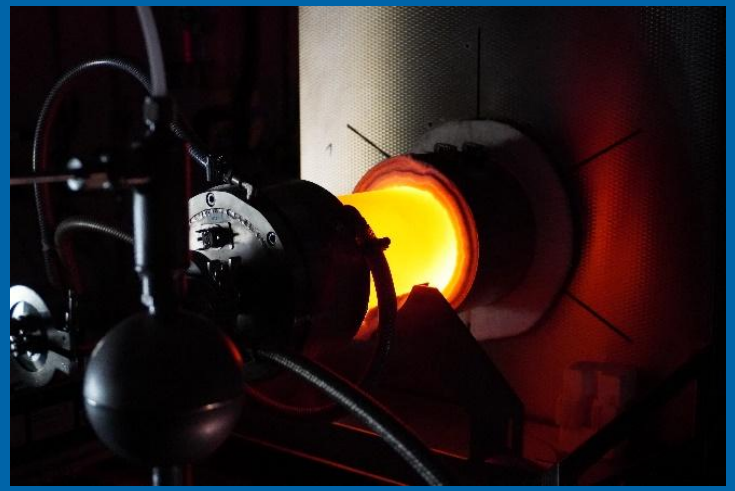
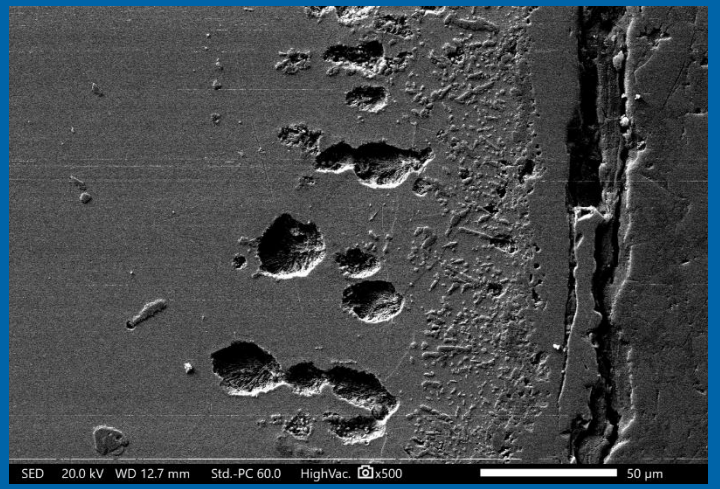
Influence of hydrogen combustion on the mechanical behaviour of heat-resistant steels in thermo-processing technology





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Motivation

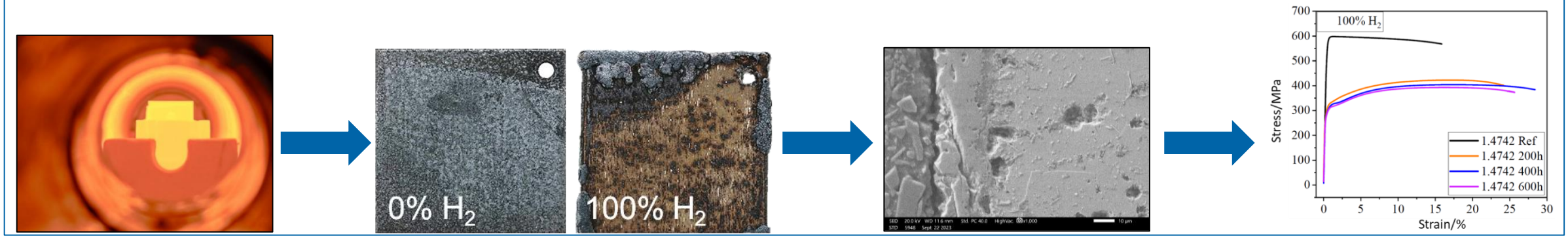
Motivation:

- Implementing **Green hydrogen** for process heat generation – **reduction of climate impact**
- Increasing adiabatic flame temperature and change of composition of process atmosphere
- The changed exhaust gas composition (**residual hydrogen, increased water content** in the exhaust gas) in combination with high temperatures leads to changed exposure cases in thermal processing plants

→ **Potentially higher impact of H_2 on material properties, due to increased corrosion**

