

Research for Sustainable Technologies



DECHEMA

FORSCHUNGSINSTITUT

Stiftung bürgerlichen Rechts

S. Madloch; M.C. Galetz

Effect of Pressure on Metal Dusting Initiation in CO-rich Syngas

KME-HTC Research Symposium 2018

Materials
Chemical Engineering
Biotechnology

- **Motivation and state of art**
- Metal dusting: experimental setups at DFI
- Testing program, materials and coatings
- Results 1 bar, cyclic 1 bar, 18 bar
- Summary

Metal dusting

Carburization and decomposition of the material to graphite and metal powder

Conditions:

- atmospheres with high carbon content $a_c \geq 1$
- temperature: 450 – 900°C
- H_2 ; CO ; CO_2 ; CH_4 ; N_2 ;

Industries:

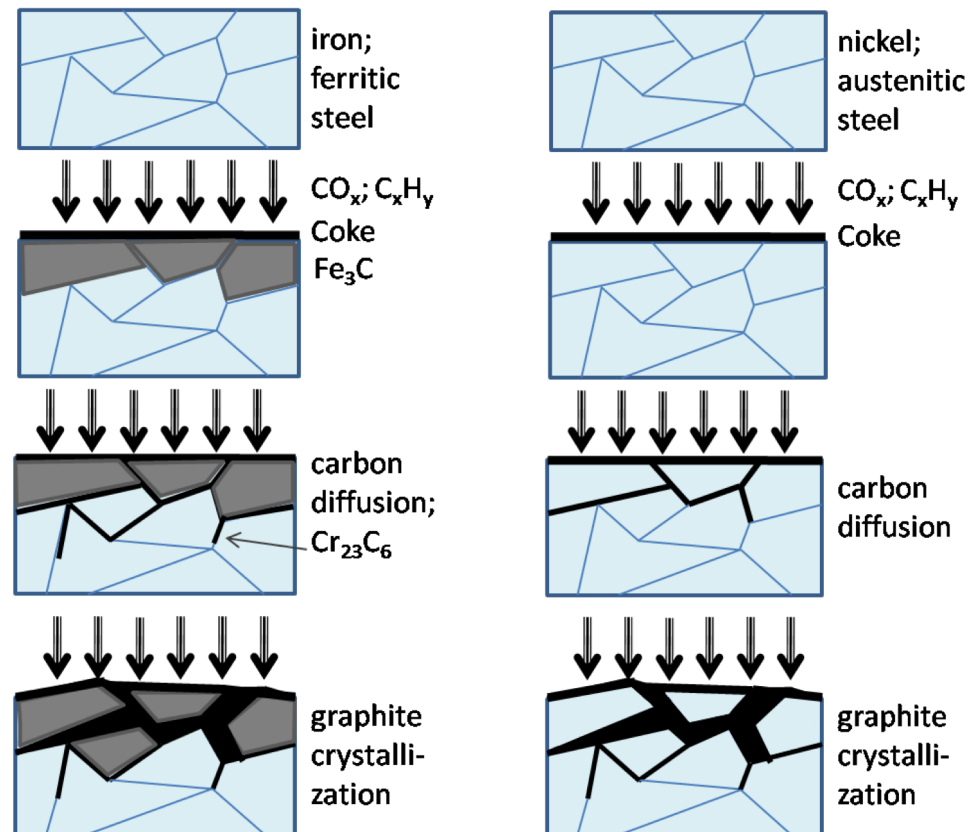
- petro chemistry
- coking plants
- steam reformer



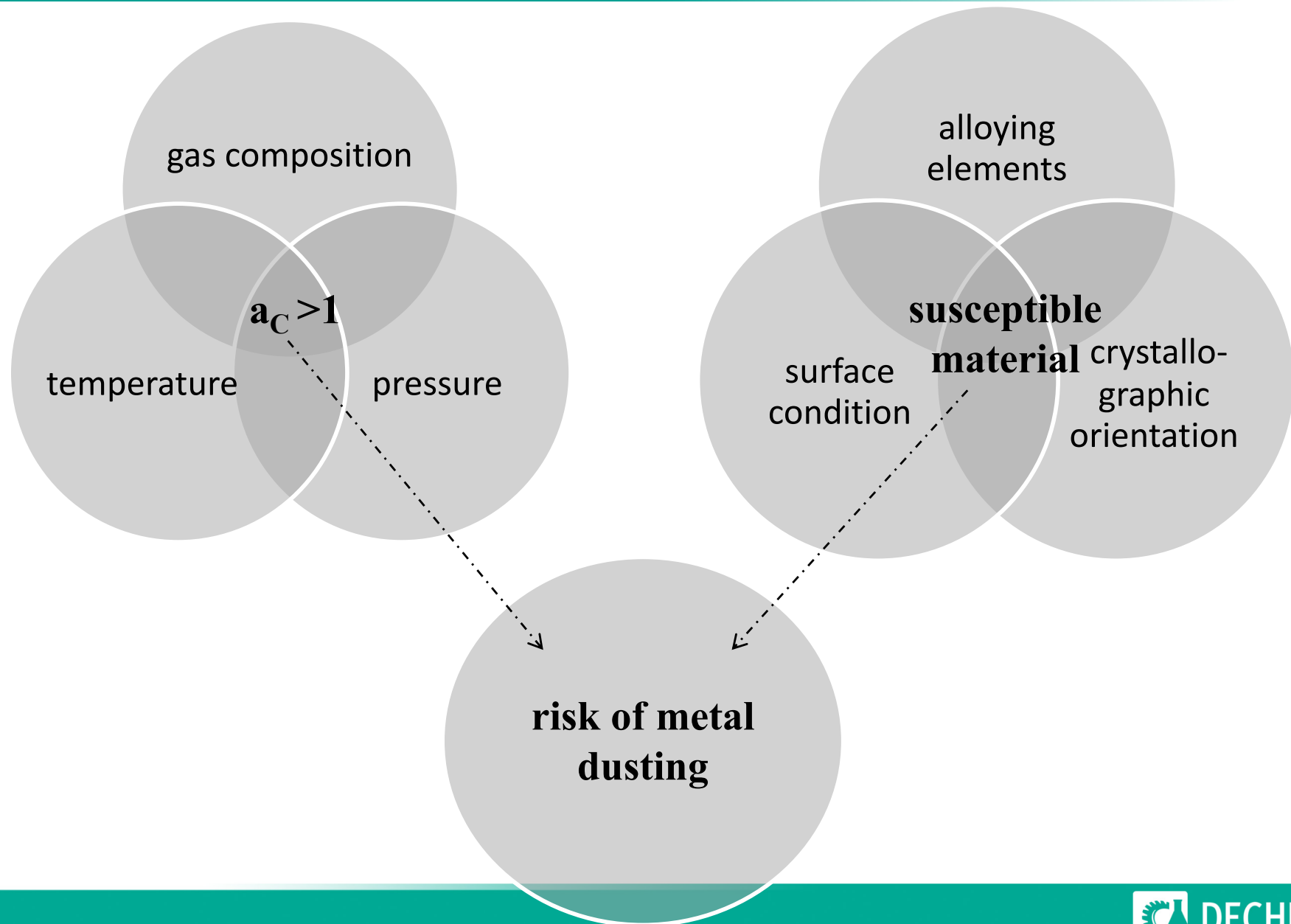
X15CrNiSi25-21

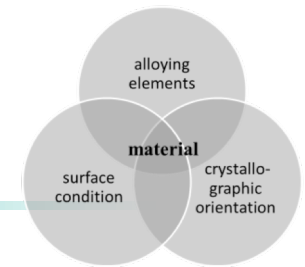
$H_2/CO/CO_2/CH_4/H_2O$ 620°C, 250h, 18 bar

2 mechanism

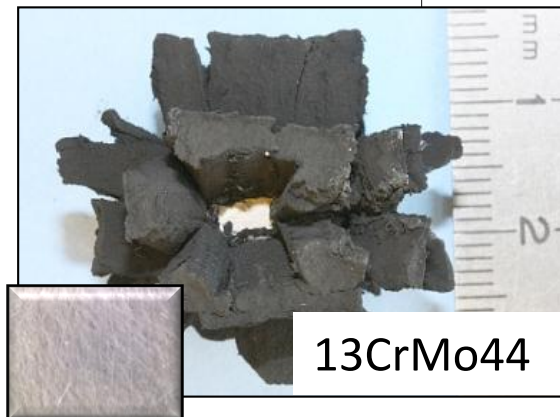
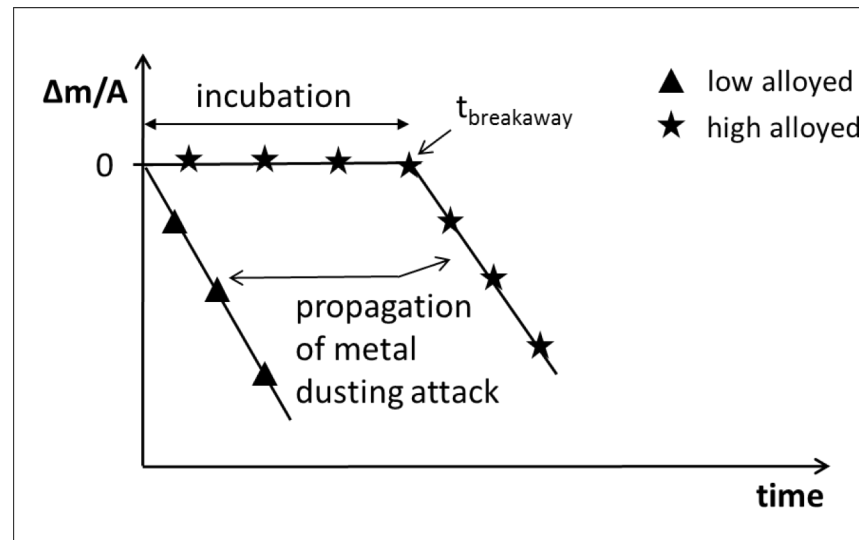


