DECHEMA FORSCHUNGSINSTITUT

DryRef II - Energy-Efficient Production of Synthesis Gas by Dry Reforming at Industrial Scale

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Introduction

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- The focus of the DryRef II project is developing the dry reforming technology for the production of CO-rich synthesis gas at industrial scale.
- Common techniques for hydrogen production such as steam reforming or partial oxidation (POx process) are based solely on fossil feedstock.
- The process consumes CH_4 and CO_2 (CO_2-recycling/-import) and has an improved efficiency by operation at elevated pressure and low steam content.

Dry reforming reaction:
(real process conditions contain low steam content)

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

T > 900 °C
p > 20 bar

Pilot plant, Linde AG (Munich)

Subproject: Metal Dusting

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Very aggressive type of high temperature corrosion

- Affected materials: Fe, Ni, Co and their alloys
- Atmospheres: H_2, CO, CO_2, CH_4, H_2O; carbon supersaturated (a_C>1)
- Temperature: 450 – 900 °C
- Leads to carburization and decomposition of the material into a dust consisting of graphite, oxides, carbides and metal particles.
- In the downstream section of the dry reforming process, CO-rich syngas at high pressure passes through the whole metal dusting temperature range.
- Material selection for downstream metal parts necessary.

→ High pressure metal dusting experiments

strongly pressure dependent reactions:
(Le Chatelier's principle)

$$H_2 + CO \rightarrow C + H_2O \quad (1)$$

$$2\,CO \rightarrow C + CO_2 \quad (2)$$

Metal sample attacked by metal dusting

Experiments

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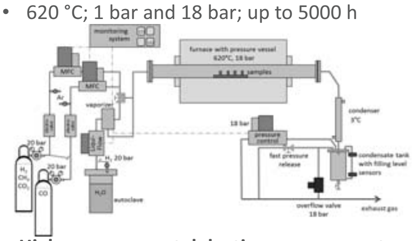
Material selection

- Austenitic steels; Ni-base alloys
- Aluminide coatings

Test conditions

- CO-rich syngas (product gas composition)
- 620 °C; 1 bar and 18 bar; up to 5000 h



High pressure metal dusting exposure set-up
[Madloch, Galetz; Oxid. of Metals, 2017]

Results

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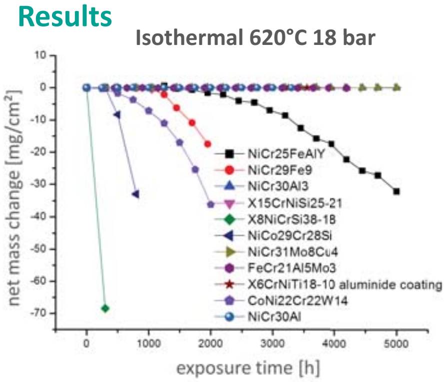
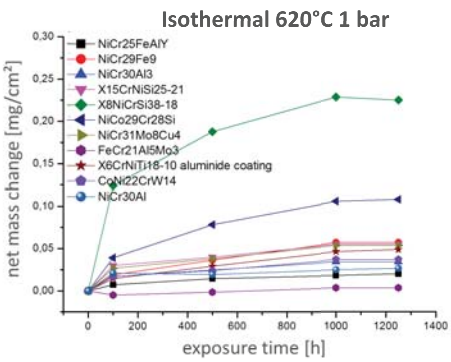
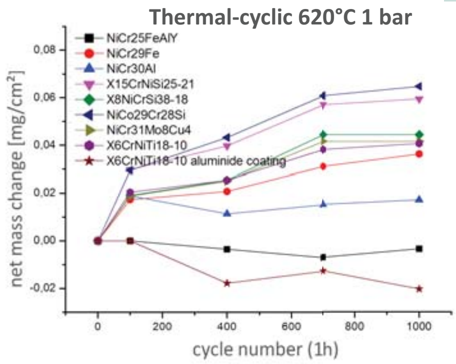


Performance of alloy 800H after exposure at different total system pressure



- Many alloys suffered mass loss by metal dusting at 18 bar after short incubation times, but no attack was found at 1 bar.
- Protective oxide scale spallation was promoted by thermal-cycling, but did not result in metal dusting attack.

→ Huge impact of total system pressure on metal dusting initiation.



- Pressure dependent reactions of protective oxide forming elements (Cr) with CO strongly affect oxide healing.
- Four alloys and an aluminide coating were identified showing superior performance at high pressure.

→ Promising candidates for application in downstream section of the DryRef-process.

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