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The Effect of Pre-heat Treatment of AluChrom 318 on the Corrosion Behavior and Cr Evaporation in SOFC Cathode Air Pre-heater

Kun Zhang, Ahmad El-kharouf, Robert Steinberger-Wilckens

Centre for Hydrogen & Fuel Cell Research

School of Chemical Engineering

University of Birmingham

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Introduction
Cathode Air Pre-Heater (CAPH)

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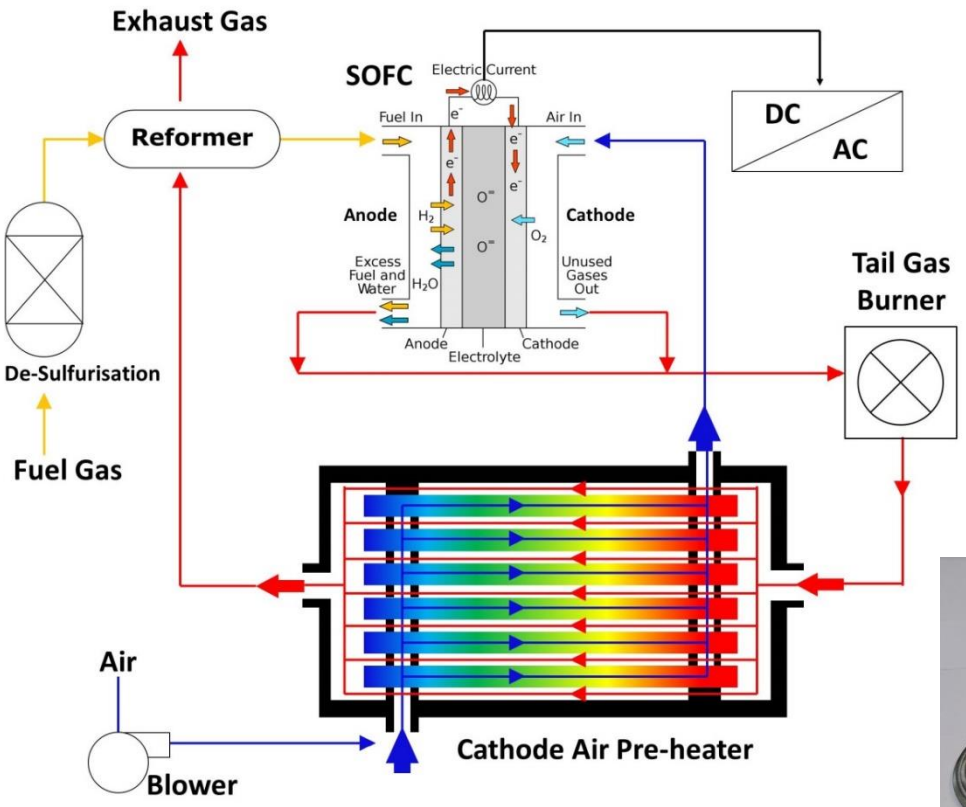
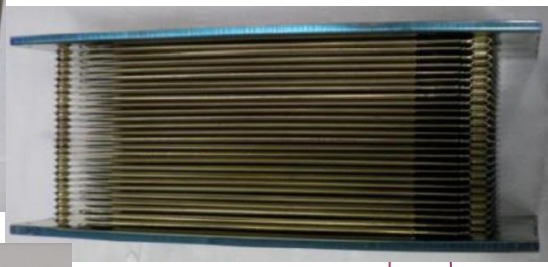


Cathode Air Pre-heater (CAPH)

1. Type: gas to gas heat exchanger; 2. Function: to recover heat from an exhaust gas to heat air to the target temperature before it enter the fuel cell; 3. Cost: One of the most expensive components within the whole CHP system; 4. Material: ceramic or metallic heat exchanger.



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Previous Results from 15th SOFC symposium Material Selection Based on Cr Evaporation

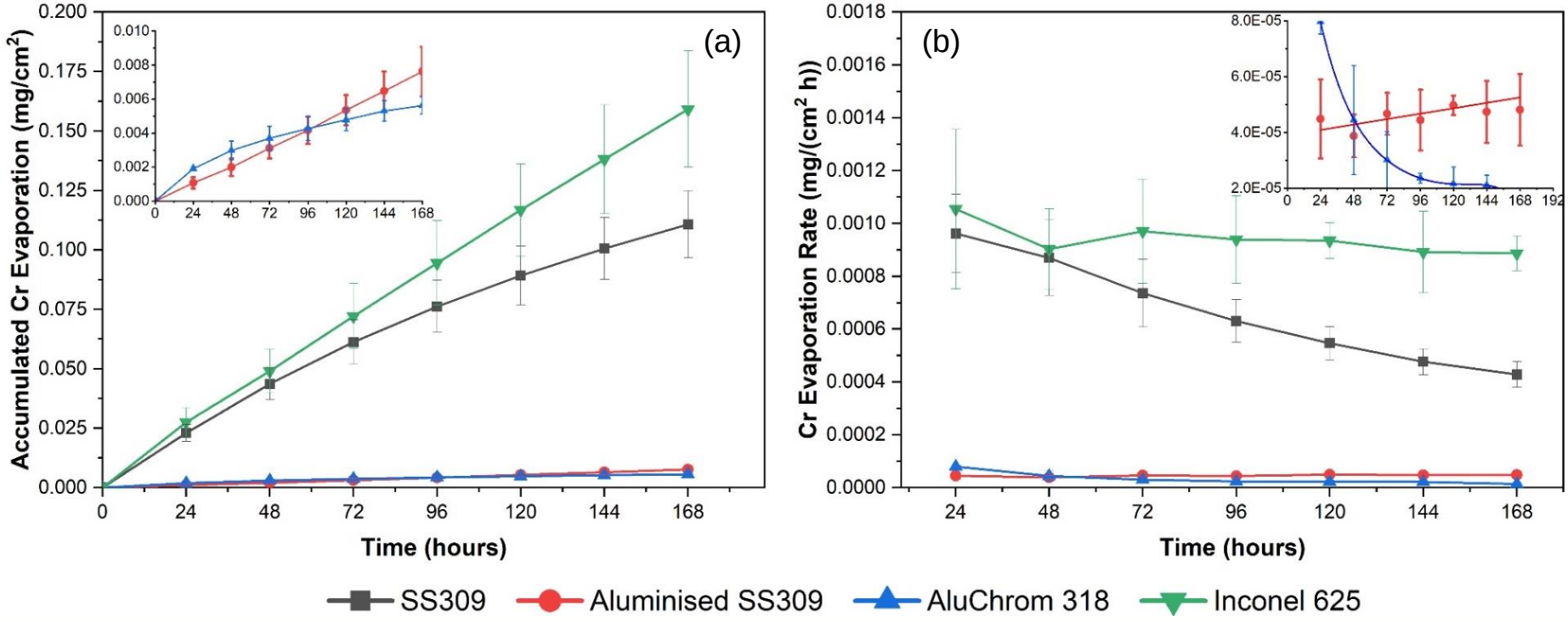


Figure. (a) Accumulated Cr evaporation and (b) Cr evaporation rates as a function of time for SS309, aluminised SS309 and AluChrom 318 exposed to 3 vol% H_2O humidified air at 850 ˚C for 168 hours.