Motivation and state of art

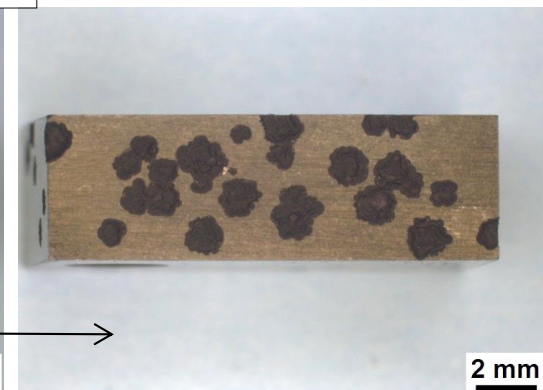




Metal dusting degradation:

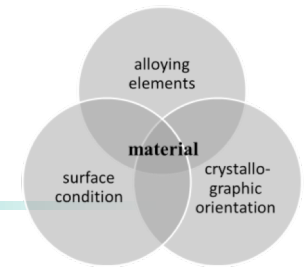


Low alloyed steels offer no protection against MD

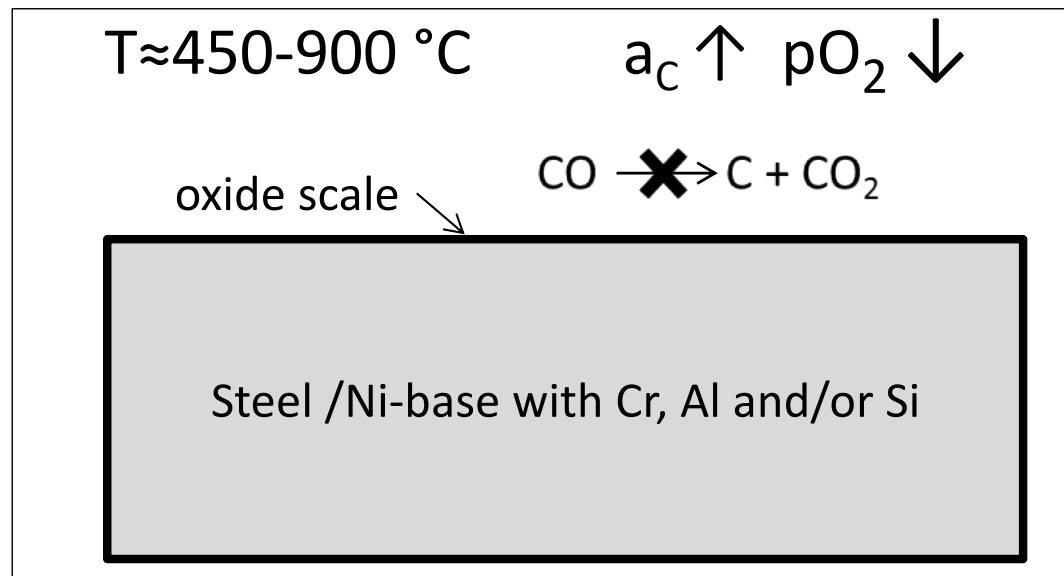


High alloyed materials show an incubation time until start of pitting and subsequent propagation of MD attack.

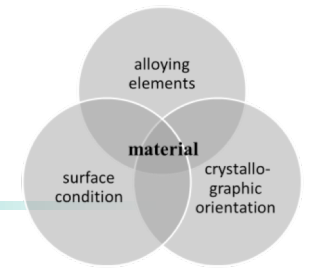
Motivation and state of art



- Metal dusting „resistant“ materials must contain high amount of oxide forming elements (Cr, Al, Si).
- Ferritic materials of high Cr content show better resistance against MD due to higher diffusion of Cr at MD temperature in ferritic compared to austenitic microstructure.



Barrier for initial reactions (no catalytic CO-dissociation $\rightarrow$ no carbon deposition)



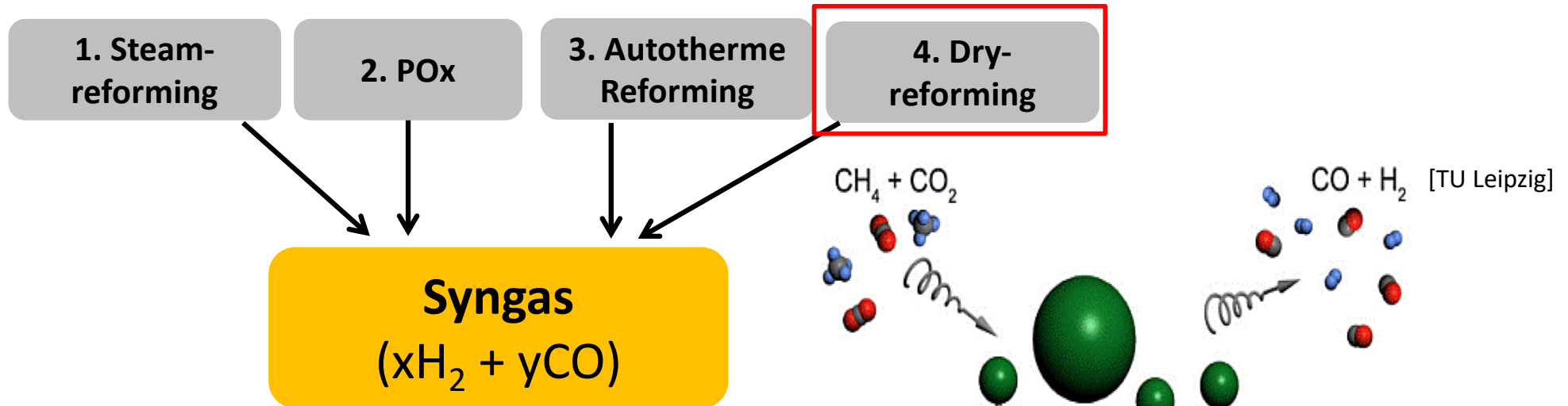
Criteria for „metal dusting resistant“ materials:

formula	source
$Cr_{equiv.} = Cr \% + 2 \cdot Si \% > 22$	Schueler, R.C., <i>Hydrocarbon processing</i> , 1972
$Cr_{equiv.} = Cr \% + 2 \cdot Si \% > 24$	Schillmoller, C.M., <i>Chem. Engineering</i> , 1986
$Cr_{equiv} = Cr \% + 3 \cdot (Si \% + Al \%) > 24$	Parks, S.B; Schillmoller, C.M., <i>Hydrocarbon processing</i> , 1996
Cr > 28 % in Ni-base (independent of Al) high Al level helps to decrease the amount of carbon deposition on the surface.	Röhnert, D.; Schütze, M.; Weber, T., <i>NACE Corrosion</i> , 2007
$Cr \% + Al \% > 33$	Hermse, C.G.M.; van Wortel, J.C., <i>Eurocorr</i> , 2008

→ many alloys that fulfill the criterion still fail under certain conditions!

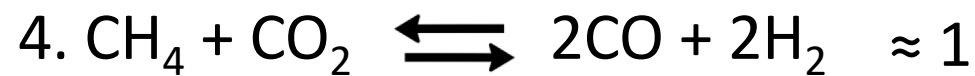
What parameters *really* influence the occurrence of metal dusting?

Syngas production

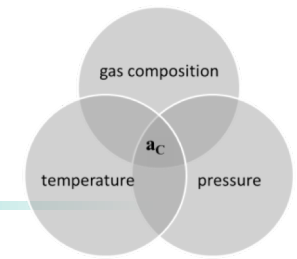


Pilot Reformer, Linde AG, München

H_2/CO :



Motivation and state of art



Factors influencing the carbon activity a_c

- **Gas composition:**

H_2 , CO , CO_2 , CH_4 , H_2O

Low in pO_2 – high enough for oxide formation of Cr, Si, Al

- **Temperature:**

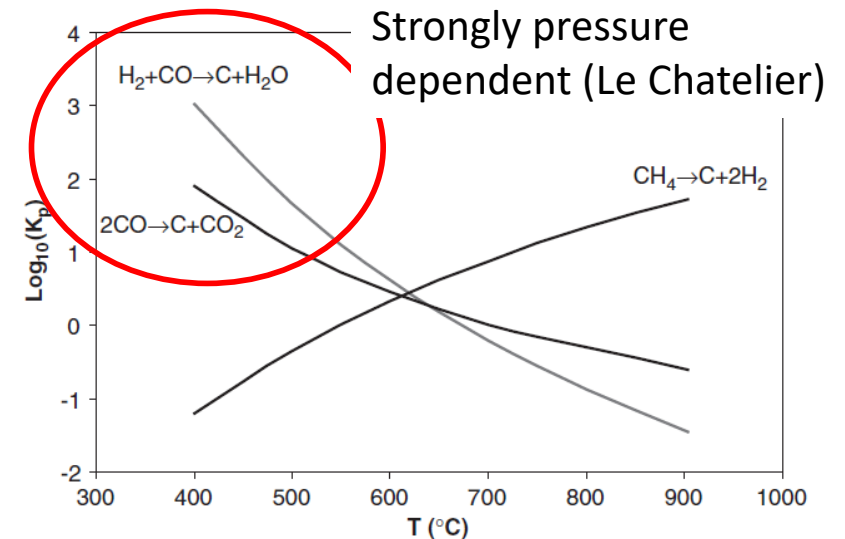
MD temperatures often too low for sufficient diffusion processes in order to develop protective scales.

- **Pressure:**

Commercial Ni-base alloys show lower incubation times in metal dusting conditions of **identical** a_c but at higher system pressures.

Natesan, K.; Zeng, Z., *Development of Materials Resistant to Metal Dusting Degradation*, U.S. Department of Energy, 2006.

