UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Al-based coating for coke reduction during ethane steam cracking

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Outline

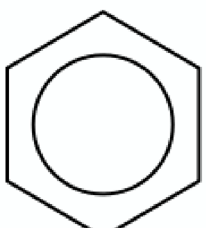
- **Introduction**
- **Experimental procedures**
- **Effluent analysis**
- **Coking rates**
- **SEM & EDX and XPS**
- **Conclusions**
- **Acknowledgments**

Steam Cracking

Main source of ethylene, propylene and other valuable hydrocarbons (i.e. olefins and aromatics)
→ **commercially prevailing petrochemical process**

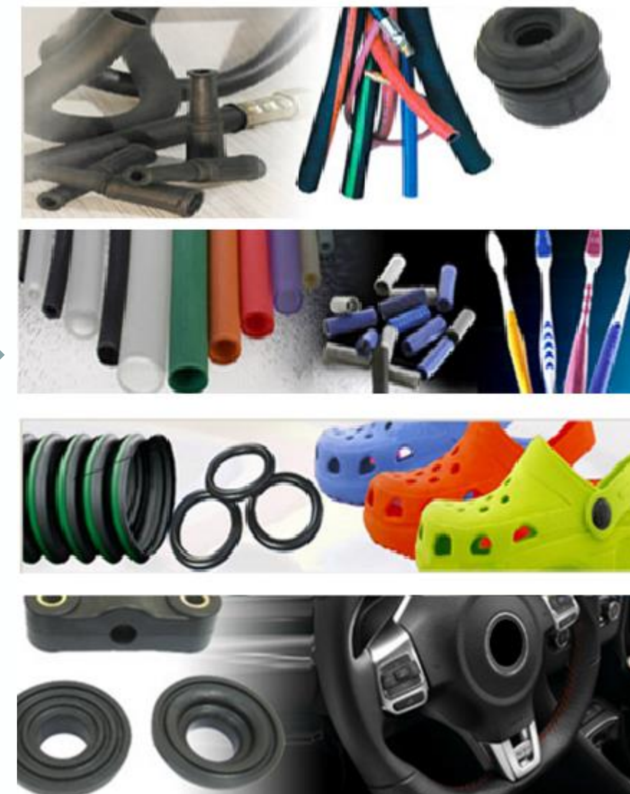
Cracker

C_2H_4, C_3H_6



POLYMERIZATION UNITS

Valuable Products



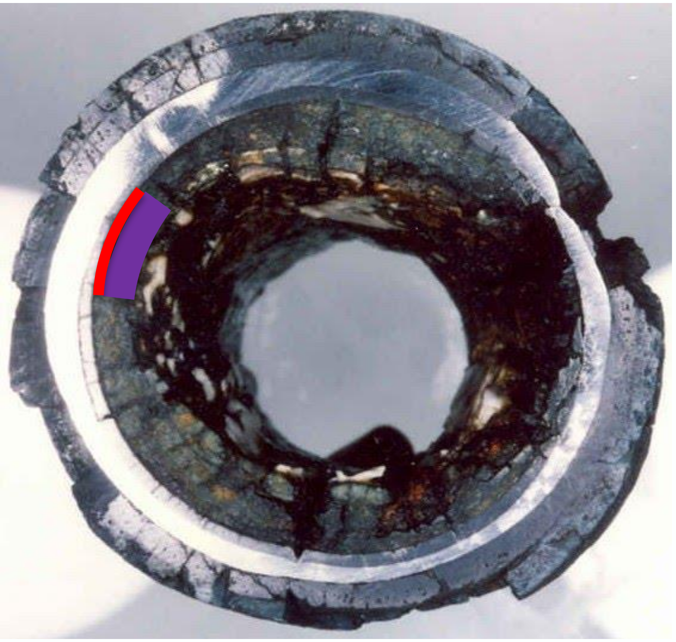
The enemy

Steam cracking is a very complex process:

- ✓ High Temperatures → < 1300 °C for the metal
- ✓ Feedstock composition → gases to heavy crude oils
- ✓ Operating conditions → steam dilution, pressure, temperature
- ✓ Reactor configuration → heat flux and mixing

→ **Coke formation**

Coke formation and Anti-coking



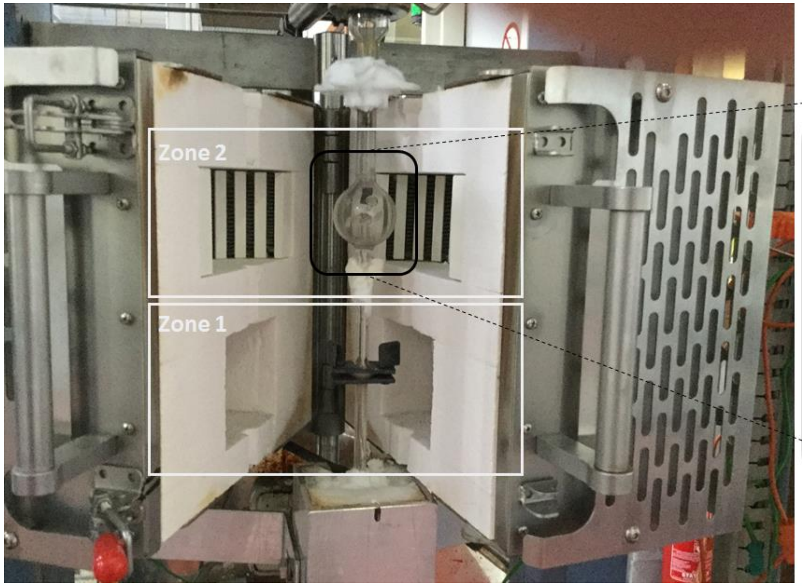
Main mechanisms lead to coke formation:

