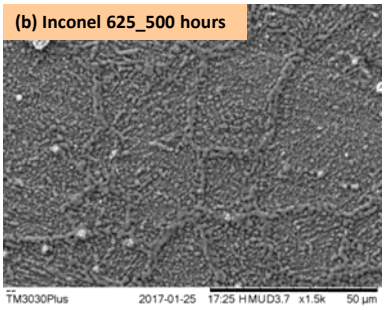
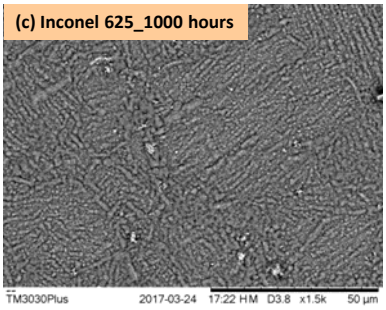
(a) Inconel 625_100 hours

(b) Inconel 625_500 hours



(c) Inconel 625_1000 hours

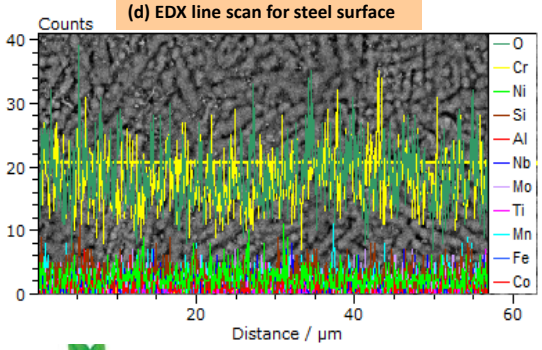


The EDX line scan confirms that the surface of Inconel 625 is completely covered by Cr_2O_3.

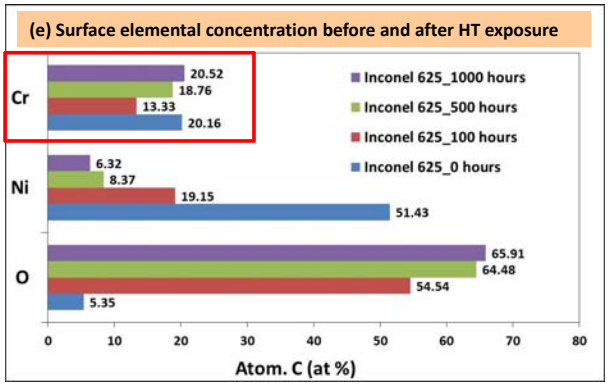
With the increase of exposure time at high temperature, more Cr_2O_3 scale grows on the steel surface.

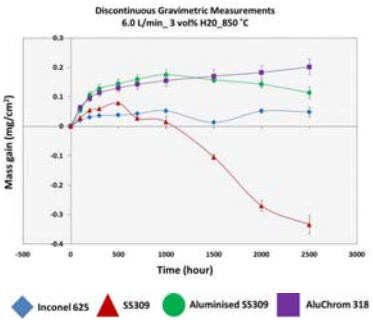
The concentration of Cr on the steel surface also increases with the increase of exposure time, which is consistent with the increase of O.