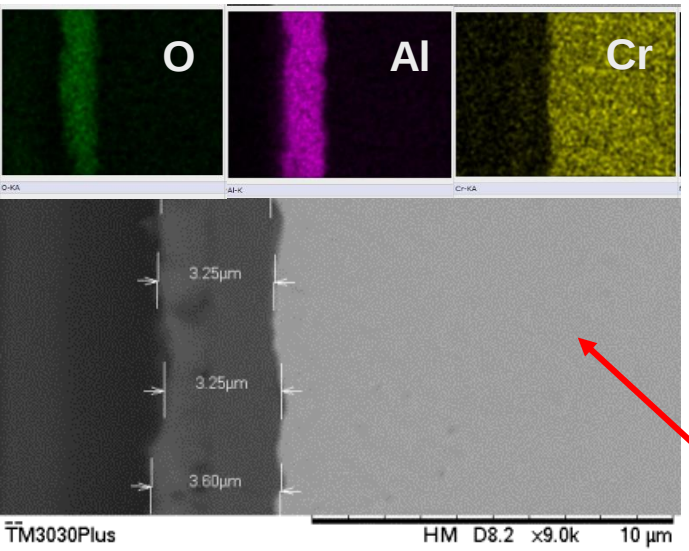
AluChrom 318 shows the best Cr retention ability.

Steel	Oxide scale
Inconel 625	Pure Cr_2O_3
SS309	(Cr,Mn) spinel
Aluminised SS309	Spalled Al_2O_3
AluChrom 318	Al_2O_3

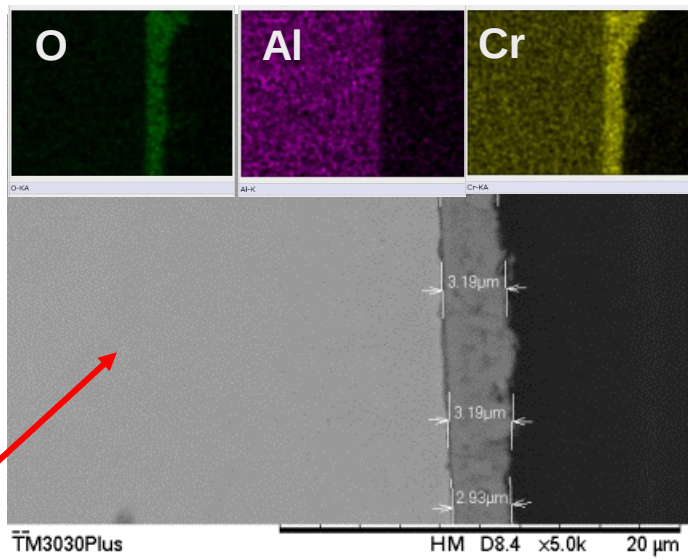
Cross-section SEM/EDX analysis for Heat Exchanger from Vaillant

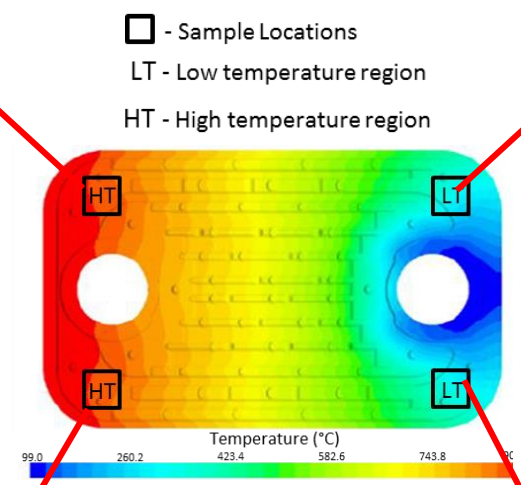
Steady state; AluChrom 318; 5800 hours; old design