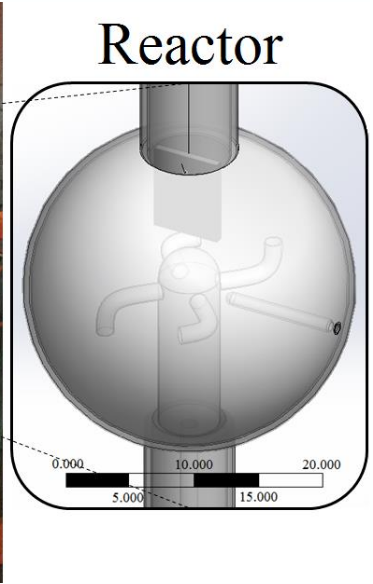
- ✓ **Catalytic** (initial catalytic behavior)
- ✓ **Radical** (long-term performance)
- ✓ **Condensation** (especially in heavy feeds)

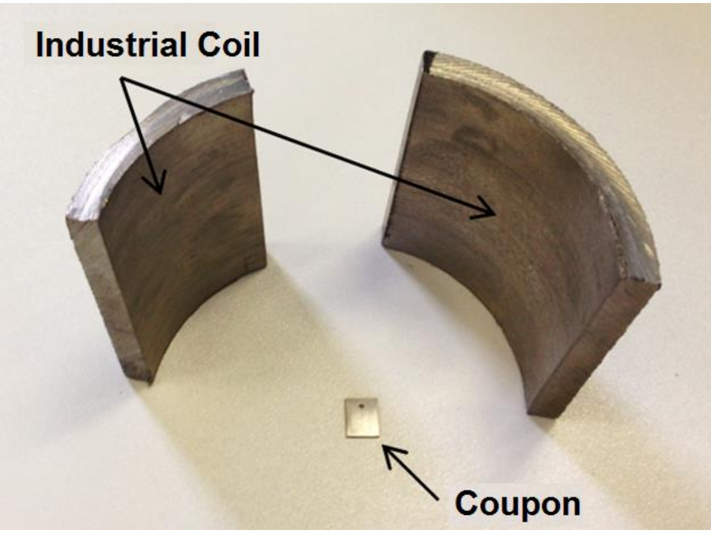
Anti-coking technologies:

- ✓3D reactor technologies
- ✓Feed additives
- ✓Surface technologies

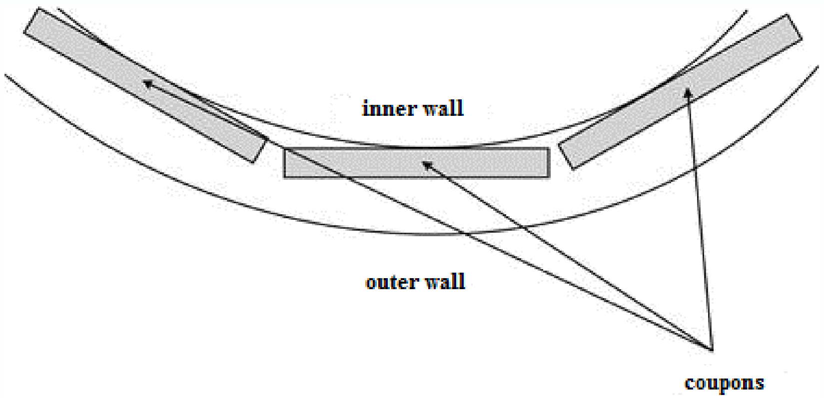
JSR set-up





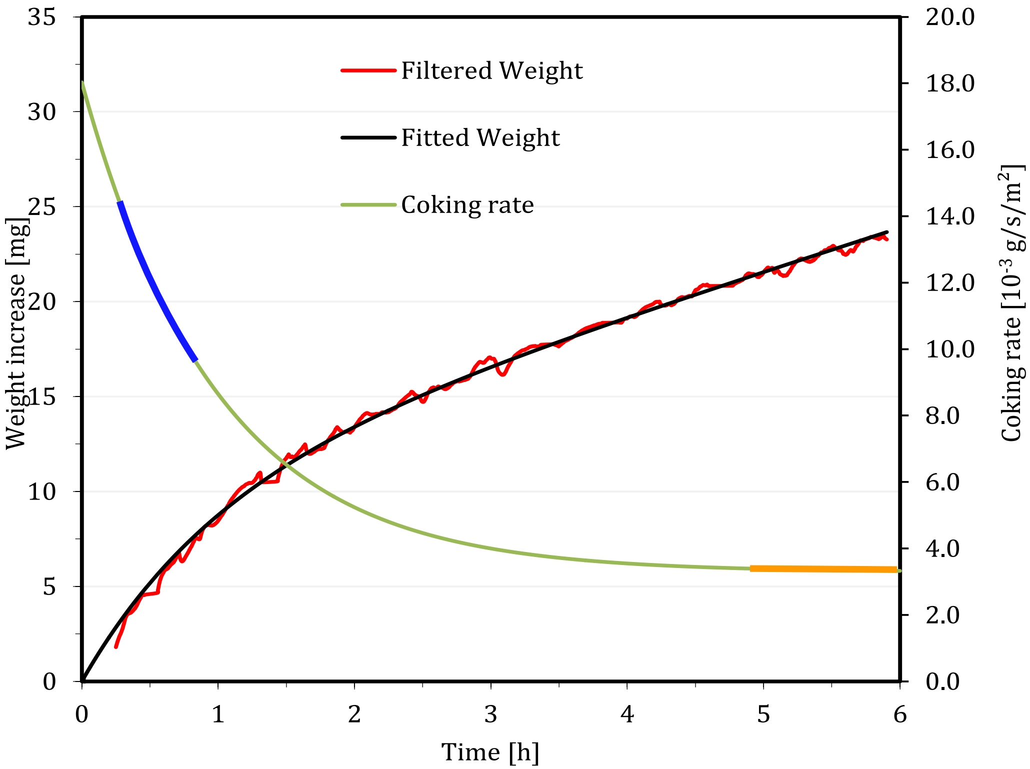


- ✓ Well mixed reactor
- ✓ Temperature measurement very close to the coupon
- ✓ No reaction before the reactor
- ✓ Mass track - accuracy of a µg/s
- ✓ Different feedstock, different conditions



Suitable for experimental validation of the effect of **material**, **process conditions** and **pretreatments** on coke formation

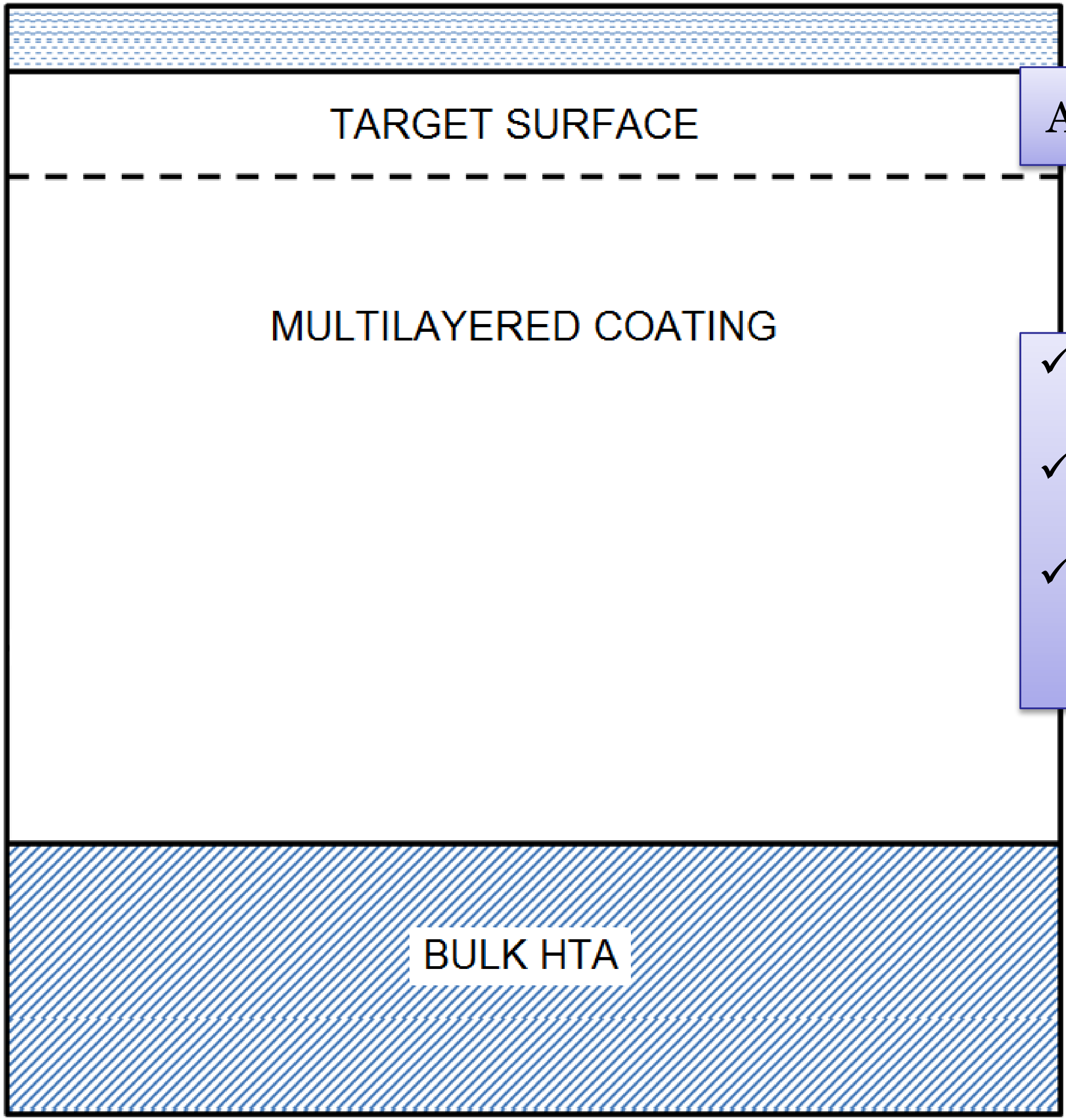
On-line measurement of coking rates



- ✓ **Initial** coking rate = Average coking rate value from 15 min - 1 h of cracking
- ✓ **Asymptotic** coking rate = Average coking rate value from 5 h - 6 h

- ✓ **Initial coking rate is representative of the catalytic coking behavior of an alloy**
- ✓ **Asymptotic coking rate refers to the long-term behavior of a material**

CoatAlloy™



Alumina forming layer

- ✓ Providing an aluminum reservoir
- ✓ Preventing inter diffusion
- ✓ Chemically inert towards the base metal

Studied conditions

Material effect
CoatAlloy or MXM
(as reference)

