FROM RESEARCH TO OPERATION: RESULTS FROM THE VALIDATION OF METAL/MEDIUM INTERACTIONS

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COMPASsCO2 Final Workshop

Back to the Future: A Forward-Thinking Approach to Concentrating Solar Technologies - Key Takeaways from the COMPASsCO$_2$ Project

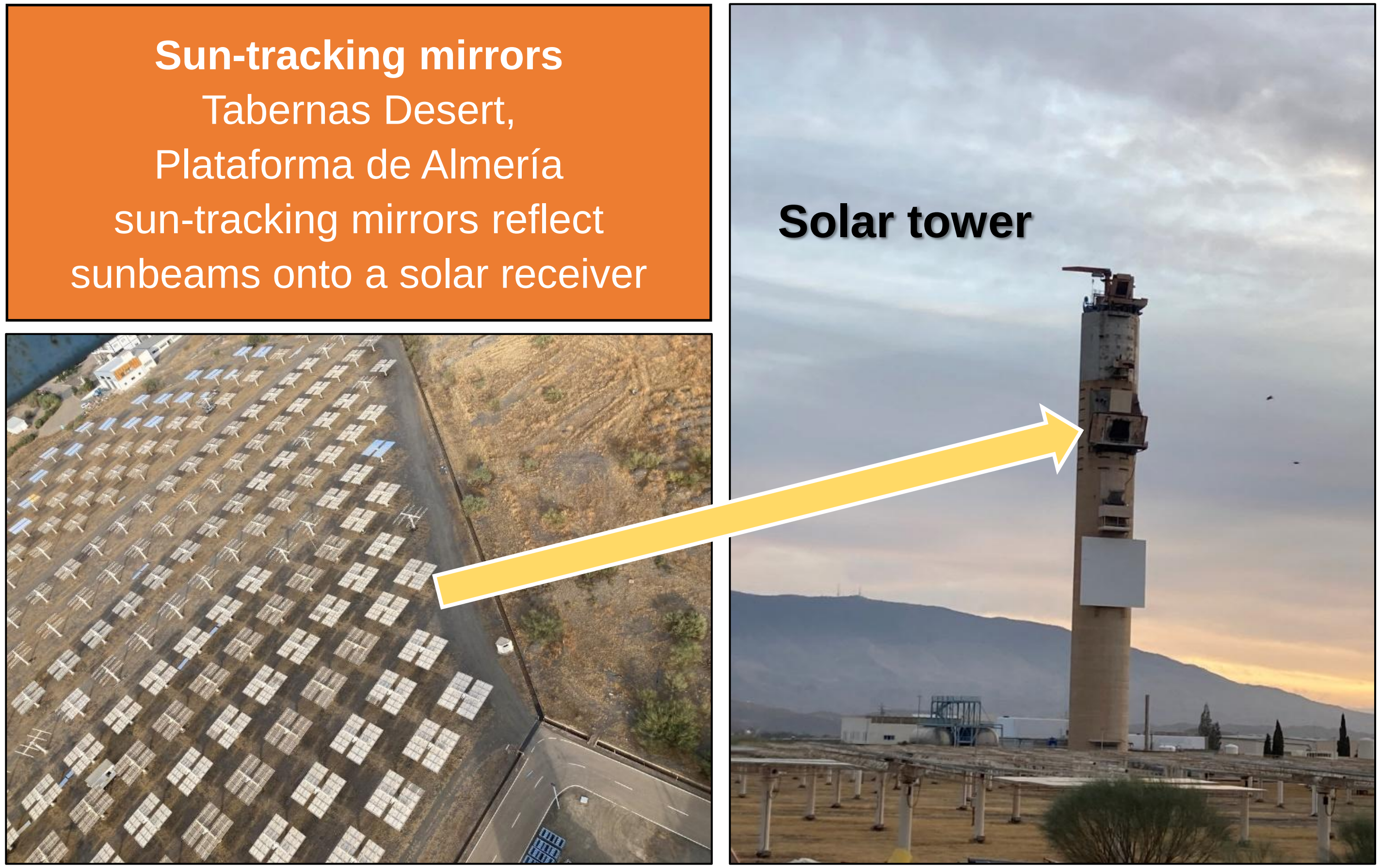
April 24th, 2025

9h30 – 14h30 CEST

Husinec u Řeže, Czech Republic & Online lifesize

CSP operating with sCO_2 and ceramic particles

Sun-tracking mirrors
Tabernas Desert,
Plataforma de Almería
sun-tracking mirrors reflect
sunbeams onto a solar receiver



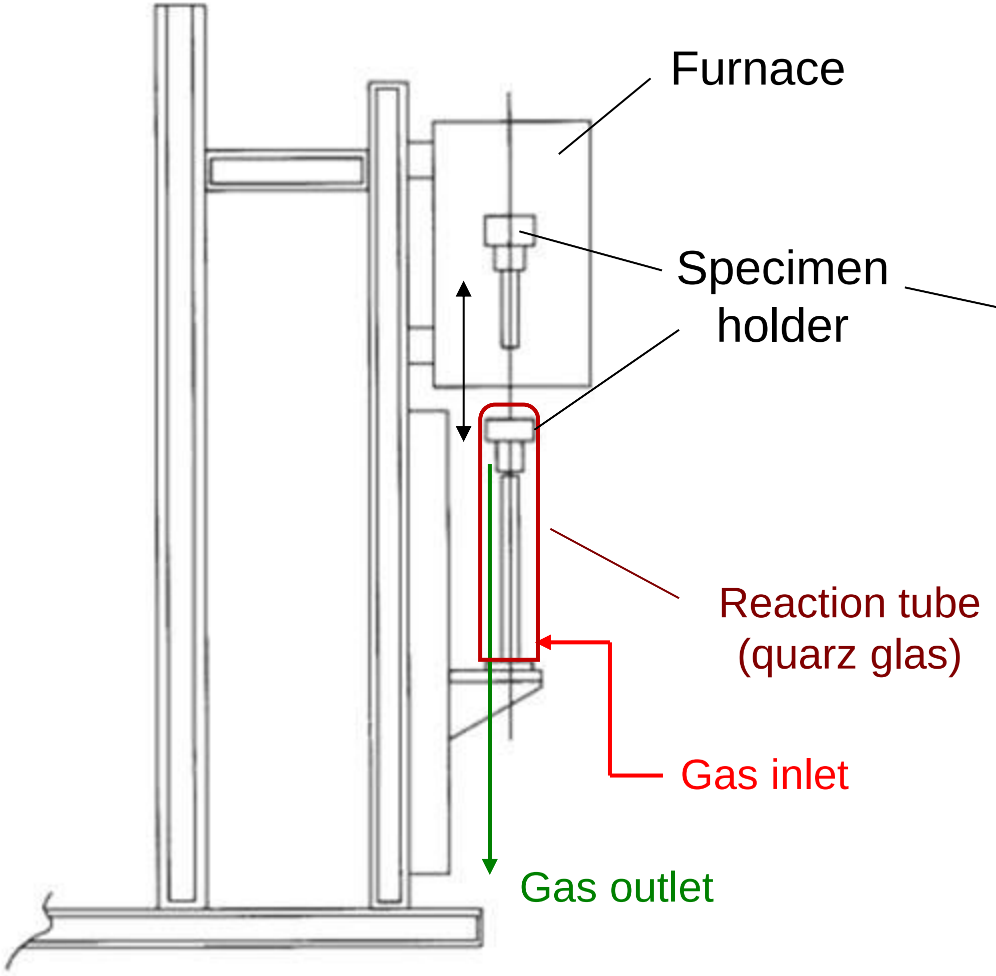
- **Instead of molten nitrates: ceramic (e.g sintered bauxite) particles** as evironment. friendly heat transfer medium; no freezing issues as molten salts, higher temperature
- **Instead of H_2O: supercritical CO_2 (sCO_2)** as working fluid to convert heat to power; potential for higher system efficiencies
- **Issues in heat exchanger (HEX):** high operating temperature and pressure, particles may produce abrasion of the tube materials, therefore, the HEX must be much more robust than the molten salt-to-water HEX

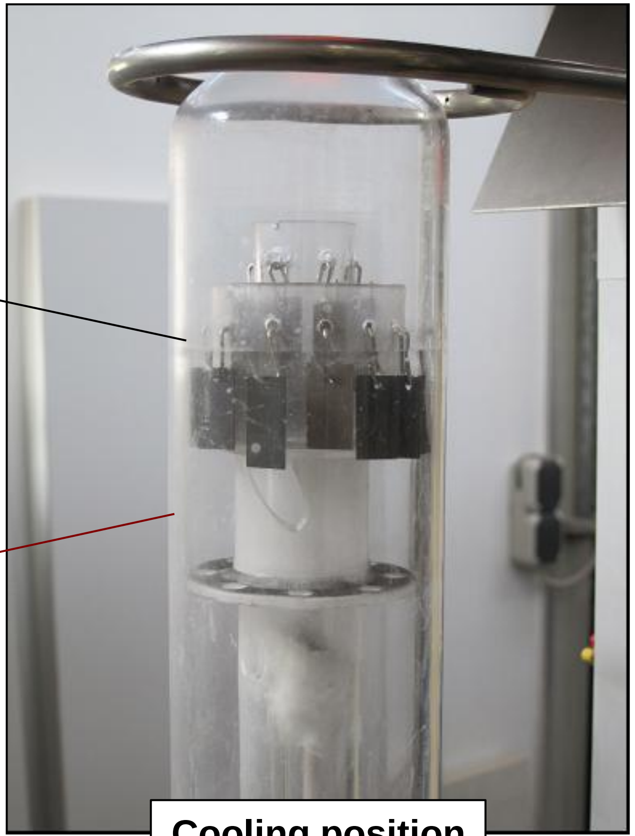
Test set-up for cyclic oxidation testing in CO_2 or air

