Corrosion behaviour of stainless steel in molten nitrate salt

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3. Results and discussion
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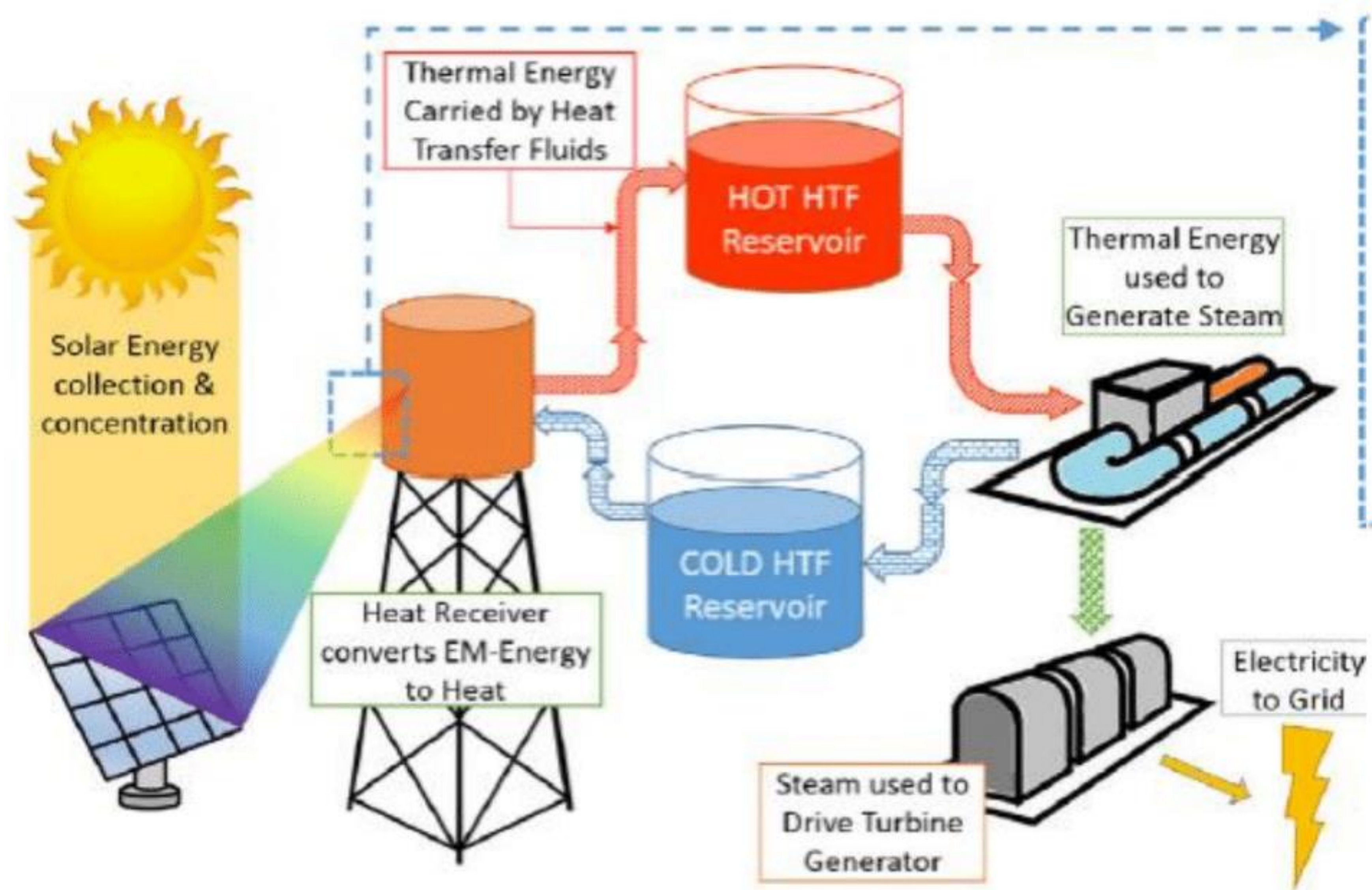
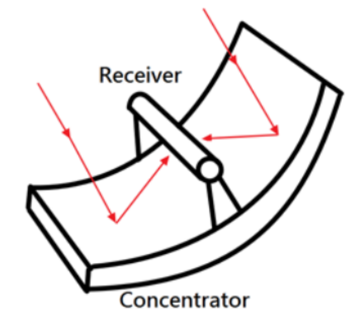
1.Introduction



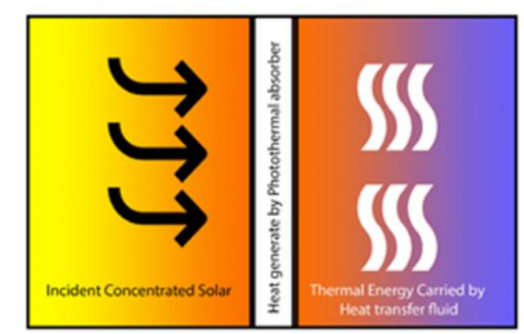
K. Vignarooban, X. Xu, A. Arvay, K. Hsu, A.M. Kannan, Applied Energy 146 (2015), 383-396.

receiver



The receiver of CSP consist of absorber coated materials. The fraction of thermal energy trans-fromed in to useful energy

Heat transfer fluid



Heat transfer fluid transfer the heat from the receiver to generater.

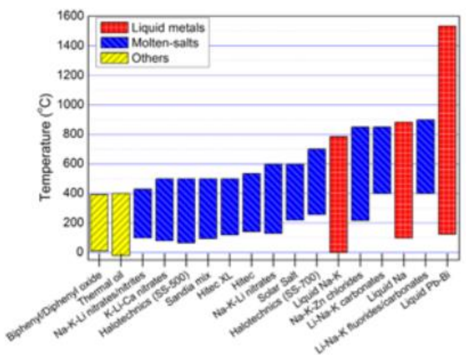
- Concentrating solar power (CSP) is currently being a new candidate for providing the majority of the renewable energy in Thailand.
- CSP focuses the solar energy and uses the resulting heat to create steam which drives a turbine generator

Heat transfer fluid

The characteristics of a heat transfer fluid includes:

- low melting point,
- high boiling point and thermal stability,
- low vapor pressure at high temperature,
- low corrosion,
- low viscosity,
- high thermal conductivity,
- high heat capacity for energy storage, and
- low cost.

molten salt



The molten salts make excellent HTFs mainly due to their thermal stability at high temperatures (generally > 500 °C).

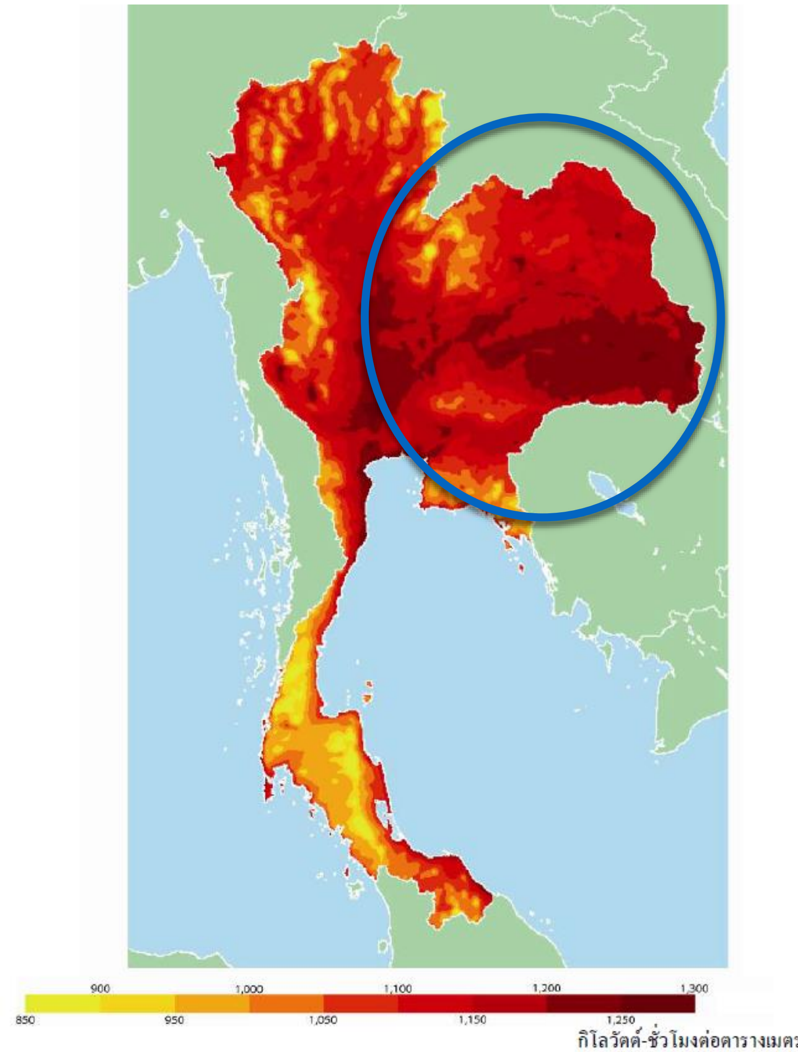
Thermal and physical properties of commonly used HTFs.

Name	Compositions (wt.%)	Melting point (°C)	Stability limit (°C)	Viscosity (Pa s)	Thermal conductivity ($W m^{-1} K^{-1}$)	Heat capacity ($kJ kg^{-1} K^{-1}$)	Cost ($/kg)	Corrosion: Rate (μm/year unless specified)	Alloy	Temperature (°C)
Molten-salts										
Solar Salt	$NaNO_3$ (60)–KNO_3 (40)	220[a]	600[a]	0.00326 (at 300 °C)[a]	0.55 (at 400 °C)[a]	1.1 (at 600 °C)[c]	0.5[b]	5	A36	316
								6–15	304	570
								15.9/4	316	600/680
								60	321	600/680
								10.4/4	347	600/680
								47	Ha230	600/680
								19.8/6	In625	
								88		
								21.7/5		
								94		

Solar salt ($NaNO_3$ – KNO_3) was first used in this research.

**Blanco, M. J., and S. Miller. "Introduction to concentrating solar thermal (CST) technologies." *Advances in Concentrating Solar Thermal Research and Technology*. 2017. 3-25.

Solar energy in Thailand



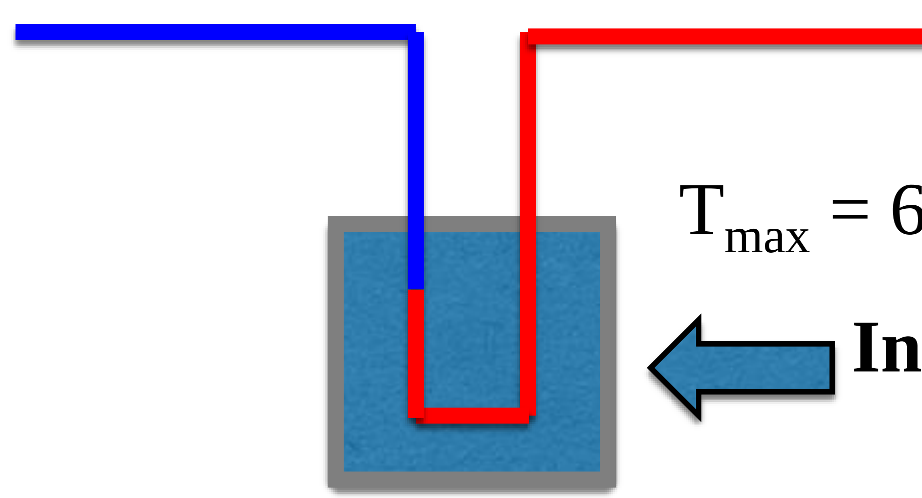
North-east zone is very interesting to be used for CSP