Pretreatment effect
N_2 and H_2O effect during stabilization and decoking

Ethane Steam Cracking

Aging effect
Cyclic (8 cc)

DMDS effect
Continuous addition (CA) of 41 ppmw S/HC and/or Presulfiding (PreS) with 500 ppmw DMDS/H_2O

Experimental sequence

			3 cc of 6 h and decoking			4 cc of 1 h and decoking			Last cc		
Pretreatment			1-3 cc	Decoking		4-7 cc	Decoking		8 cc	Decoking	
1023 K	1023 K → 1173 K	1173 K	1173 K	1023 K → 1173 K	1173 K	1173 K	1023 K → 1173 K	1173 K	1173 K	1023 K → 1173 K	1173 K
Air	N_2 + Air or H_2O/Air	H_2O/Air	C_2H_6 + H_2O	N_2/Air or H_2O/Air	H_2O/Air	C_2H_6 + H_2O	N_2 /Air or H_2O/Air	H_2O/Air	C_2H_6 + H_2O	N_2 /Air or H_2O/Air	H_2O/Air
12-14 h	30 min	15 min	6 h	30 min	15 min	1 h	30 min	15 min	6 h	30 min	15 min

Only before the 1cc

Cooling down

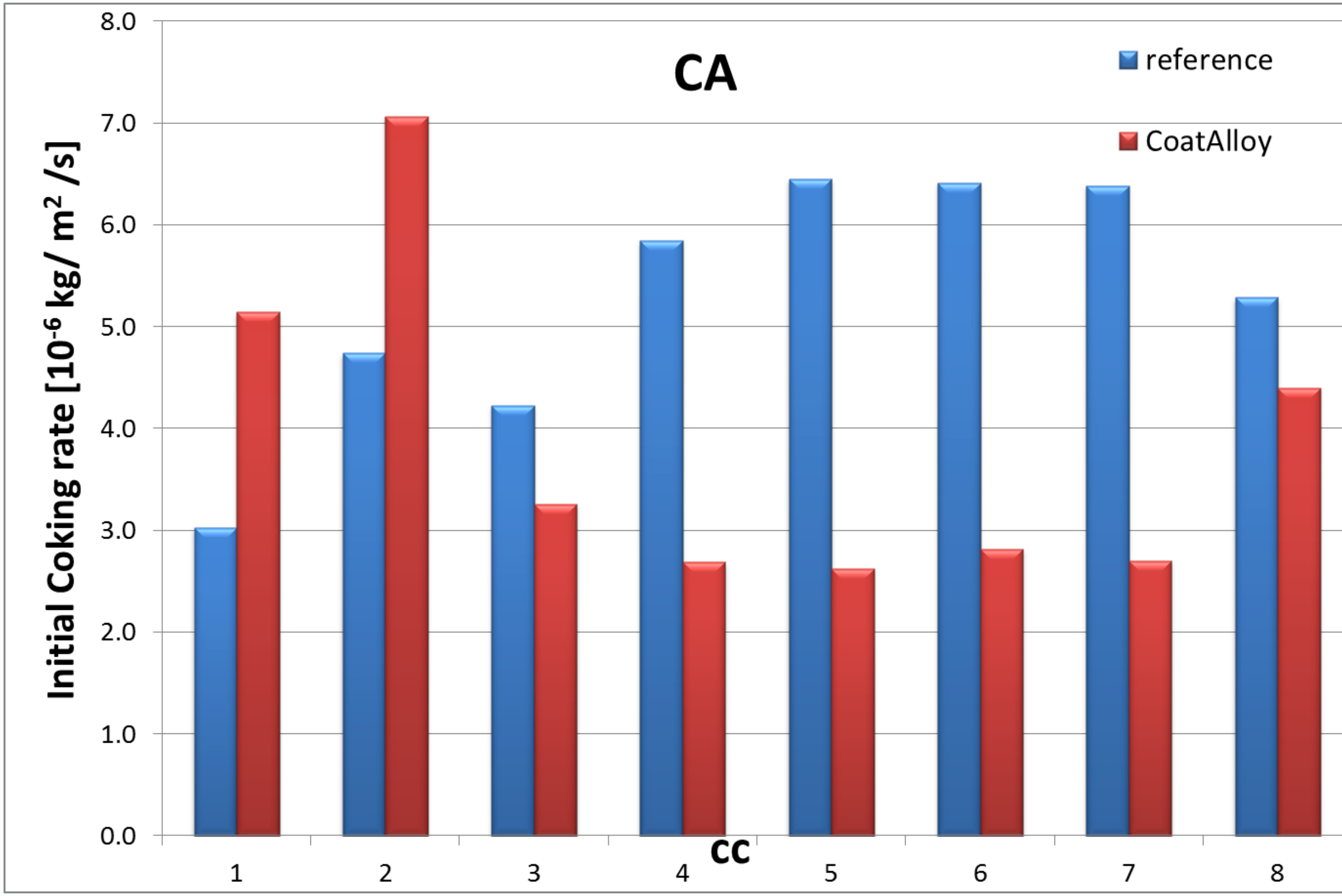
- ✓ Absence of Nitrogen during stabilization points
- ✓ Only Steam/Air treatment is applied for CoatAlloy