Hot Zone Outside

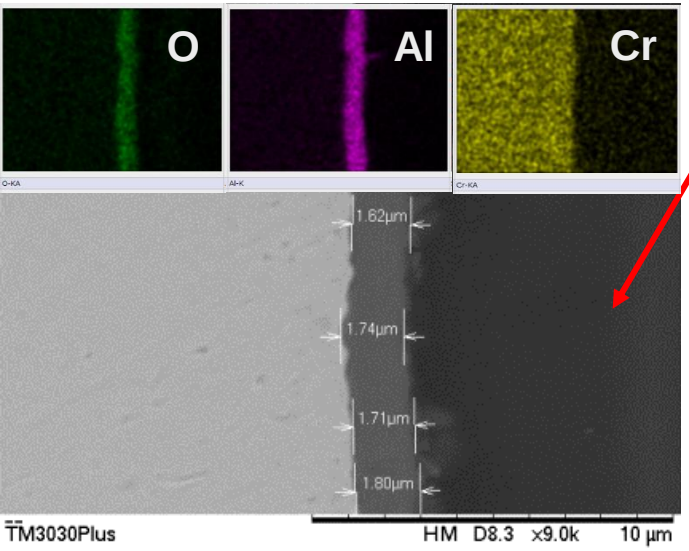


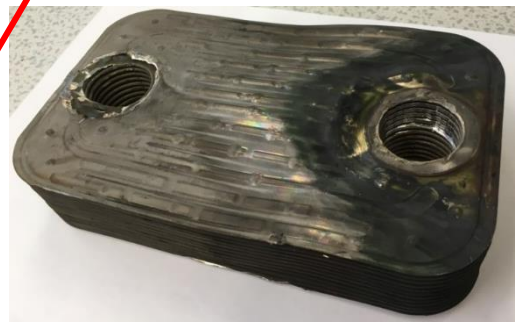
Cold Zone Outside



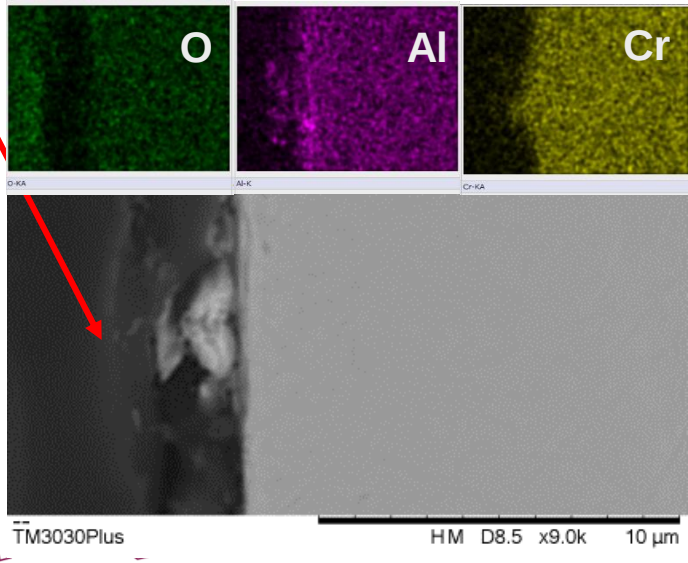


Hot Zone Inside





Cold Zone Inside



Pre-treatment for AluChrom 318

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(wt.%)	Fe	Cr	Mn	Al	Ni	Si	Nb	W	others
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

Variables: (1) Temperature; (2) Time.

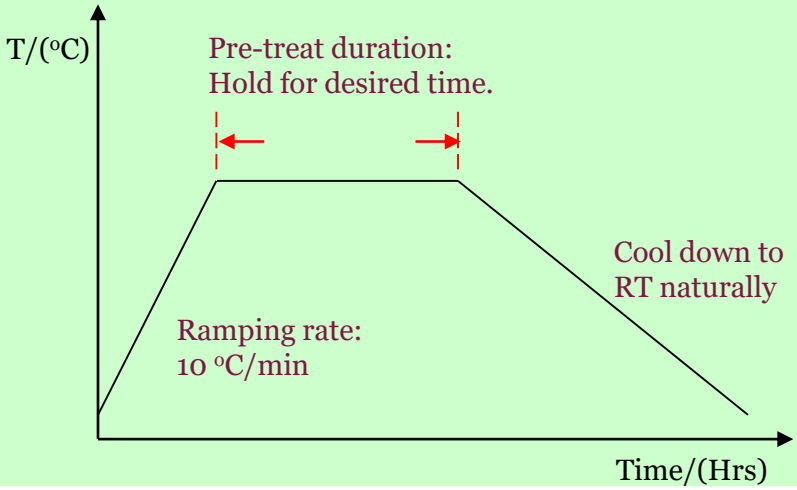
800 °C: 1 hour, 2 hours, 4 hours.

900 °C : 1 hour, 2 hours, 4 hours.

1000 °C : 1 hour, 2 hours, 4 hours.

1100 °C : 30 mins, 1 hour, 2 hours.

Atmosphere: Air (No flow)



The expected effect of pre-heat treatment:

1. To form the stable α-Al_2O_3 on the surface prior to exposure in SOFC environment;
2. To stop the Cr_2O_3 formation in cold zone;
3. To slow down the Al oxidation rate in hot zone.

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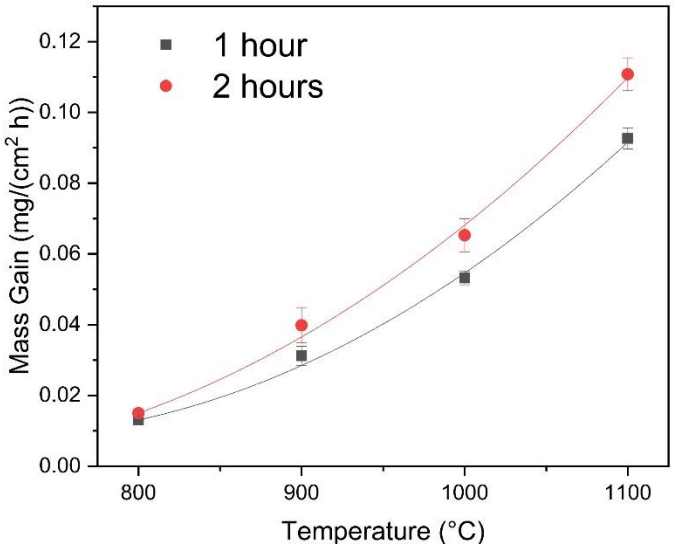
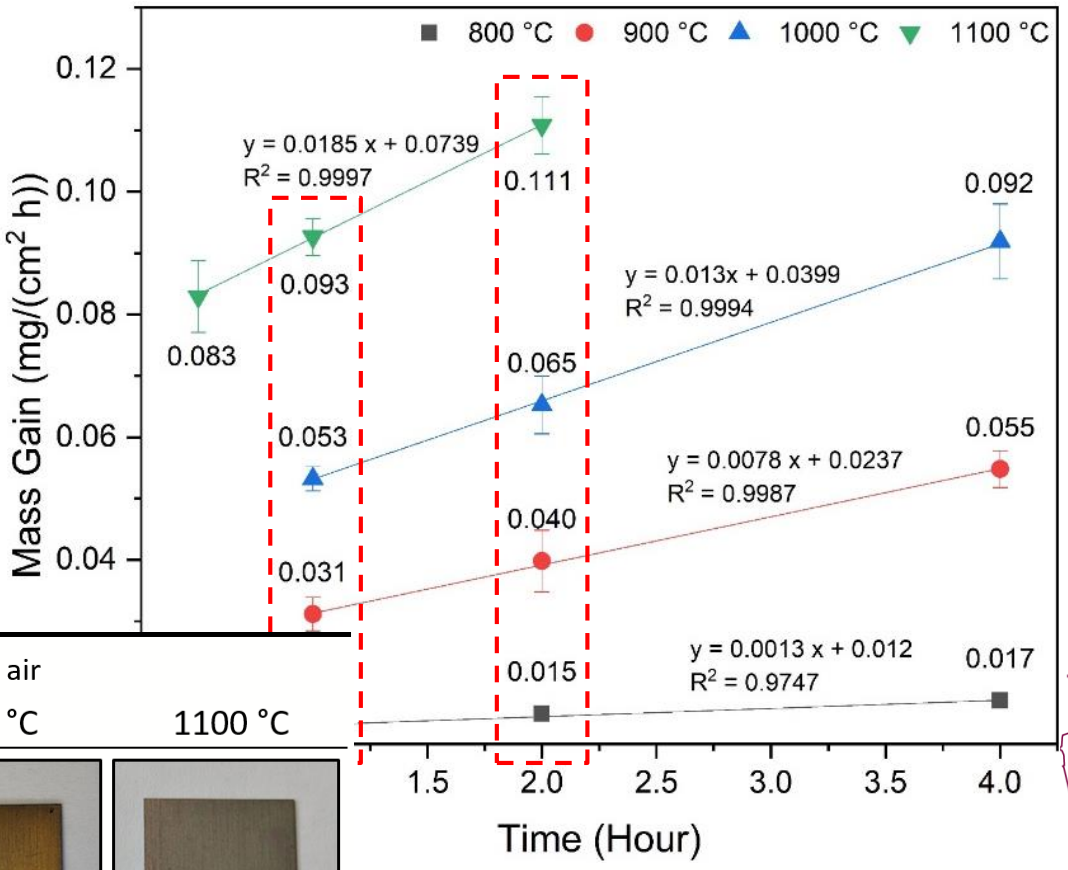
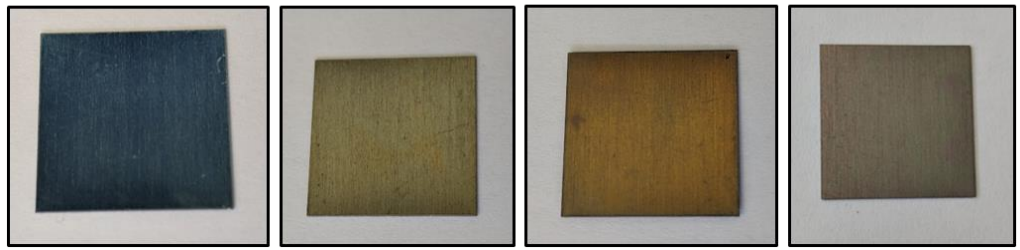
Effect of Time and Temperature on the Pre-treatment