16-22 MJ/m^2-day

E_{max} in Feb - May

J. Serm, **Solar radiation**, Silpakorn University, 2014

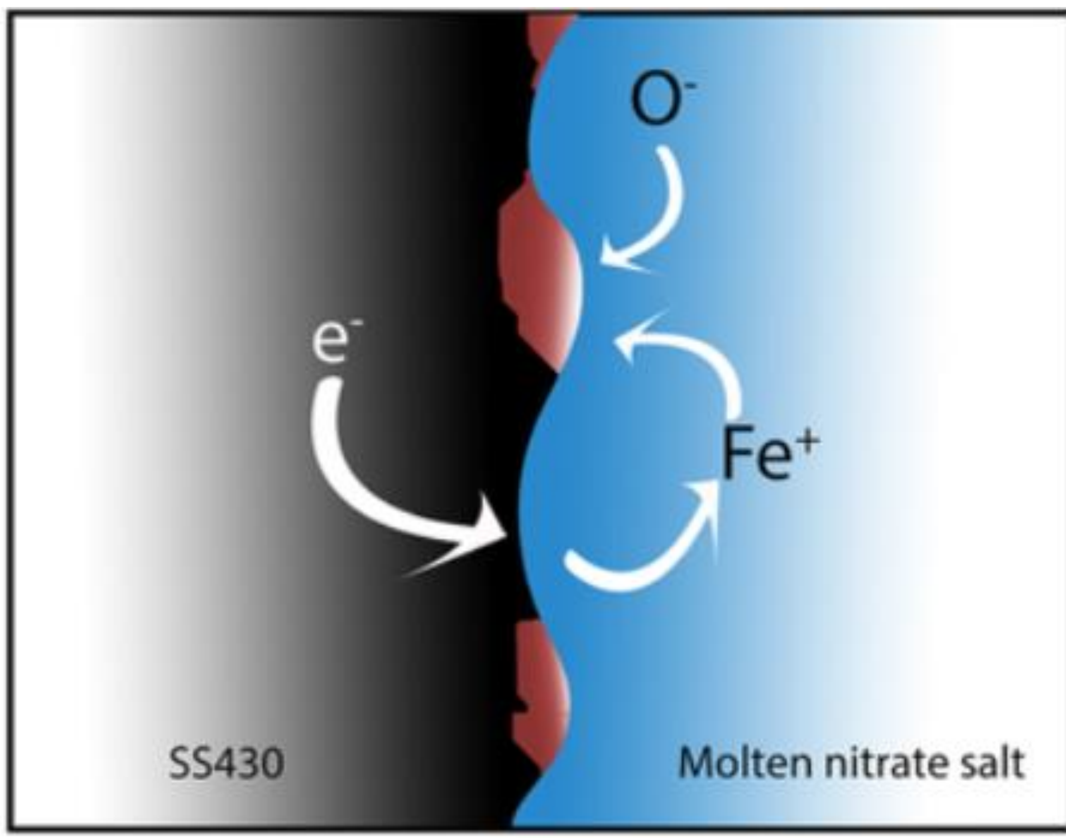
The 1st experiment was tested in Udonthani province (North-East of Thailand) in order to produce hot water in food industry (Chili sauce).



Solar salt (60%wt $NaNO_3$+40%wt KNO_3) (Industrial grade impurity 5%)

Problem

- Due to the expensive materials (Ni-base superalloys) , ferritic stainless steels such as AISI430 was used instead of Inconel625.
- However, the AISI430 was aggressively corroded in molten nitrate salt at high temperature with reaction as follows:



The corrosion reaction of molten nitrate salt at high temperature.

$$NO_3^- + 2e^- \leftrightarrow NO_2^- + O^{2-}$$

$$Fe + O^{2-} \leftrightarrow FeO + 2e^-$$

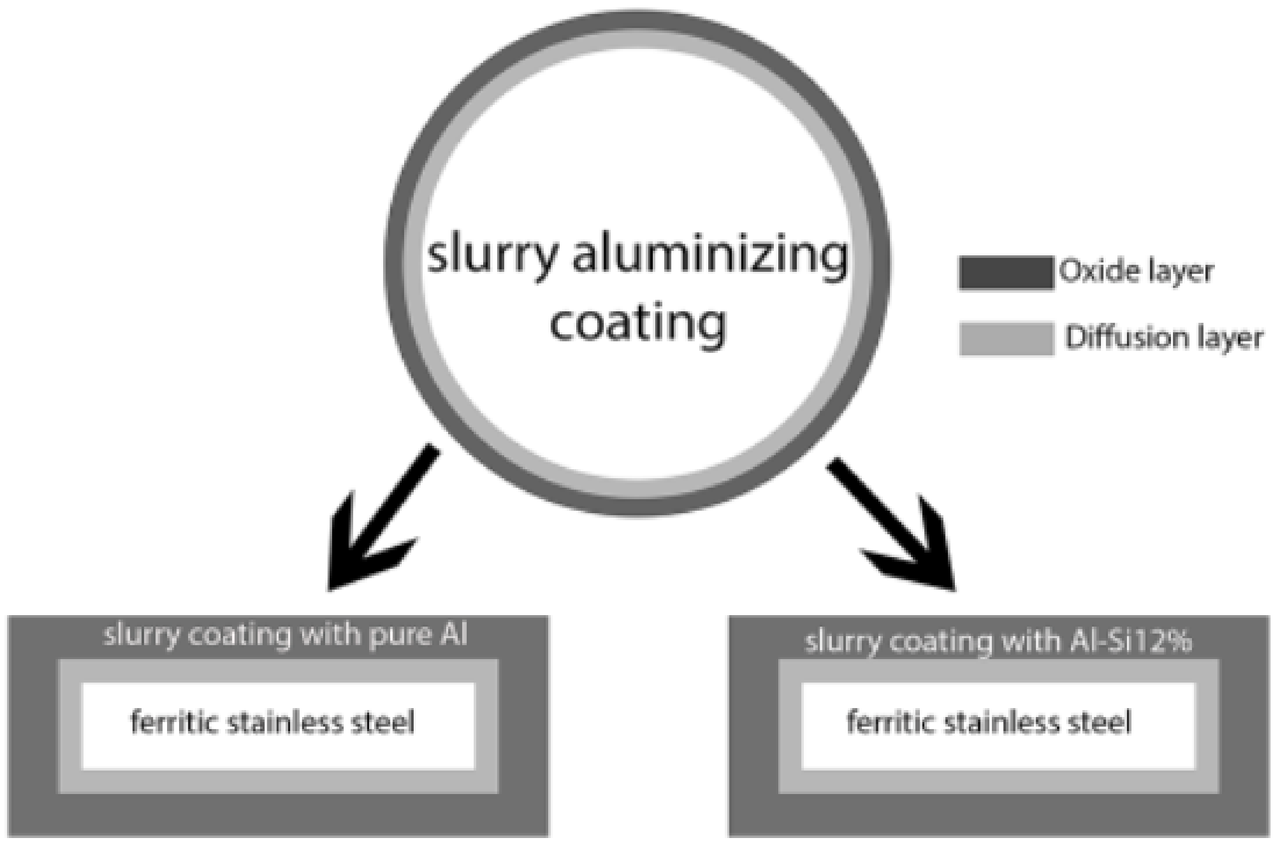
$$3FeO + O^{2-} \leftrightarrow Fe_3O_4 + 2e^-$$

$$2Fe_3O_4 + O^{2-} \leftrightarrow Fe_2O_3 + 2e^-$$

$$2Cr + 3O^{2-} \leftrightarrow Cr_2O_3 + 6e^-$$

$$Fe + Cr_2O_3 + O^{2-} \leftrightarrow FeCr_2O_4 + 2e^-$$

Prevention

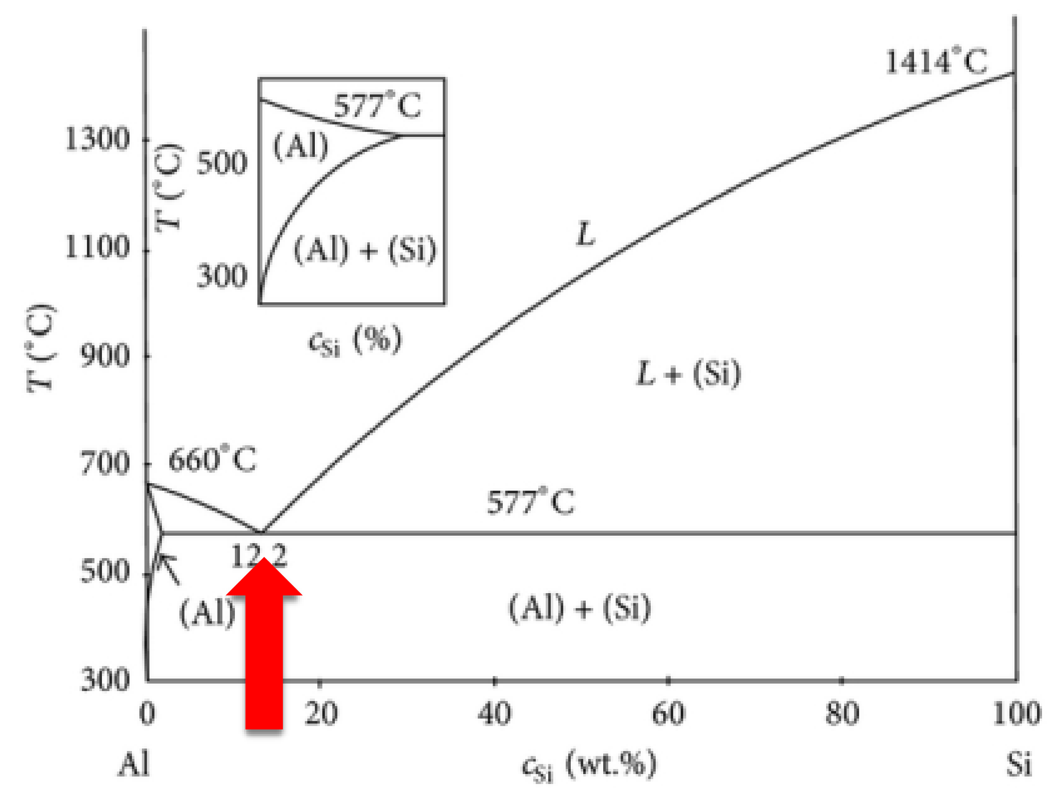


Slurry aluminize coating are improved the corrosion resistance of the base material via the formation of aluminium oxide layer(Al_2O_3) and diffusion layer (iron aluminize)

oxide layer	The Al particle are oxidised to hollow alumina spheres
diffusion layer	Aluminium diffuse to the sub-state via formation Fe-Al to increase corrosion resistance

- Due to eutectic point of Al-Si phase diagram, 12%Si was added in the Al powder.
- Adding Si may lead to continuous diffusion layer and improve crack resistance.

- **In this research, Al and Al-12%Si slurry coating will be studied.**



Objective

Corrosion behaviour of SS430 coated by Al and Al-12%Si slurry was studied with:

- Corrosion kinetics with immersion test in molten nitrate salt for 1, 25, 50, 100 h at 600°C
- Electrochemical test in molten nitrate salt at 600°C
- Surface characterization with SEM equipped EDS and XRD

Research methodology

1. Sample preparation

SS430 sheet (18%Cr) was cut into flat coupon (20 x 20 mm^2)

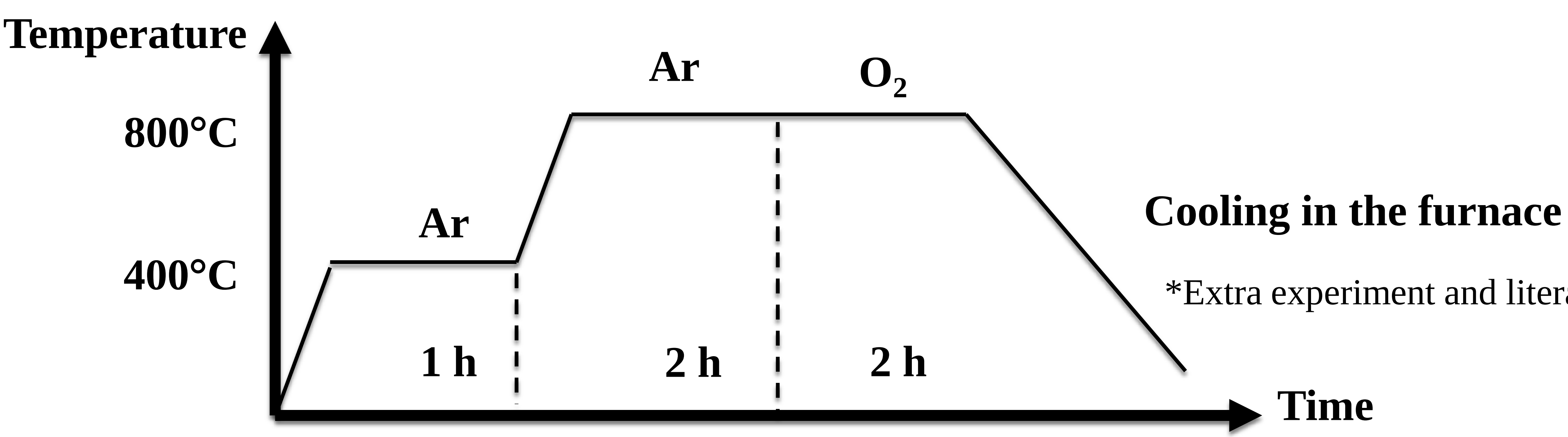
→ Al, or 12%Si-Al, and PVA and alcohol were mixed for slurry solution