Effluent analysis

Alloy	reference	CoatAlloy	reference	CoatAlloy
Pretreatment	Fe-Ni-Cr optimal	Improved only steam	Fe-Ni-Cr optimal	Improved only steam
id	CA		CA+PreS	
Cracking Temperature (K)	1173		1173	
N_2 during stabilization	no		no	
dilution	0.33		0.33	
CA DMDS (ppmw S per HC)	41		41	
PreS (ppmw DMDS per H_2O)	0		500	
component				
H_2	4.25	4.23	4.26	4.24
CO_2	0.003	0.003	0.002	0.003
CO	0.01	0.01	0.01	0.01
CH_4	7.05	7.14	7.08	7.17
C_2H_6	30.21	29.96	30.02	29.88
C_2H_4	49.76	50.42	49.87	50.41
C_3H_8	0.11	0.12	0.11	0.12
C_3H_6	0.76	0.77	0.76	0.77

- ✓ No differences are observed in C oxides between coating and reference
- ✓ No effect of the material in the product distribution

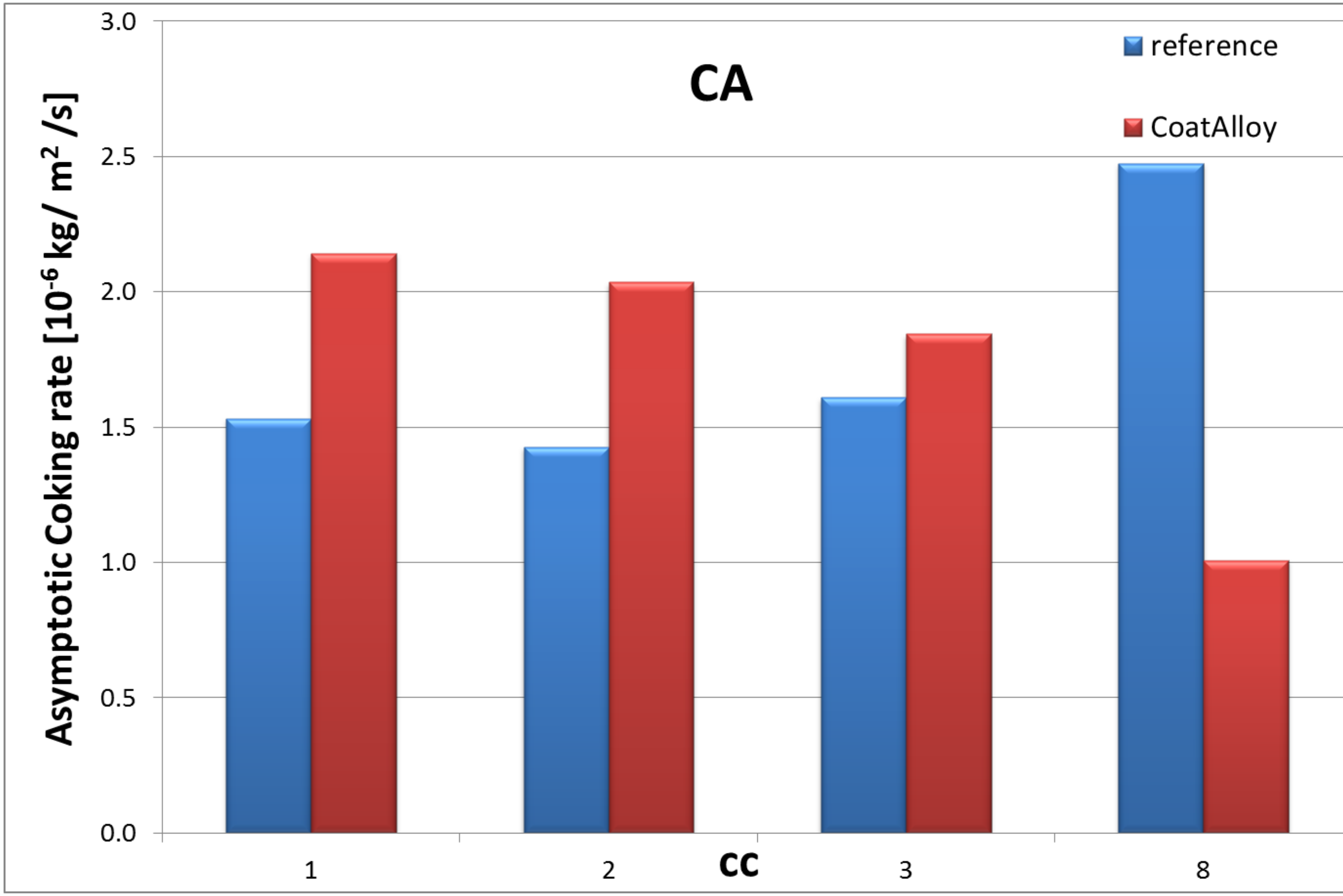
CA effect – Initial Rate



- ✓ 70 % ethane conversion
- ✓ T_{gas}= 1173 K
- ✓ 41 ppmw S/HC of DMDS

➢ CoatAlloy **supresses** catalytic coking in comparison with the reference

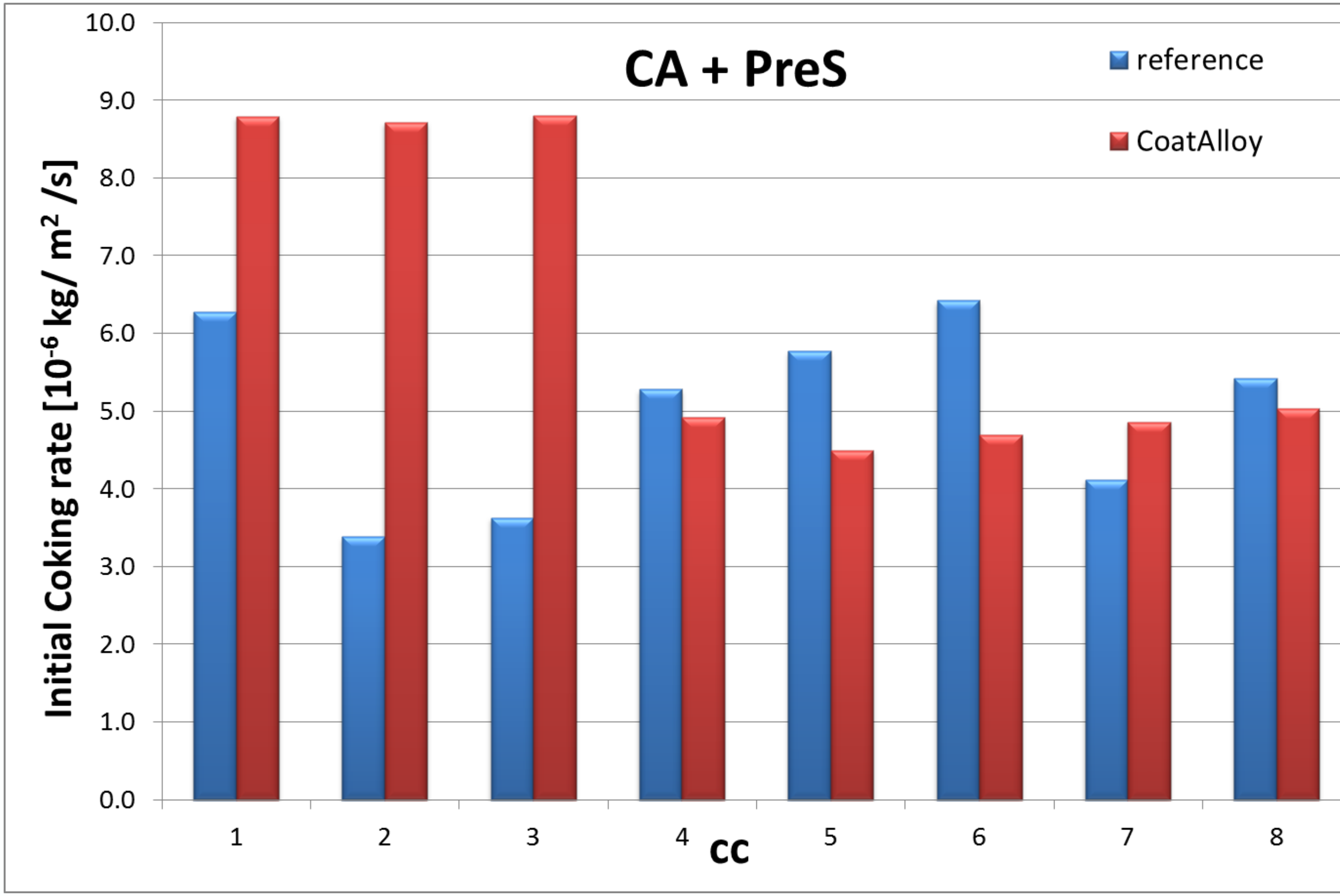
CA effect – Asymptotic Rate



- ✓ 70 % ethane conversion
- ✓ T_{gas}= 1173 K
- ✓ 41 ppmw S/HC of DMDS