One hour pre-oxidation in dry air

800 °C 900 °C 1000 °C 1100 °C



, 900 °C for 1 , 2 and 4 hours, 1000 °C for 1, 2 and 4

EDX: Surface Element Concentration

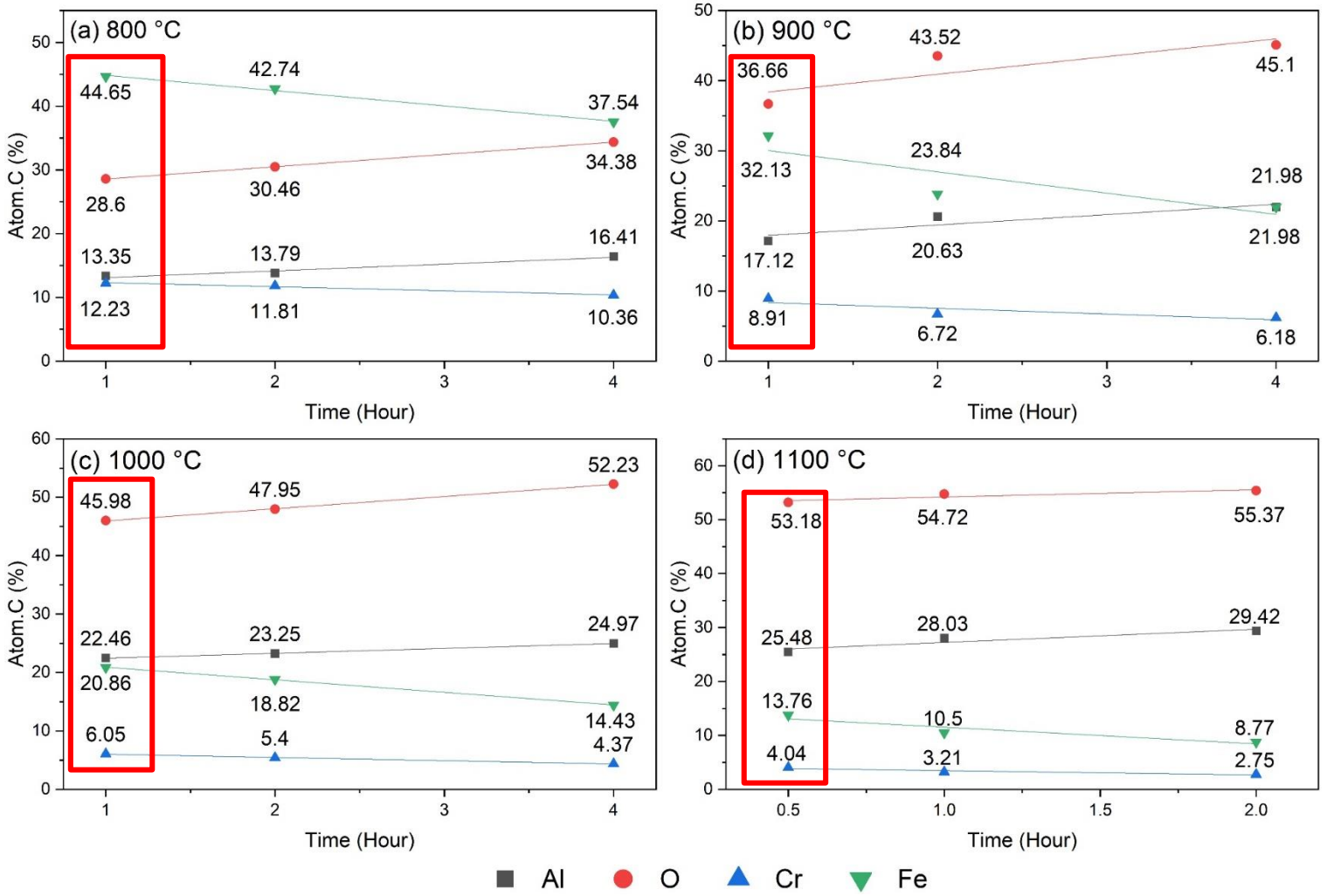


Figure. EDX elemental concentration of AluChrom 318 surface pre-heated at (a) 800 °C for 1, 2 and 4 hours, (b) 900 °C for 1 , 2 and 4 hours, (c) 1000 °C for 1, 2 and 4 hours and (d) 1100 °C for 0.5, 1 and 2 hours.