Solution approach:

- Investigation of common high-temperature materials under hydrogen combustion atmospheres



Determination of the boundary conditions
Temperatures, Exhaust gas composition, Materials

Exposure temperatures: 1000 °C, further experiments are planned at 800 °C and 1150 °C

Exposure time: 600 h (3 x 200 h)

Composition of atmosphere [vol.-%]: H0 (Methane combustion) and **H100** (hydrogen combustion) at flame temperature and air factor λ = 1,1

Scenario	H_2O	O_2	CO_2	CO	N_2	H_2
H0: 0 % H_2, 100 % CH_4	17.1	1.8	8.4	0.2	71.9	0.1
H100: 100 % H_2, 0 % CH_4	30.8	1.8	0	0	66.1	0.46

Materials:

- Ferritic heat-resistant steels 1.4742 and 1.4762
- Austenitic heat-resistant steels 1.4835 and 1.4841

Investigations after atmospheric treatment:

- Gravimetric measurements, optical microscopy, planned: SEM/EDS
- Tensile tests with micro tensile specimens

Chemical composition of the materials examined

Determination of chemical composition using GDOES

1.4742

C	Si	Mn	P	S	Cr	Al
≤ 0,12	0,7–1,4	≤ 1,0	≤ 0,04	≤ 0,015	17,0–19,0	0,7–1,2
0,06	1,2	0,4	0,03	0,013	20,0	0,9

1.4762

C	Si	Mn	P	S	Cr	Al
≤ 0,12	1,4	≤ 1,0	≤ 0,04	≤0,015	23,0–26,0	1,2–1,7
0,06	1,3	0,8	0,03	0,006	26,7	1,3

1.4835

C	Si	Mn	P	S	Cr	Ni	N	Ce
0,05–0,12	1,4–2,5	≤ 1,0	≤ 0,045	≤ 0,015	20,0–22,0	10,0–12,0	0,12–0,20	0,03–0,08
0,10	1,5	0,5	0,032	0,006	24,3	10,8	0,2	*