→ Samples were coated with slurry by brush, then dried in air at room temperature

→ Coated samples were annealed in Ar at 400°C for 1 h in order to eliminate binder

→ All samples were then annealed in Ar at 800 °C for 2 h in order to form diffusion layer

→ All samples were finally annealed in O_2 at 800 °C for 2 h in order to form oxide layer



*Extra experiment and literature reviews

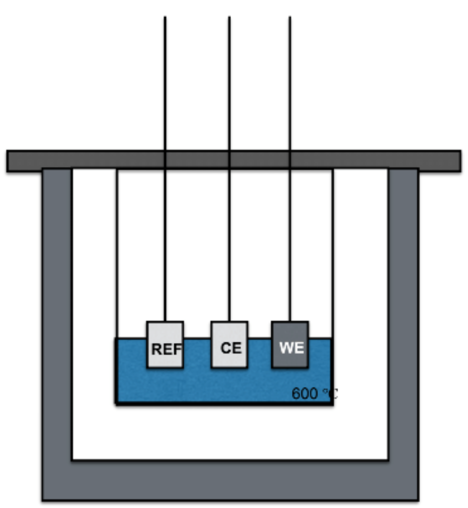
Research methodology

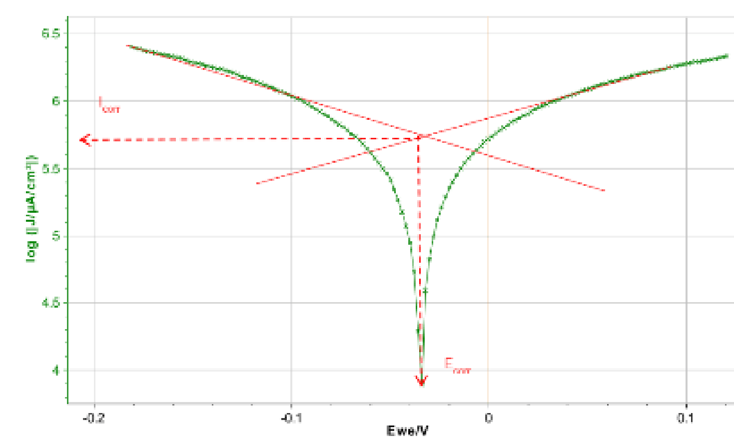
2. Physico-chemical characterization

1. Corrosion kinetics:

- All samples were immersed in molten nitrate salt (60%wt $NaNO_3$+40%wt KNO_3) for 1, 25, 50, and 100 h at 600°C.
- After test, samples were cleaned.
- The weight change were investigated with microbalance (1 µg)

2. Electrochemical test for 1h in 600°C molten nitrate salt





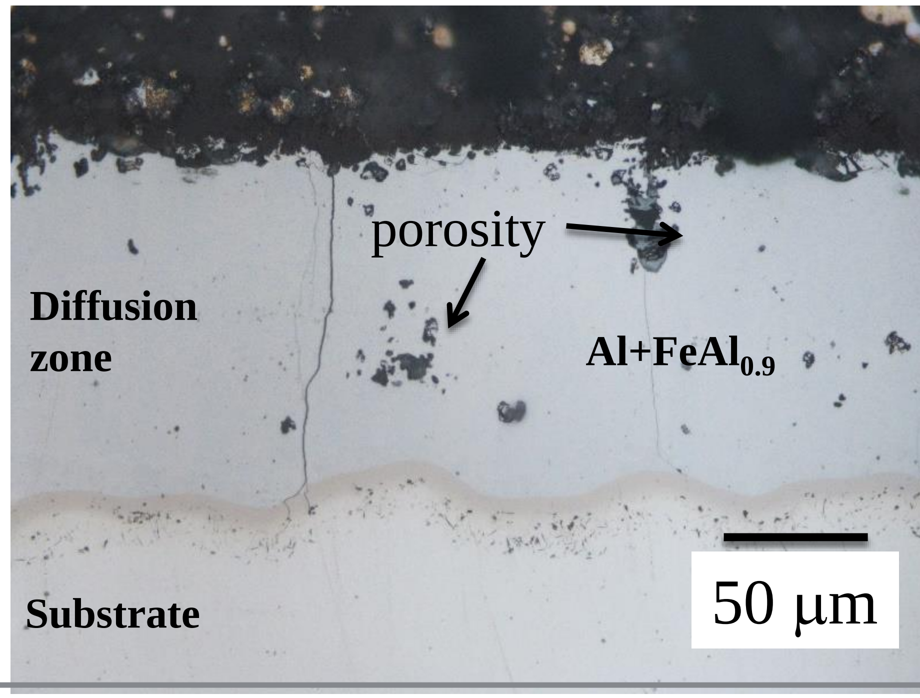
3. Surface characterization: OM, SEM equipped EDS and XRD