(d) EDX line scan for steel surface



(e) Surface elemental concentration before and after HT exposure





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SEM/EDX: SS309

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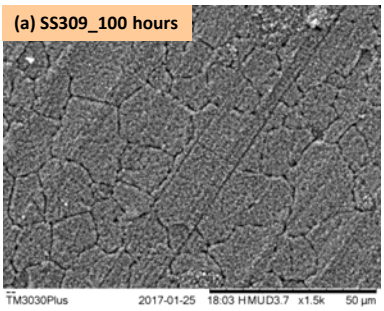
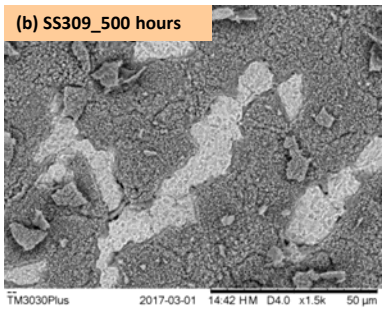
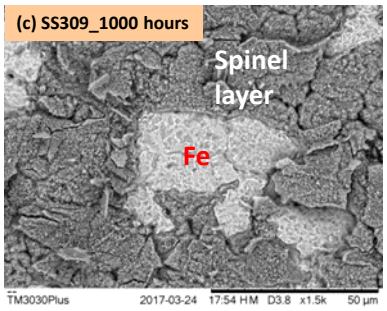
(a) SS309_100 hours



(b) SS309_500 hours



(c) SS309_1000 hours

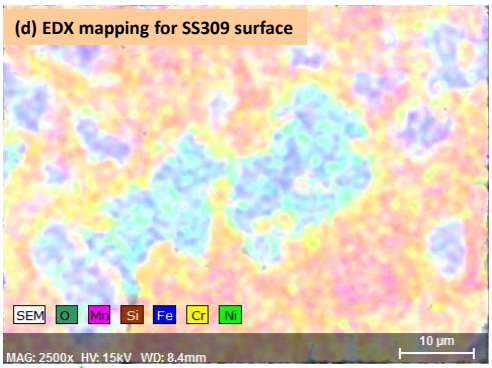


The spinel layer is formed on the surface after 100 hours of exposure at high temperature.

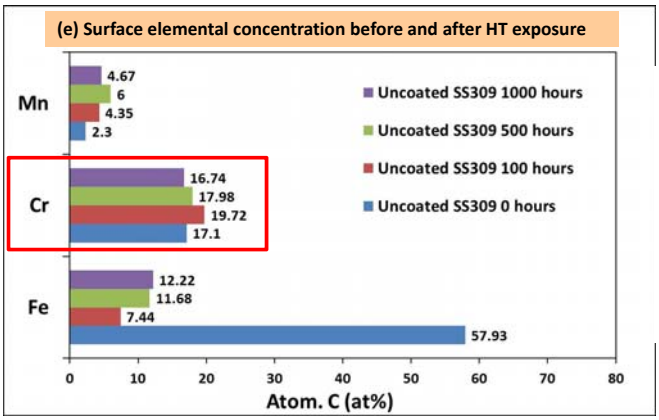
However, this material suffered serious spallation of the oxide layer after 500 hours exposure. Fe started to be exposed on the surface.

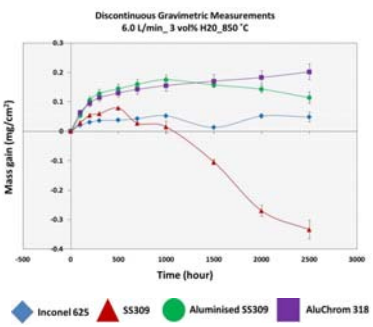
In figure (e), the concentration of Cr decreases with the increase of exposure time, because this material is loosing Cr due to the spallation of the spinel layer.