XRD Analysis

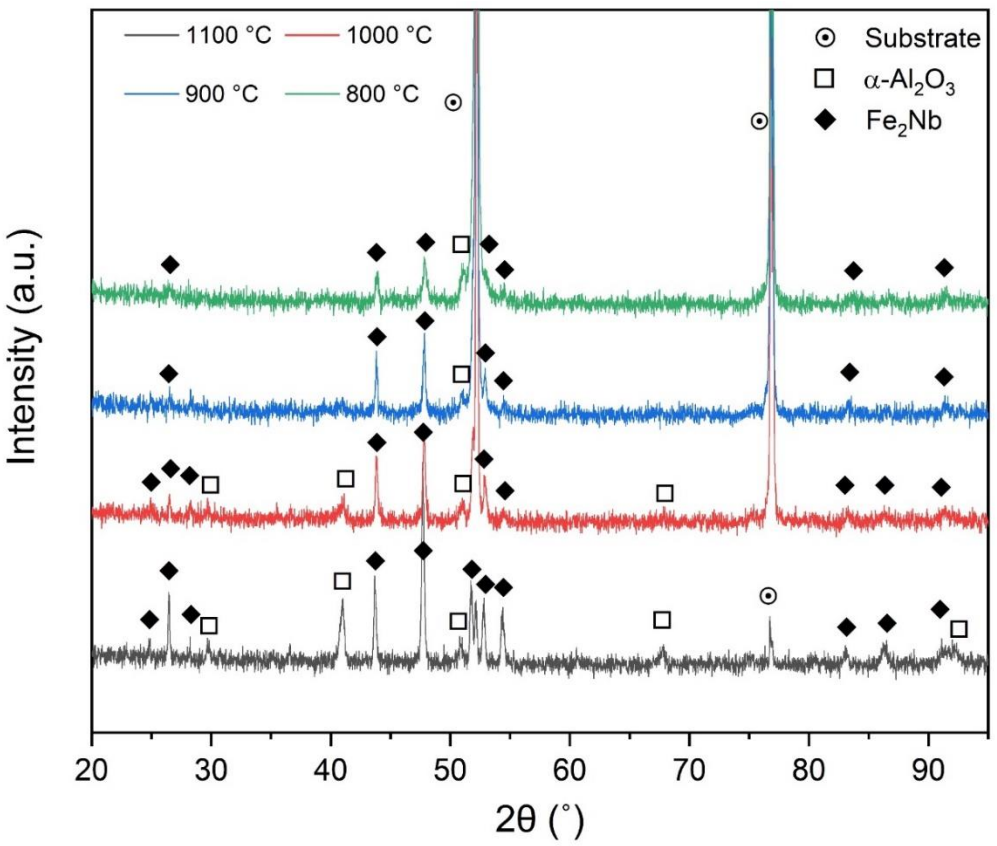


Figure. XRD patterns of the AluChrom 318 pre-treated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour.

- **Formation of Fe_2Nb Laves phase has been detected for all the pre-treated samples;**
- **Formation of corundum-type α-Al_2O_3 has been detected for samples pre-treated at 1000 °C and 1100 °C for 1 hour;**
- **The alumina scale formed on the samples pre-treated at 800 °C and 900 °C cannot be detected by XRD.**
- **The alumina form at 800 °C and 900 °C is mainly in metastable phases (γ- or θ-Al_2O_3) due to their easy nucleation at low temperature while the amount of the alumina formed is too low and below the detection limit of the XRD technique.**
- **The 1100 °C used for pre-treatment promotes faster phase transformation of metastable alumina formed during temperature ramping stage to the stable α-Al_2O_3 phase.**

SEM/EDX Analysis

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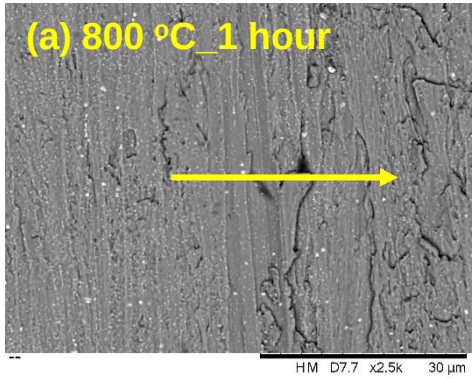
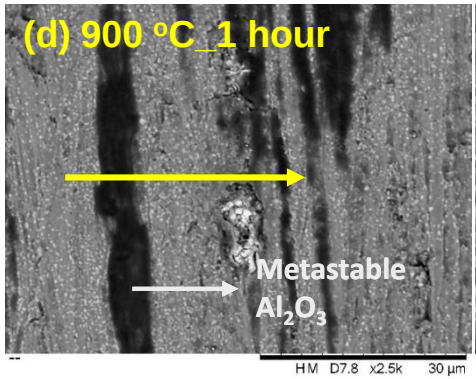
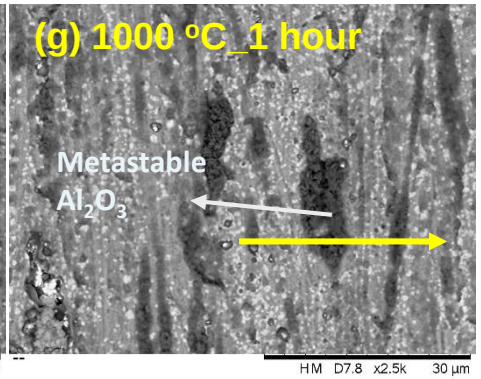
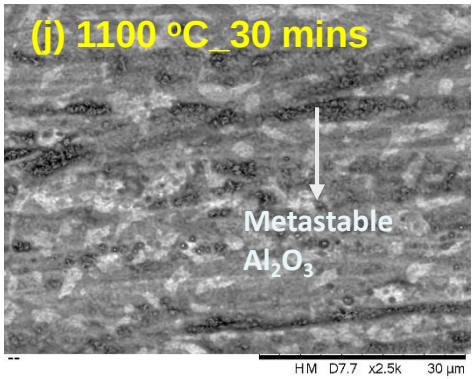
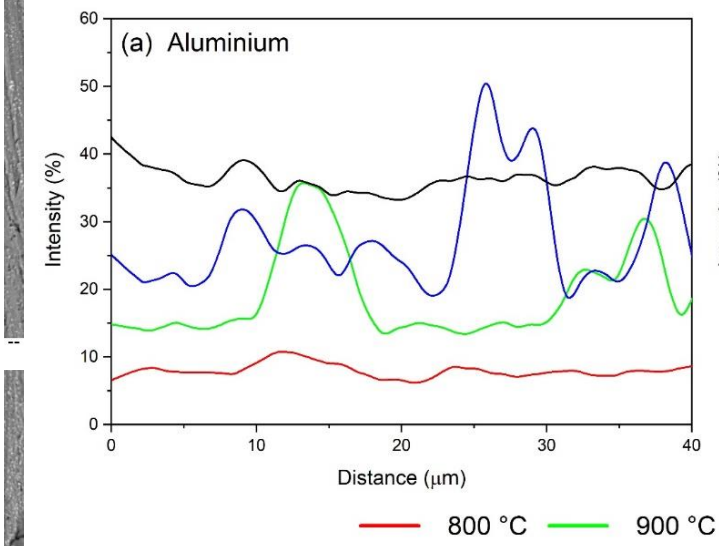
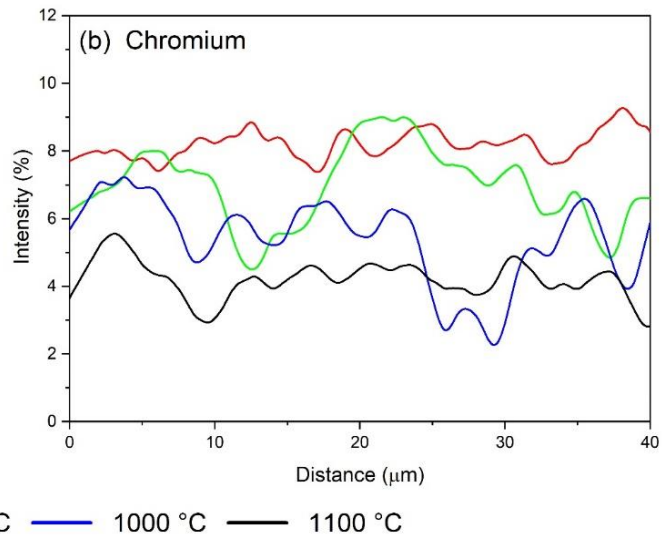