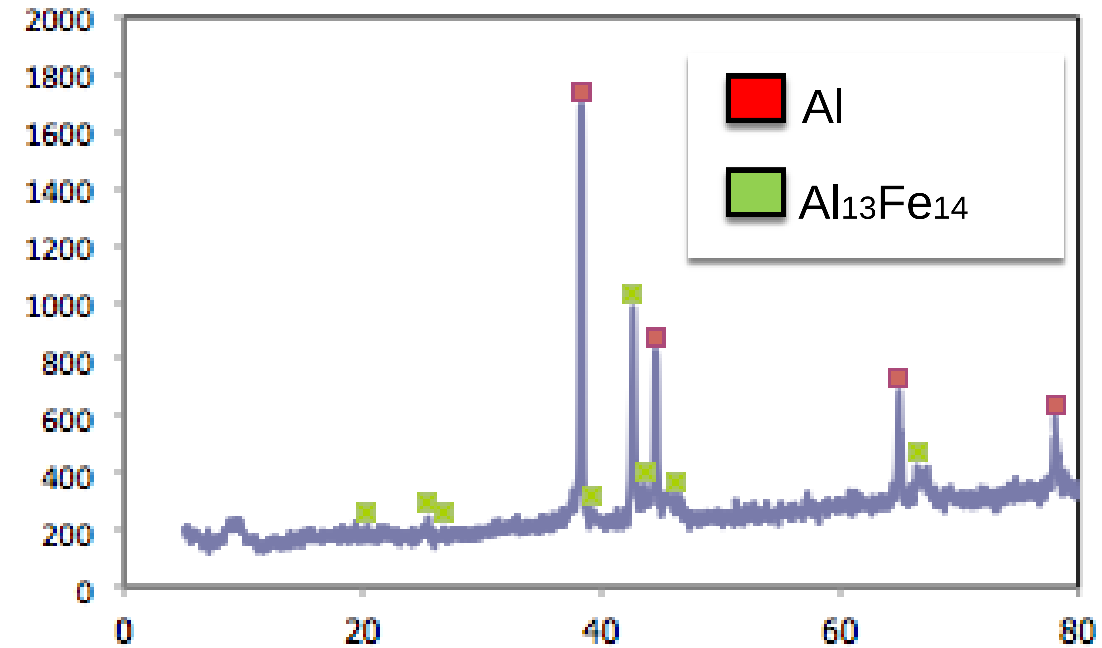
Result and discussion

After coating with slurry

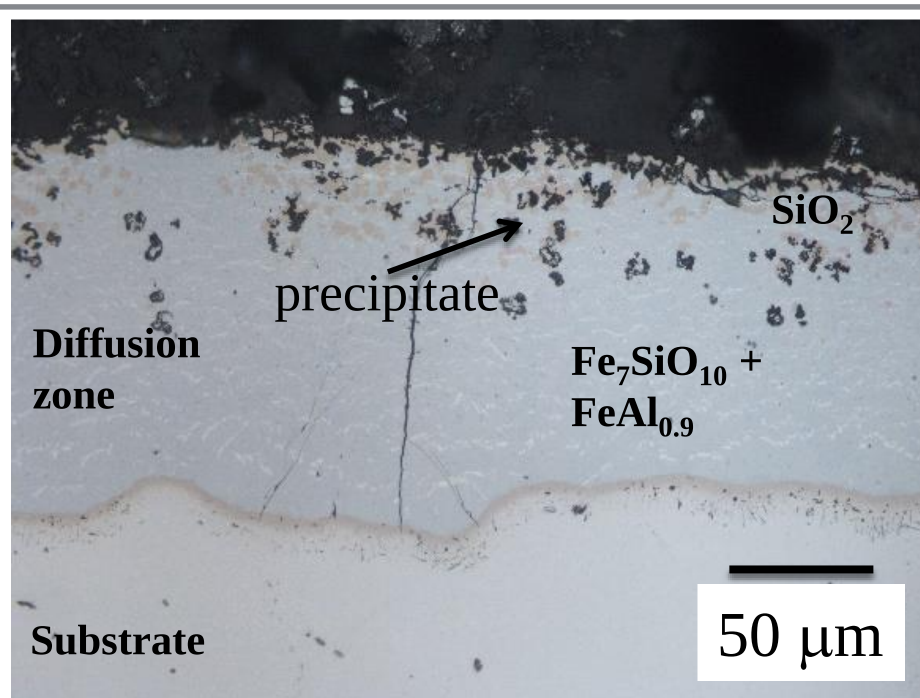
OM | XRD results

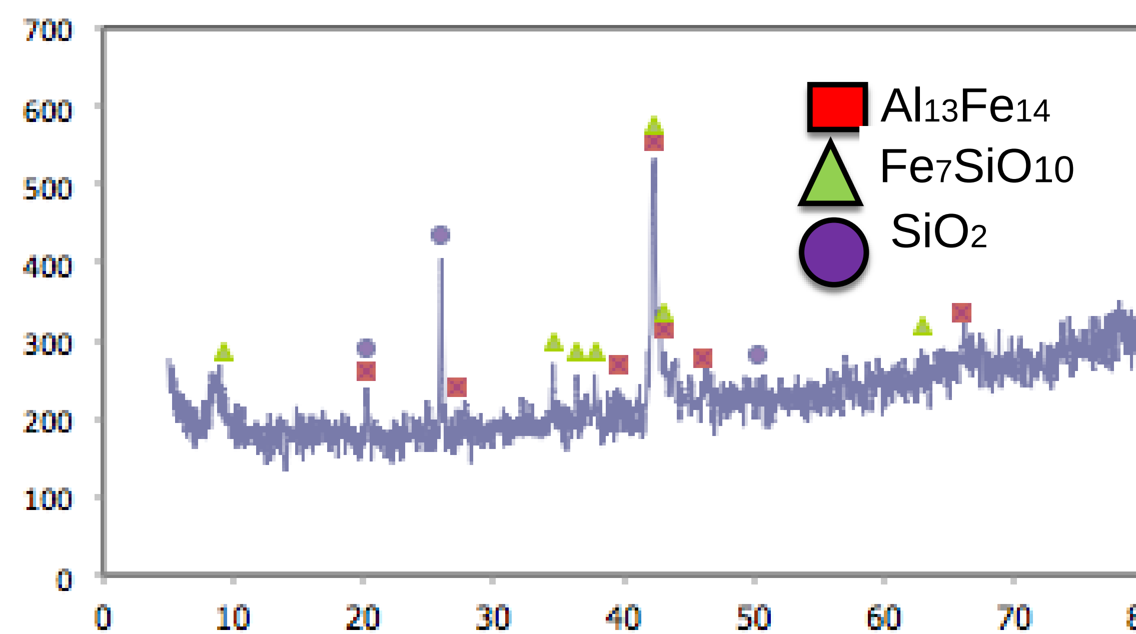
Al slurry coating





Al-Si slurry coating

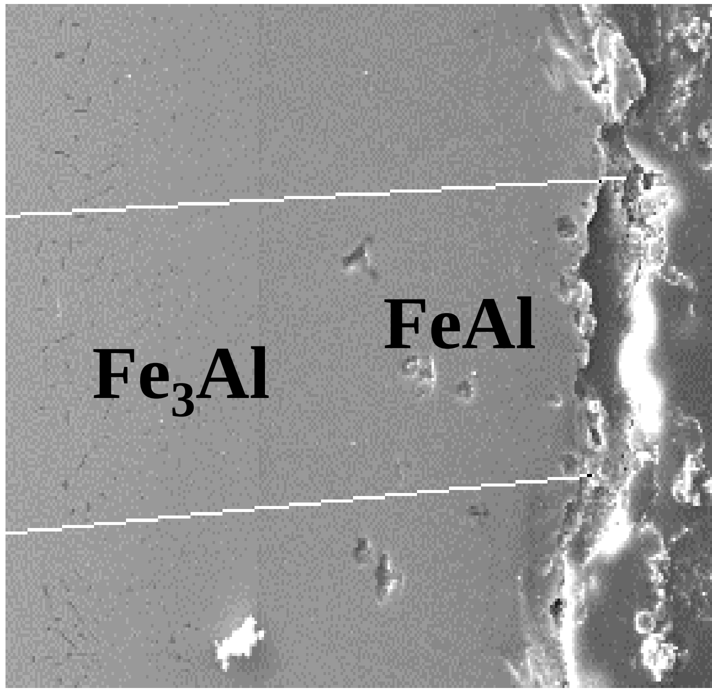


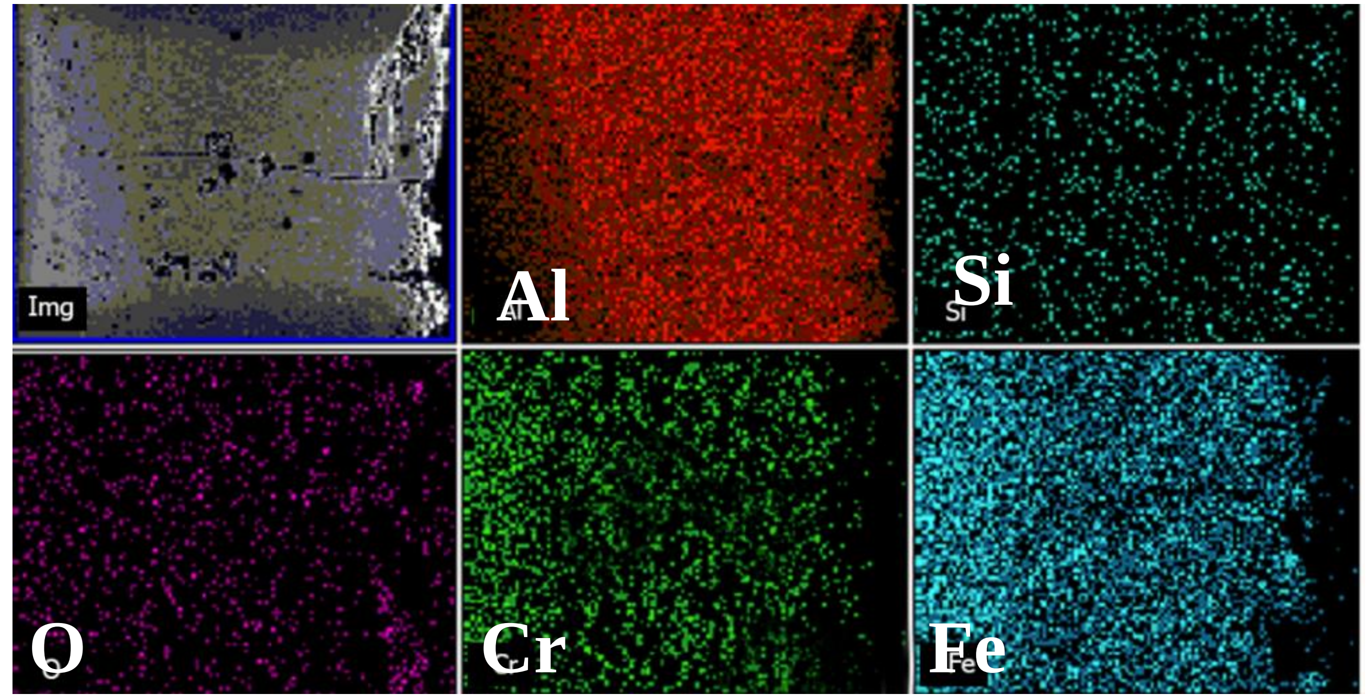


Diffusion layer ~100 µm.

SEM and EDS results

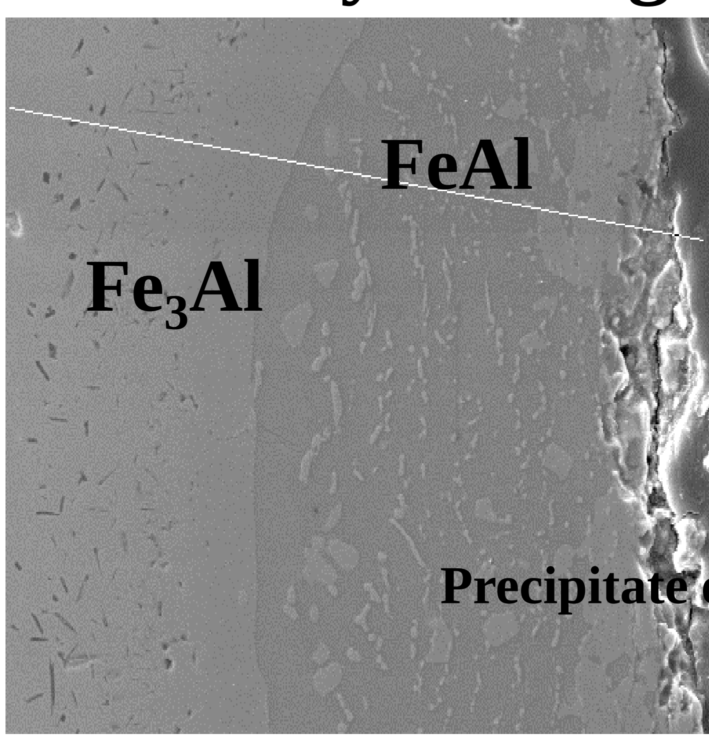
Al slurry coating

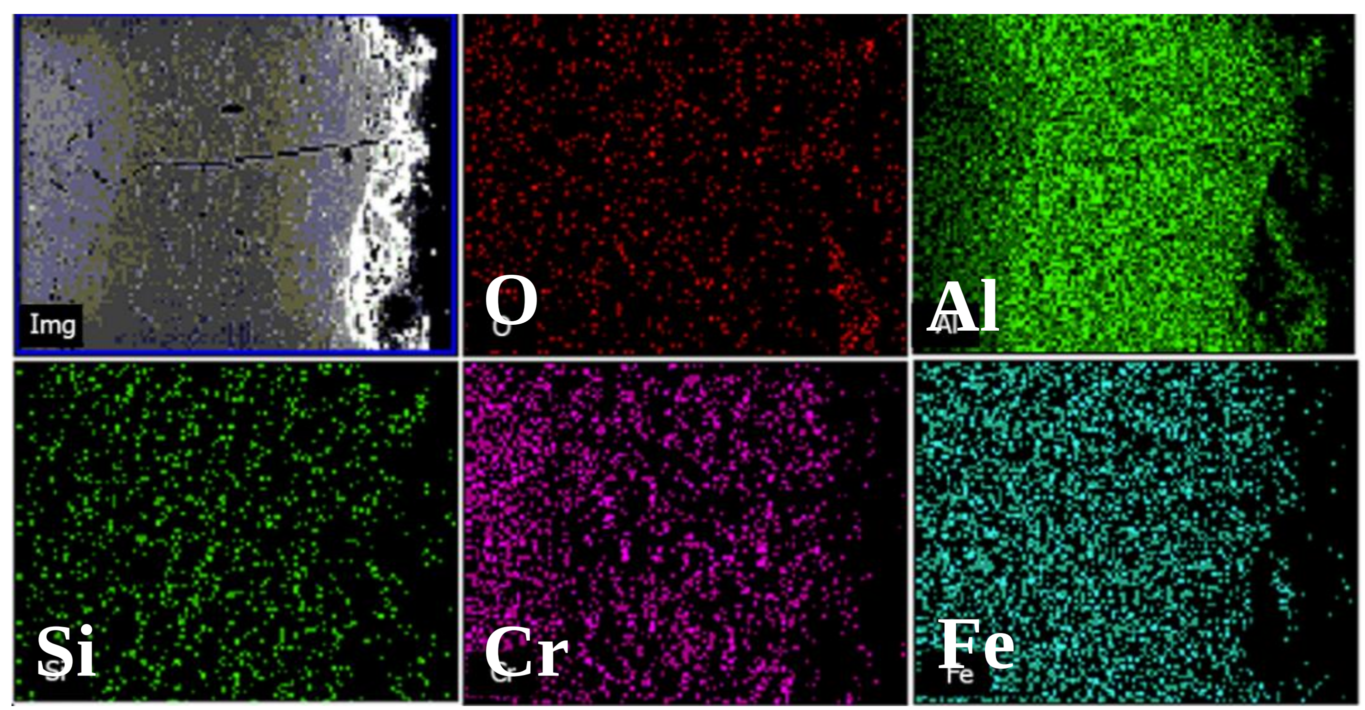




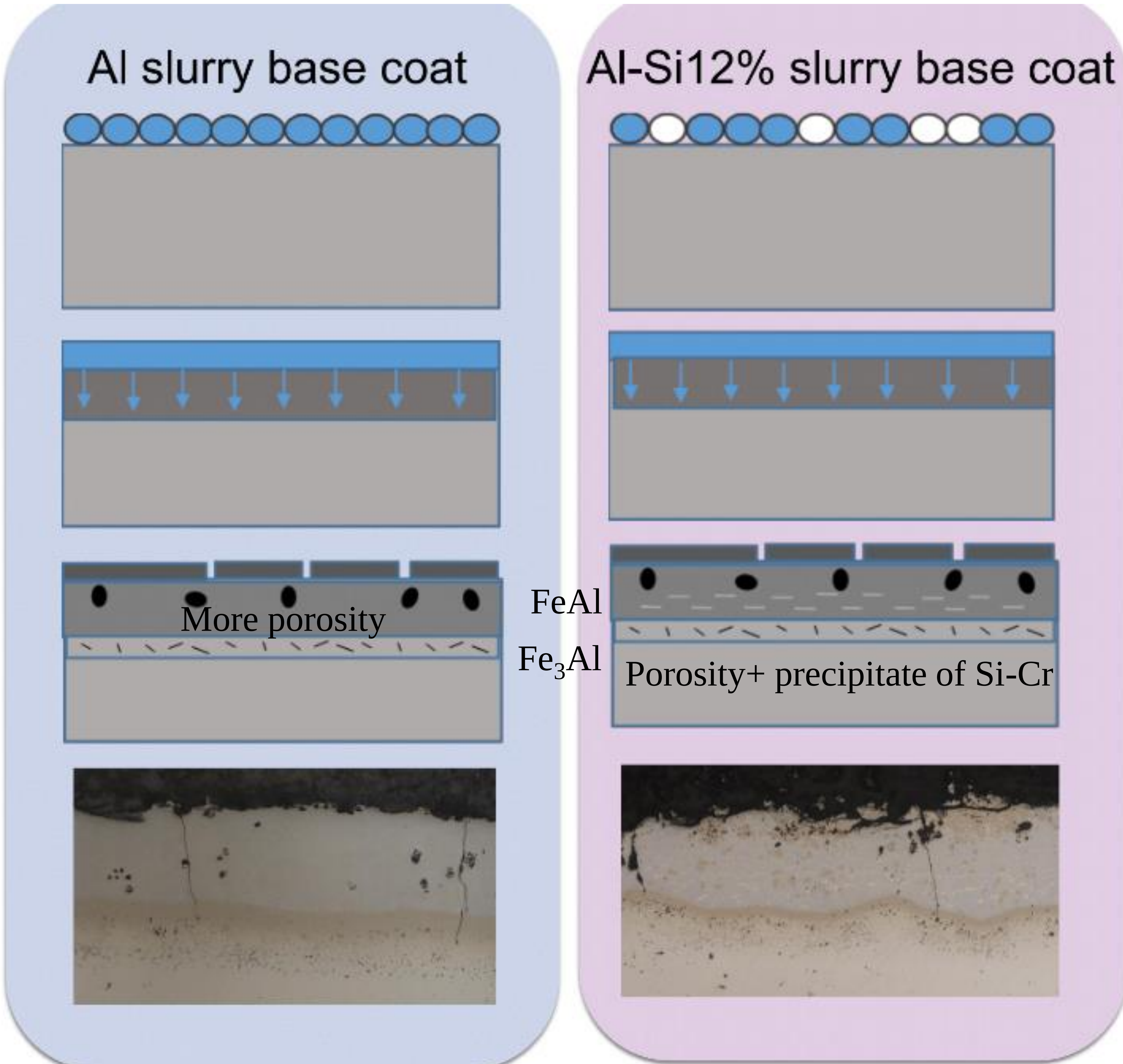
The diffusion layer shows 2 zones with different Fe- Al intermatallic compound