Influence of pressure → lack of understanding



Young, D.J., *High Temperature Oxidation and Corrosion of Metals*, 2008

$$a_c = K \cdot \frac{p_{H_2} p_{CO}}{p_{H_2O}} = \exp\left(\frac{-\Delta G^0}{RT}\right) \cdot \frac{p_{H_2} p_{CO}}{p_{H_2O}}$$

$$a_c = K \cdot \frac{p_{CO}^2}{p_{CO_2}} = \exp\left(\frac{-\Delta G^0}{RT}\right) \cdot \frac{p_{CO}^2}{p_{CO_2}}$$

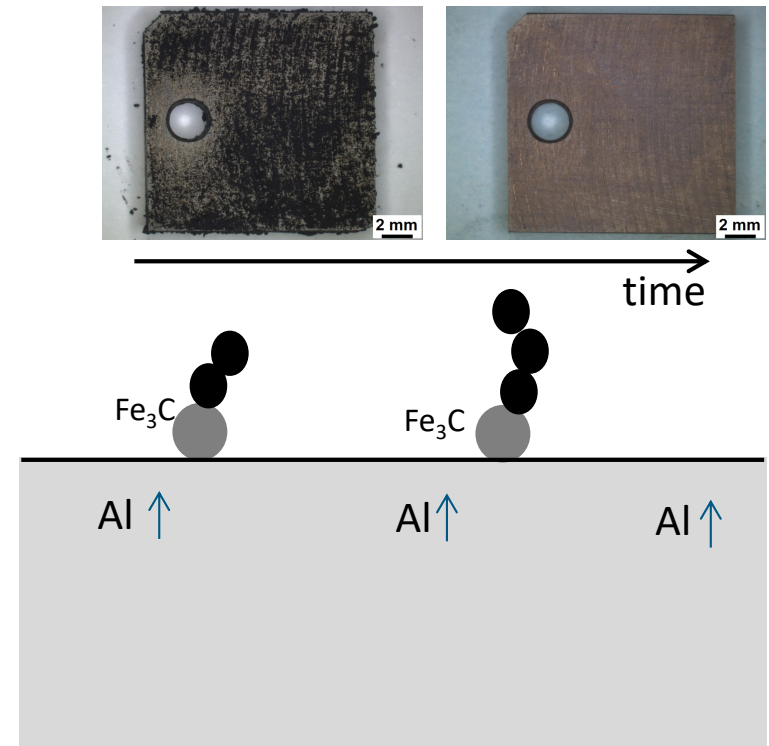
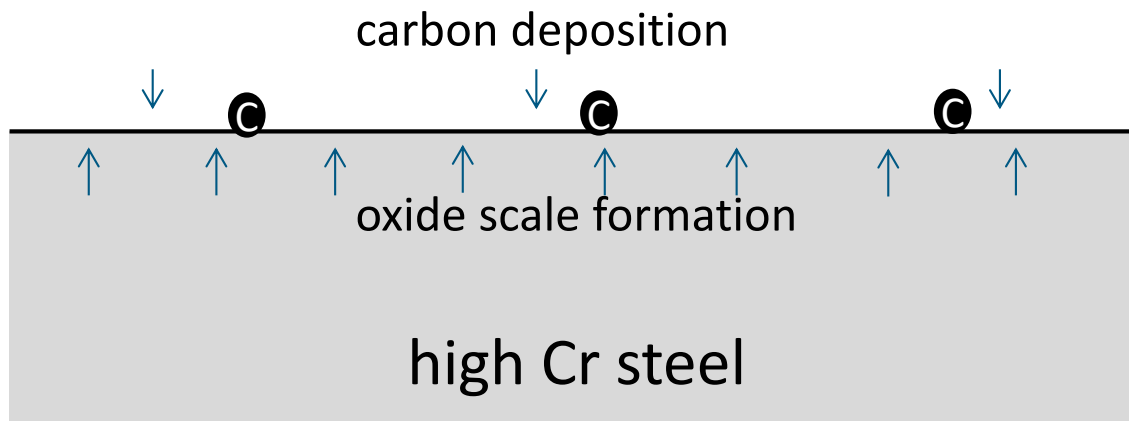
Motivation and state of art

- **Thermodynamics**: pO_2 high enough for oxide formation and also $a_c > 1$
→ coking
- Competition between oxide scale formation and C-deposition
- Initiation of MD is dependent on a_c **and** the number of catalytically active surface sites, which are limited. → **kinetically** controlled threshold for carbon deposition

This work:

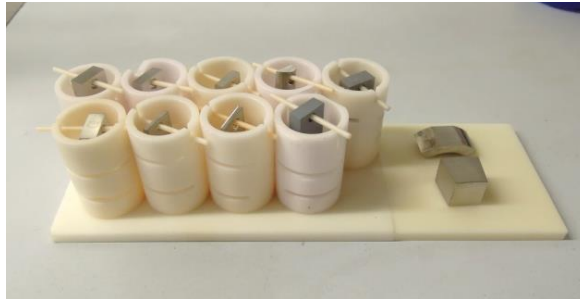
→ fixed **gas composition, temperature,**

→ variation of **system pressure**

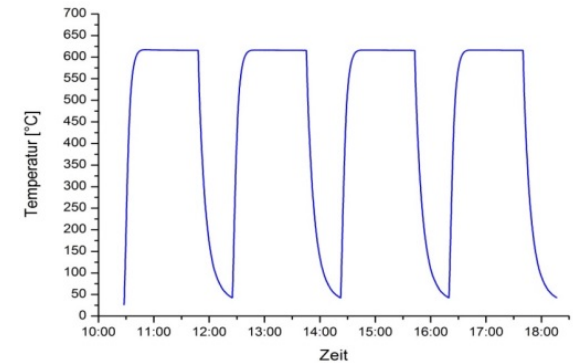


Metal dusting: experimental setups at DFI

3 setups for metal dusting testing



$T = 450\text{--}900\text{ }^{\circ}\text{C}$
(usually $620\text{ }^{\circ}\text{C}$)
gas mixtures contain
 CO , H_2 , H_2O and/or CH_4 , CO_2
flowing gas conditions



isothermal

- standard test
- quasi-isotherm
system is cooled
down for
inspection

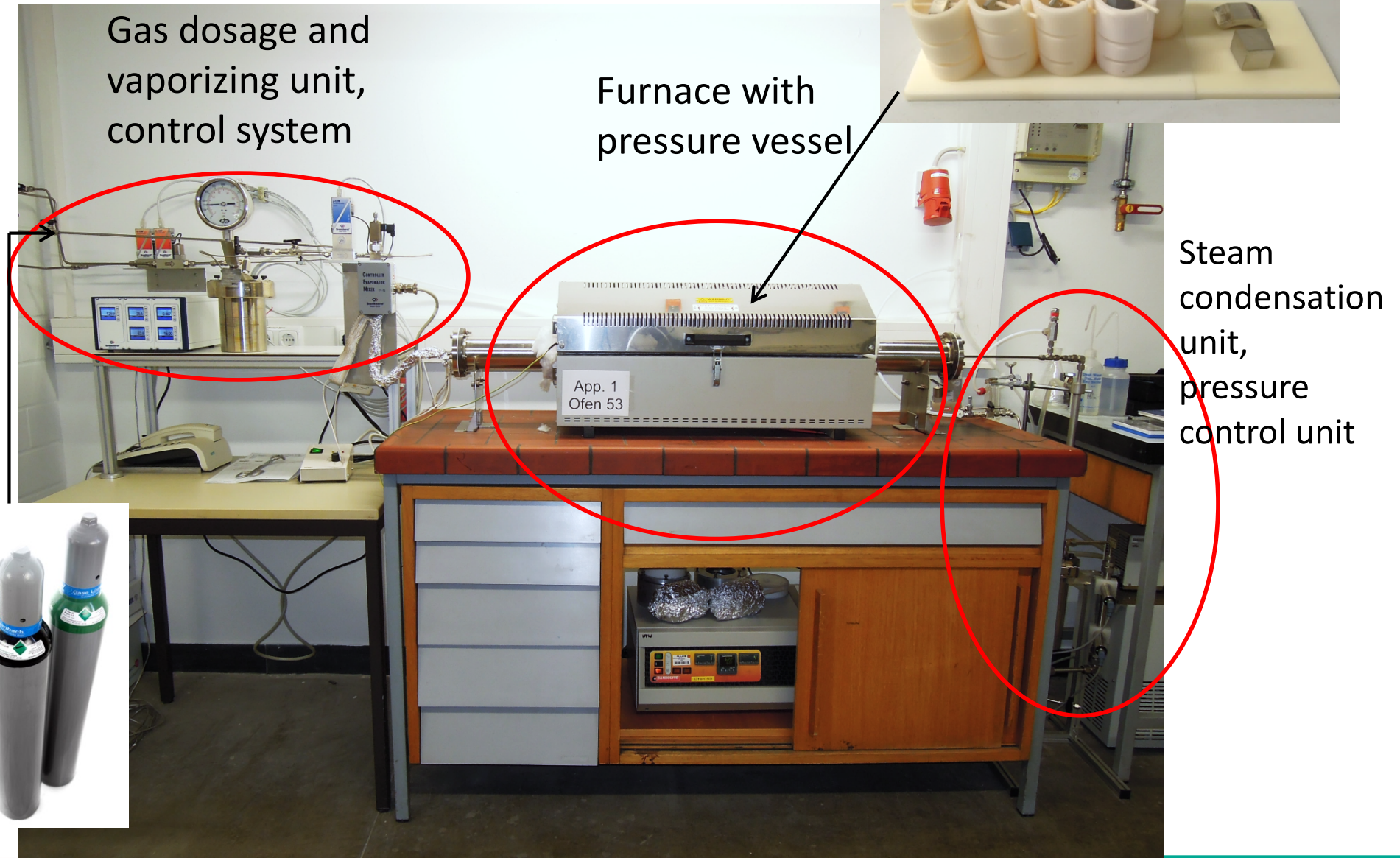
high pressure

- system pressure up to
18 bar
- dosage- and vaporizing
unit produces accurate
steam content under
high pressure