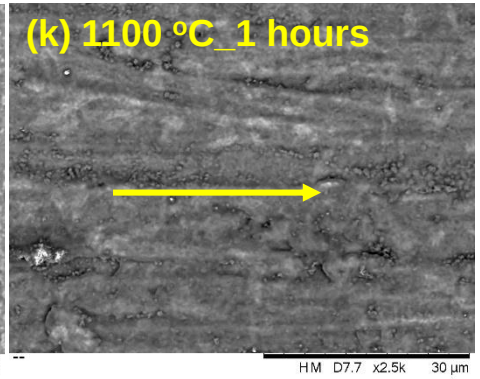








800 °C 900 °C 1000 °C 1100 °C



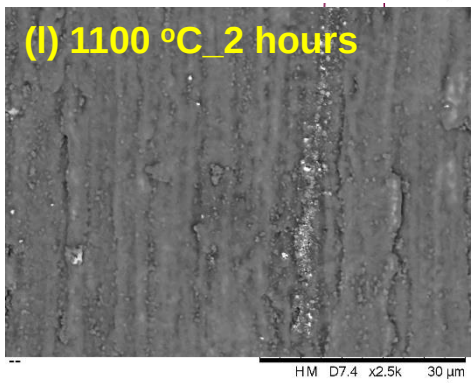


Figure. EDX line scan of Al (a) and Cr (b) for the AluChrom 318 pre-heated at 800 °C, 900 °C, 1000 °C and 1100 °C for 1 hour along the line indicated in the micrographs.

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Exposure Test

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- **Materials:**
  - Pre-treated AluChrom 318
- **Experiment:**
  - **High Temperature Oxidation Test: 500 hours**

    Normal Tubular Glassware
  - **Quantification of Cr Evaporation: 168 hours**

    Denuder Technique (ICP-OES)
- **Test Condition:**
  - 850 ˚C; 6.0 L/min air flow; 3% humidity
- **Post-analysis:**

  Mass measurement; Surface SEM/EDX; X-ray Diffraction.

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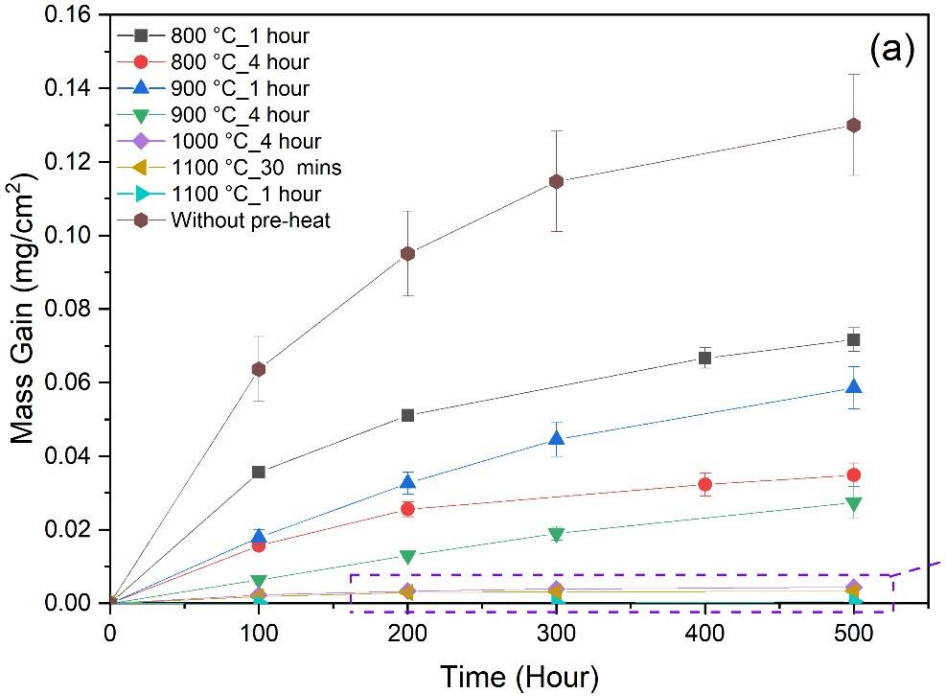
Corrosion Testing-Mass Gain