Al-Si slurry coating

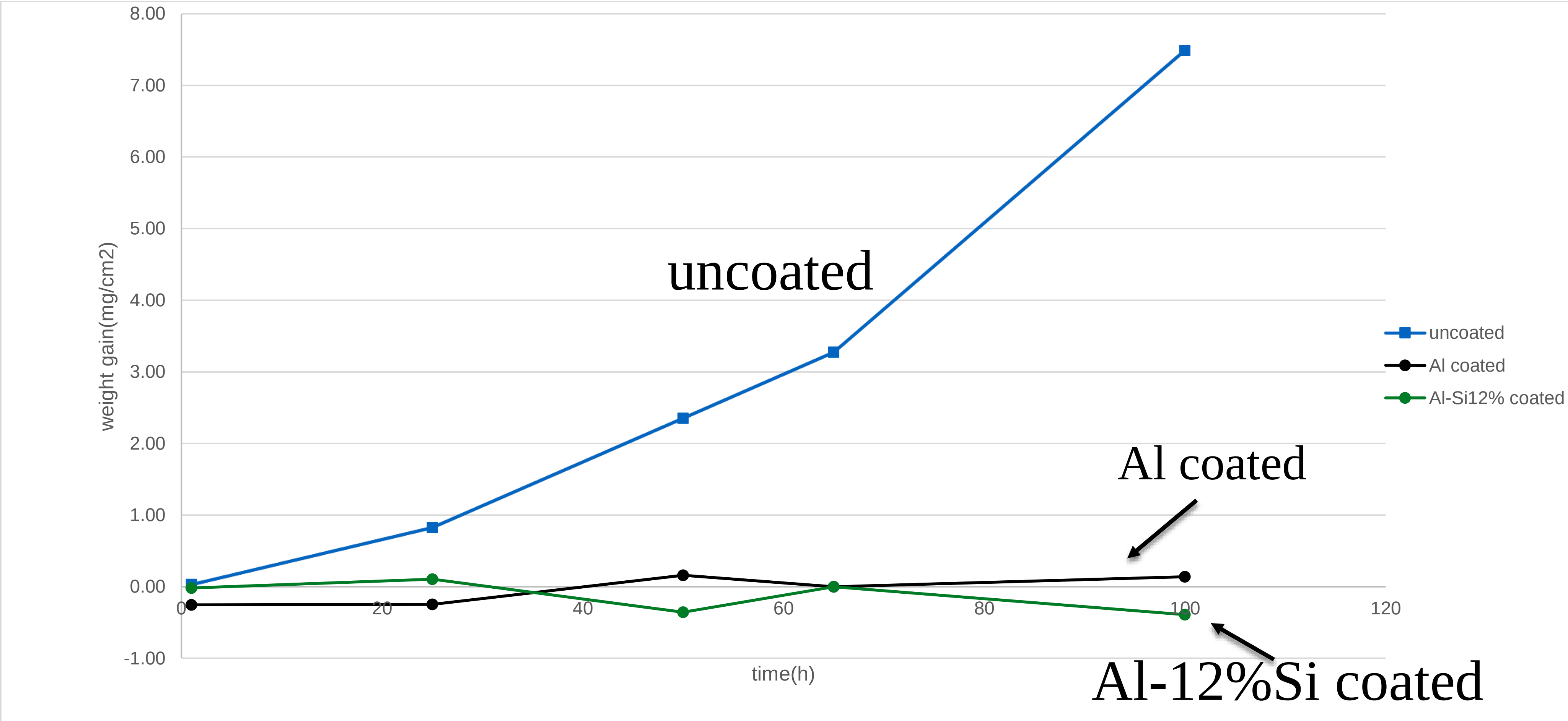




The diffusion layer also shows different Fe- Al intermetallic compound zone with precipitate of Si-Cr


Al slurry base coat
Al-Si12% slurry base coat
More porosity
FeAl
Fe3Al
Porosity+ precipitate of Si-Cr

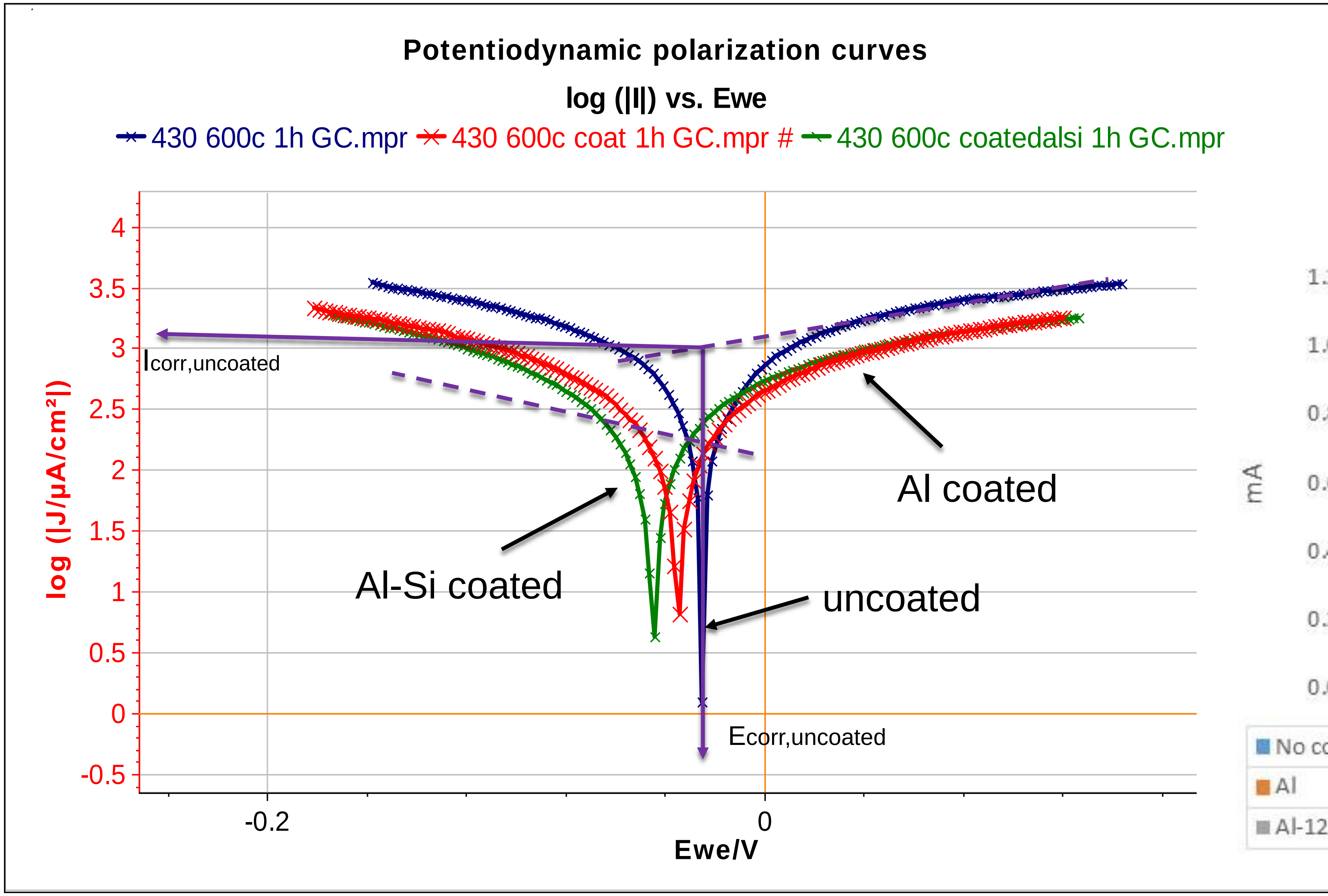
Corrosion kinetics after testing in molten salt

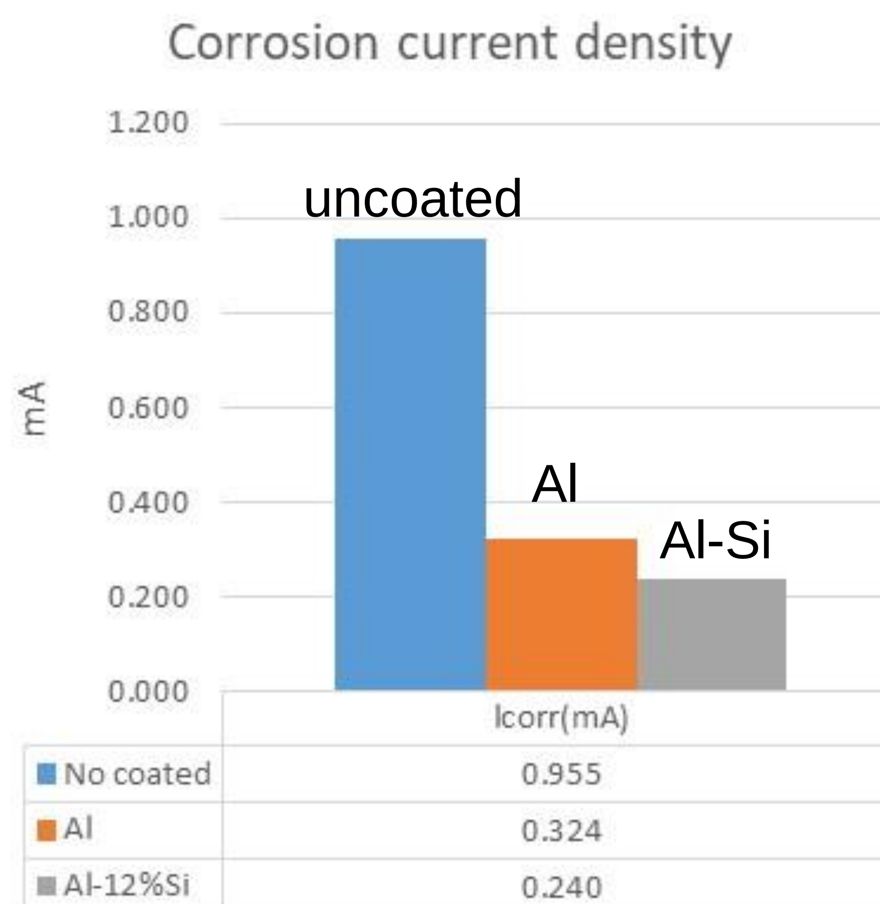


- The weight gain of uncoated sample was higher than that of coated samples.
- There was no different weight change for coated samples.
- Weight loss occurred due to the spallation of oxide scale.
- The rate of weight loss (oxide spallation) and weight gain (oxide formation) may be almost identical for coated samples.