thermo-cyclic

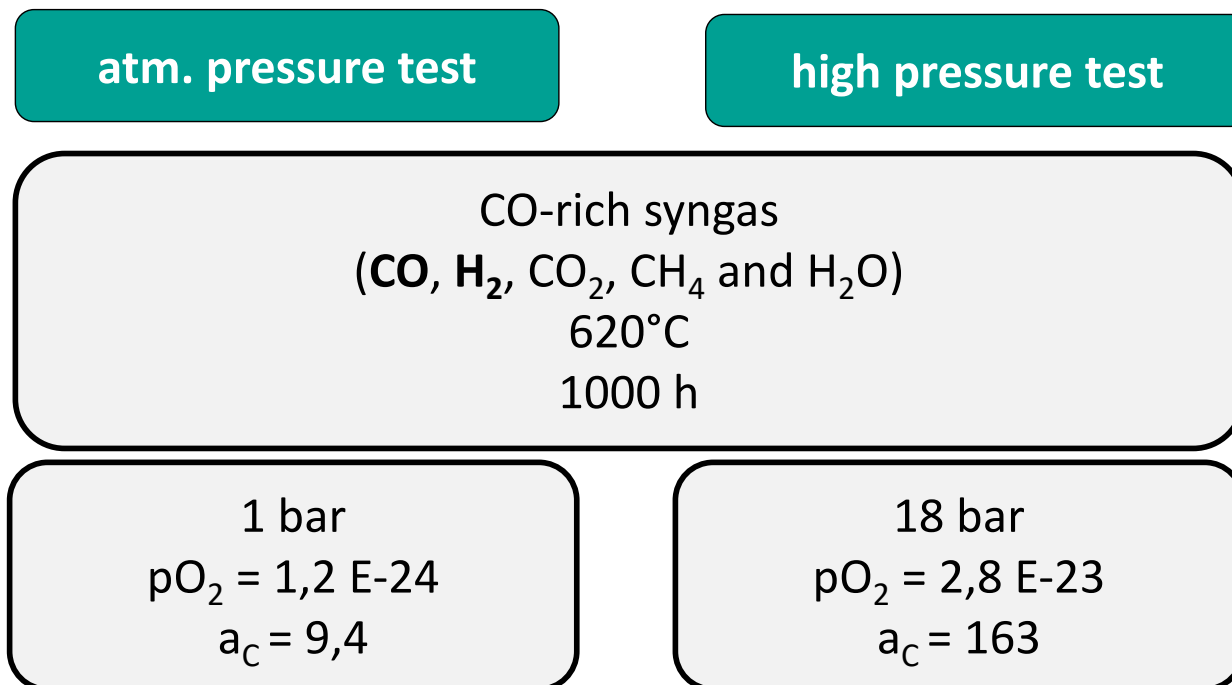
- Control system enables
automated time-
temperature programs
(hot and cold dwell times
adjustable, no. cycles...)
- according to ISO 13573
($T_{\text{cold}} < 50\text{ }^{\circ}\text{C}$)

Metal dusting: high pressure setup



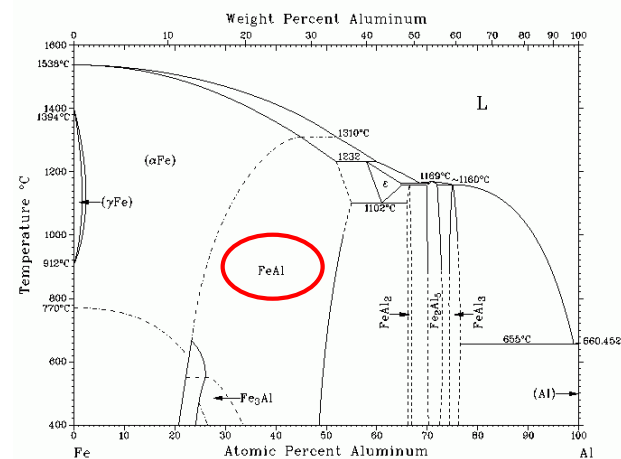
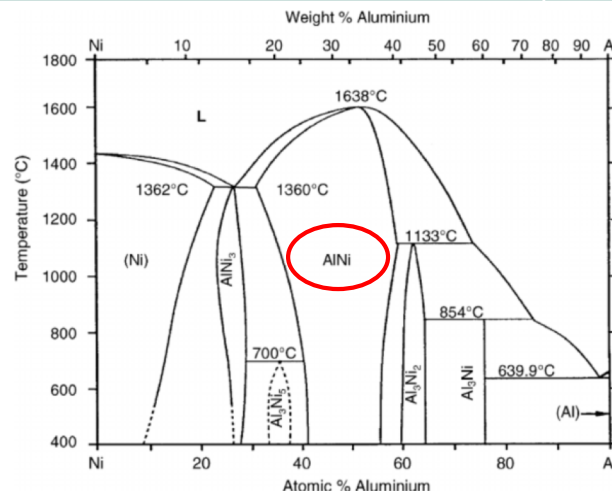
Testing program, materials and coatings

Exposure of several commercial alloys in identical gas composition and temperature but different system pressures.



Testing program, materials and coatings

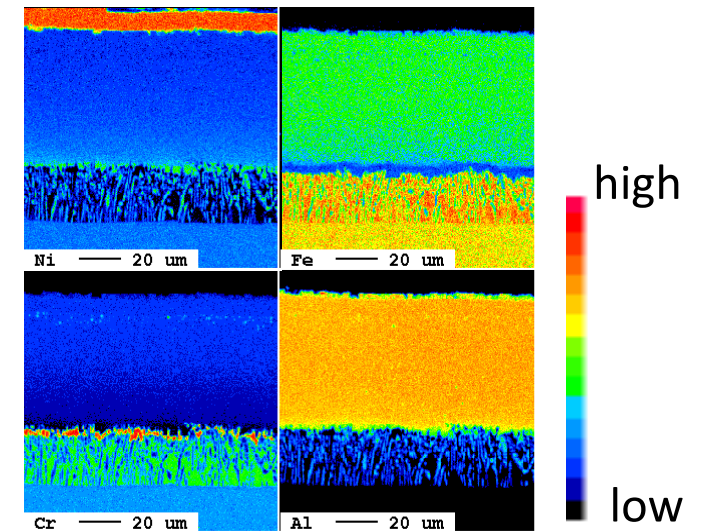
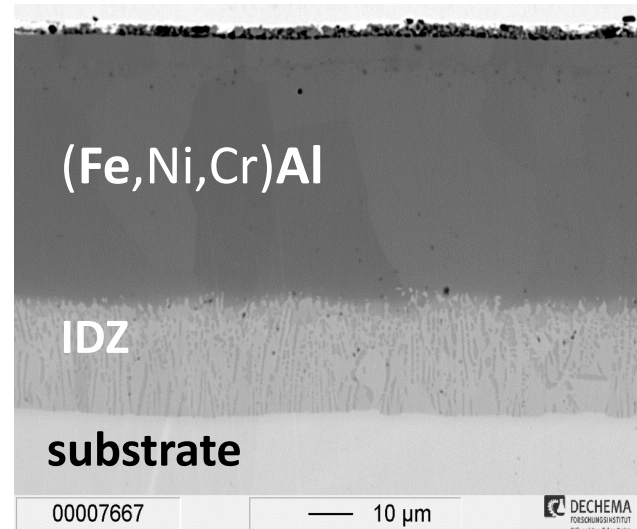
Materials and coatings	Alloy type (important alloying elements in brackets, not complete)
NiCr15Fe/ Alloy 600	Ni-base (15% Cr)
NiCr15Fe/ Alloy 600 Ge-modified aluminide coating	Ni-base (15% Cr) with NiGeAl-diffusion coating
NiCo29Cr28Si/ 2.4880	Ni-base (29% Co; 28%Cr; 2,75% Si)
X6CrNiTi18-10/ 1.4541 aluminide coating	Fe-base (18% Cr) with FeAl-diffusion coating
X8NiCrSi38-18 / 1.4862	Fe-base (18% Cr; 2% Si)
X10NiCrAlTi32-20/ Alloy 800H	Fe-base (20% Cr; 0,3% Al)
Kanthal APMT	Fe-base (21% Cr; 5% Al; 3% Mo)



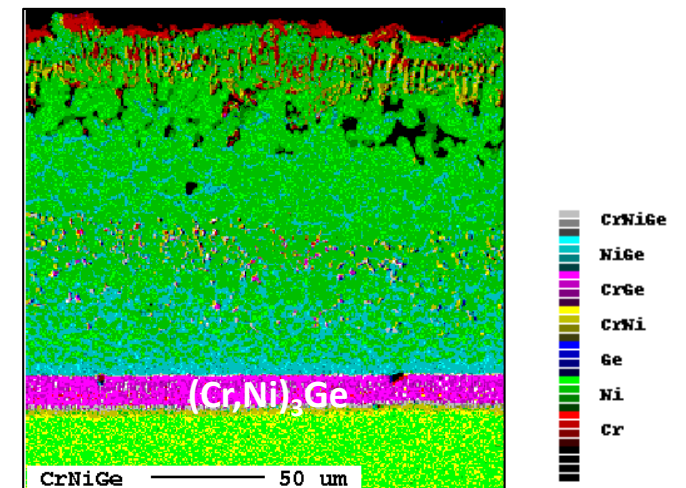
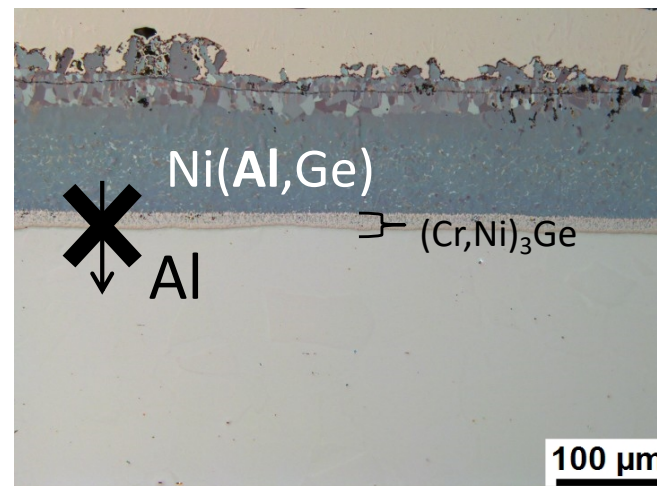
...and others

Testing program, materials and coatings

Pure aluminide coating
(pack
cementation)