Cyclic oxidation: Heating / cooling

CO_2 cyclic oxidation rig

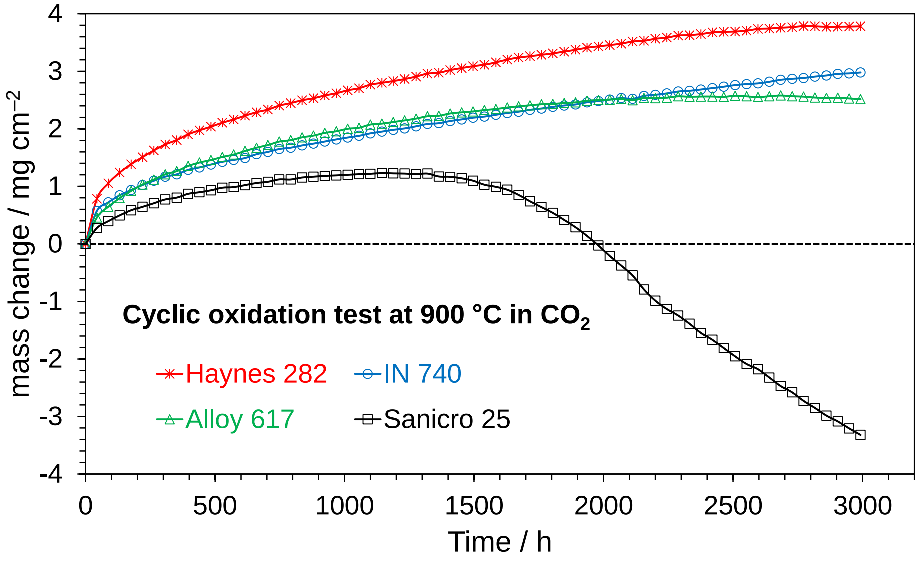
Schematic automated rig

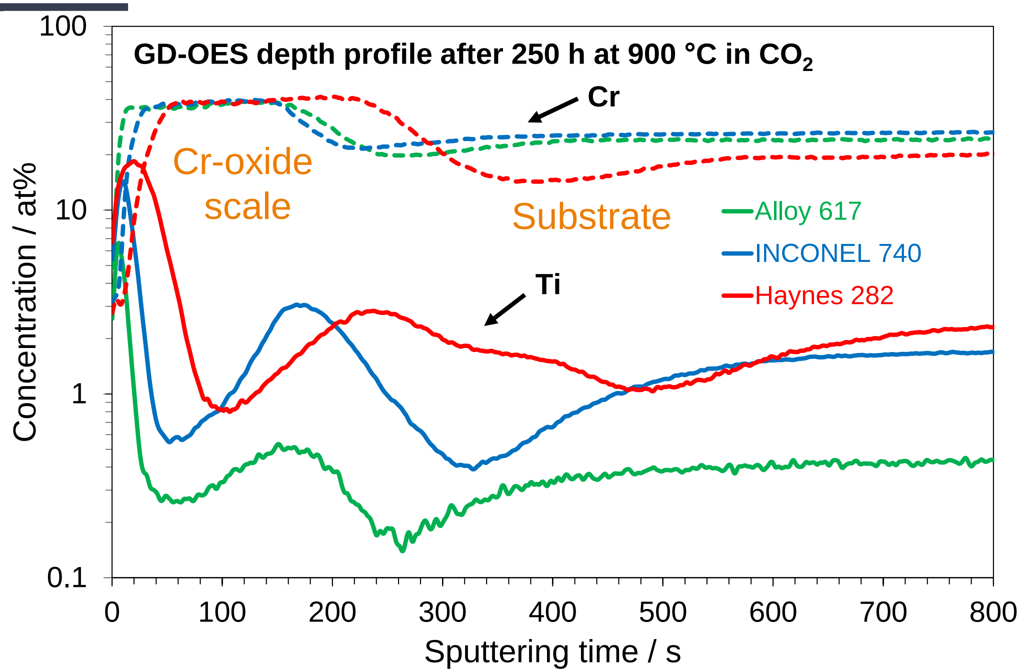


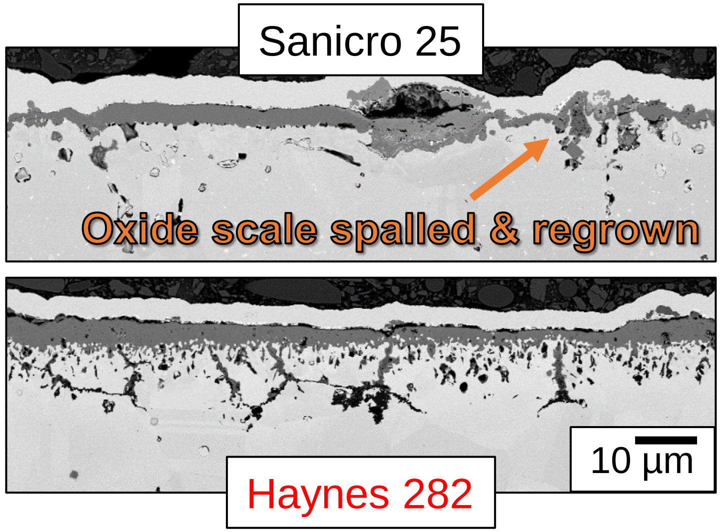


Cooling position

Internal wall investigation





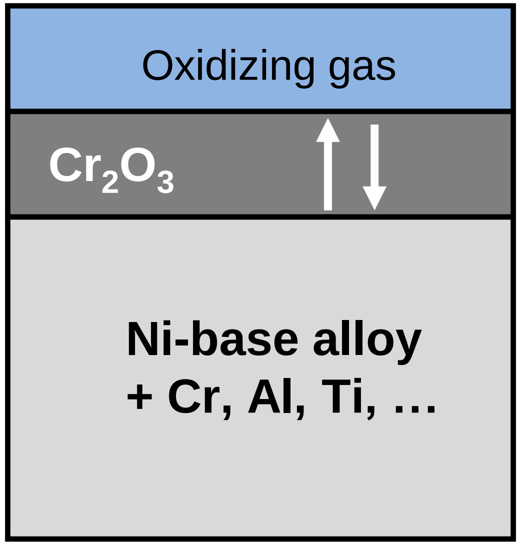


- Candidate materials initially undergo **parabolic oxidation**; the austenitic steel Sanicro 25 shows substantial scale spallation during long-term service at 900 °C
- Ti addition in Ni-base alloys for stabilisation of γ' strenghthening phase

(See results in Deliverable 4.1)

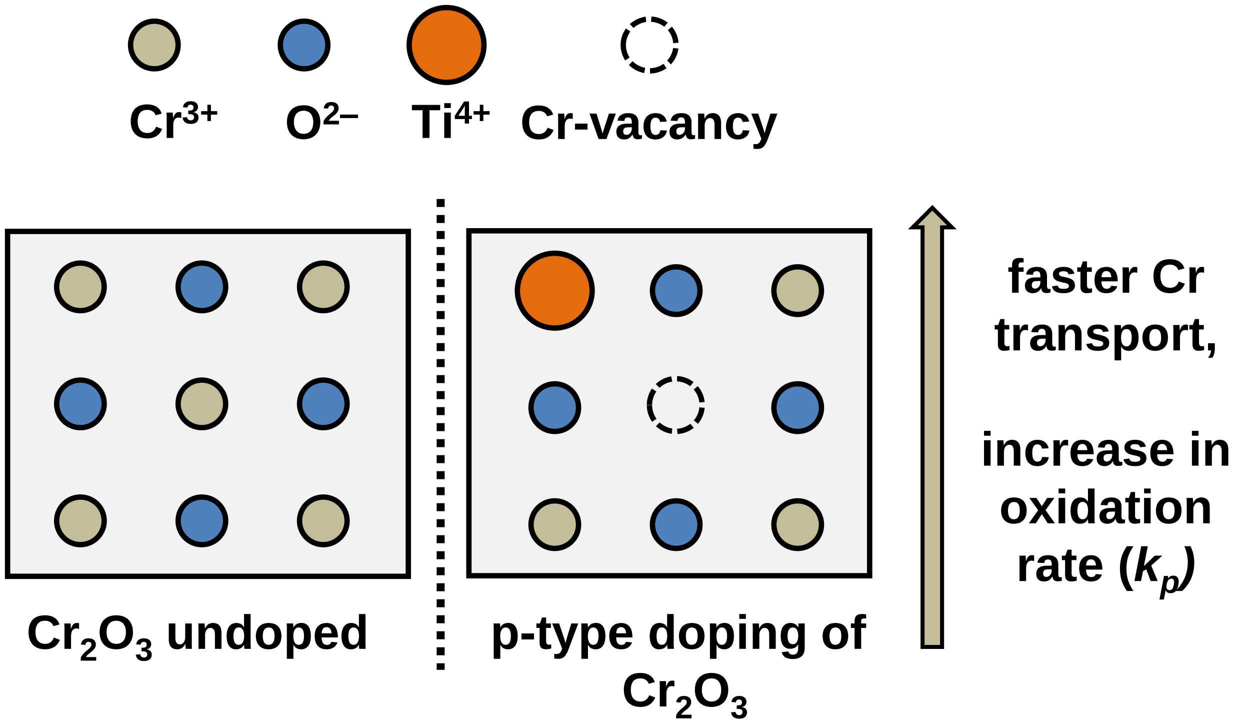
Internal wall investigation

High-temperature results in formation of protective oxide scales preventing access of O_2 to metal surface



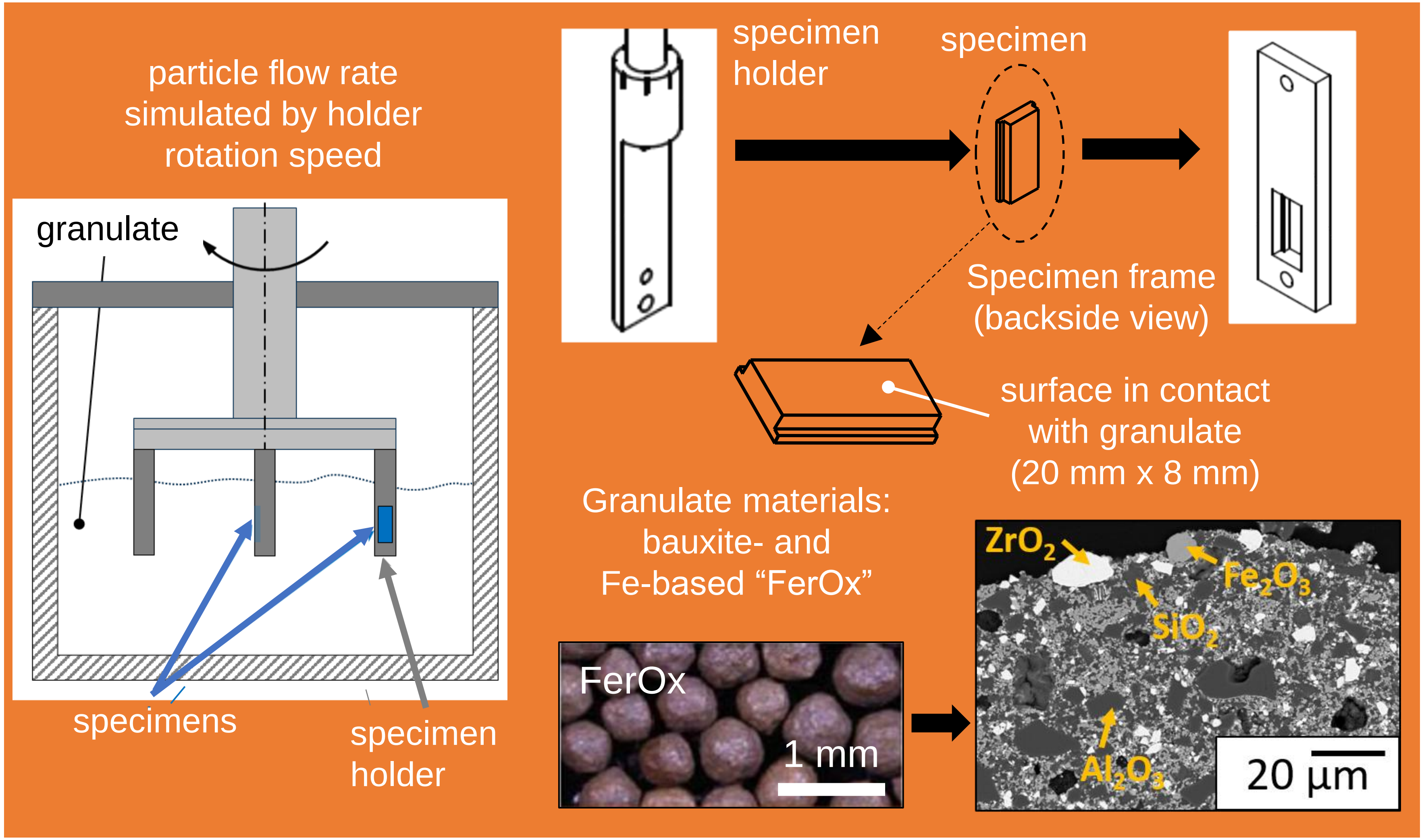
Diffusion of species through the scale **e.g. Cr^{3+}, O^{2-}** rate limiting step

Why do we observe different kinetics?