t=100h

Electrochemical results



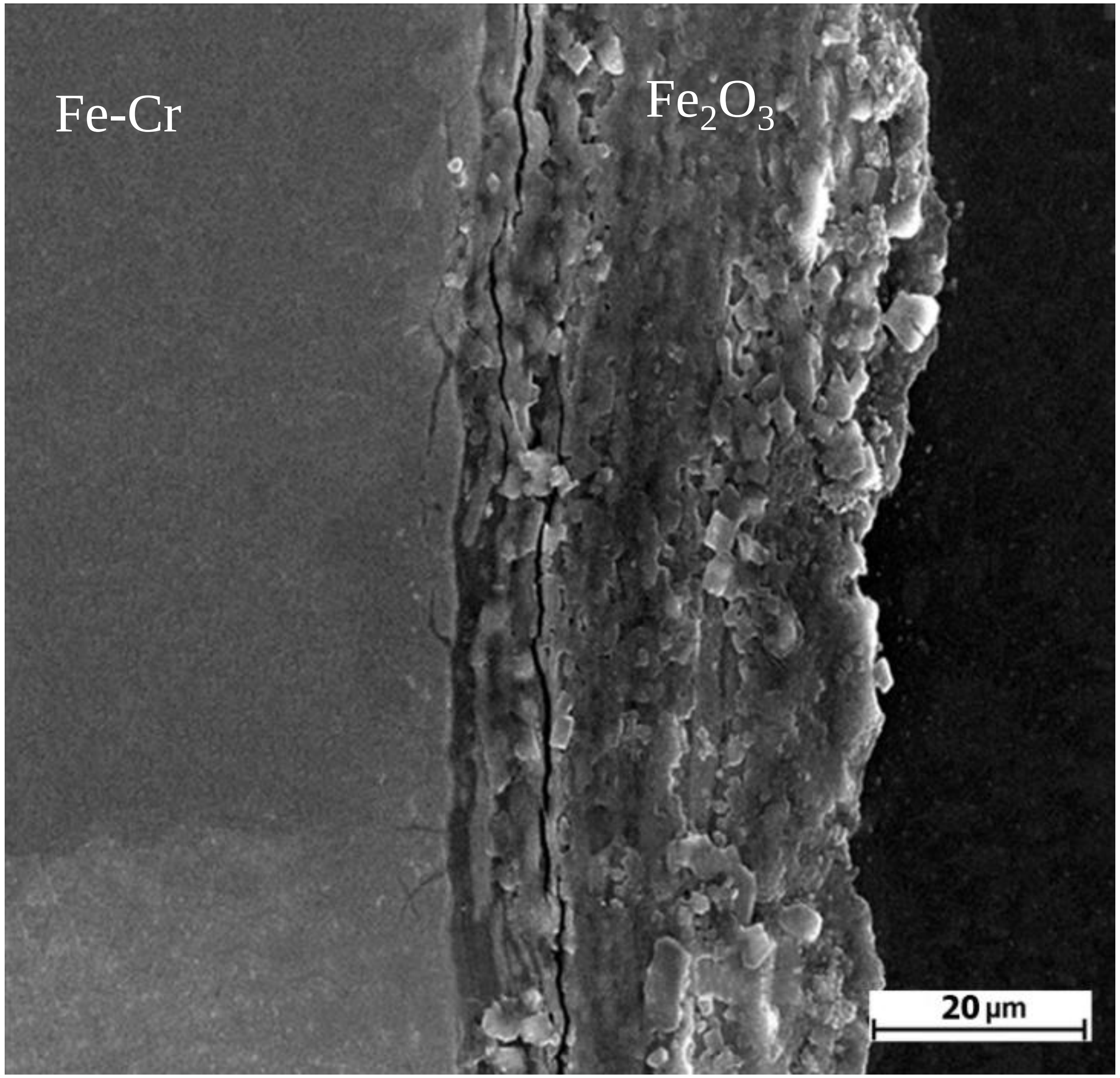


- Uncoated sample showed the highest corrosion current density .
- The sample coated with Al-12%Si showed the lower current density than that of samples coated with pure Al.

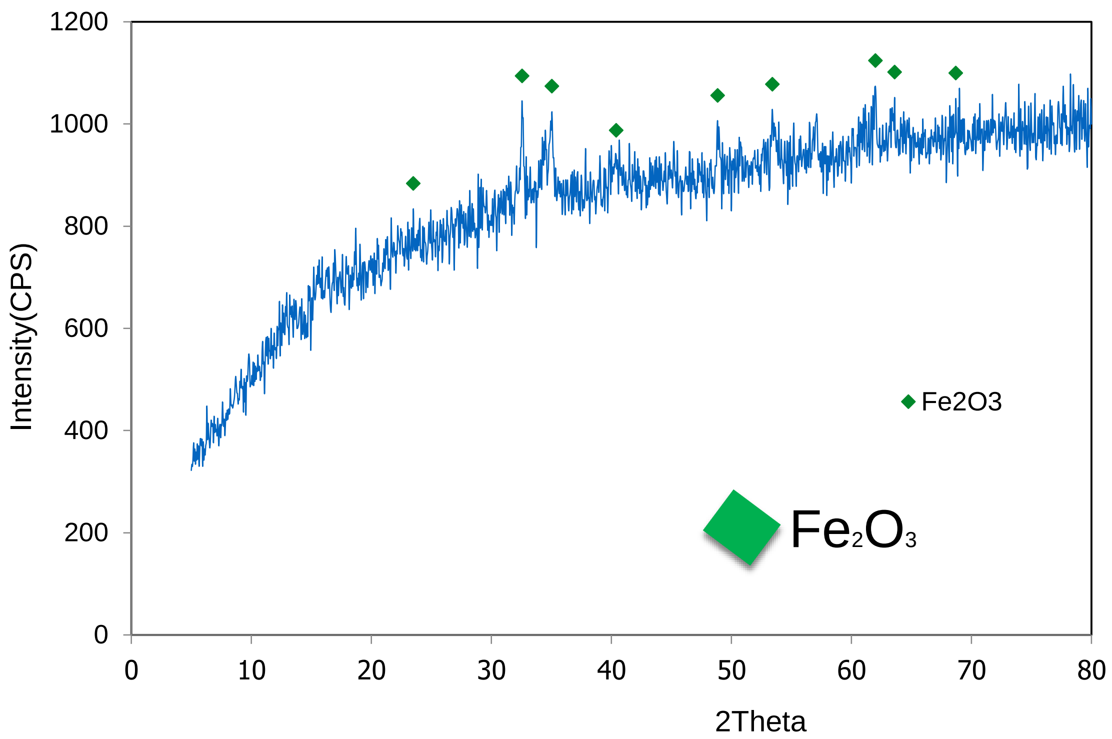
Surface characterization

Uncoated samples after testing in molten salt for 100h at 600°C

SEM result



XRD result



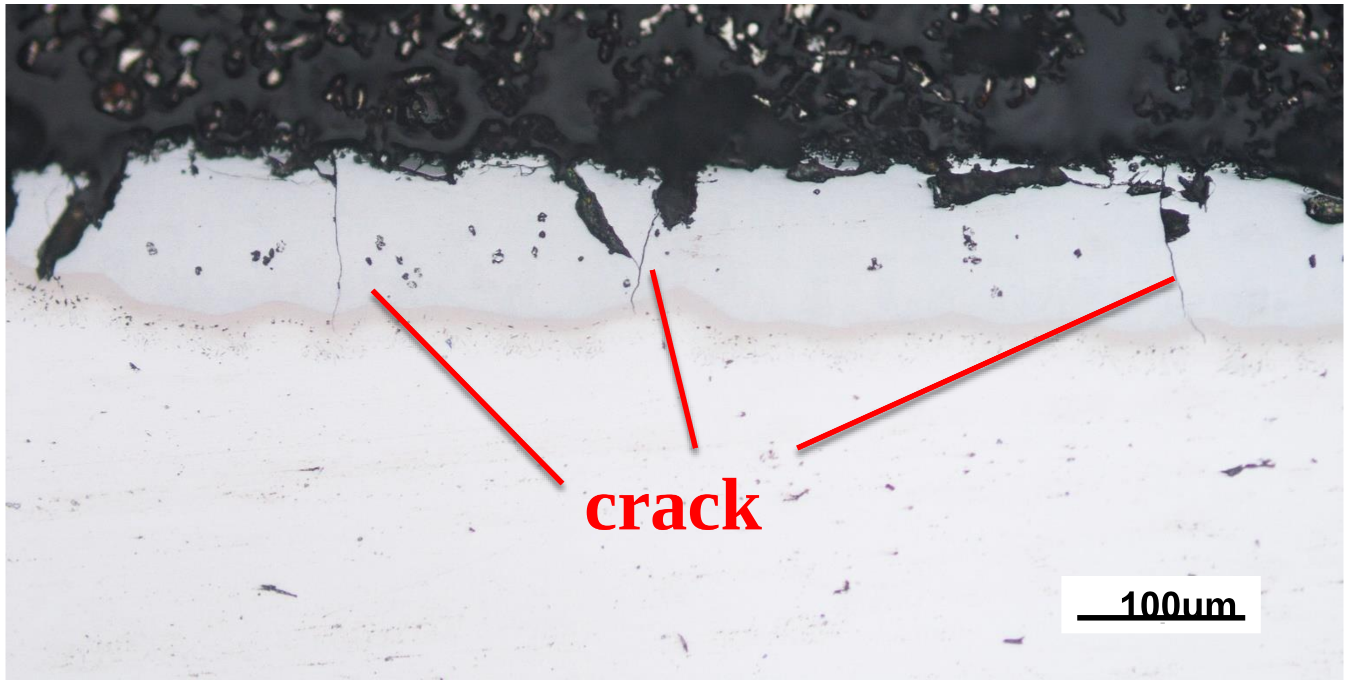
Fe_2O_3 was the major oxide scale.

There was no Cr_2O_3 detected apparently

Surface characterization

OM results

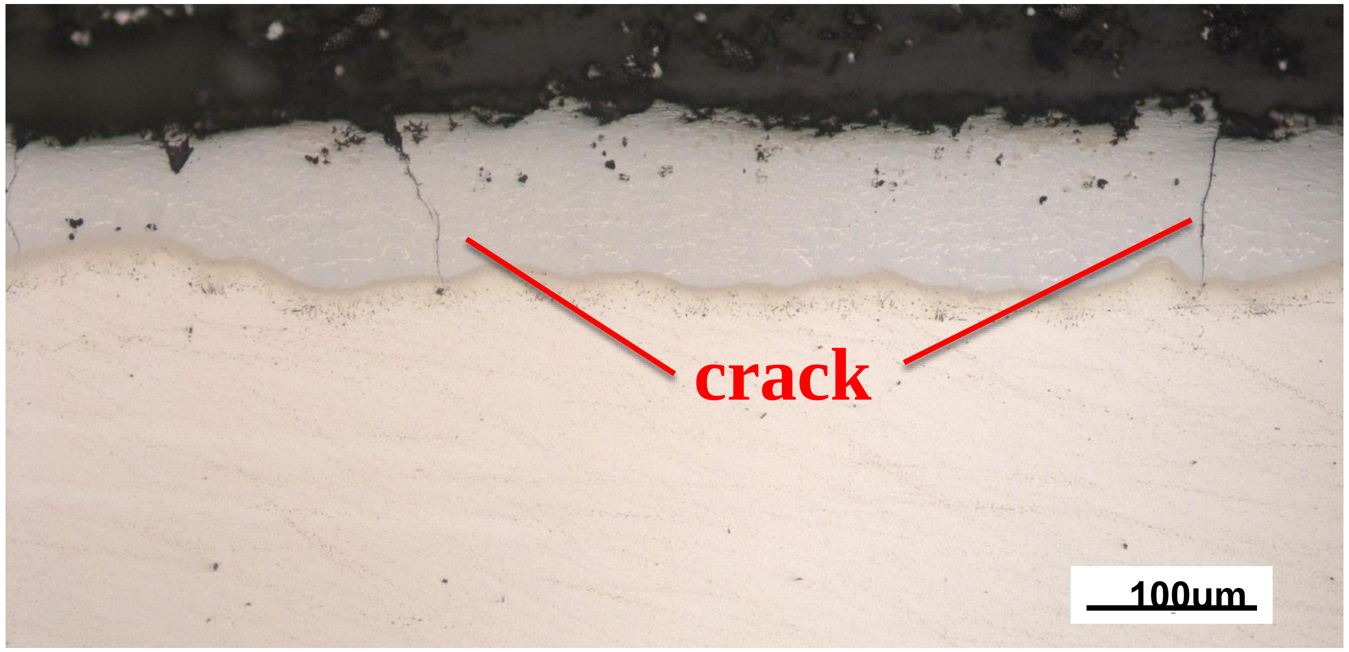
Al slurry coated



A lot of crack and porosity in diffusion layer were apparently observed in the Al coated samples.

Cracks may lead to the pitting corrosion.