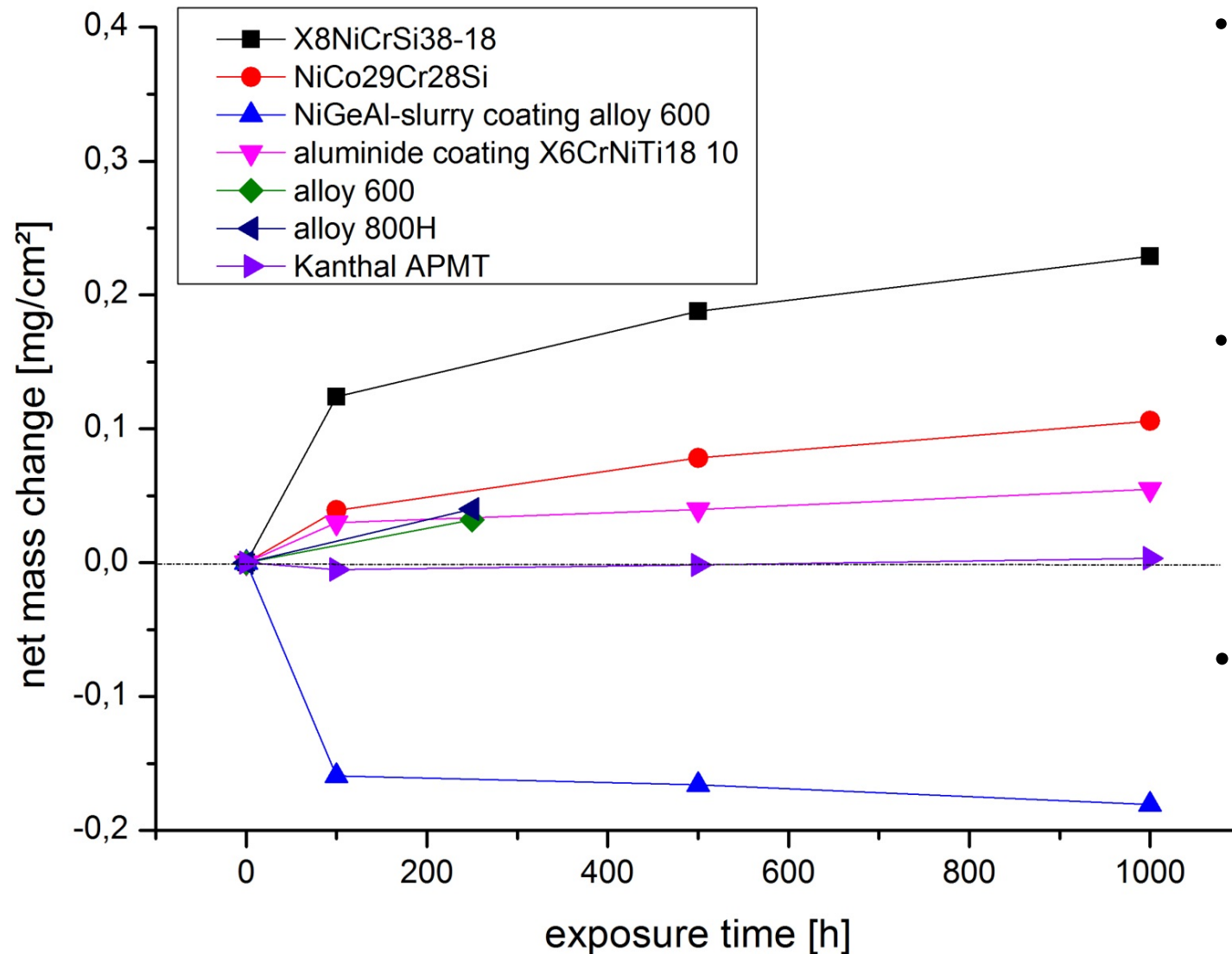
Ge-modified aluminide coating
(slurry diffusion)



Agenda

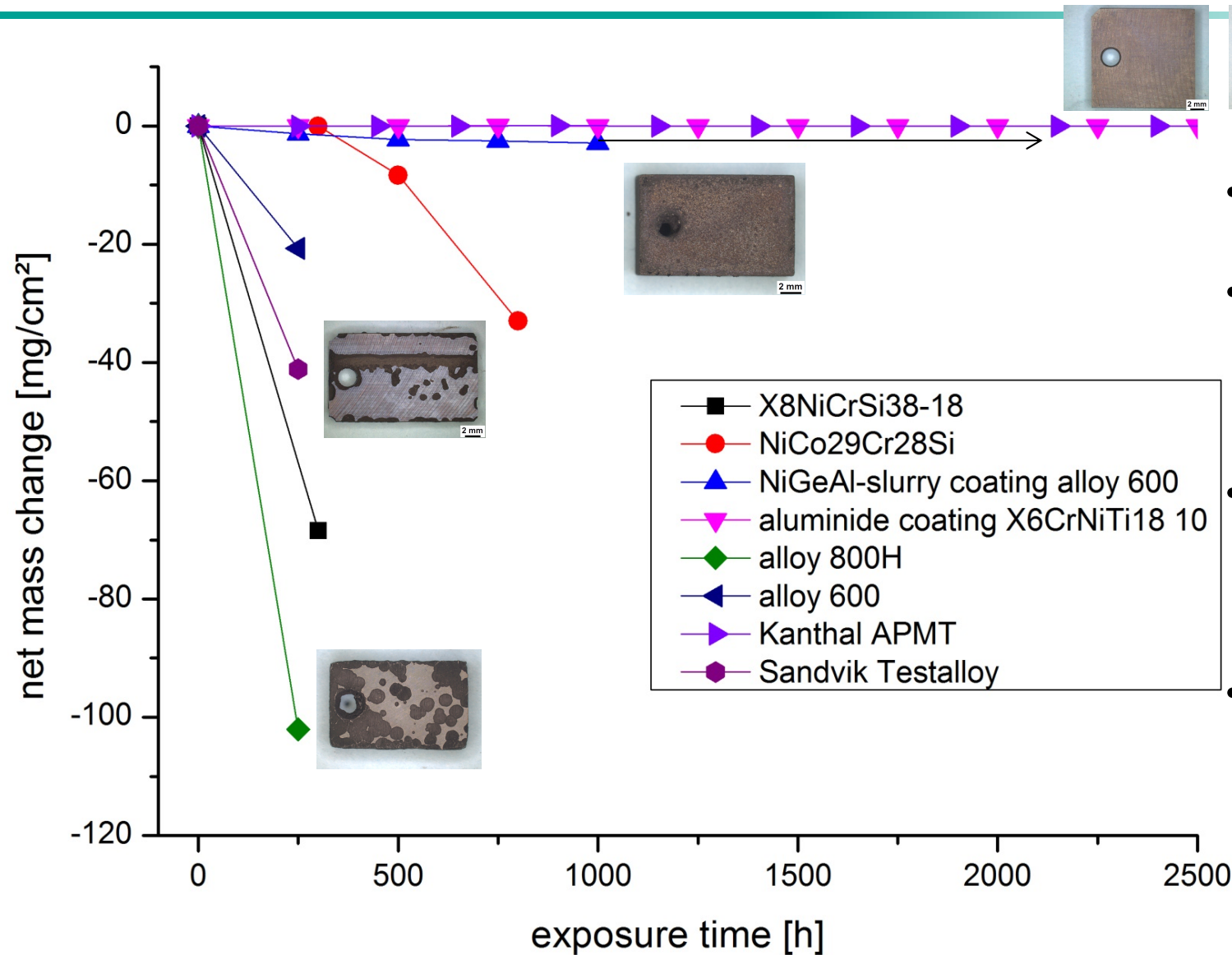
- Motivation and state of knowledge
- Metal dusting: experimental setups at DFI
- Testing program, materials and coatings
- **Results**
- Summary

Metal dusting test – $\text{H}_2\text{-CO-CO}_2\text{-CH}_4\text{-H}_2\text{O}$ – 620°C - 1 bar



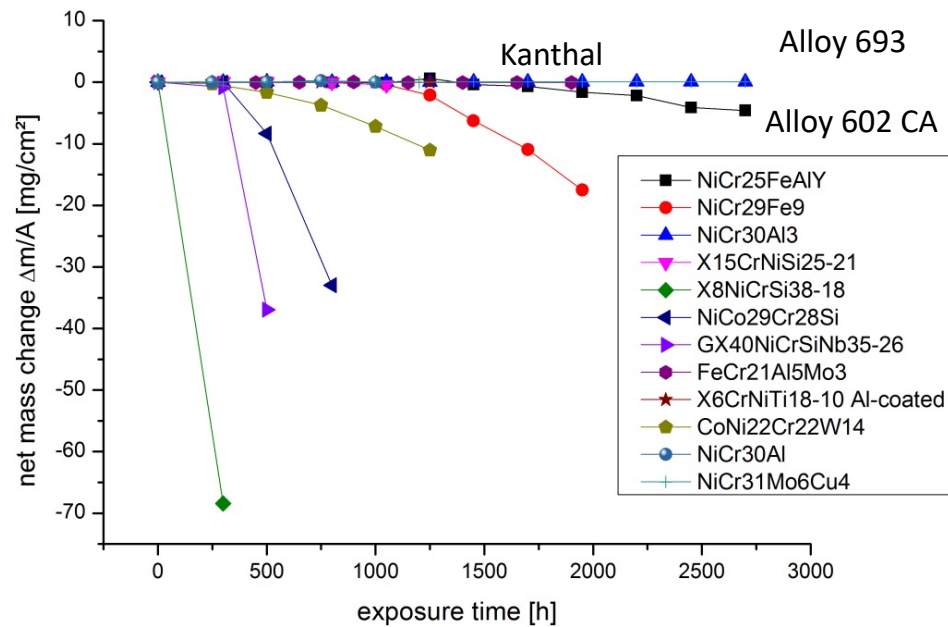
- All alloys and the aluminide coating show very low mass gains. Oxide scale growth follows parabolic behavior.
- The slurry coating shows slight weight loss after the first exposure due to spallation of undiffused particles.
- **No coking or metal dusting observed.**

Metal dusting test - $\text{H}_2\text{-CO-CO}_2\text{-CH}_4\text{-H}_2\text{O}$ – 620°C - 18 bar