(d) EDX mapping for SS309 surface



(e) Surface elemental concentration before and after HT exposure





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SEM/EDX: Aluminised SS309

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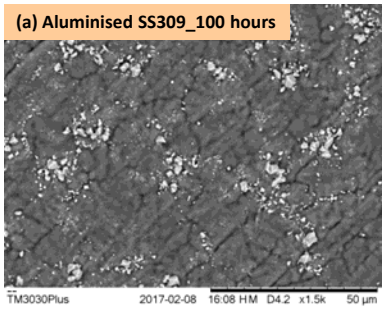
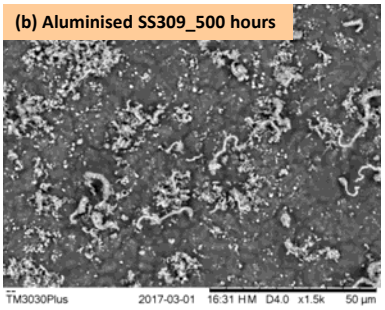
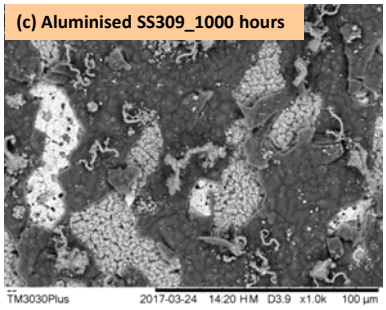
(a) Aluminised SS309_100 hours



(b) Aluminised SS309_500 hours



(c) Aluminised SS309_1000 hours

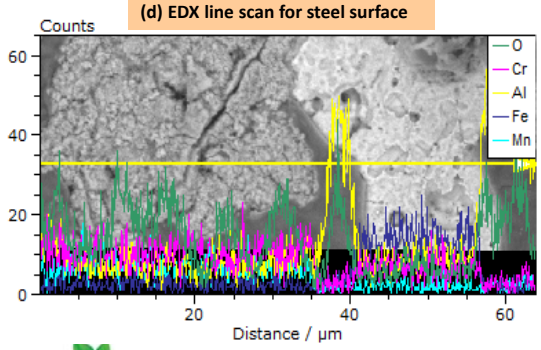


The Al formed Al_2O_3 on the surface after 100 hours of HT exposure.

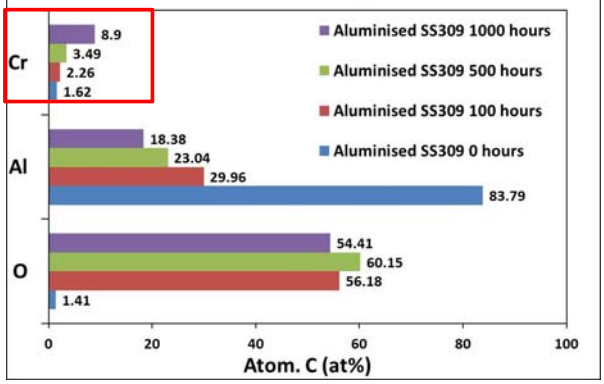
The Al_2O_3 coating starts to crack after 1000 hours exposure.

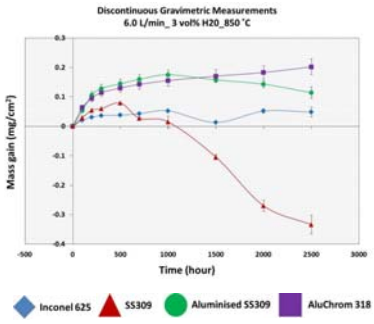
In figure (e), the surface concentration of Cr subsequently increases to 8.9 %.

(d) EDX line scan for steel surface



(e) Surface elemental concentration before and after HT exposure





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SEM/EDX: AluChrom 318

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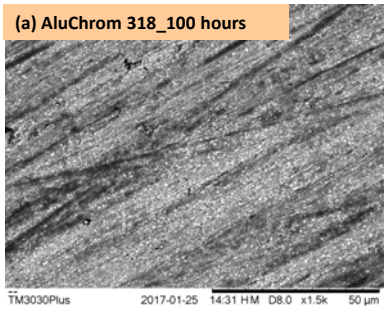
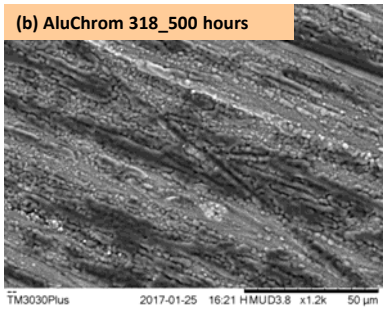
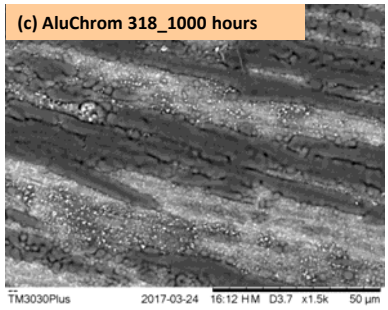
(a) AluChrom 318_100 hours