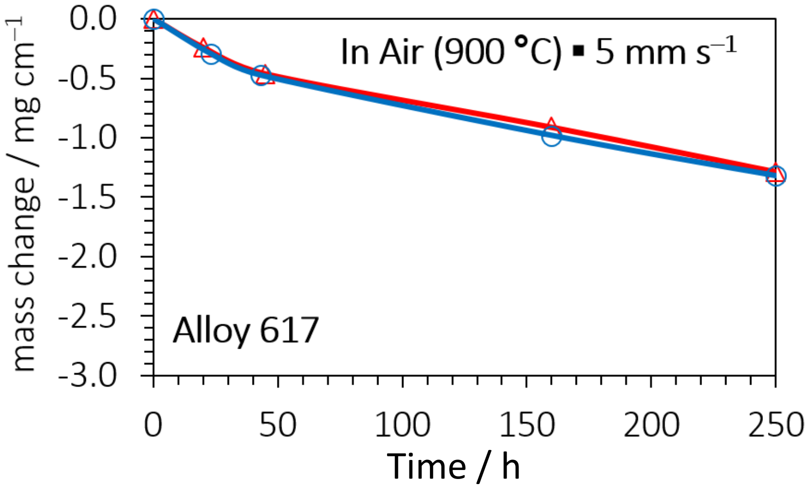


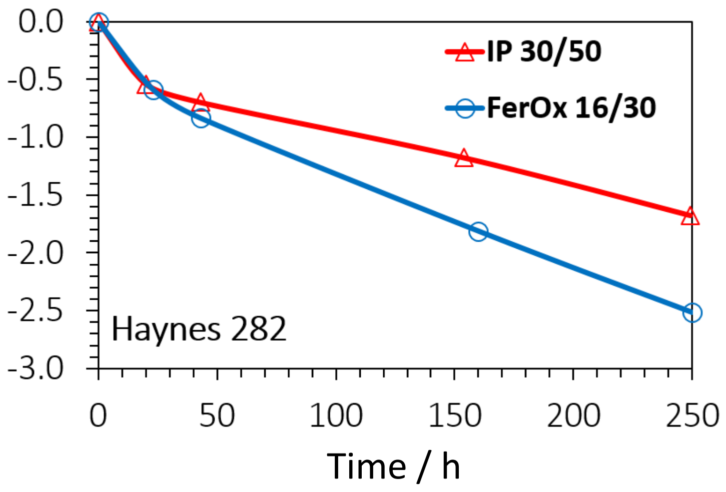
- Ti addition in Ni-base alloys **increase growth rate of chromia scales** due to p-type doping leading to pore formation within the scale

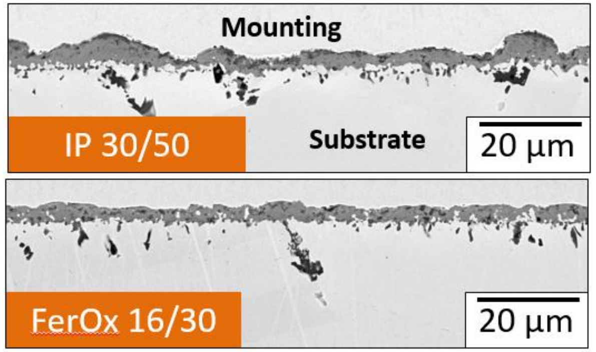
Test set-up for hot erosion-oxidation testing



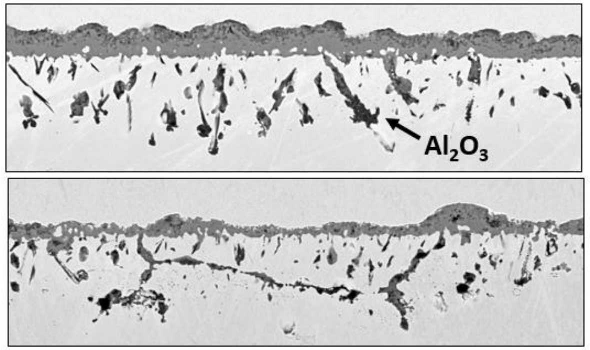
External wall investigation – uncoated SOTAs



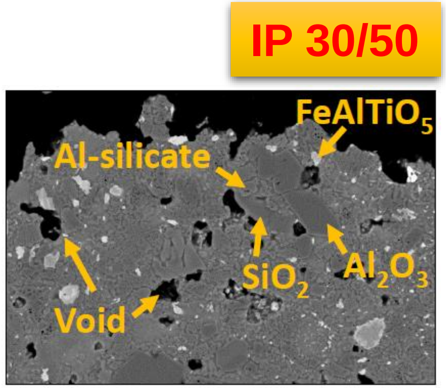


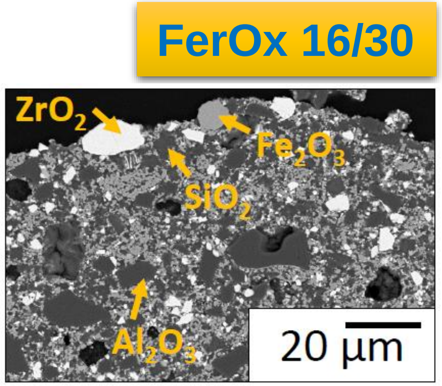


versus



- Erosion testing demonstrates that the oxide scale microstructure (porosity) has a significant influence on the erosion wear resistance of studied alloys
- Microstructure and mechanical properties of the granulate material appear also to influence the erosive wear rate





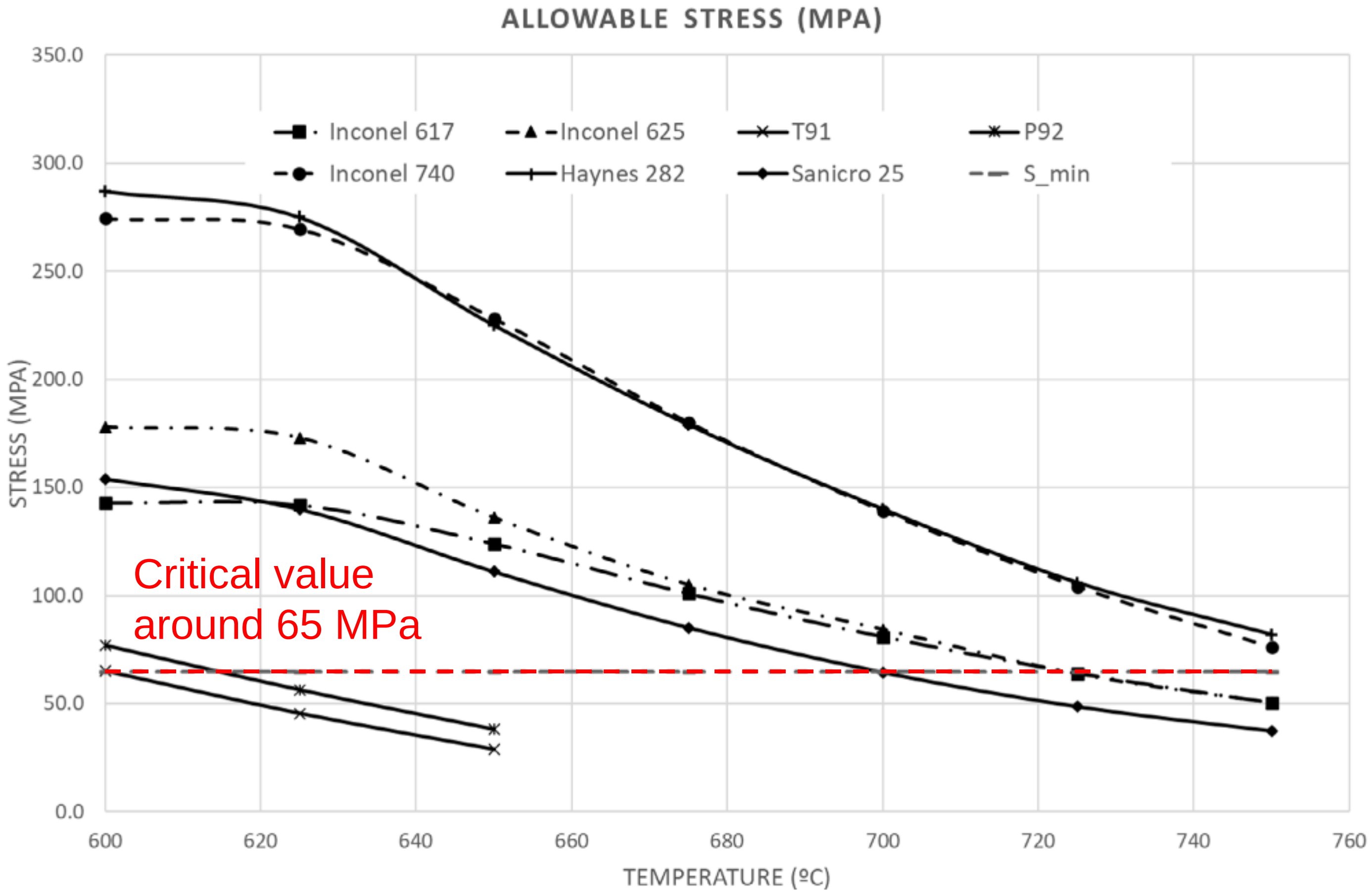
(See results in Deliverable 4.2)

Key outcomes, conclusions & lessons learnt

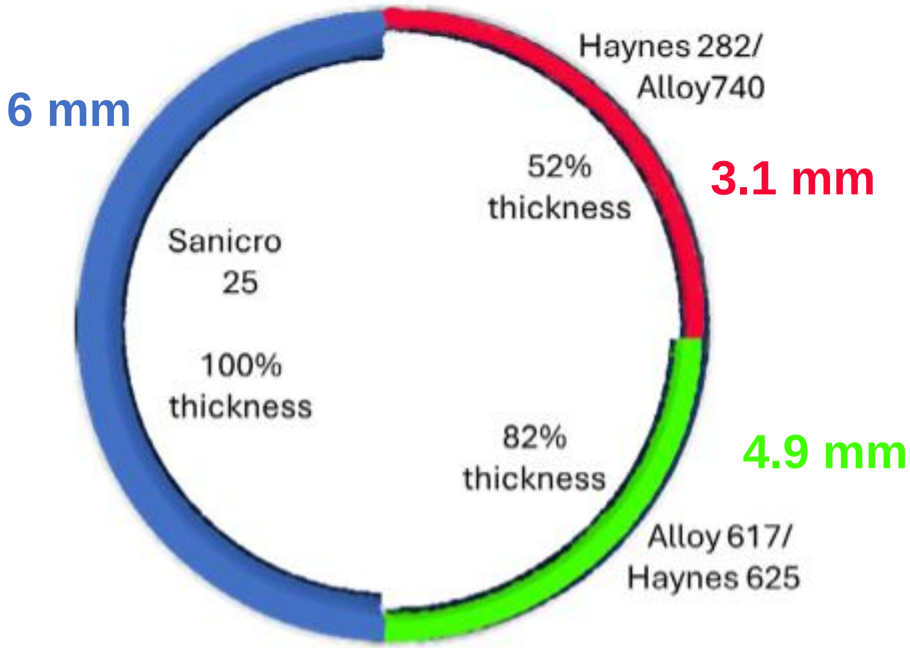
- Growth rates of Cr-oxide scales on Ni-base alloys can be strongly influenced by strengthening alloying additions, such as Ti
- While creep strength may be expected to provide additional benefits (Haynes 282), is does not necessarily imply higher erosion resistance in contact with granulate flow
- Ti doping of Cr_2O_3 promotes high cation vacancy content resulting in formation of faster growing oxide scales with substantial amount of porosity, which are susceptible to erosion
- The denser the oxide scale, the higher the erosion resistance was observed (Alloy 617 vs. Haynes 282)
- The phase composition, porosity and corresponding mechanical properties of ceramic granulate appear to affect the erosion wear of studied alloys
- Coatings such as CrSi can provide protection of base materials susceptible to erosion

Candidate materials for HEX from a mechanical standpoint

Maximum allowable stress following ASME standard B31.1 [1]



Wall thicknesses required for candidate alloys for a 40 mm Ø tube with 25 MPa internal pressure at 700 °C [1]



[1] M. Galetz et al. Material Challenges and Alloy Selection for Particle/s-CO 2
Heat Exchangers in Concentrated Solar Power Systems, Adv. Eng. Mater. 2402060 (2025)