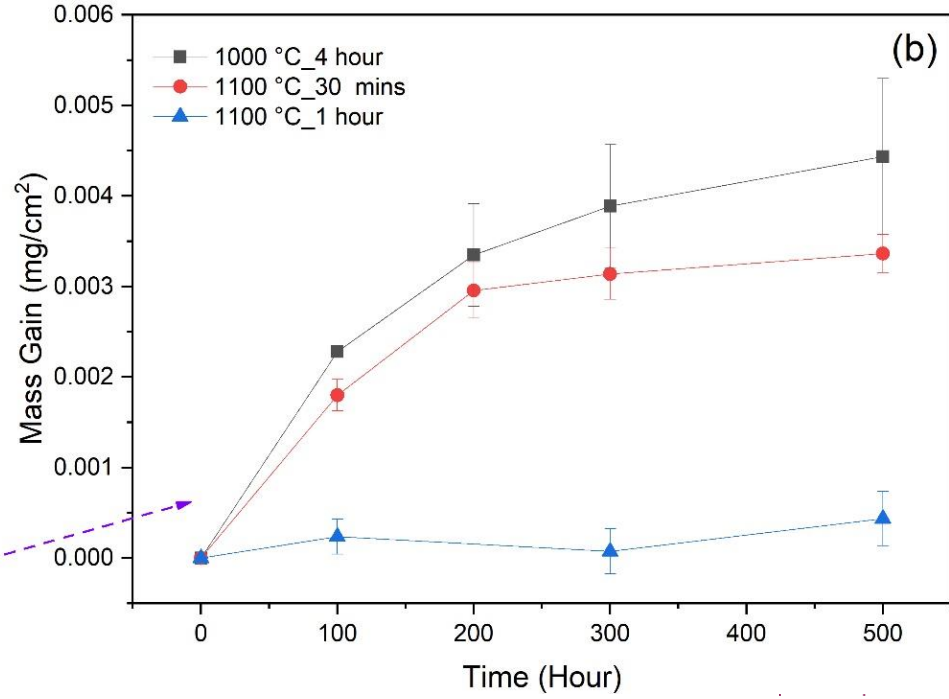
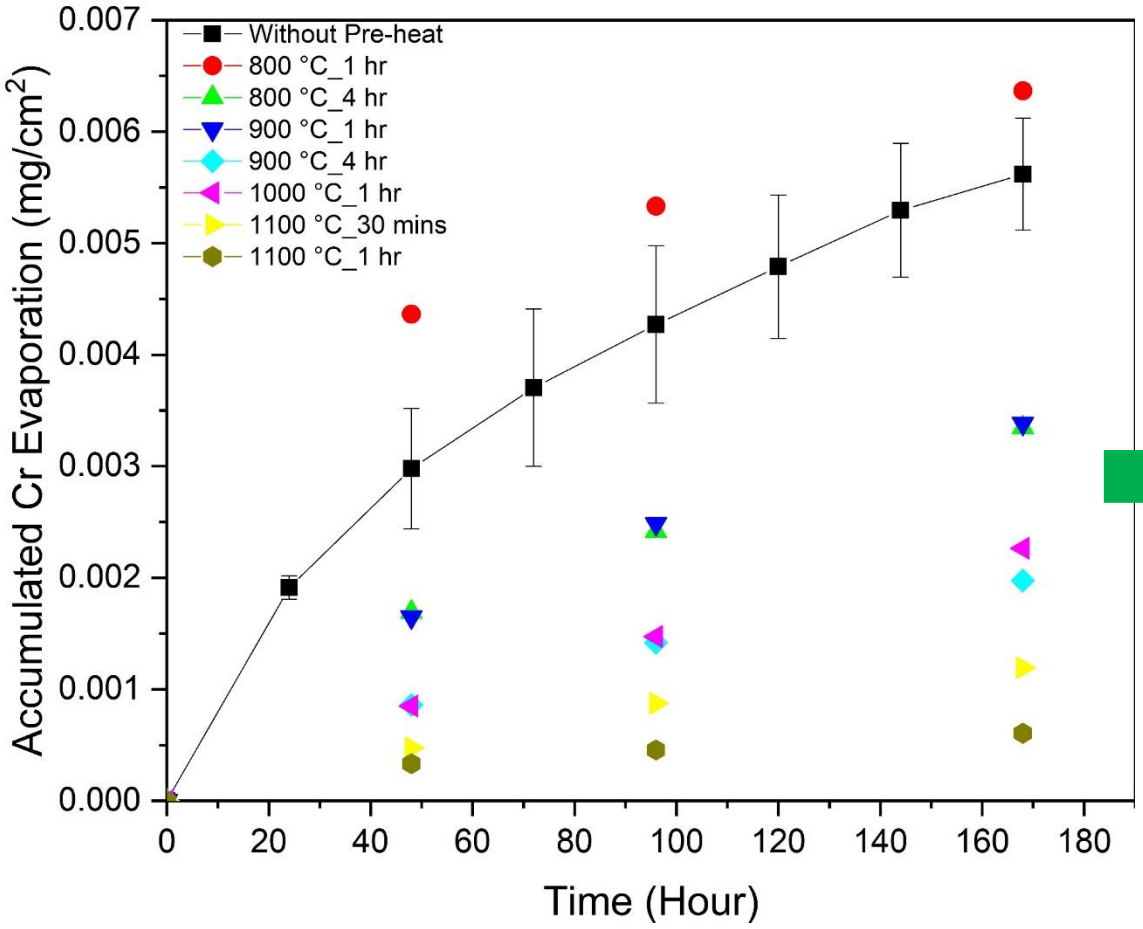


Figure. Discontinuous mass measurements of the non-treated and pre-treated AluChrom 318 exposed to 3% H_2O humidified air (6.0 L/min) at 850 °C for 500 hours.

AluChrom 318 pre-treated at 1100 °C for 1 hour shows a **98% reduction** of oxidation rate.

Cr Evaporation Test



Samples	Cr Evaporation (mg/cm²)
Non-treated sample	5.62E-03
800 °C_1 hour	6.37E-03
800 °C_4 hours	3.35E-03
900 °C_1 hour	3.38E-03
900 °C_4 hours	1.98E-03
1000 °C_1 hour	2.26E-03
1100 °C_0.5 hour	1.19E-03
1100 °C_1 hour	6.07E-04

Figure. Accumulated Cr evaporation as function of time for the non-treated and pre-heated AluChrom 318 exposed at 850 °C in 3 vol% humidified air for 168 hours.

AluChrom 318 pre-treated at 1100 °C for 1 hour shows a **90% reduction** of Cr evaporation.