(b) AluChrom 318_500 hours



(c) AluChrom 318_1000 hours

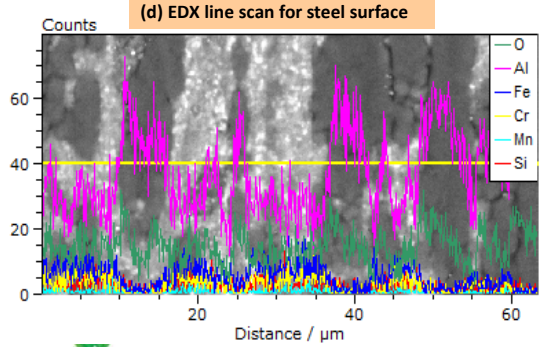


The EDX line scan confirms the steel surface is covered with AL_2O_3.

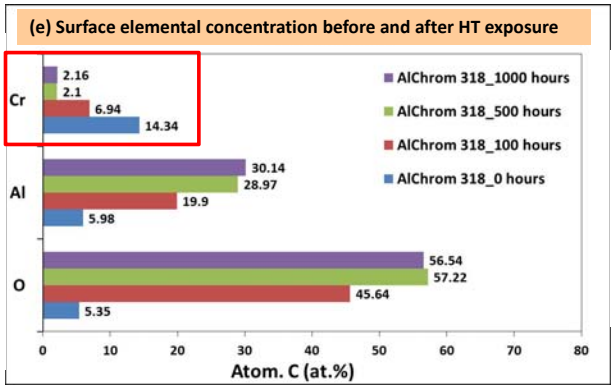
The thickness of the AL_2O_3 layer increases with the length of exposure at 850 ˚C.

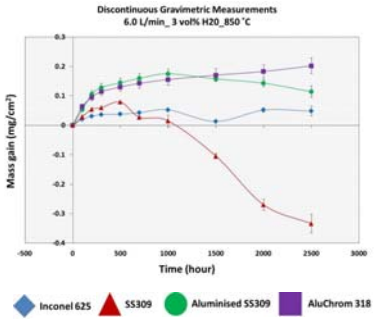
The concentration of Cr on the steel surface remains at 2.16% after 1000 hours exposure at 850 ˚C.

(d) EDX line scan for steel surface



(e) Surface elemental concentration before and after HT exposure





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Cross-section SEM of AluChrom 318