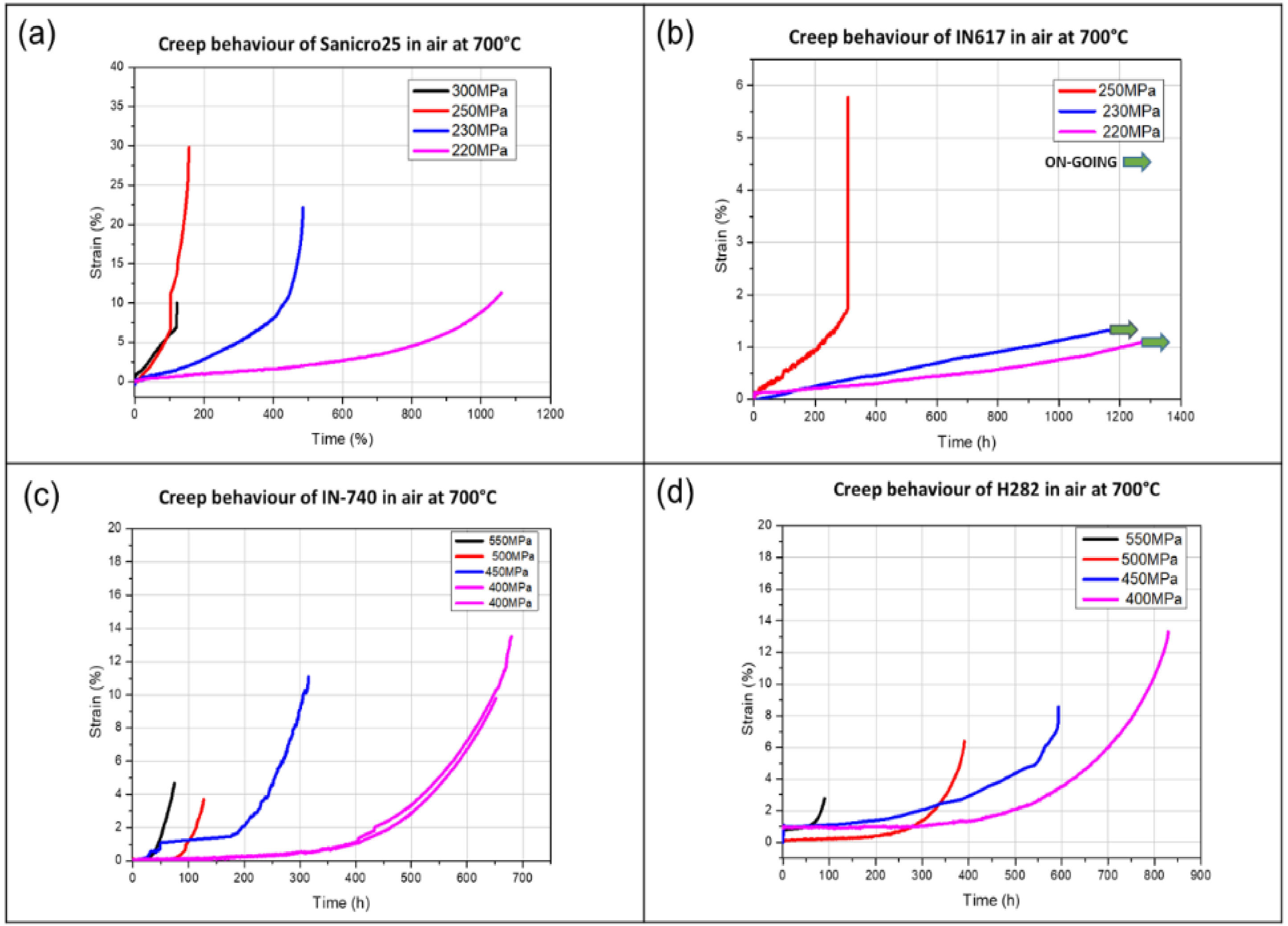
Creep testing campaign

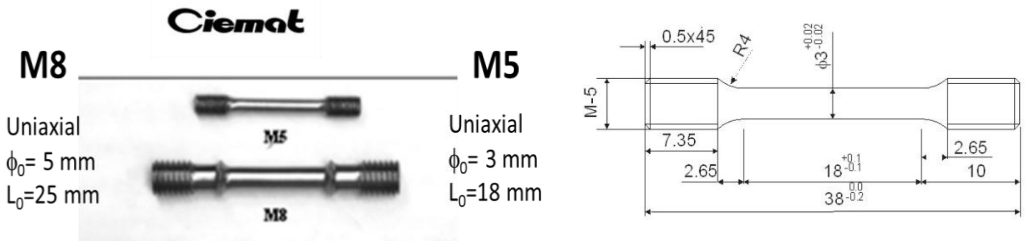
- Creep tests in air and in flowing CO_2 (3.0 purity) of candidate alloys at 700°C under varying loads
- Key parameters: ***Minimum creep rate* < 10^{-6} s^{-1}*** and rupture lifetime
- Cross-sectional investigation → characterization of depletion zones and carburization (?)
- ***Influence of atmosphere*** on the creep behavior of candidate alloys

Alloy	**Nominal Composition [wt.%]**												
	Ni	Cr	Fe	Co	Al	Ti	Nb	W	Cu	Mo	Mn	Si	C
Sanicro 25	25	22.5	Bal.	1.5	-	-	0.5	3.6	3	-	0.5	0.2	≤ 0.1
IN-617B	Bal.	21-23	≤ 1.5	11-13	0.8-1.3	0.25-0.5	≤ 0.6	-	-	8-10	≤ 0.5	≤ 0.3	0.05-0.08
IN-740	Bal.	25	0.7	20	0.9	1.8	2.0	-	-	0.5	0.3	0.5	0.03
Haynes-282	Bal.	20	≤ 1.5	10	1.5	2.1	-	-	-	8.5	≤ 0.3	≤ 0.15	0.06

*Key performance indicator (KPI) limit: minimum creep rate <10^{-6} s^{-1} at 200 MPa and 600-800°C

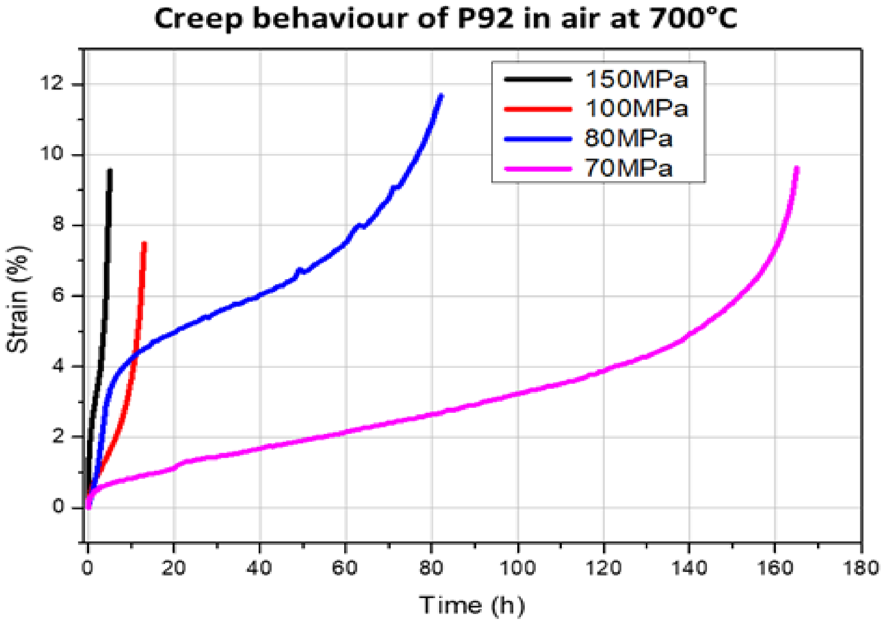
Creep tests in air (CIEMAT)

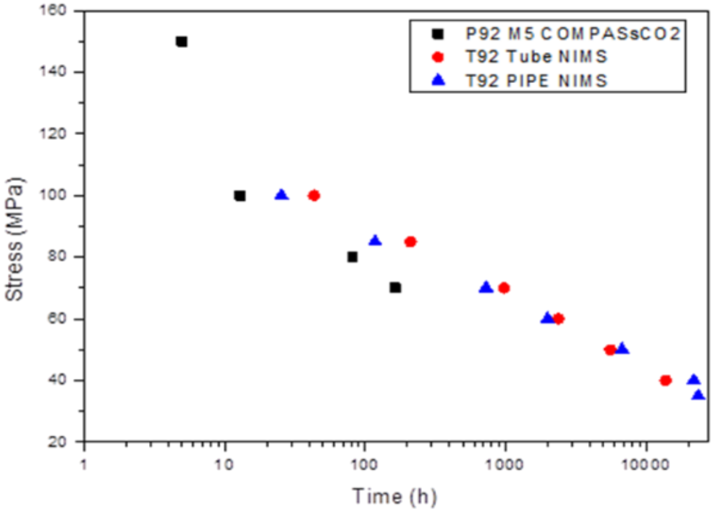


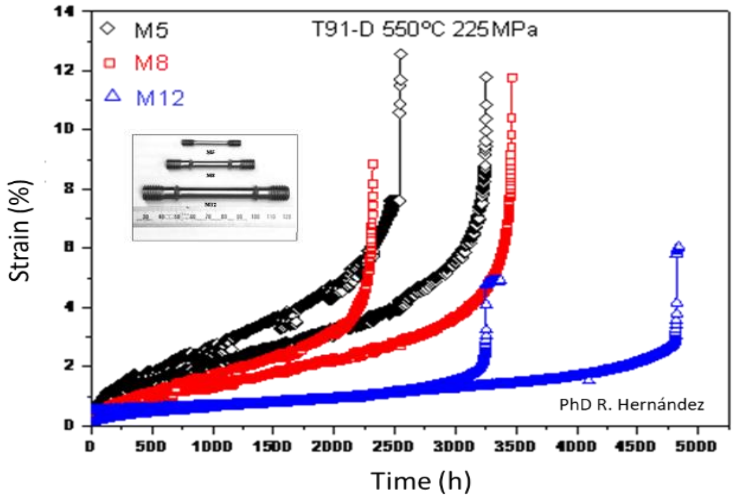


- Sanicro 25 shows high creep elongation as expected for an austenitic steel.
- IN617 (solid-solution strengthened Ni-based alloy) showed a significantly longer creep rupture life than Sanciro25 steel under the same creep test conditions.
- For the γ'-strengthened nickel base alloys, H282 shows higher creep rupture life compared to IN740.

Influence of sample geometry on creep behavior



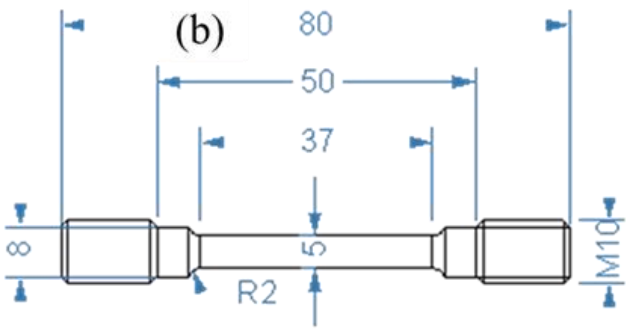




- For comparative purposes, corresponding data for T92 (tube and pipe from NIMS) results are included. Rupture times for P92 (M5 specimens) are shorter than the T92 (Tube and pipe).
- An effect of the specimen size could be detected (previous projects) → shorter rupture durations for thinner samples
- Valid information in the comparison of materials