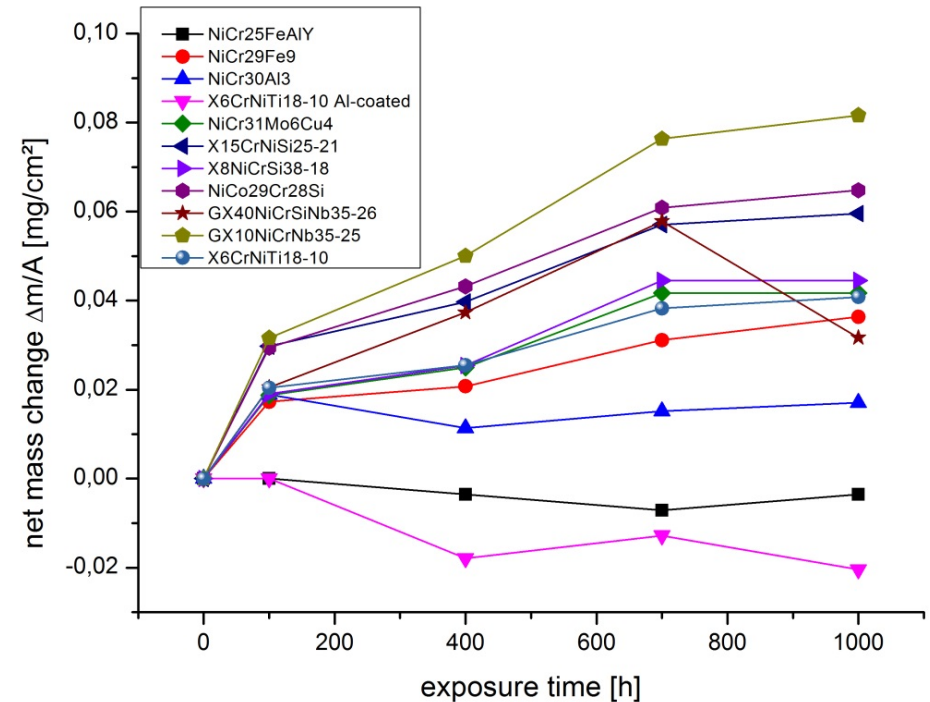


- Most alloys suffered severe attack.
- Kanthal APMT performs superiorly for more than 4000 h.
- Aluminide coating protects X6CrNiTi18 10 more than 2500 h.
- NiGeAl-slurry coating increases lifetime of alloy 600.

Metal dusting test - $\text{H}_2\text{-CO-CO}_2\text{-CH}_4\text{-H}_2\text{O}$ – 620°C - 18 bar vs. cyclic 1 bar



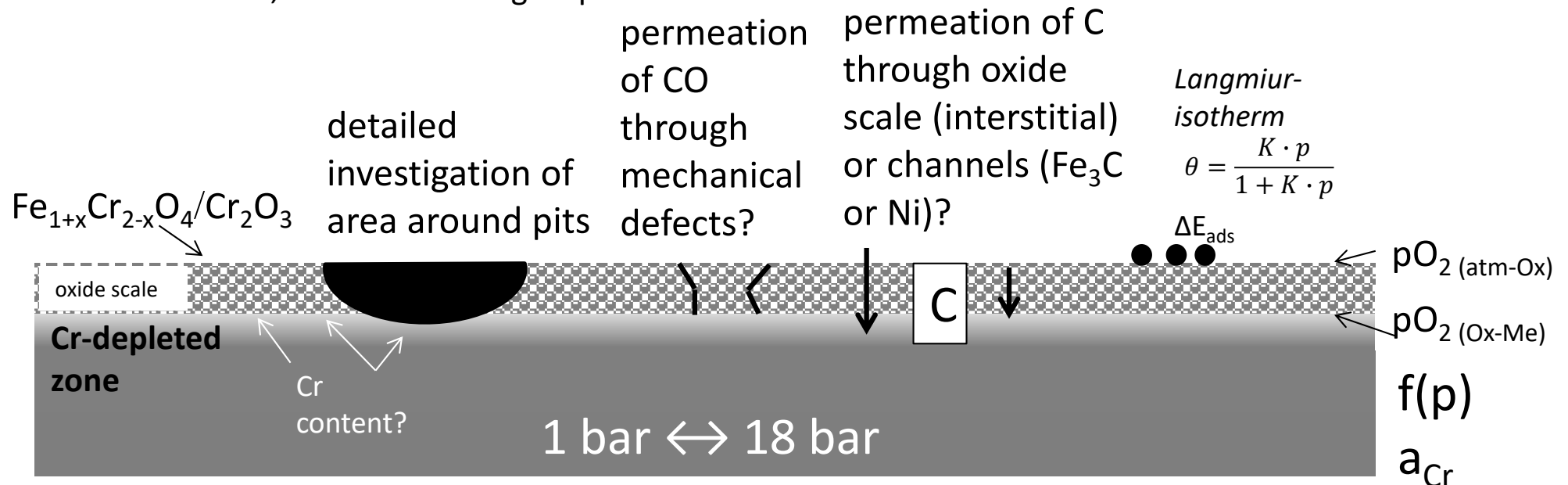
Isothermal test 18 bar



Thermocyclic test 1 bar

Impact of pressure: Competition between oxide formation and C-deposition

- **Oxide scale** → oxide composition, pressure dependency of oxide formation → growth stress & isostatic compression, crack initiation, transport properties, permeation of carbon through oxide layers?
- **Subsurface region** → Cr content below oxide scale, conditions for oxide formation altered by pressure, higher a_{Cr} in substrate necessary at high pressures?
- **Surface reactions** → effect of pressure on surface coverage and surface energy, catalytically active sides, rate determining step



Impact of pressure: Thermodynamics

CO-rich syngas
(CO, H₂, CO₂, CH₄ and H₂O)
620°C
1000 h

Gas phase

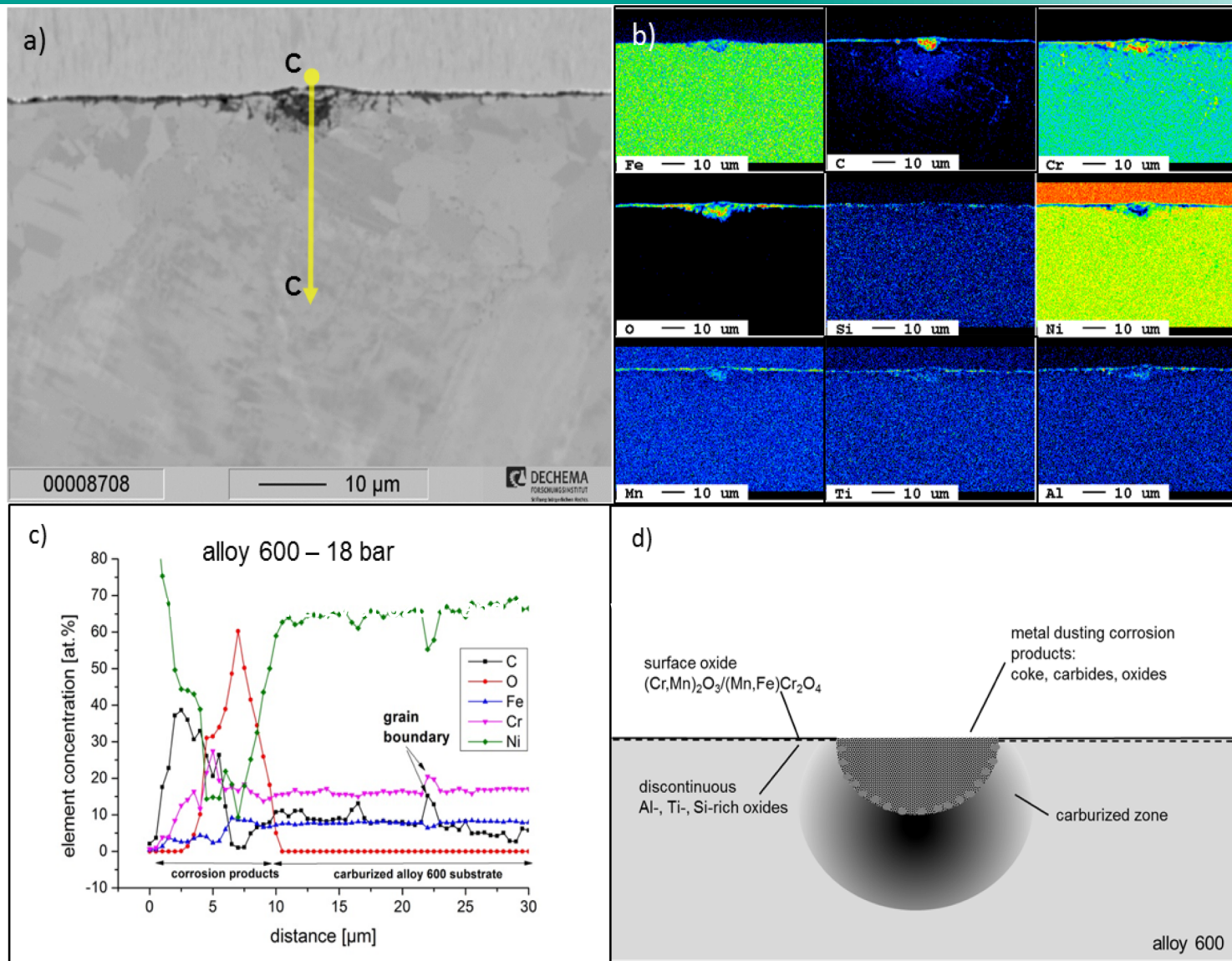
1 bar
pO₂ = 1,2 E-24
a_C = 9,4

18 bar
pO₂ = 2,8 E-23
a_C = 163

	$\Delta G_{620^\circ\text{C}}^{1 \text{ bar}} \text{ [kJ/mol]}$	$\Delta G_{620^\circ\text{C}}^{18 \text{ bar}} \text{ [kJ/mol]}$
$2\text{Cr}_{(s)} + 3\text{CO}_{2(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3 \text{CO}_{(g)}$	-278.8	-278.8
$2\text{Cr}_{(s)} + 3\text{H}_2\text{O}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3 \text{H}_{2(g)}$	-292.5	-292.5
$2\text{Cr}_{(s)} + 3\text{CO}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3 \text{C}_{(s)}$	-328.8	-393.3
$\frac{27}{2}\text{Cr}_{(s)} + 3\text{CO}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + \frac{1}{2}\text{Cr}_{23}\text{C}_{6(s)}$	-519.4	-583.8