✓ CoatAlloy performs **a factor 2 better** than the reference after cyclic aging

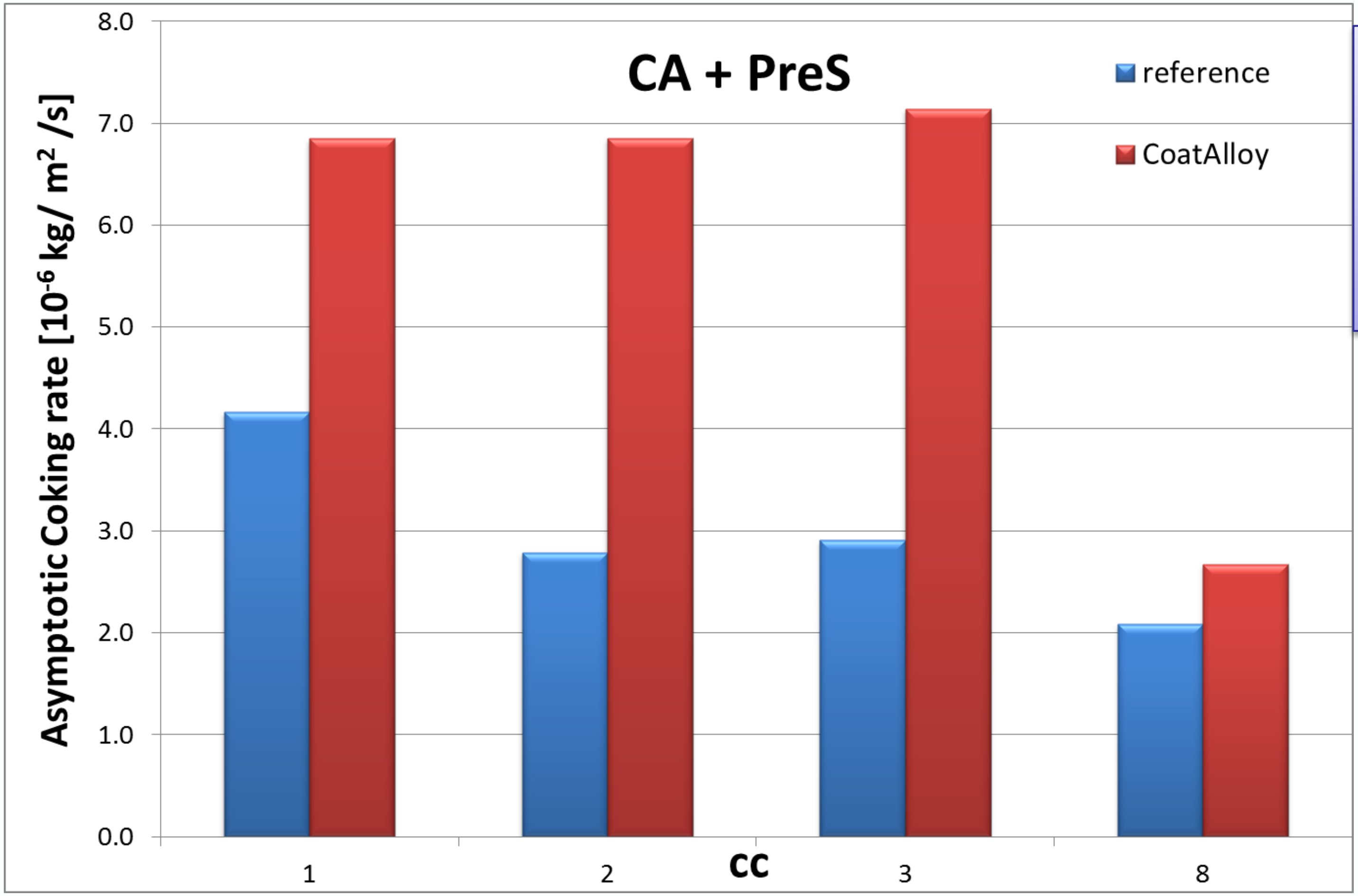
CA + PreS effect – Initial Rate



- ✓ 70 % ethane conversion
- ✓ T_{gas}= 1173 K
- ✓ 41 ppmw S/HC of DMDS
- ✓ 500 ppmw DMDS/H_2O

✓ PreS has a less pronounced effect on the reference when is combined with CA → the two materials coke similarly

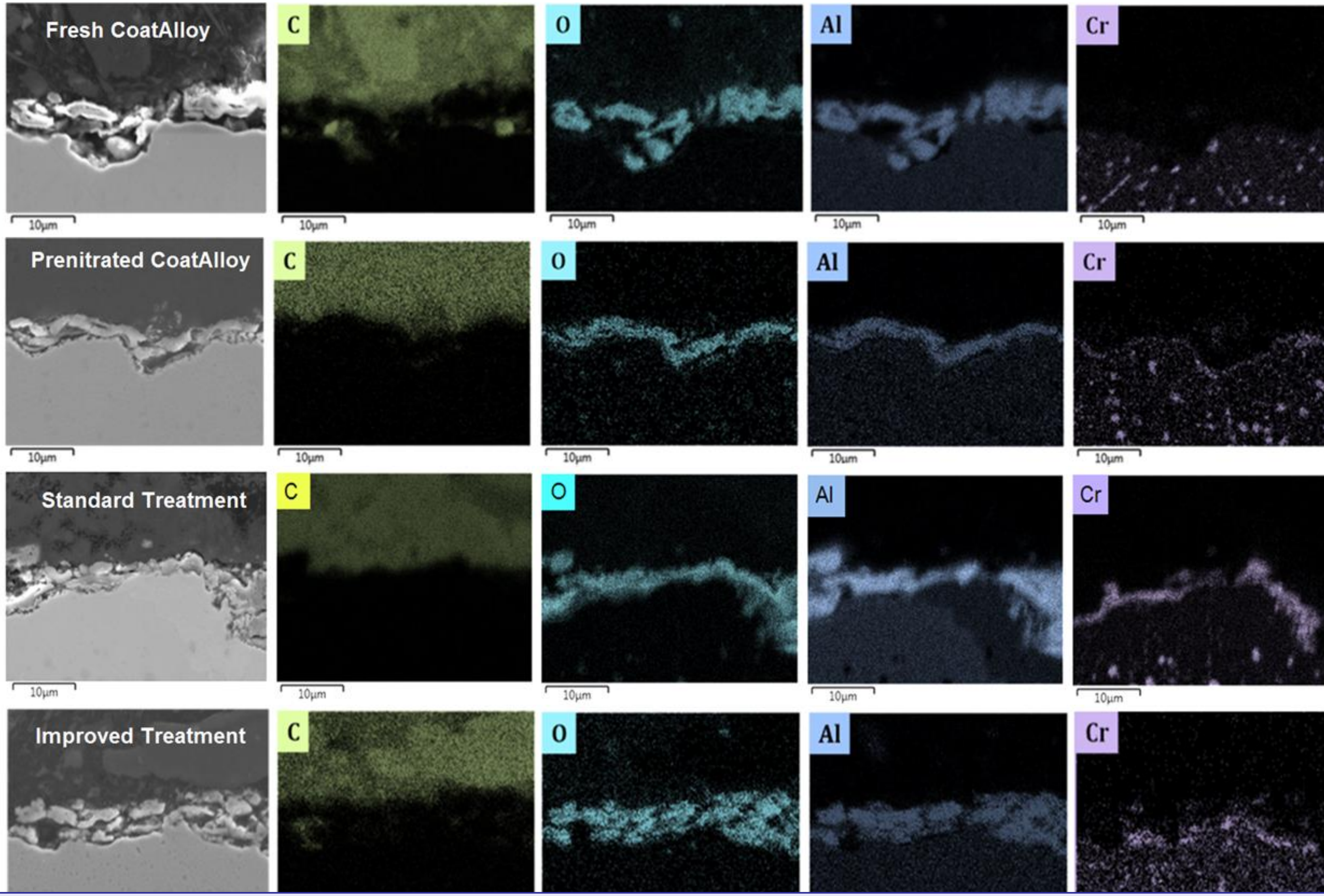
CA + PreS effect – Asymptotic Rate



- ✓ 70 % ethane conversion
- ✓ T_{gas}= 1173 K
- ✓ 41 ppmw S/HC of DMDS
- ✓ 500 ppmw DMDS/H_2O