Surface Morphology After Exposure Tests

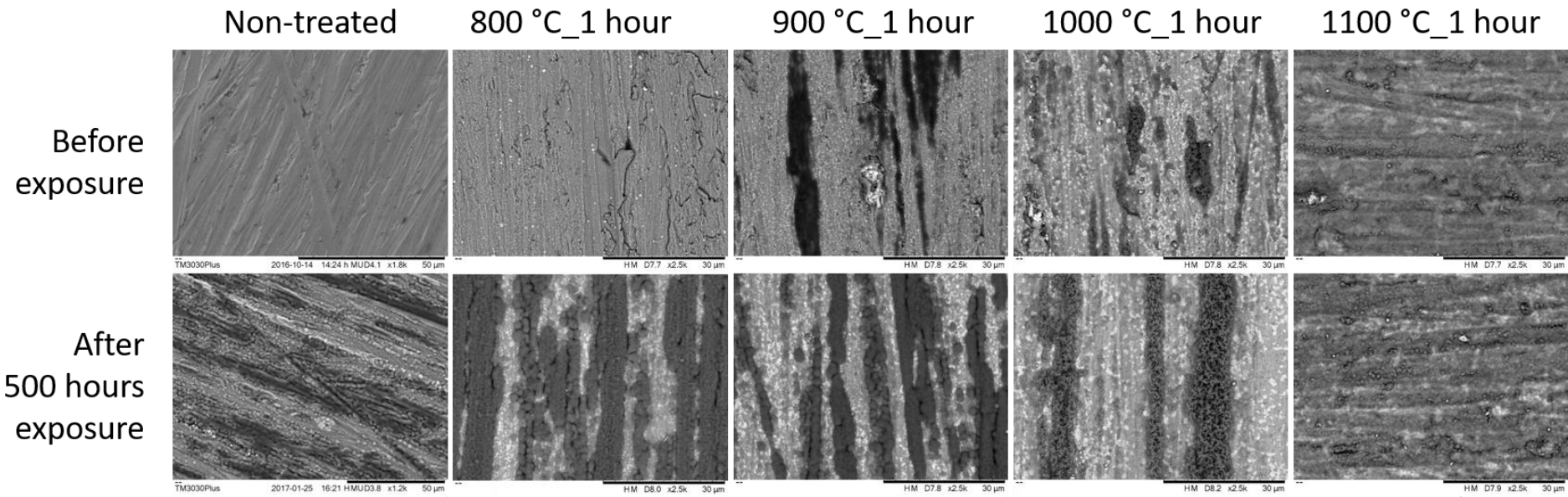


Figure. Surface SEM images of the non-treated AluChrom 318 (a) and the AluChrom 318 pre-treated for 1 hour at 800 °C, 900 °C, 1000 °C and 1100 °C before and after exposed for 500 hours at 850 °C in 3% humidified air (6.0 L/min).

Expansion of long ridged alumina (Metastable alumina) after exposure tests:
800 °C_1 hour > 900 °C_1 hour > 1000 °C_1 hour > 1100 °C_1 hour

Pre-treatment for single AluChrom 318 heat exchanger plate

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Non-treated plate

1000 °C_1 hour

1100 °C_1 hour

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Conclusions

- The oxidation rate and Cr evaporation of the AluChrom 318 at 850 °C in humidified air was shown to be dramatically decreased by pre-treatment.
- It can be assumed that the kinetics of oxidation rate and Cr release for the pre-treated AluChrom 318 is governed by the phase formation of alumina on the alloy surface during pre-treatment. High temperature with short time is more effective than low temperature with long time.
- Pre-treatment at 800 °C and 900 °C resulted in less improvement in the oxidation resistance and Cr retention capability than at 1000 °C and 1100 °C due to the formed metastable alumina scale which allows relatively faster Al and Cr outward diffusion.
- The best corrosion resistance was observed for the samples pre-treated at **1100 °C for 1 hour** with **a 98% reduction of oxidation rate and 90% reduction of Cr evaporation** compared to the non-treated AluChrom 318 due to the formation of a compact and homogenous α-Al_2O_3 scale which can effectively prevent the Al and Cr from outward diffusion in the simulated SOFC environment.

Acknowledgements

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HEATSTACK Project:	**All the collaborators**
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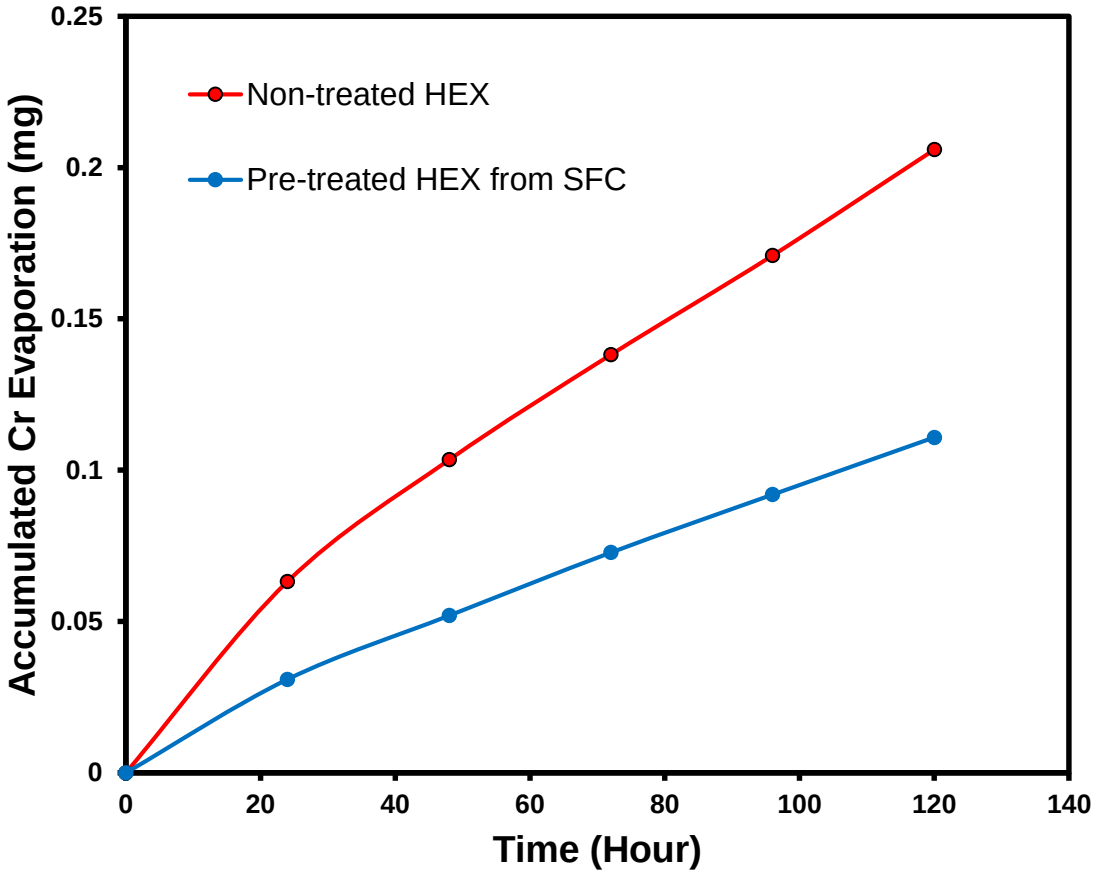
Funding:	**European Union's Seventh Framework Programme No.700564**

Cr evaporation of pre-treated AluChrom 318 single heat exchanger plate



Non-treated plate after exposure