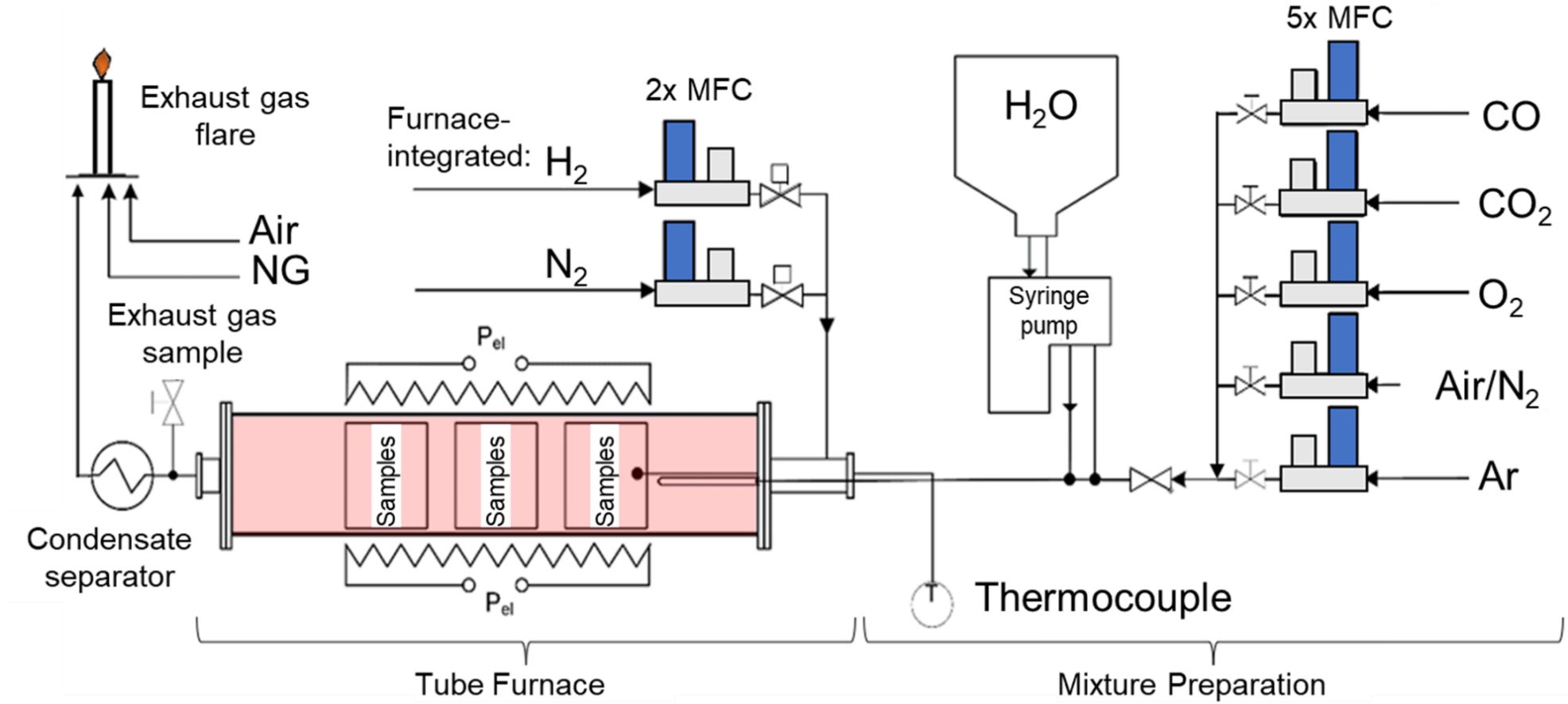
1.4841

C	Si	Mn	P	S	Cr	Ni	N
≤ 0,20	1,5–2,5	≤ 2,0	≤ 0,045	≤ 0,015	24,0–26,0	19,0–22,0	≤ 0,11
0,05	2,6	2,2	0,035	0,007	30,6	20,9	0,01

* Not determined by GDOES
- upper line: tolerance range from data sheet
- lower line: sample measurement

Test rig for long-term exposure tests – Tube furnace setup

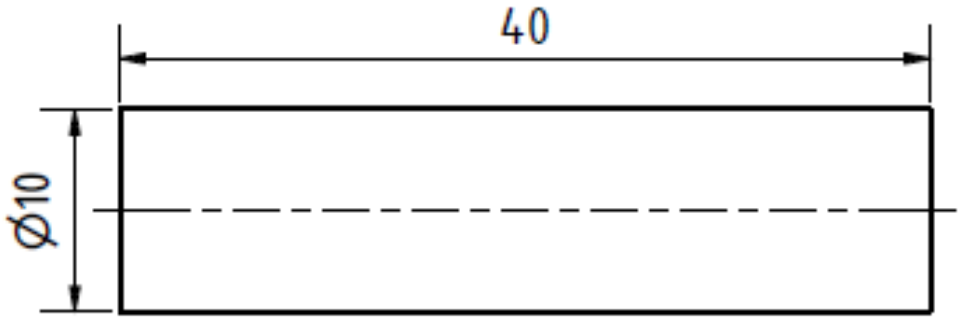
- Tube furnace test rig for exposure tests over 600 h (divided in 200 h blocks)
- Temperature: up to 1600 °C, experiments carried out at 1000 °C
- Atmosphere species: H_2O, H_2, CO_2, CO, N_2, O_2, Ar