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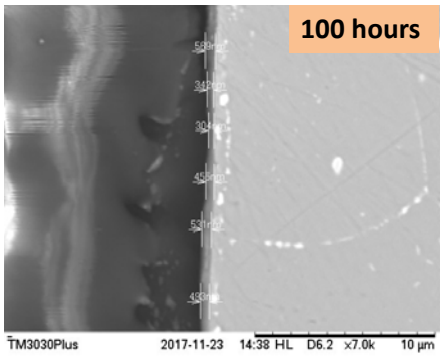
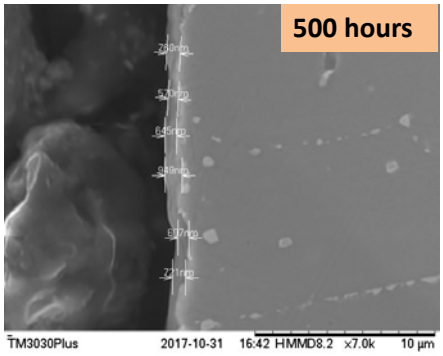
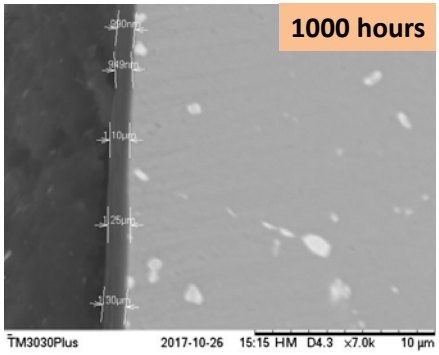
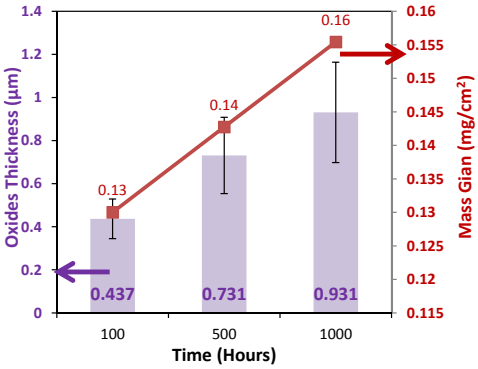
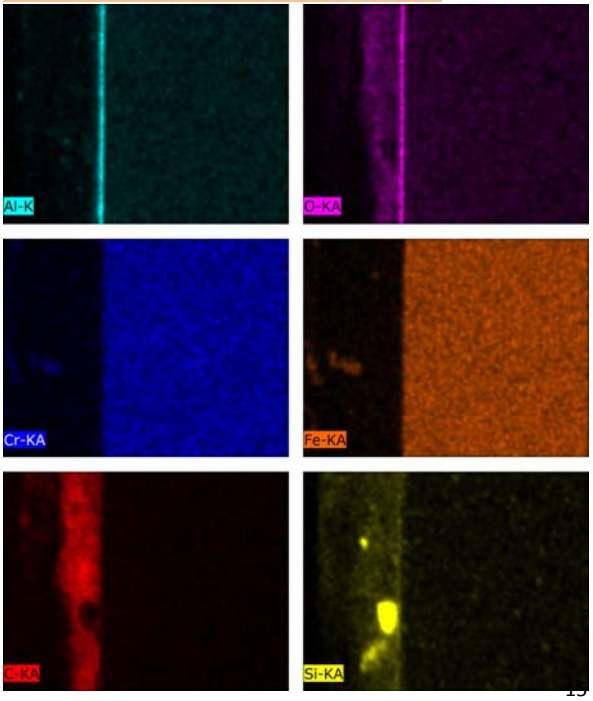








EDX mapping 1000 hours sample



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XRD Analysis for Al-containing Steels

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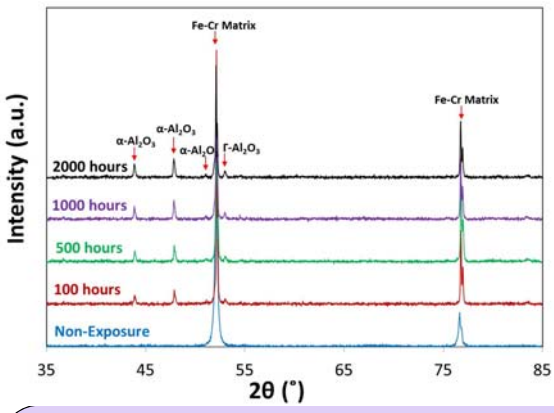
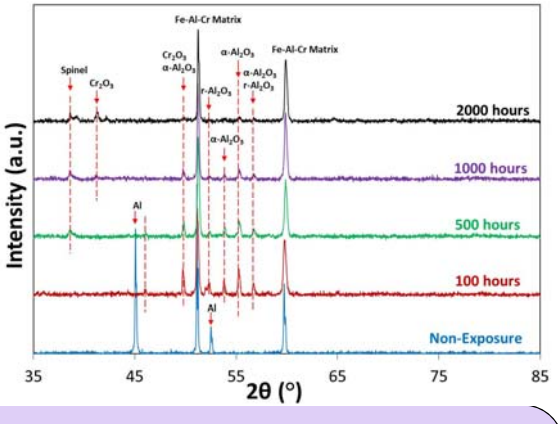
AluChrom 318