Al-Si slurry coated



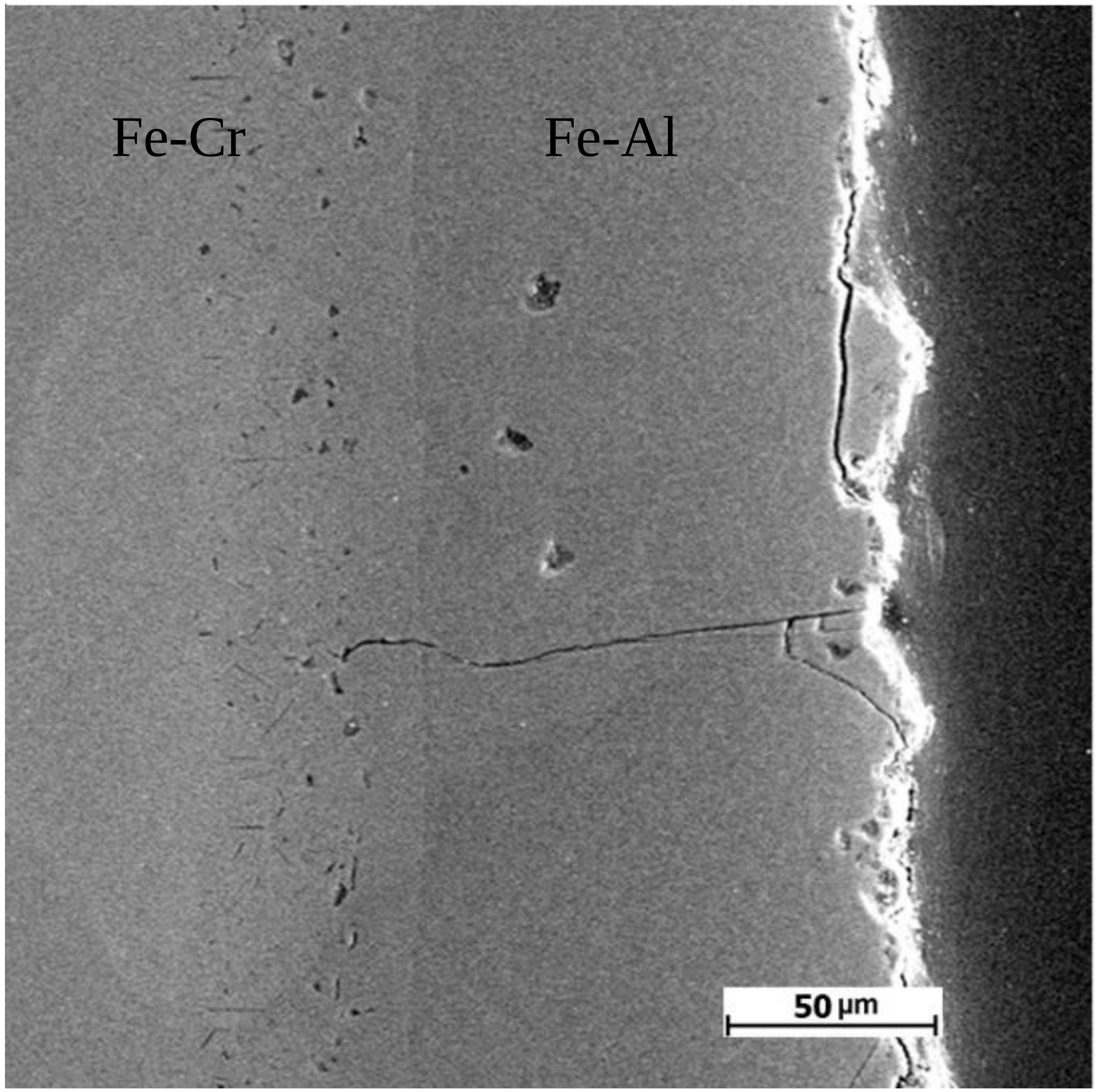
Compared with the Al slurry coated samples, there were cracks less than in the Al slurry coated samples.

Precipitation of Si-Cr may reduce crack, showing higher corrosion resistance.

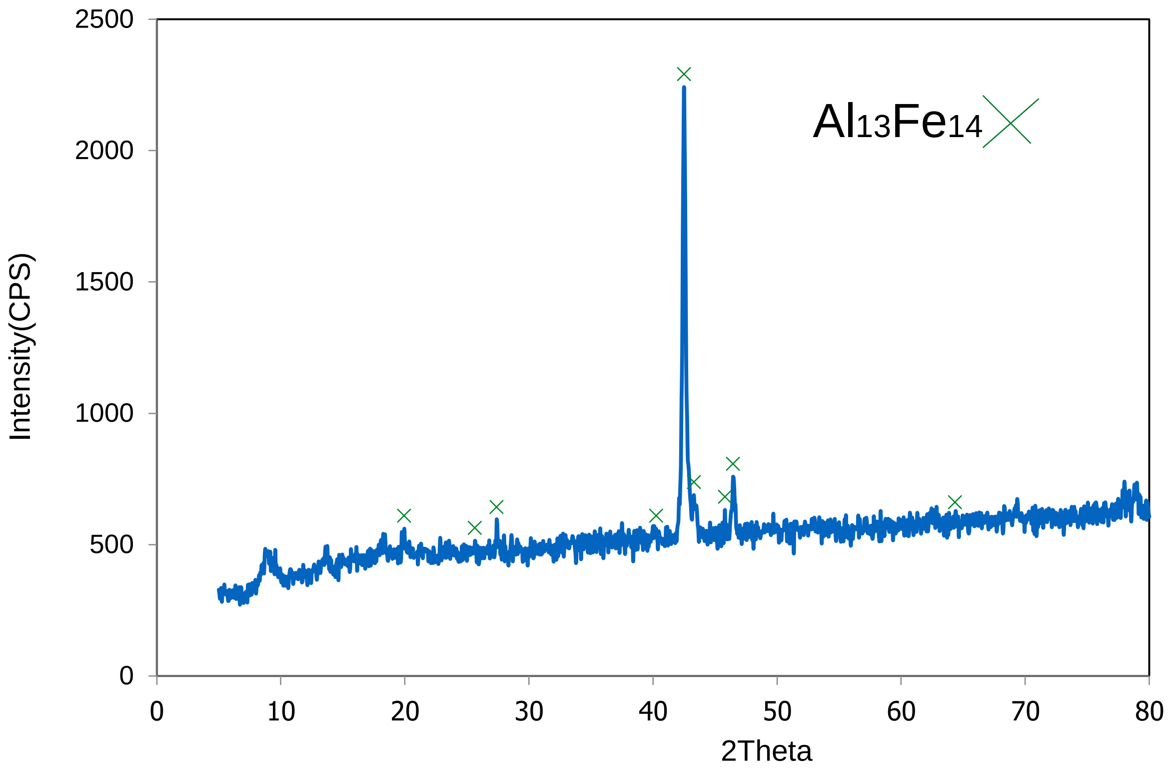
Surface characterization

Al coated samples after testing in molten salt for 100h at 600°C

SEM result



XRD result



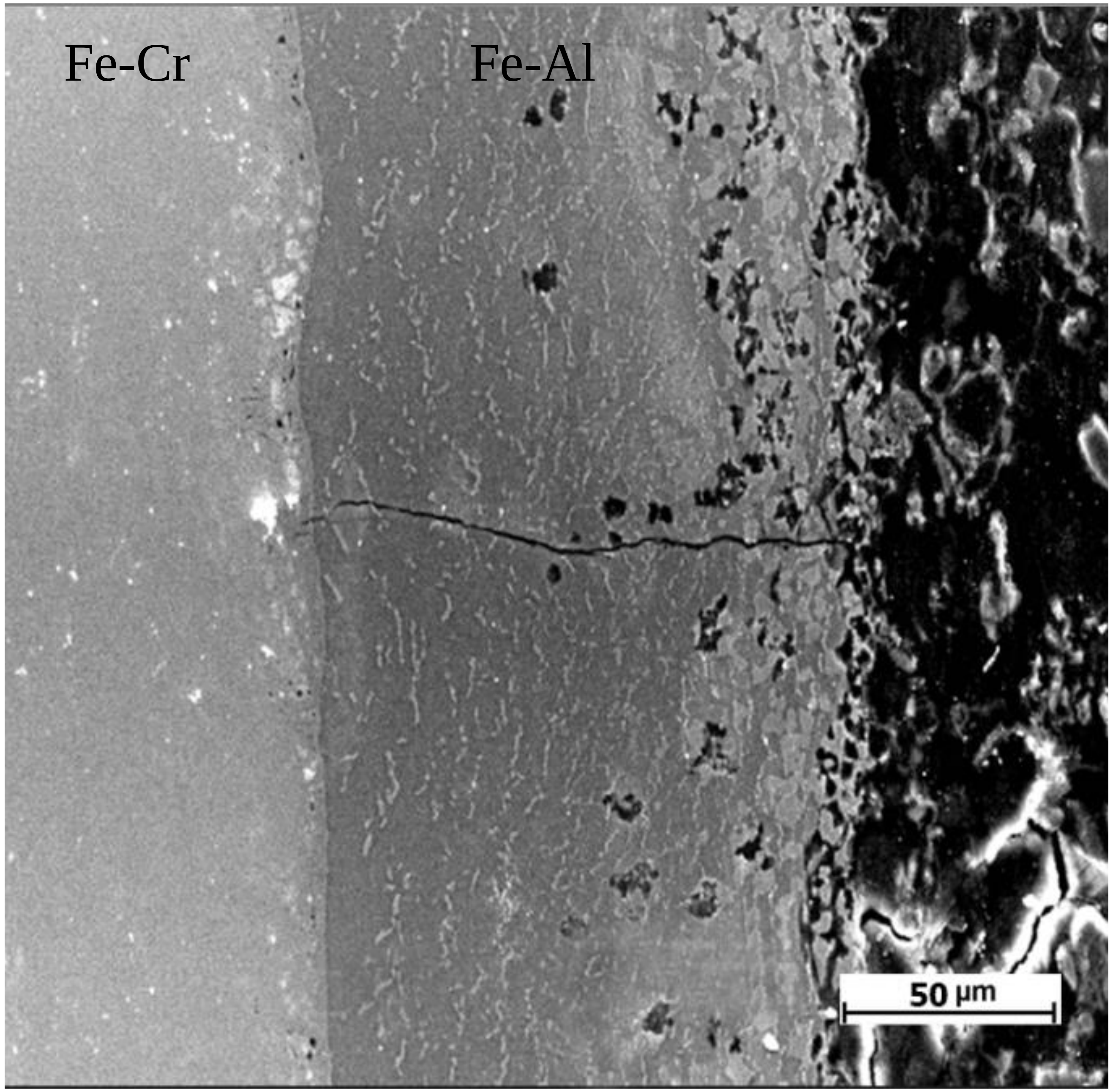
In no crack zone, there was no significant difference compared with samples before immersion test except for the loss of Al_2O_3 layer.

Some crack occurred in the diffusion layer.