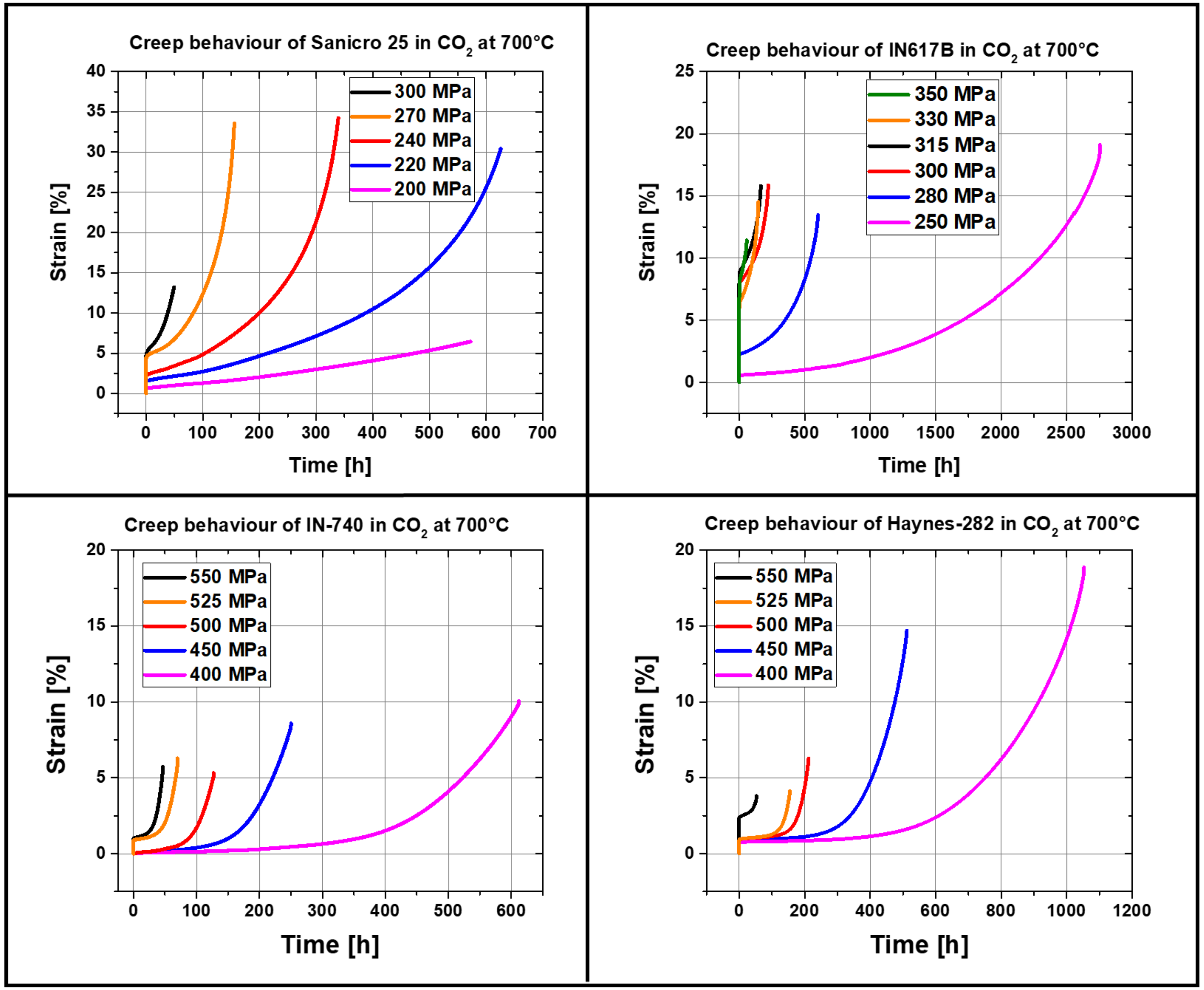
Creep tests in CO_2 (DFI)

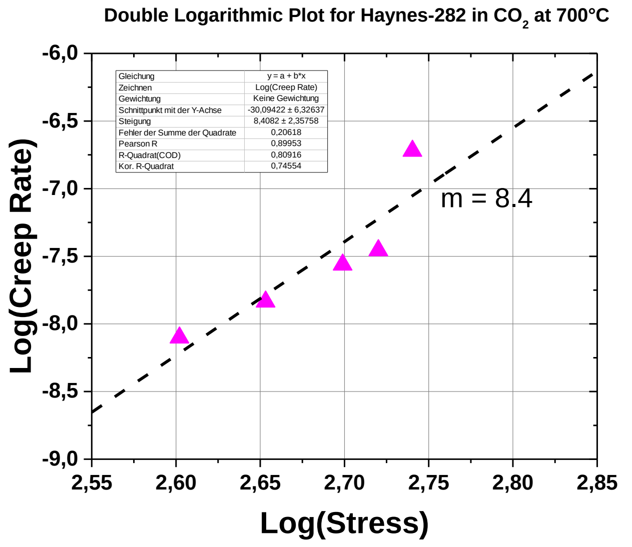
- Creep tests in flowing (4 L/h) CO_2 at 700°C
- CO_2 purity level 3.0 (≥ 99.9%)
- Gas impurities: O_2 + N_2 ≤ 500 vol. ppm, H_2O ≤ 250 ppm, others ≤ 250 ppm
- M8 specimens with a gauge length of 37 mm
- Test campaign with a total of 21 creep tests



Alloy	Sanicro 25	IN617B	Haynes 282 and IN740
Stress (MPa)	300, 270, 240, 220, 200	350, 330, 315, 300, 280, 250	550, 525, 500, 450, 400

Creep tests in CO_2



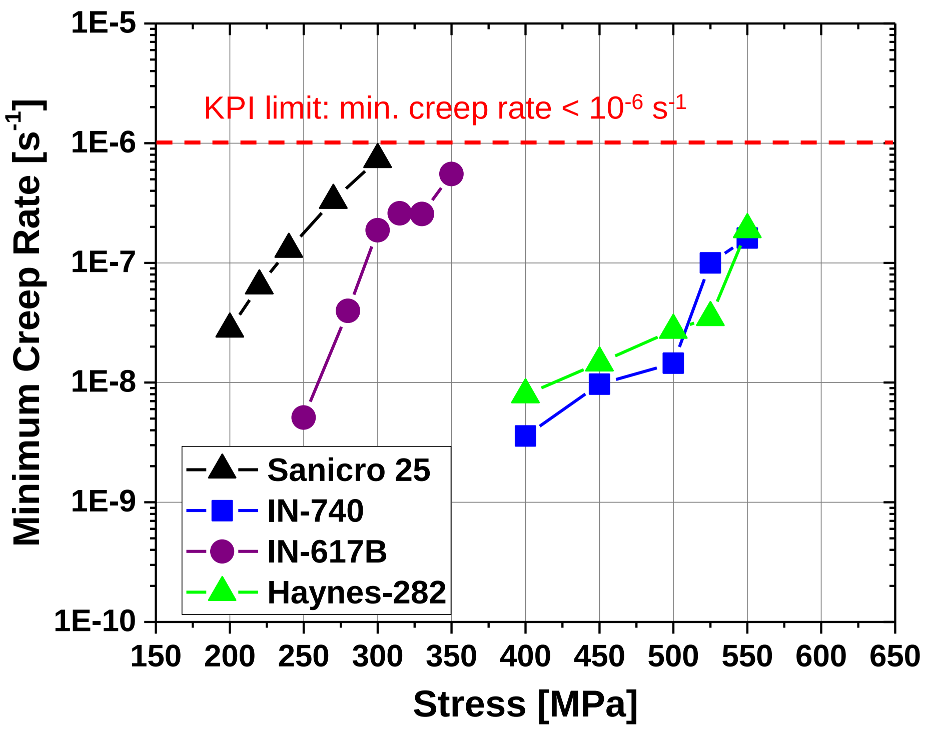


$$\dot{\varepsilon} = A \cdot \sigma^{n}$$

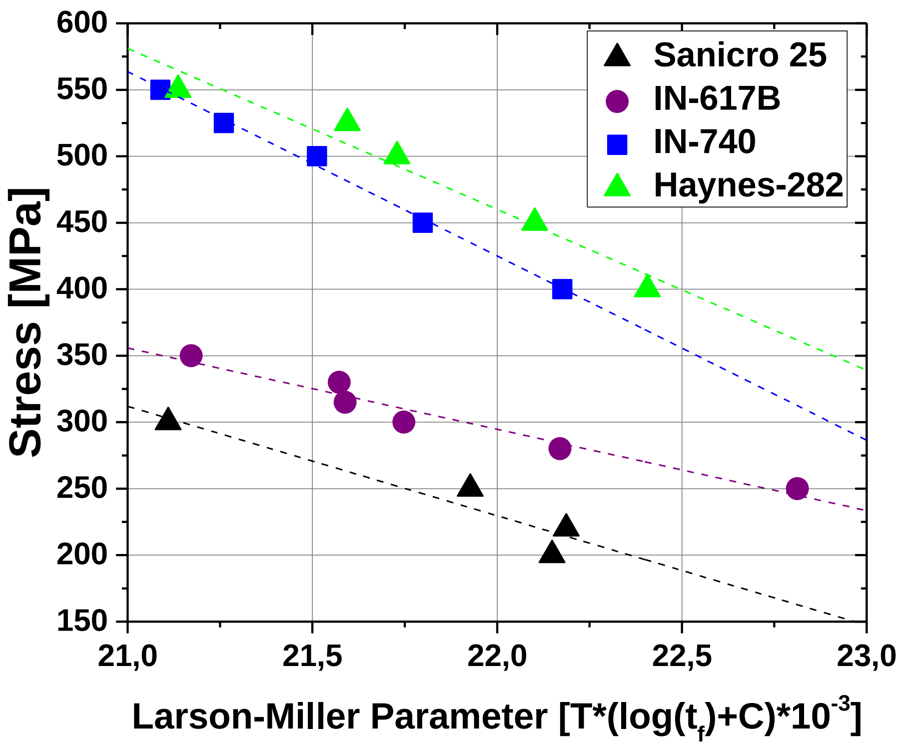
Alloy	Norton Stress exponent
Sanicro 25	8.0
IN-617B	13.8
IN740	11.8
Haynes-282	8.4

Minimum creep rate and rupture lifetime

Minimum creep rate as f(σ)



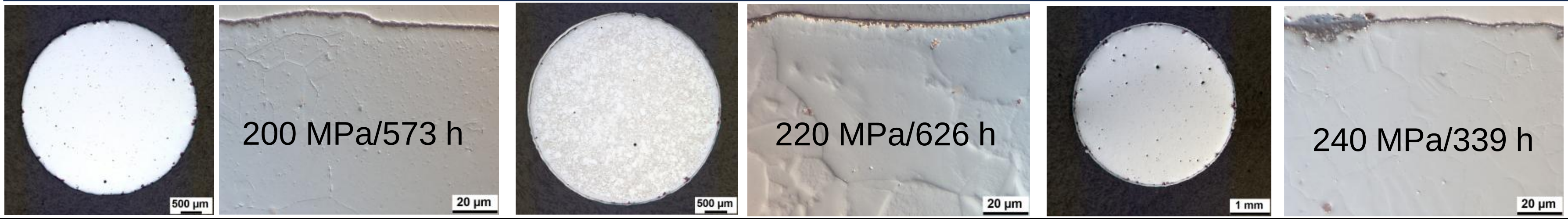
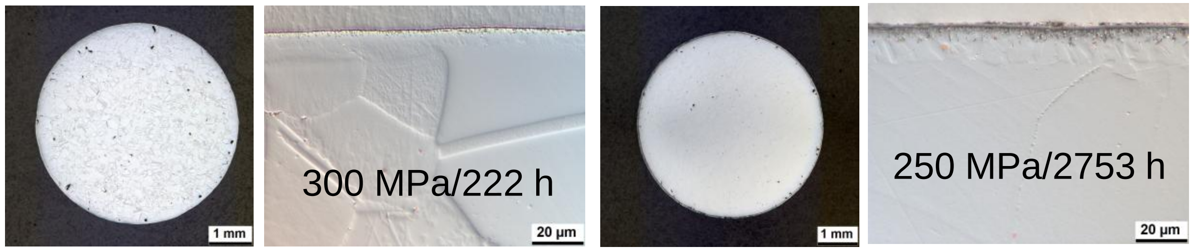
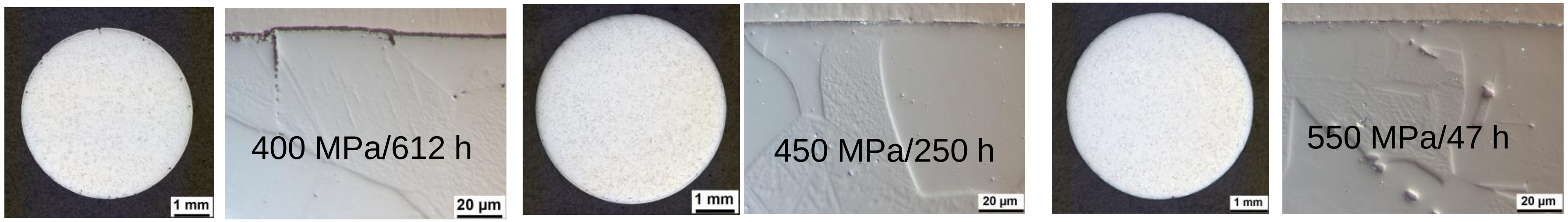
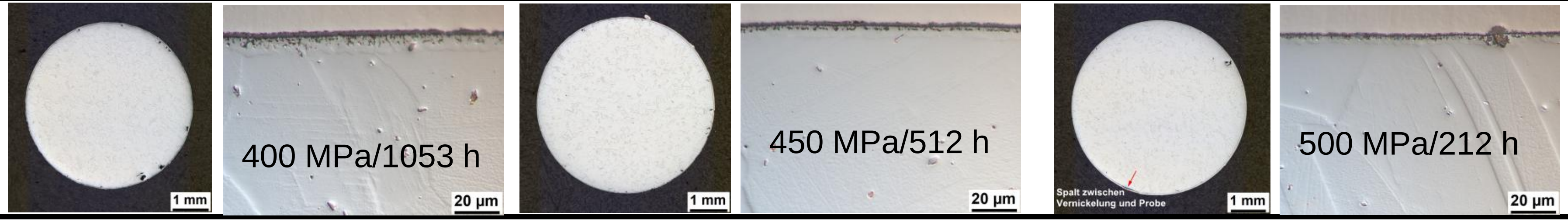
Creep rupture lifetime as f(LMP)