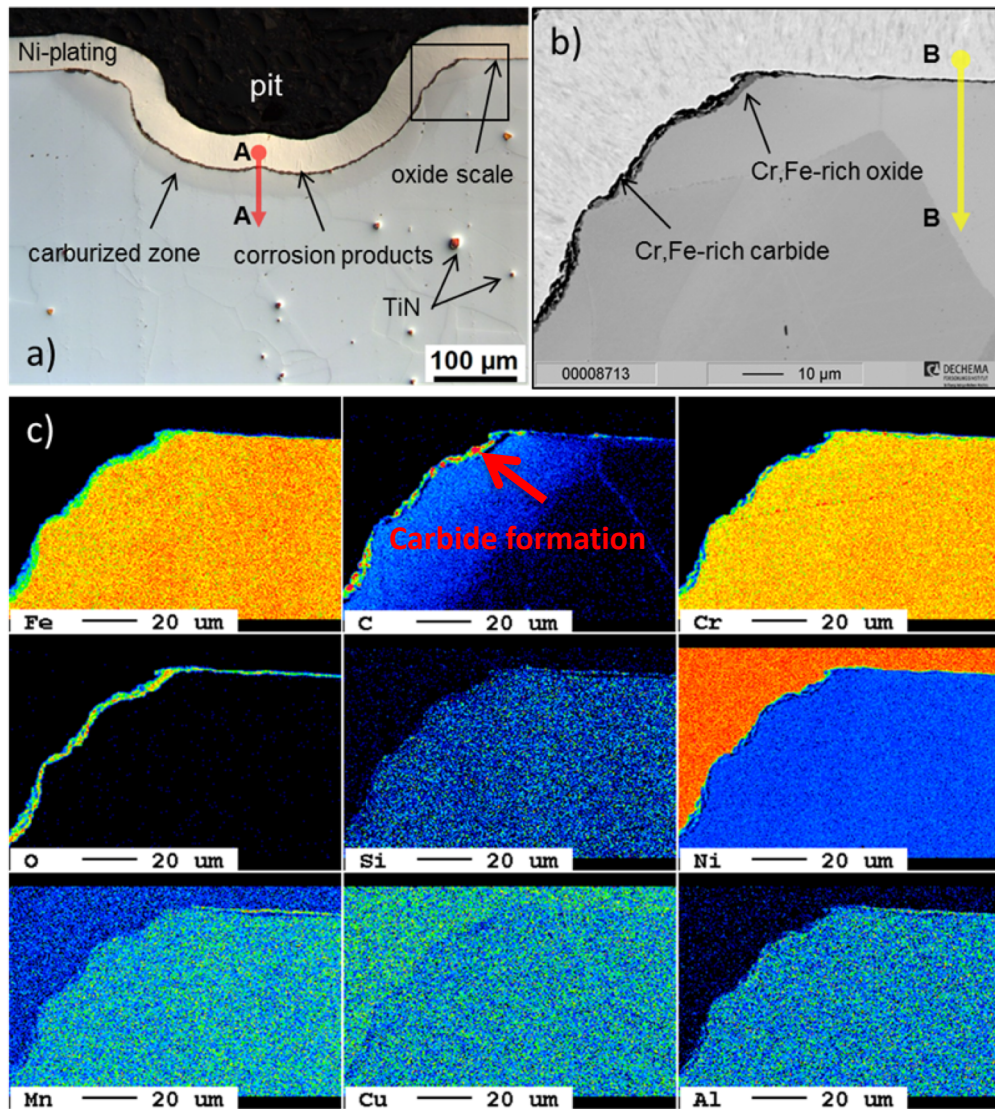
Reactions
„Le Chatelier’s
principle“

Pit Propagation



Alloy 600
250h,
620°C, 18 bar

Exposure tests reveal a strong impact of the system pressure on the incubation time of MD.

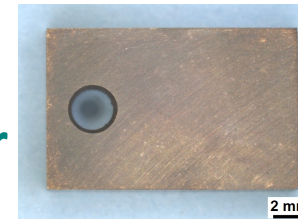


Alloy 800H
250h,
620°C, 18 bar

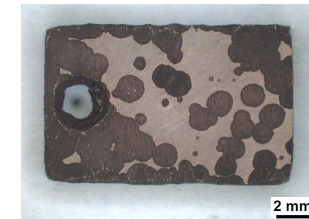
Summary

Tests revealed a **strong impact** of the **system pressure** on the onset of metal dusting. **At 1 bar no attack.**

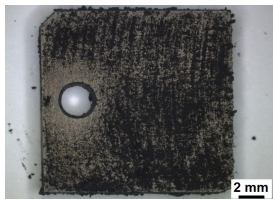
Pressure more severe than cyclic loading.



250 h 1 bar

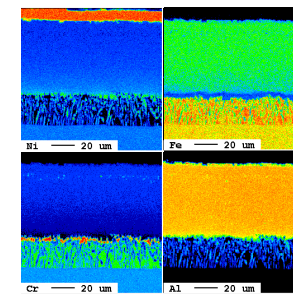


250 h 18 bar



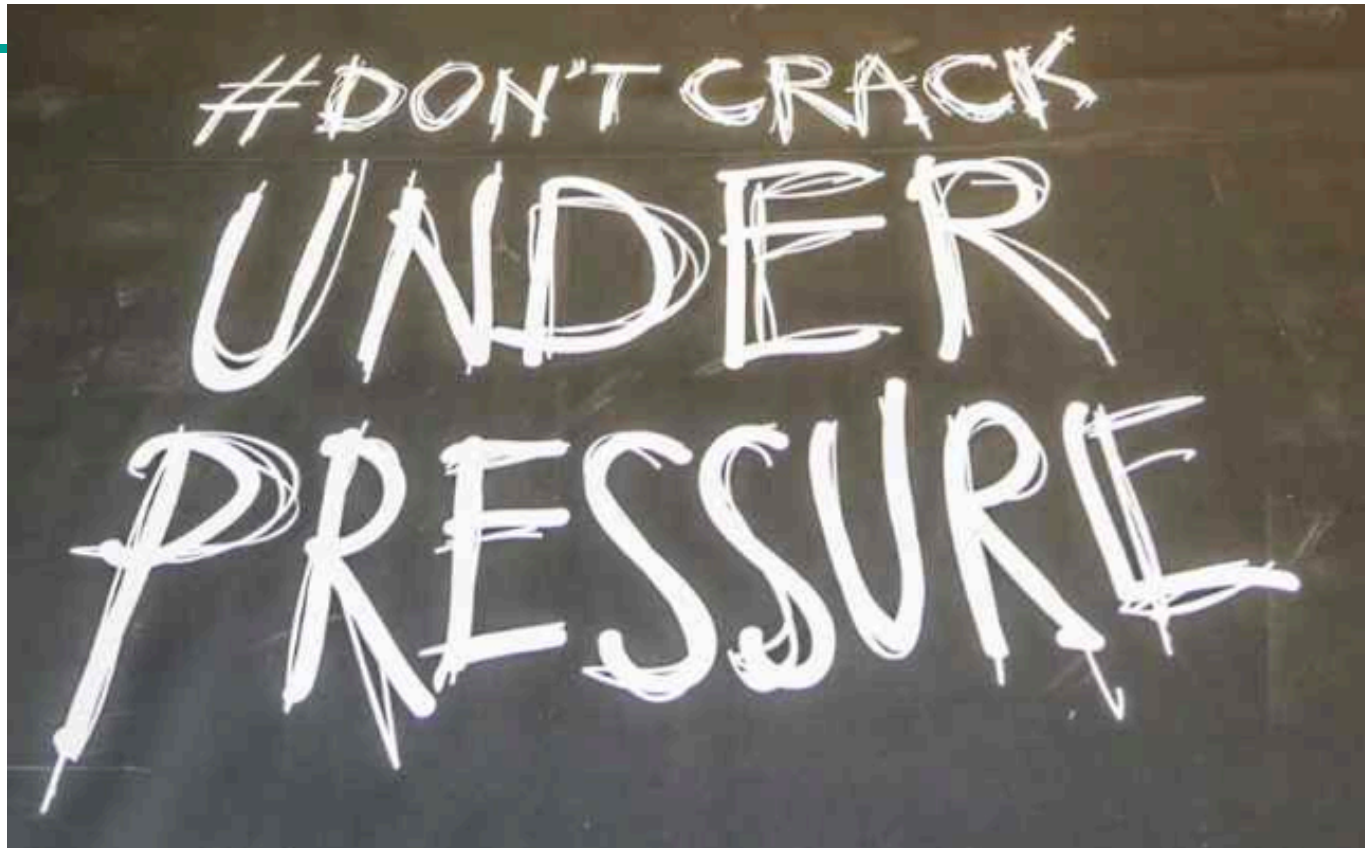
Al containing alloys such as Kanthal APMT or alloy 693 do not show pits in the high pressure test (now) for more than 4000 h.