Aluminised SS309



- The formation of a surface scale of α-Al_2O_3 was observed for both materials.
- The peak intensity of α-Al_2O_3 for AluChrom 318 shows an increasing trend.
- The XRD peaks of α-Al_2O_3 for aluminised 309 almost disappeared after 2000 hours.
- For aluminised 309, the peaks spinel and Cr_2O_3 started to appear after 500 hours exposure.
- The alumina layer formed on Aluchrom 318 is much stronger than that on aluminsed 309.

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Heat Exchanger from Vaillant

Steady state; AluChrom 318; 5800 hours; old design

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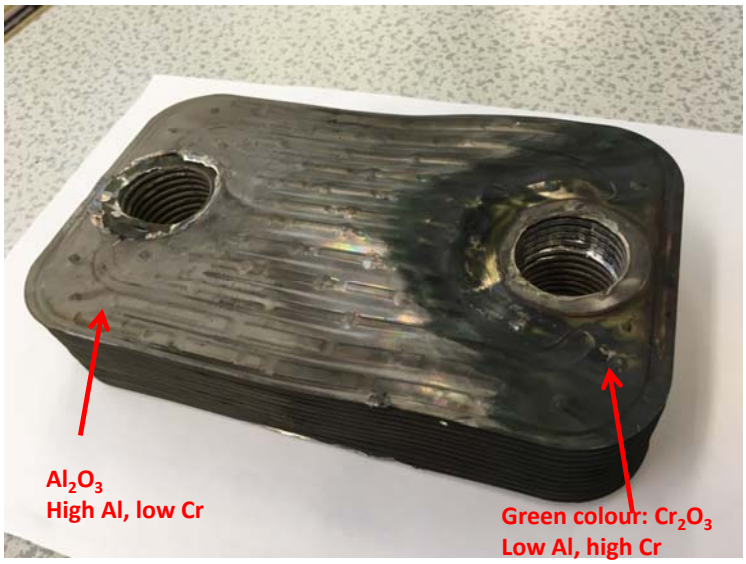
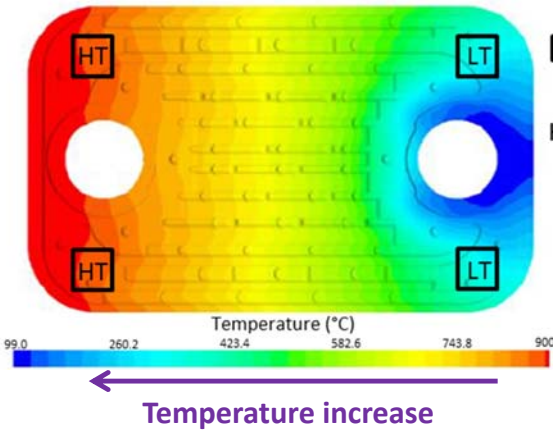


Hot Zone
900 ˚C

Cold Zone
100 ˚C



- **The green colour on the left image is chromium oxide. This region is the cold zone and the temperature is about 100 ˚C. The temperature is not high enough for the Al_2O_3 to form, so the Cr_2O_3 forms on the surface first.**
- **The hot zone shows an extremely low concentration of Cr and high concentration of Al, which means the plate surface is completely covered with a very thick Al_2O_3 coating.**
- **A (pre-)heat treatment procedure is still required for the AluChrom 318.**