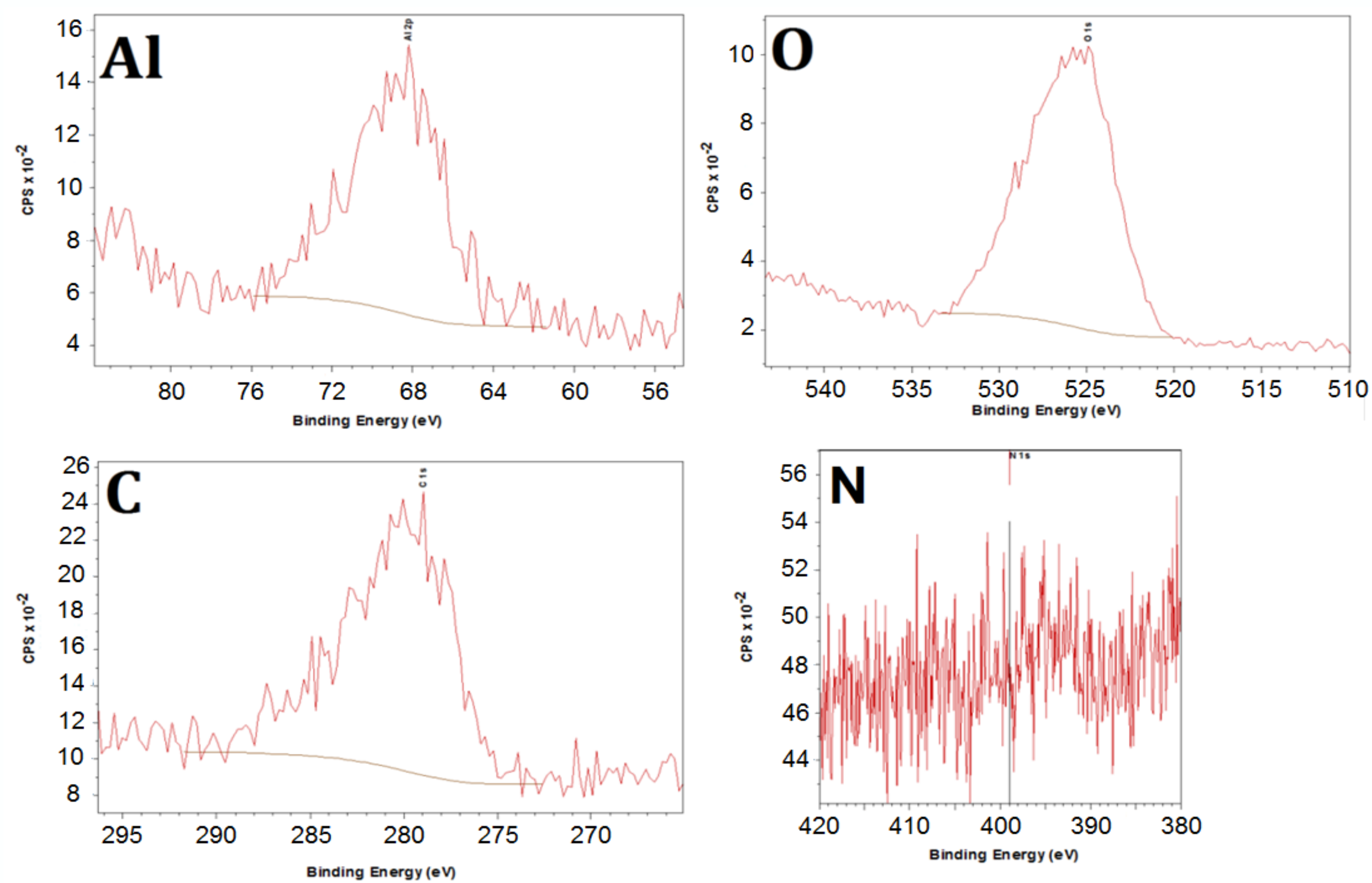
✓ CoatAlloy and MXM perform similarly after cyclic aging

SEM & EDX cross sectional analysis



- ✓ Increased uniformity of the coating is observed after application of steam
- ✓ The absence of nitrogen during stabilization points is beneficial

XPS analysis pre-nitrated sample



- ✓ No nitrogen is identified on the surface of CoatAlloy after exposure to nitrogen
- ✓ No nitrates are expected to be formed

Conclusions

- ✓ CoatAlloy performs better than the reference under industrially relevant conditions
- ✓ The coating stability, thickness and homogeneity is not affected throughout the cyclic aging experiments
- ✓ Addition of steam during the in-situ decoking and pretreatment of the coating improves its subsequent coking behavior
- ✓ Presulfiding shows no beneficial impact on the coking behavior of CoatAlloy
- ✓ The presence of pure N_2 has a negative effect on the homogeneity of the coating
- ✓ The optimization of the pretreatment depending on the material composition and properties is of great interest

Acknowledgments

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Questions