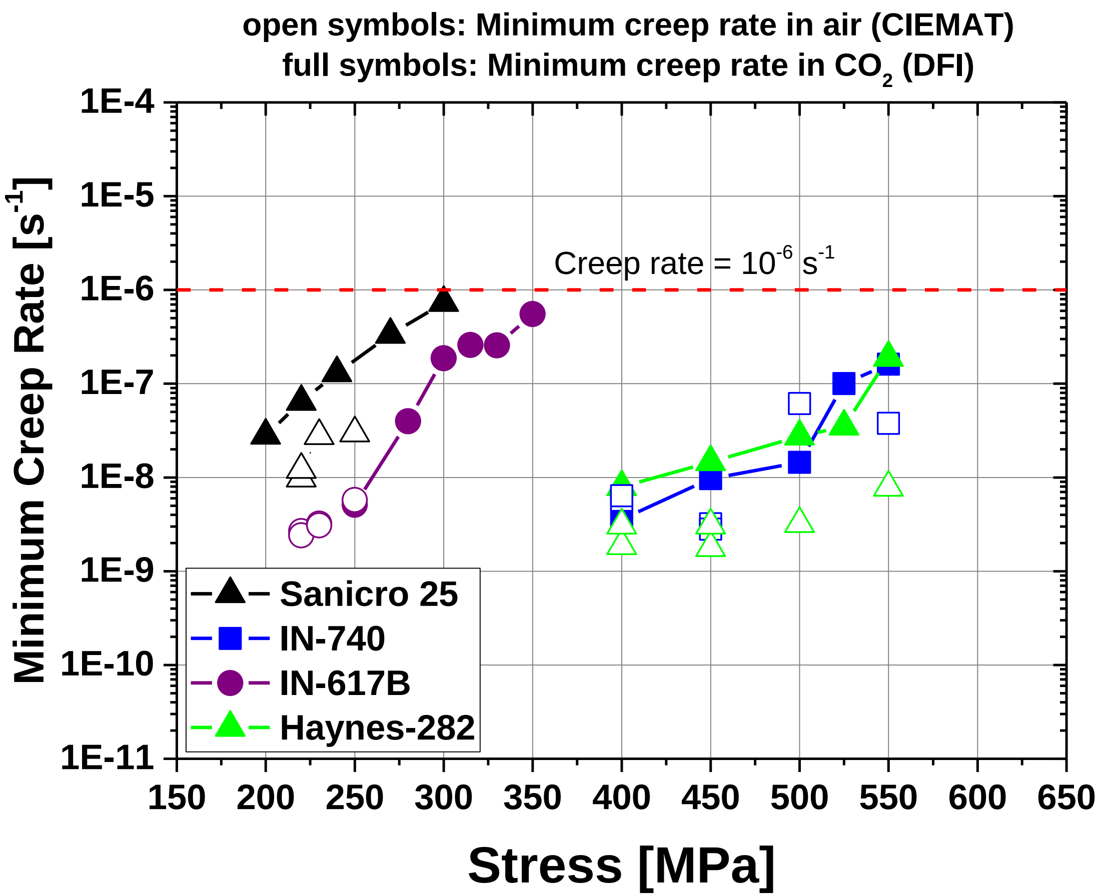
Creep strength ranking in CO_2:
Sanicro 25 < IN-617B << IN-740 ≤ Haynes-282

Cross-sectional analysis of crept samples in CO_2

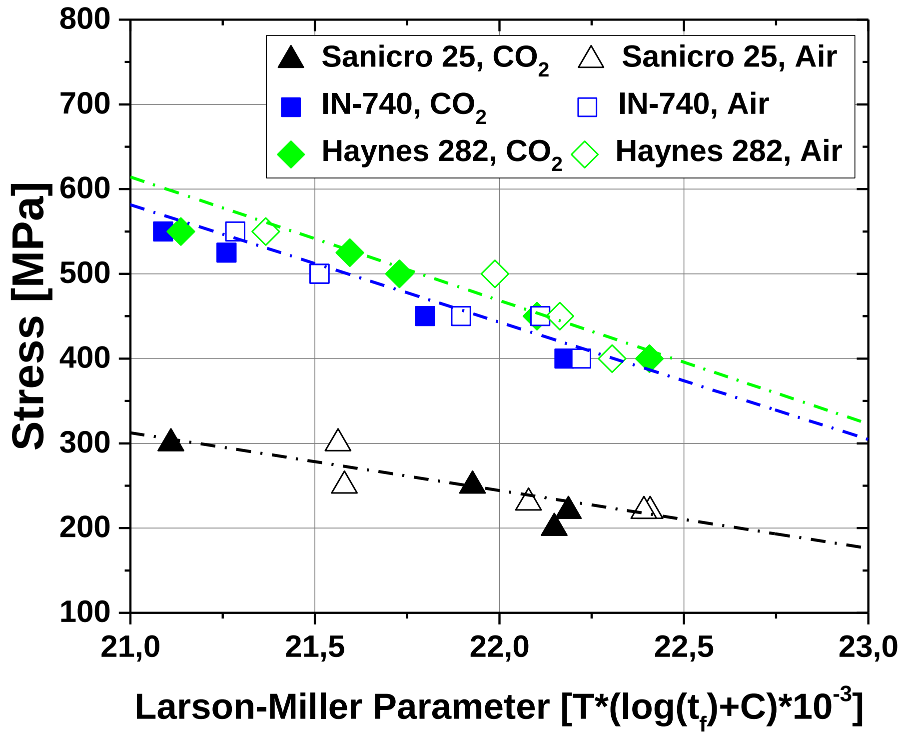
Increasing Load usually equals to decreasing rupture lifetime

Material	Cross-sections	Result
Sanicro 25		Very thin (5-15 µm) depletion zones identified
IN-617B		Very thin (5-15 µm) depletion zones identified
IN-740		Very thin (3-6 µm) depletion zones identified
H-282		Very thin 5-9 µm) depletion zones identified

Influence of atmosphere

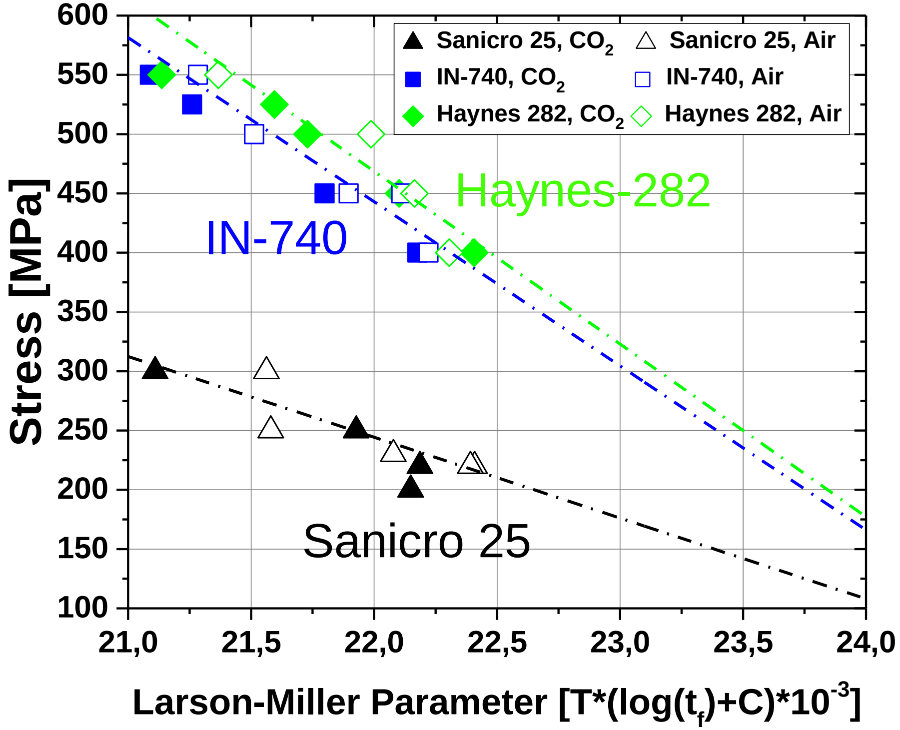


- Good agreement for IN-617B
- Scattering for Ni-based alloys
- Higher creep rate in CO_2 for Sanicro 25

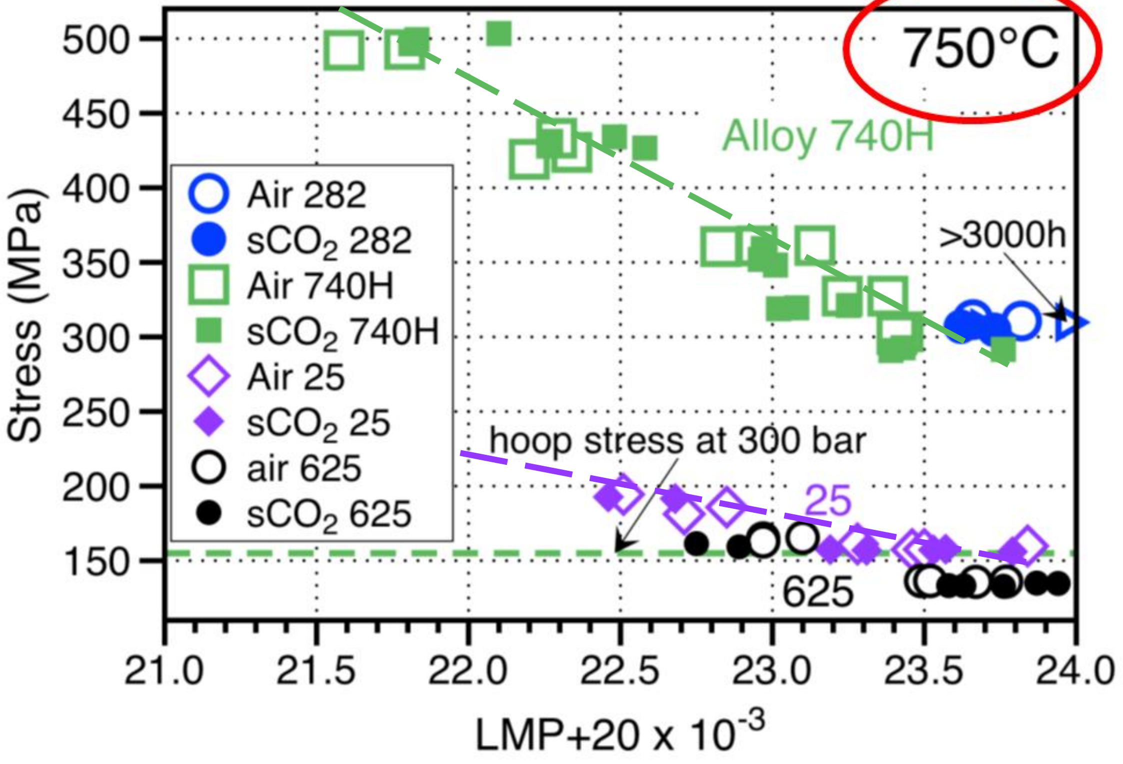


- Rupture lifetime in CO_2 and in air show a good agreement for all investigated alloys

Comparison with literature data



Pint & Pillai (2019) ORNL/SPR-2019/1134, conducted at Brayton Energy, LLC (BE)



- Results in flowing CO_2 and in air are in line with the results from ORNL publication
- Less influence of atmosphere (air, CO_2 or sCO_2) at the testing temperatures on the creep behavior

Key outcomes, conclusions & lessons learnt

- All tested alloys showed a creep strength in accordance with the KPI requirement.
- γ'-strengthened alloys exhibited a higher creep strength.
- Testing atmosphere did not have a strong influence on the creep rupture lifetime at 700°C.
- All alloys formed thin oxide scales and IOZ (for Ni-based alloys).
- Results were in agreement with the data from the literature (including sCO_2 testing).