Aluminide diffusion coatings offer **protection** of highly affected alloy 600 substrate from MD. **No coke formation.**



	$\Delta G_{620^\circ\text{C}}^{1 \text{ bar}}$ [kJ/mol]	$\Delta G_{620^\circ\text{C}}^{18 \text{ bar}}$ [kJ/mol]
$2\text{Cr}_{(s)} + 3\text{CO}_{2(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3\text{CO}_{(g)}$	-278.8	-278.8
$2\text{Cr}_{(s)} + 3\text{H}_2\text{O}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3\text{H}_{2(g)}$	-292.5	-292.5
$2\text{Cr}_{(s)} + 3\text{CO}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + 3\text{C}_{(s)}$	-328.8	-393.3
$\frac{27}{2}\text{Cr}_{(s)} + 3\text{CO}_{(g)} \rightarrow \text{Cr}_2\text{O}_{3(s)} + \frac{1}{2}\text{Cr}_{23}\text{C}_{6(s)}$	-519.4	-583.8

Long way to go to understand MD or the **impact of total pressure**



Thank you very much for you attention

DryRef2 - Energy-efficient production of synthesis gas by dry reforming at industrial scale; subproject: Metal Dusting

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e-mail: madloch@dechema.de

Funded by: BMWi

Project funding reference number: 03ET1282E

Period: 01.04.2015 – 30.09.2017

Supported by:



on the basis of a decision
by the German Bundestag

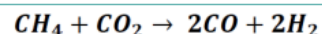
Dry Reforming Process



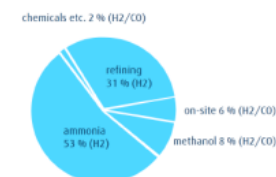
Pilot plant, Linde AG

The demand of hydrogen and synthesis gas for several chemical synthesis processes increase every year. Common techniques for hydrogen production such as steam reforming or partial oxidation (POx process) are based solely on fossil feedstock. The focus of the DryRef2 project is developing the dry reforming technology for the production of CO-rich synthesis gas at industrial scale. A pilot plant has been installed on the Linde AG site in Munich. The process consumes CH₄ and CO₂ (CO₂-recycling/-import) and has an improved efficiency by operation at elevated pressure and low steam content. Such syngas is highly aggressive for reactor components due to its ability to induce metal dusting.

For the process, a new generation of catalysts, which is not based on the common Ni-system, has been developed. The new catalyst system, which is fabricated by BASF SE, performs stable at 20 bar for >500 h at very low steam/carbon (S/C) ratio without deactivating coke formation. Catalyst screening is conducted by hte GmbH, while KIT contributes reaction simulations.



Dry reforming reaction in an ideal case
(real process conditions contain low steam content and CH₄-/CO₂ slip)



Worldwide hydrogen and synthesis gas demand.

Total installed syngas capacity ≈ 70 mill. Nm³/h (2011). [1]

[1] A. Behrens (Linde AG), NGCS 11; Tromsø/ Norway 2016



Process design
Pilot testing



Catalyst
Scale up



Catalyst screening
Testing



Reaction
Simulation



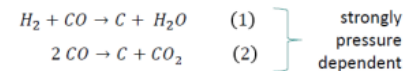
Material Selection
Testing

Subproject: Metal Dusting

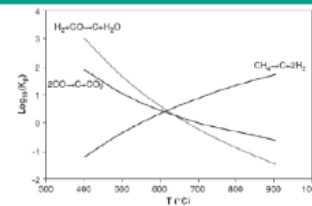
Metal dusting is a severe form of high temperature corrosion, that occurs in carbonaceous environments with carbon activities >1 in the temperature range of 450 - 900 °C. Dissociation of carbon containing gas species, catalytically induced by Fe, Ni, Co and their alloys, result in carbon uptake and subsequent graphite precipitation in the micro structure of the material. The mechanical stresses induced by the precipitates lead to the full disintegration of the metal.

In the downstream section of the dry reforming process, CO-rich syngas under high pressure passes through the whole metal dusting temperature range. This provides a high risk for metal dusting and thus increased requirements on the metal components.

The two following reactions are the main carbon producing processes:



According to Le Chatelier's principle, increasing pressure shifts the equilibrium toward product side (volume decrease).



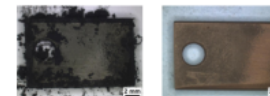
Equilibrium constants for gas phase carbon producing reactions. [2]



Alloy specimens after metal dusting test at 620 °C.

Material selection:

- Austenitic steels
- FeCrAlMo alloys
- Ni-base alloys
- Co-base alloys
- Aluminide coatings

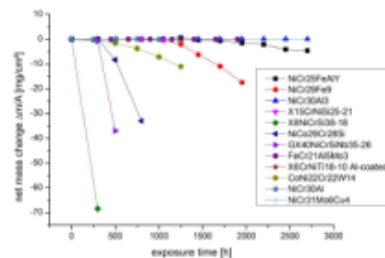


Austenitic steel X6CrNiTi18-10 after 1050/1000 hours exposure in high pressure test (left) and thermo cyclic test (right)

[2] Young, Zhang, Geers, Schütze; *Mat. Corrosion* (2011)



Exposure setup of high pressure tests



Net mass change vs. exposure time of tested alloys

High pressure testing

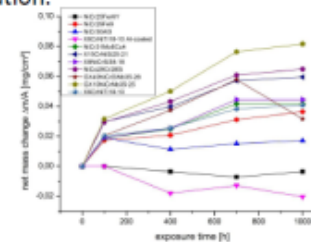
Dry reforming product gas:
CO-rich syngas, low steam content
620°C
18 bar
 $a_c=163$

Test conditions according to dry reforming downstream section.
High alloyed materials fail after few hundred hours exposure time.
Huge influence of pressure on materials' incubation times.
Most stable alloys will be considered for application in dry reforming downstream section.

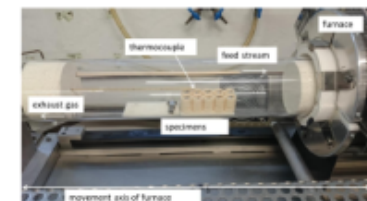
Thermo cyclic testing

Dry reforming product gas:
CO-rich syngas, low steam content
620°C
1 bar
 $a_c=9.4$

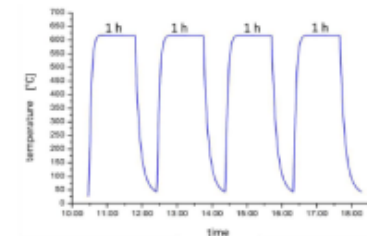
Thermo cyclic conditions promote oxide scale spallation.



Net mass change vs. exposure time of tested alloys



Exposure setup of thermo cyclic tests



Successive thermal cycles [ISO 13573]

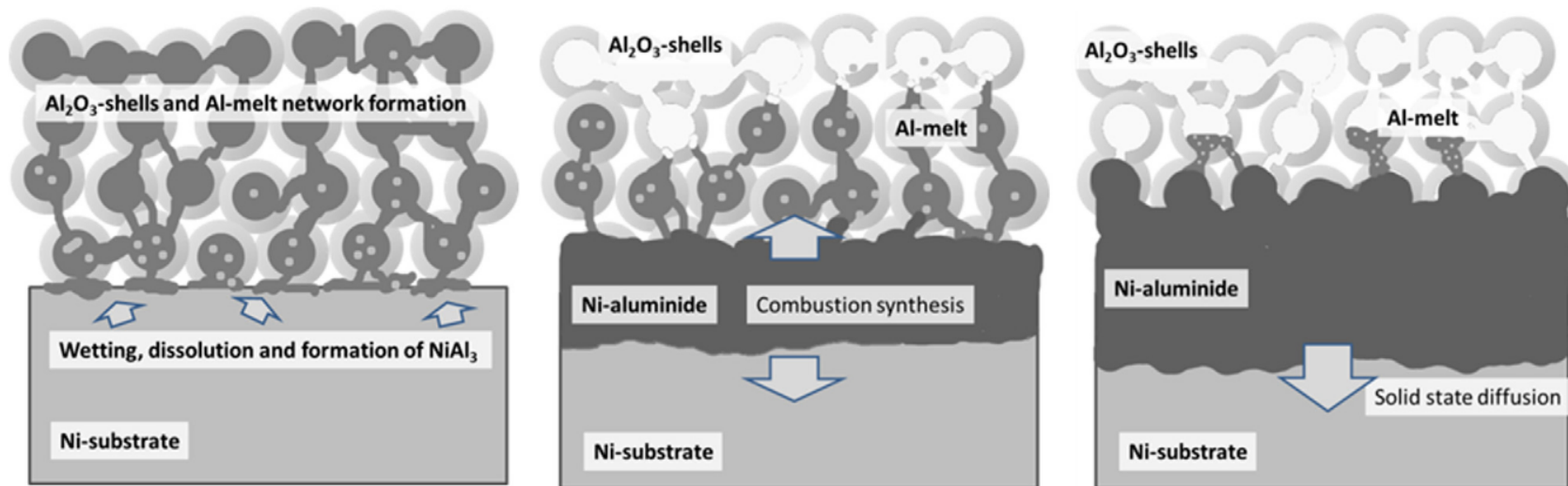
Back up

Slurry aluminization



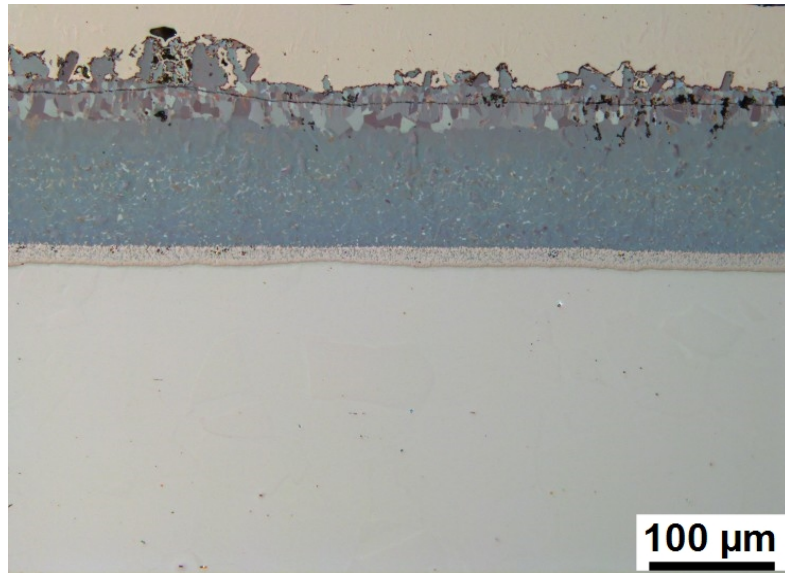
Ge slurry
($T_m=938^\circ\text{C}$)

AlSi slurry
($T_m=577^\circ\text{C}$)



Galetz, M.C.; Montero, X.; Mollard, M.; Günthner, M.; Pedraza, F.; Schütze, M., *Intermetallics*, 2014

Back up NiGeAl-slurry coating



NiGeAl-coating after
exposure in high pressure
setup for 1000 h