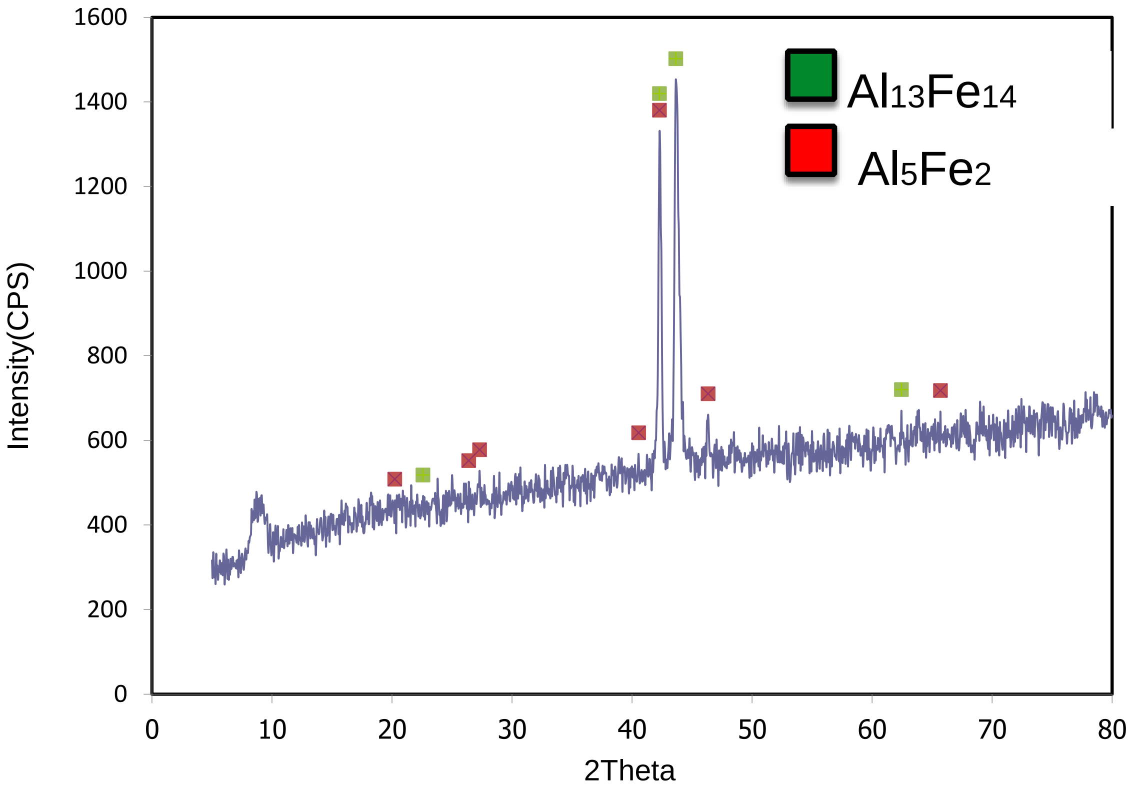
Surface characterization

Al-Si coated samples after testing in molten salt for 100h at 600°C

SEM result



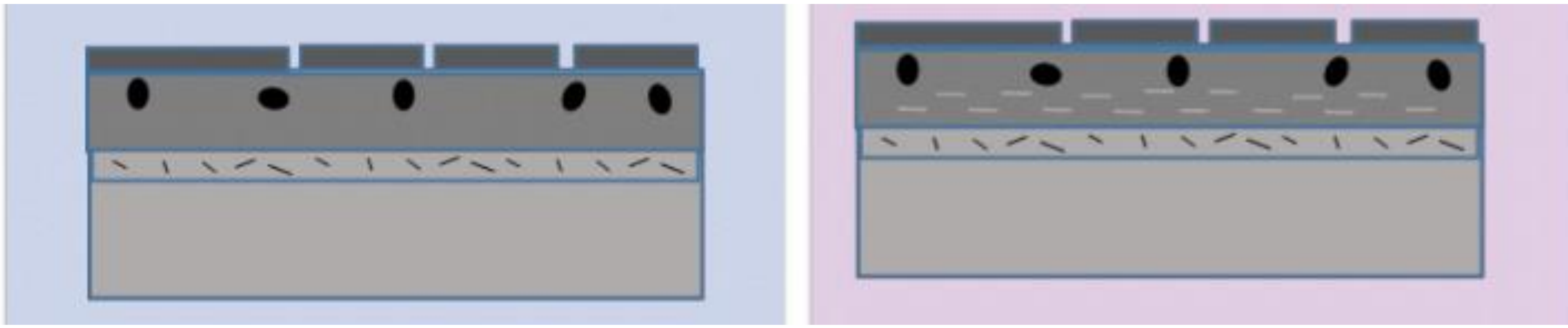
XRD result



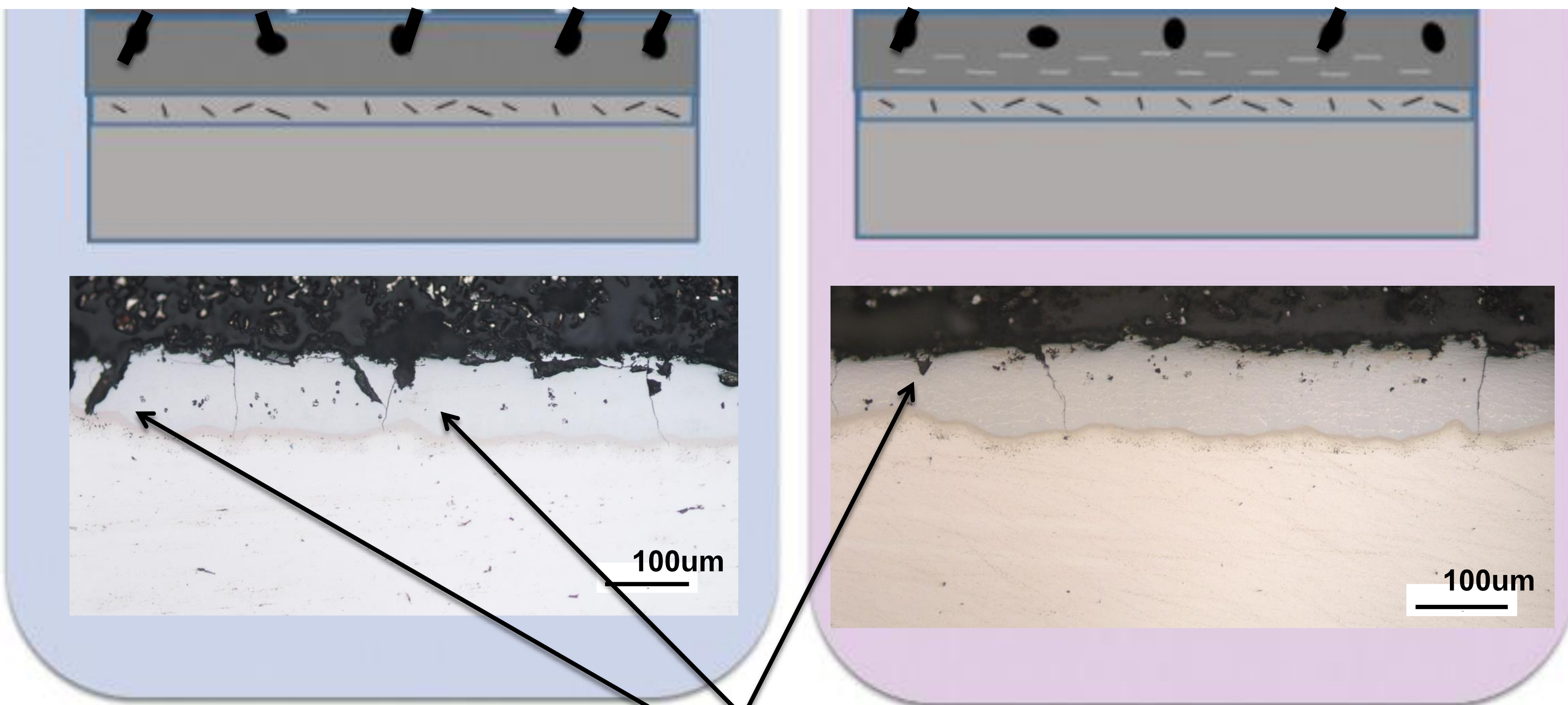
Fe_2Al_5 was formed in the diffusion layer.

Before corrosion test

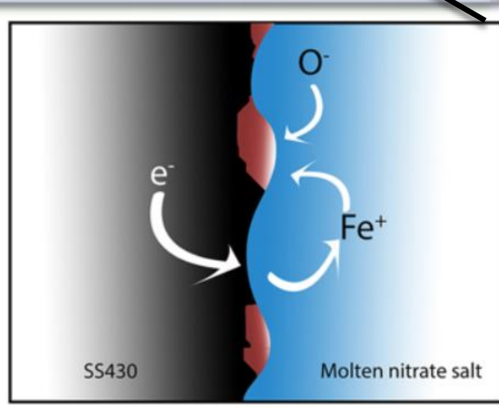
Al coating | Al –Si coating



After corrosion test



Pitting corrosion:



The corrosion reaction of molten nitrate salt at high temperature.

$$NO_3^- + 2e^- \leftrightarrow NO_2^- + O^{2-}$$

$$Fe + O^{2-} \leftrightarrow FeO + 2e^-$$

$$3FeO + O^{2-} \leftrightarrow Fe_3O_4 + 2e^-$$

$$2Fe_3O_4 + O^{2-} \leftrightarrow Fe_2O_3 + 2e^-$$

$$2Cr + 3O^{2-} \leftrightarrow Cr_2O_3 + 6e^-$$

$$Fe + Cr_2O_3 + O^{2-} \leftrightarrow FeCr_2O_4 + 2e^-$$

Conclusion

1. The corrosion resistance of the samples with slurry aluminizing coating were apparently higher than that of uncoated samples in the molten nitrate salt.

2. The weight change of coated samples are almost identical due to the same rate of spallation and formation of oxide.

3. However, the corrosion current of Al-Si coating samples was lower than that of Al coating samples, resulting to the increasing of corrosion resistance in molten salt.

4. Fe_2O_3 was a major oxide scale of uncoated samples after immersion testing.

5. The intermetallic compounds of Fe and Al, possible FeAl and Fe_3Al, were found in the diffusion zone. In addition Fe_2Al_5 was found in Al-Si coating samples after immersion testing.

6. The Si-Cr precipitation in Al-Si coating samples led to crack resistance, showing less pitting corrosion.

Prospective

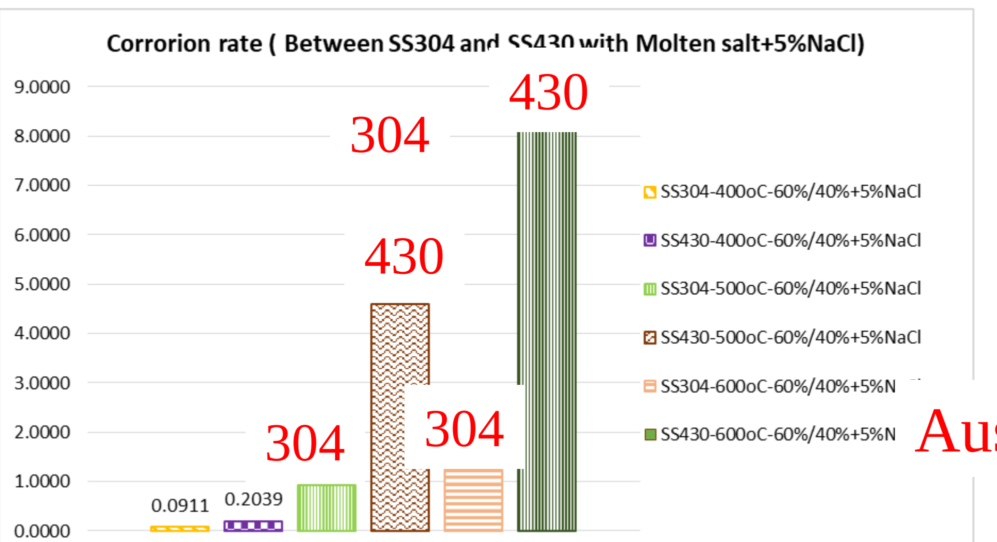
HTF

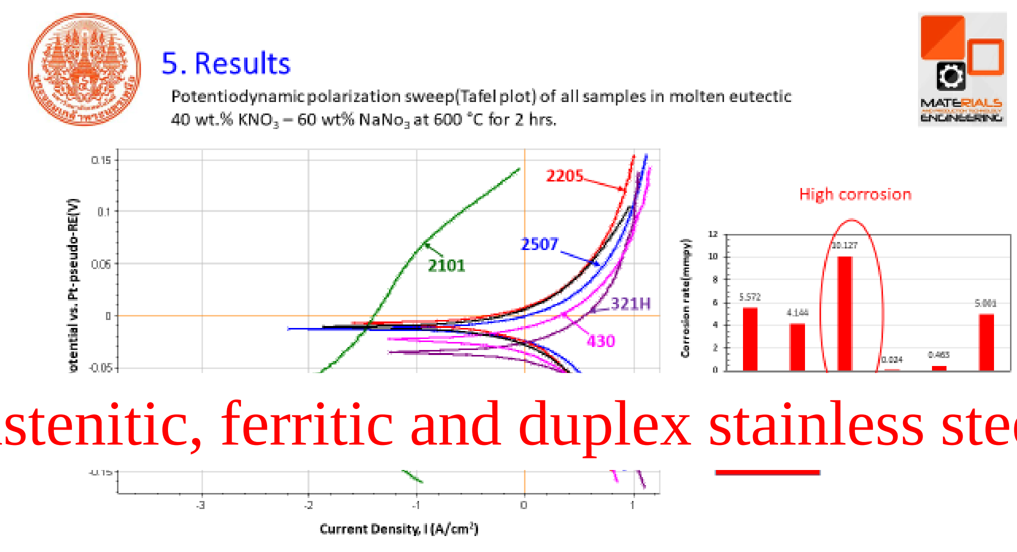
The local salt in Thailand may be used as HTF, the protection from molten salt corrosion should be intensively studied. (Addition of NaCl)

Solar salt (60%wt $NaNO_3$+40%wt KNO_3+ 5%NaCl) → **P. Kettrakul**

Materials

Several types of stainless steel were used instead of 430 for this application (**In progress**)





Austenitic, ferritic and duplex stainless steels

→ **P. Kettrakul**

→ **N. Kanjanaprayut**

molten salt induce intergranular corrosion??

Slurry coating

1. The new procedure of slurry coating should be investigated in order to reduce crack in the diffusion zone and also for tube coating.
2. The effect of other elements in slurry coating should be studied.

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Thank you for your attention