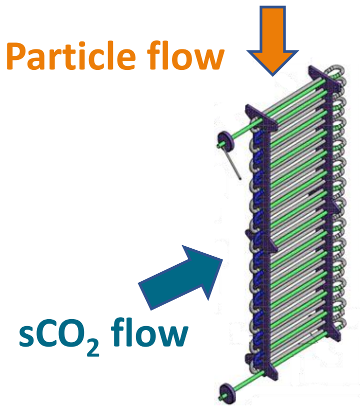
Further details on creep tests can be found in Project **Deliverable 4.2 “Wear and mechanical properties evaluation**”

HEX candidate materials – sCO2 interactions

CVŘ Research Centre Řež

- Selection of candidate state-of-the-art materials (Ni-based alloys, austenitic SS)
- Novel Cr-based materials
- Protective coatings

EVALUATION for their resistance to sCO2-induced corrosion in real operation conditions



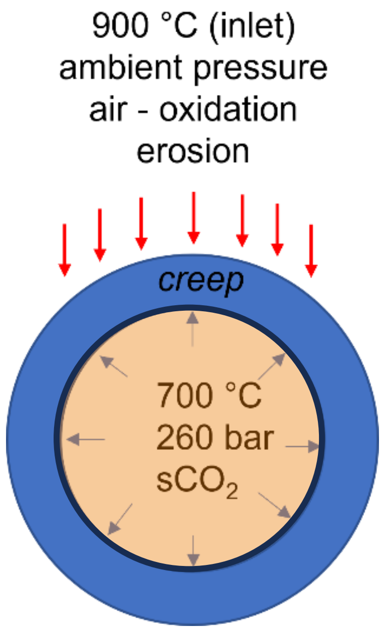
HEX Requirements

- High mechanical strength at high temperatures
- Creep resistance under long-term operation
- **Corrosion and oxidation resistance in sCO2** (high press./temp.)
- Long-term thermal stability
- Abrasion resistance against particle impact
- Cost-effectiveness for commercial application

Key Material Challenges in Supercritical CO_2 Environments

sCO2 environment

- Dry sCO2 is relatively inert
- sCO_2 is more corrosive in the presence of **water** or **impurities** as SOx, NOx, O_2, CH_4, H_2S
- Carburization, carbonic acid formation
- HEX operates at higher p and T
- Material selection and sCO2 purity control are key
- Design to secure mechanical strength and safety, ensuring efficiency and material longevity

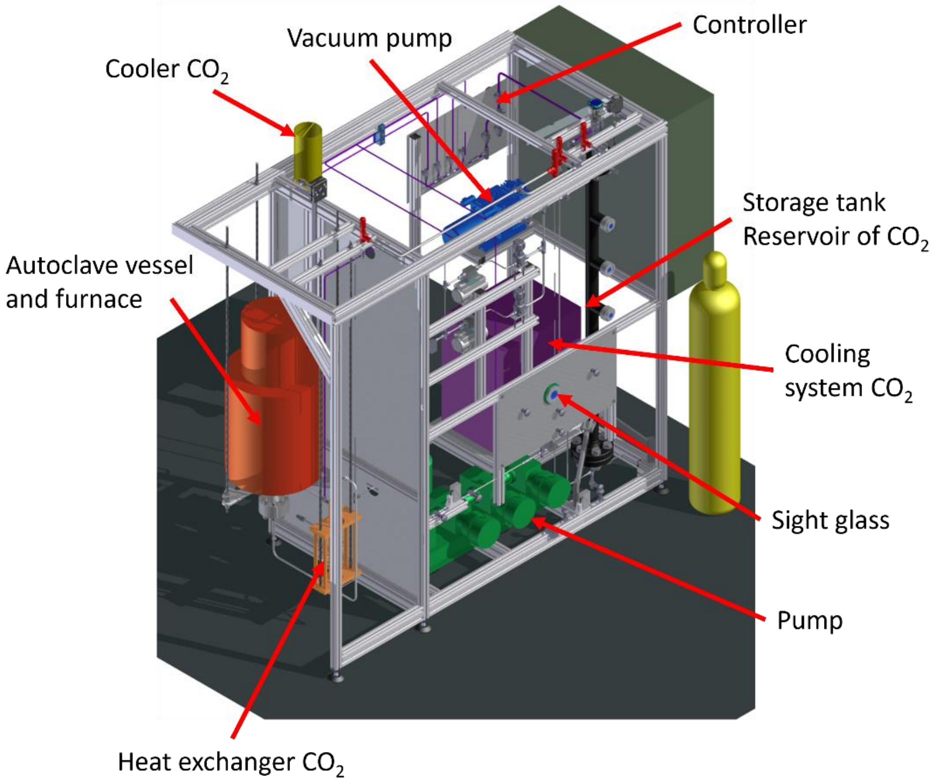


Material requirements

- High Temperature Corrosion/Oxidation Resistance
- Resistance to carburization (low reactivity with carbonic acid)
- Ideal materials form **protective oxide layers** (e.g., Cr_2O_3 or Al_2O_3) that inhibit further corrosion
- To meet COMPASsCO_2 targets, oxidation/carburization rates must stay below 0.5% of tube wall thickness per year, ensuring a 25-year service life

sCO_2 Corrosion Testing in CVR

- Supercritical CO2 Autoclave (IN625)
- Test Conditions: **700 °C**, **120 bar**, IG CO_2 (99.995% purity), 3 L/h flow, in-line moisture monitoring BARTEC (available from 3rd campaign)
- Materials Tested (9):
  - SOTA: Sanicro 25, IN617B, IN740, Haynes 282
  - Novel: Pure Cr, Cr5Ni5Al, Cr5Ni5Al10Fe
  - Coatings: Cr-Si on Sanicro 25 and IN617B
- Custom sample holder (IN625 + TiAlSiN) for 100 specimens
- Two test campaigns (1000, 2000 h), with interim analysis
- Characterization: Gravimetry, LOM, SEM-EDX, XRD



sCO_2 Autoclave (ScCAc) – Development & Testing Highlights

2022 | 2023 | 2024 | 2025

Design & Manufacturing
- Autoclave design finalized
- Manufacturing and completion

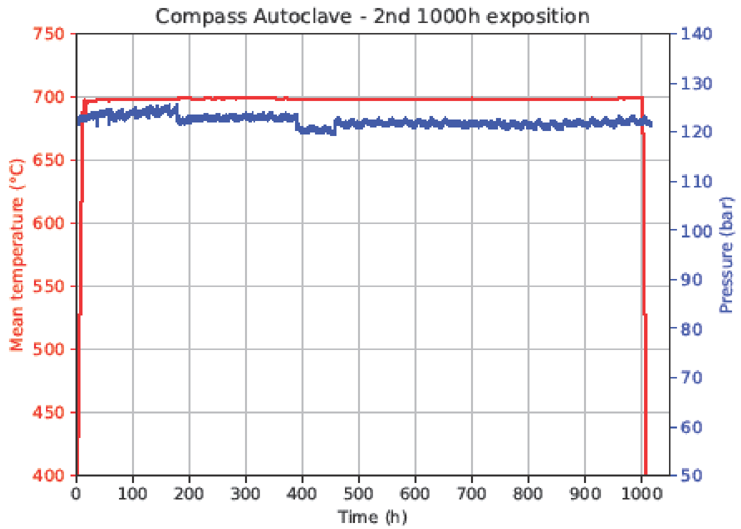
Commissioning & System Setup
- System commissioned
- Initial test at 100°C/ 25 MPa, duration 500 hours

System Challenges & Repairs
- Pump fault, diagnostics & repair
- Leak repairs (storage tank resealing)

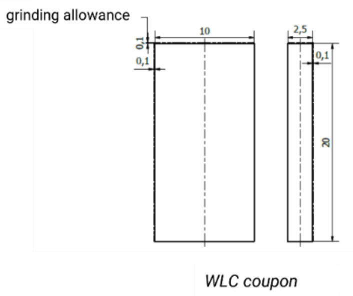
Advancements & Upgrades
- Test at 300°C / 25 MPa, duration 500 hours
- **High-temperature sealing**
- New autoclave head design with **thermocouple feedthroughs**
- **Optimization** for phase transitions (liquid ⇄ supercritical)

Corrosion Testing in sCO_2
- Pre-test system prep (700°C / 12 MPa)
- **Nov 2024–Jan 2025** – 1000 h corrosion test
- **Jan–Feb 2025** – 2000 h corrosion test
- **Mar–Apr 2025** – Final 3000 h exposure completed