Heat Exchanger from Vaillant

Steady state; AluChrom 318; 5,800 hours; old design

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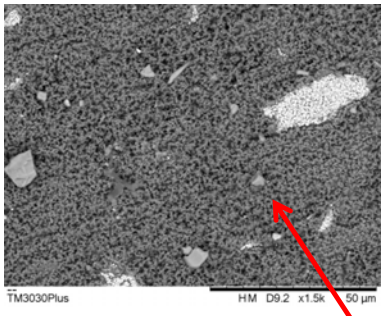
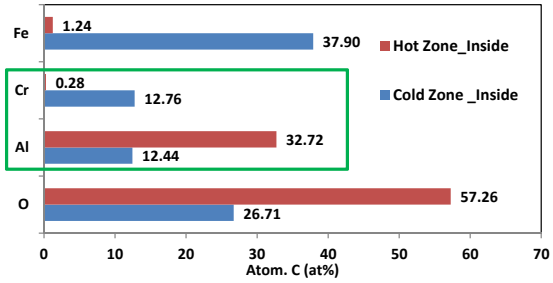
SEM for **hot** zone of inside plate



Comparison of the elemental concentration between hot zone and cold zone (inside of the stack plate)

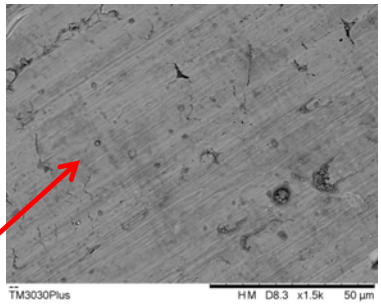


Hot Zone
700 ˚C

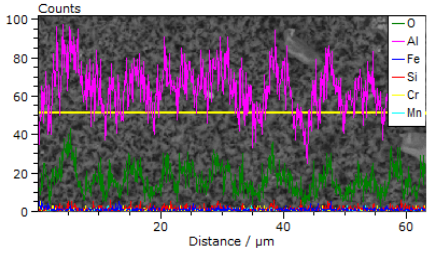
Temperature increase

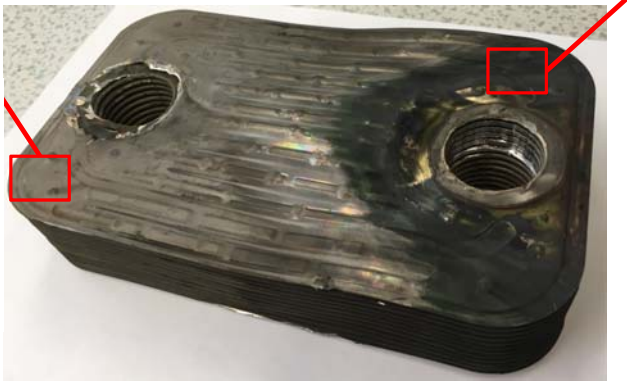
Cold Zone
100 ˚C

SEM for **cold** zone of inside plate

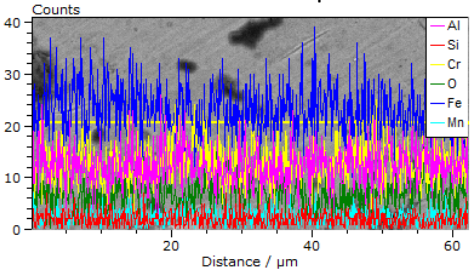


EDX line scan
for **hot** zone of inside plate



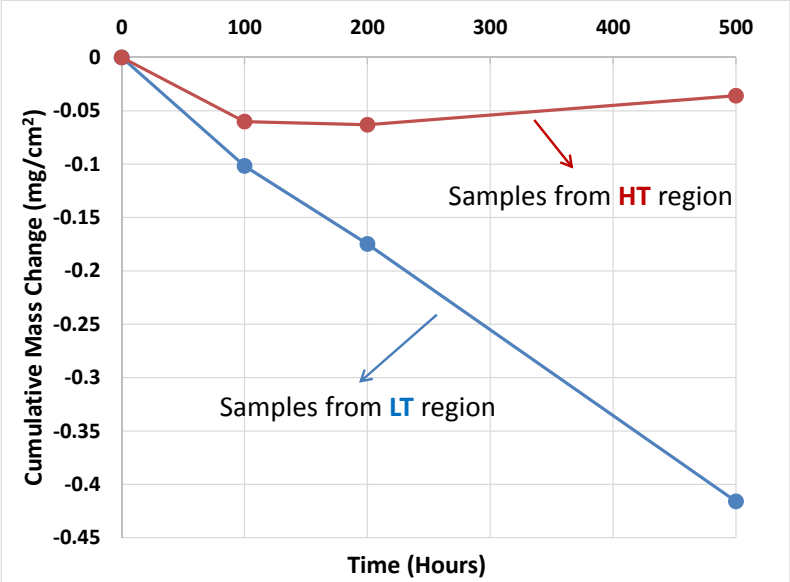


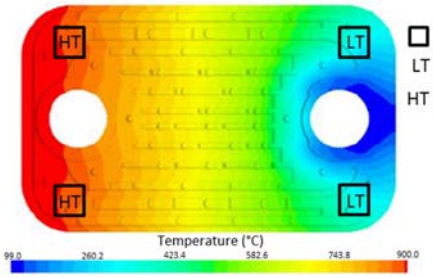
EDX line scan
for **cold** zone of inside plate



Mass Gain Measurements

850 °C, 6.0L/min air flow + 3 vol% H_2O





Sample from HT regions:

- Thick alumina layer covered both inside and outside of the plate;
- The slight decrease of mass before 200 hours maybe due to a small amount of alumina spallation.

Sample from LT regions:

- Outside is covered with thick Cr_2O_3, inside is covered with think alumina.
- The large amount of mass decrease is due to the large amount of Cr evaporation from outer and internal surface of plate.

Since the alumina coverage of the internal face of plate in the cold zone is not enough, it will cause much high Cr evaporation compared to the internal face of plate in the hot zone. Therefore, pre-heat treatment in air is necessary to prevent Cr_2O_3 formation in both hot and cold zone.

Conclusions