Design optimization → safe and reliable long-term operation

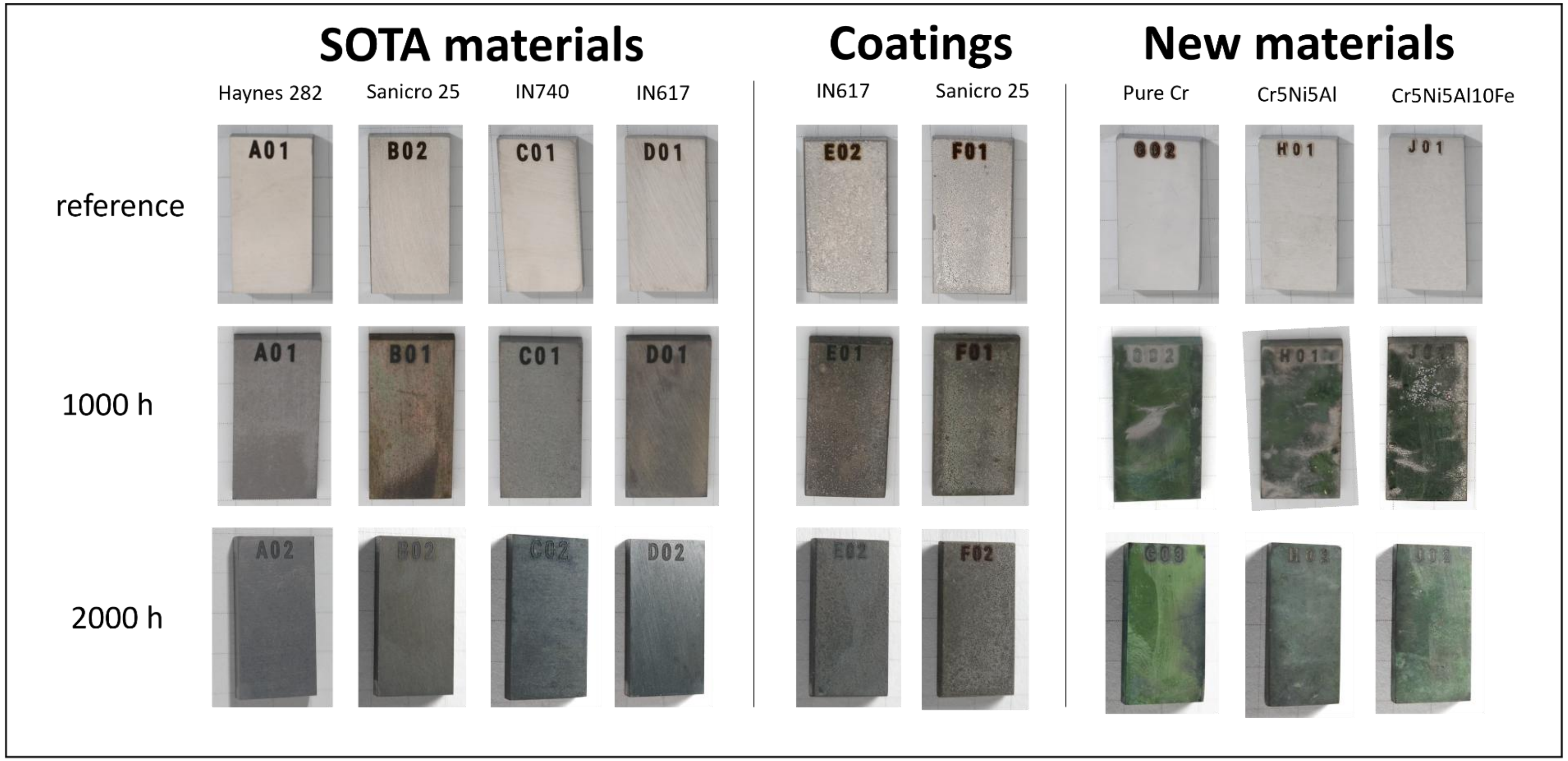


sCO_2 exposure – evaluation after 2000 hours



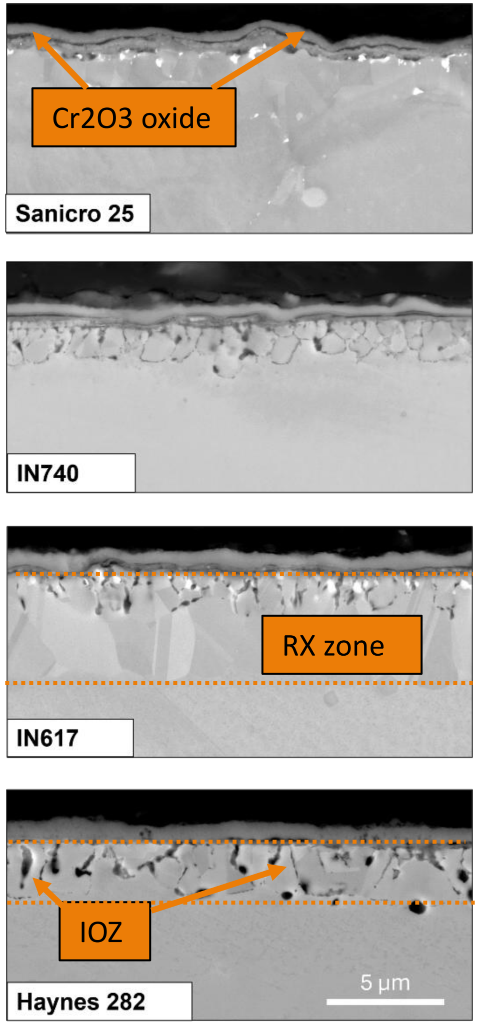
sCO2 - Industrial gas 99.995% purity
T = 700 °C
p = 120 bar

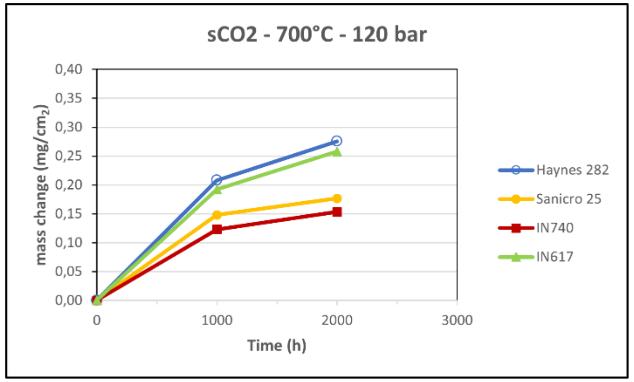
- all samples showed surface oxidation after exposure
- SOTA materials – colour change indicating oxide increase in thickness
- new materials – non-uniform oxide layers, thickness increase after 2000h

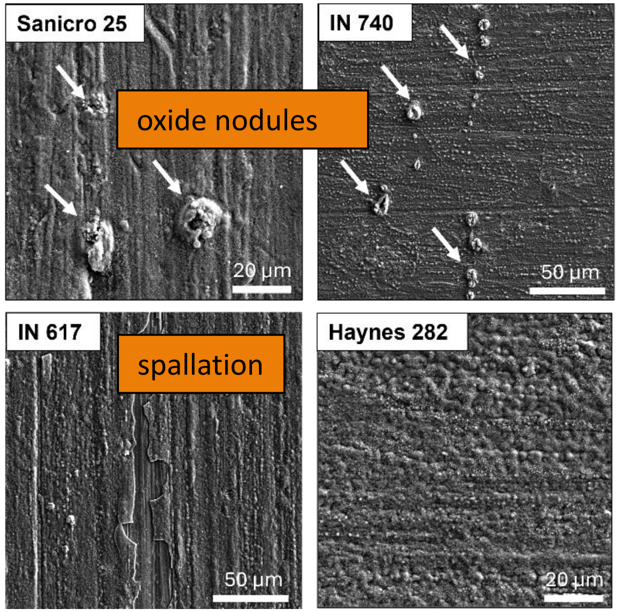


Key Findings – state-of-the art materials

- Weight Gain (Parabolic Law):
  Haynes 282 > IN617B > Sanicro 25 > IN740
  ⇒ all materials meet the KPI
- Oxide scales thickened over time
- Spallation and nodules after 2000h
- Ni-based materials showed protective chromia scale, Cr-depletion and internal oxidation zone
- **Recrystallized zones** observed, most prominent in Haynes 282 and IN617B
- **Best performer: IN740** (0.8 µm oxide after 2000 h)
- XRD: **Cr_2O_3**, spinels, TiO_2 (Haynes 282),
- **carbides** in Sanicro 25 & IN617B



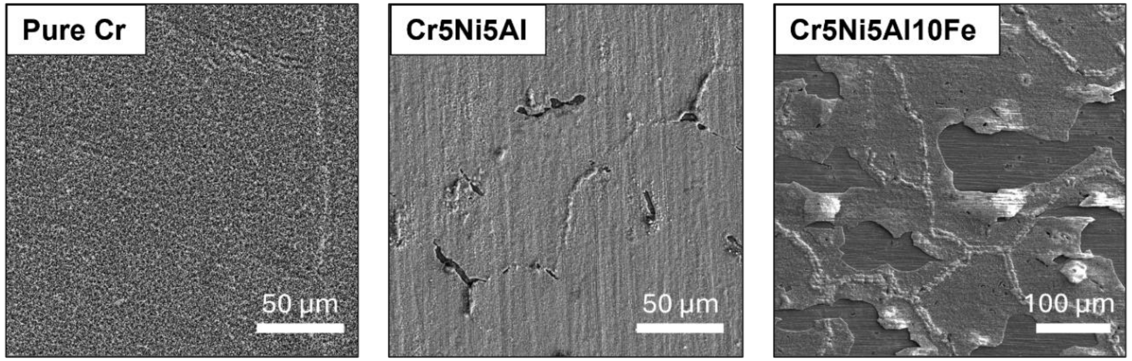


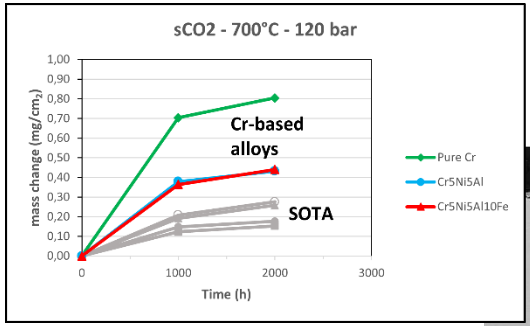


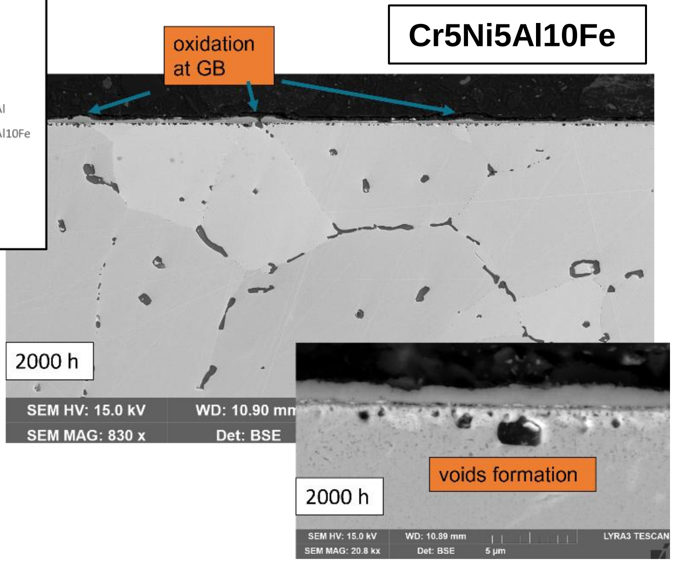
Key Findings – Novel Materials

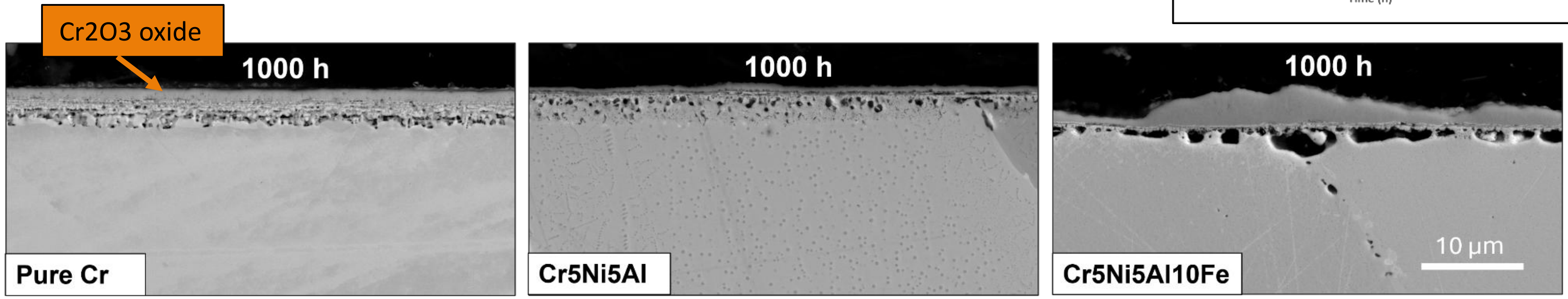
- All novel alloys showed higher corrosion rates than state-of-the art materials
- Weight Gain: Cr5Ni5Al < Cr5Ni5Al10Fe < Pure Cr
- Pure Cr: Thick but uniform oxide (3.5 µm at 2000 h), **carbides formation**
- Cr5Ni5Al: Thin oxide, prone to internal oxidation & grain boundary attack →Cr-depleted boundaries become susceptible to intergranular cracking
- Cr5Ni5Al10Fe: Irregular, spalling-prone oxide; Fe addition not beneficial

Comparison of the material surfaces covered by oxide scales after 2000 h exposure









Key outcomes, conclusions & lessons learnt

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- Successfully developed, manufactured, and commissioned a device for testing candidate materials under real supercritical CO_2 conditions
- Test: Exposure at 700 °C for up to 2000 hours in Supercritical CO_2 Autoclave
- State-of-the-art materials:
  - Materials met the COMPASsCO_2 KPI thresholds
  - Formed layered protective chromia/spinel oxide scales
  - Haynes 282: highest oxidation rate
  - Inconel 740: best corrosion resistance
  - Recrystallized zone affected diffusion & corrosion behavior
  - Carbides in Sanicro 25 & IN617B linked to higher weight gain and carburization
- Novel Cr-based alloys:
  - Higher corrosion rates than state-of-the art materials but still within KPI thresholds
  - Ni+Al additions led to preferential grain boundary oxidation
  - Cr5Ni5Al10Fe: early oxide spallation (after 1000 h), reduced protection
  - Promising properties but require further development for sCO2 applications

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THANK YOU

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