- **Inconel 625** shows the **largest amount of Cr evaporation** because the surface is totally covered with Cr_2O_3.
- Uncoated **SS309** also exhibits serious **Cr leakage** due to the spallation of the spinel layer ($(Mn, Cr)O_X$).
- For **AluChrom 318**, the α-Al_2O_3 formed on the surface could effectively **prevents Cr evaporation** in the long term.
- For **aluminised SS309**, the α-Al_2O_3 produced by PVD can dramatically reduce Cr evaporation in the beginning. However, the spallation of the Al_2O_3 coating was detected after long term exposure, followed by **increased Cr leakage**.
- A heat treatment process is needed for the heat exchanger plate prior to operation.

Future Work

- For Cr evaporation tests:
  - To run short term (one week) Cr evaporation test on **welded AluChrom 318** (repeat 3 times),
  - To run **long term (1,000 hours)** Cr evaporation test for Inconel 625, SS309, aluminised SS309, AluChrom 318 and welded AluChrom 318.
- For high temperature oxidation tests:
  - Aim to complete 10,000 hours.
- Post- test analysis:
  - Cross-section SEM/EDX for Inconel 625, SS309 and aluminised SS309 (include: **0, 100, 500 and 1,000 h** samples),
  - Surface SEM/EDX for Inconel 625, SS309, aluminised SS309 and AluChrom 318 (including **5,000 and 10,000 h samples**).
- Heat exchanger plates from Vaillant
  - To find a temperature for **pre-heat process** of heat exchanger plate,
  - To analyse chromium evaporation and weight gain of 'used' heat exchanger plates.

Thank you for your attention!
Any Questions?

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