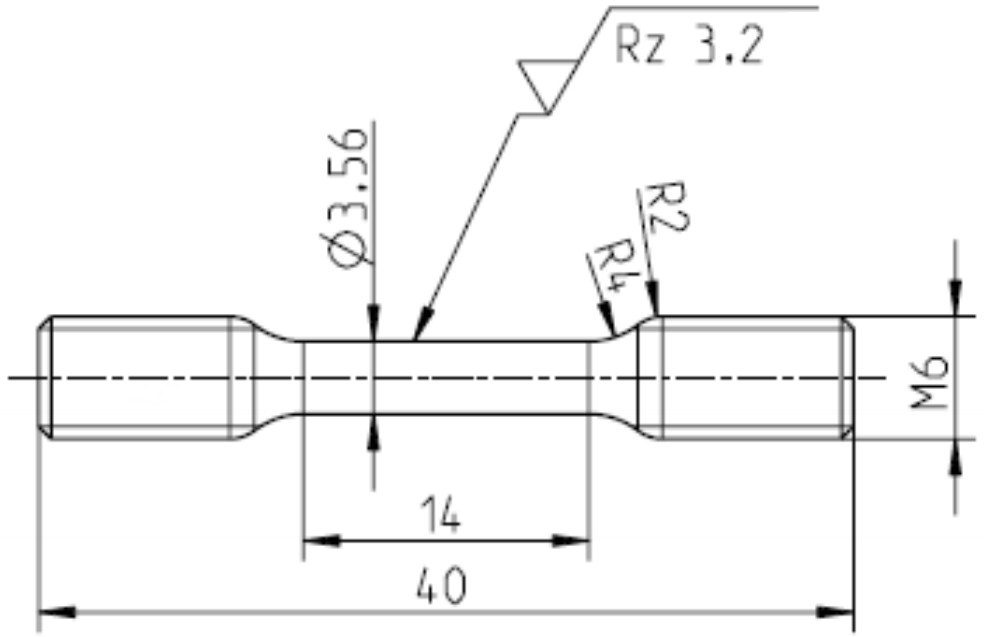
Preparation of samples

Exposure tests are carried out at two different types of samples:

Round bar samples for corrosion tests (gravimetric analysis and microscopy)



Tensile specimen for tensile tests

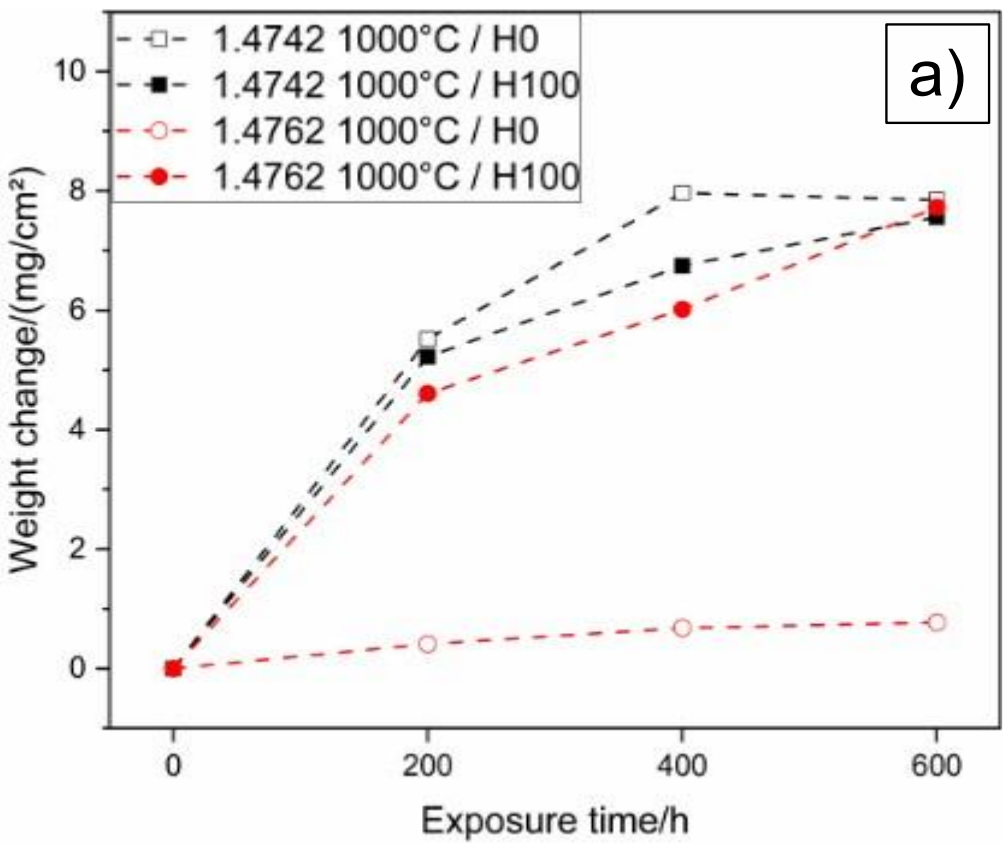


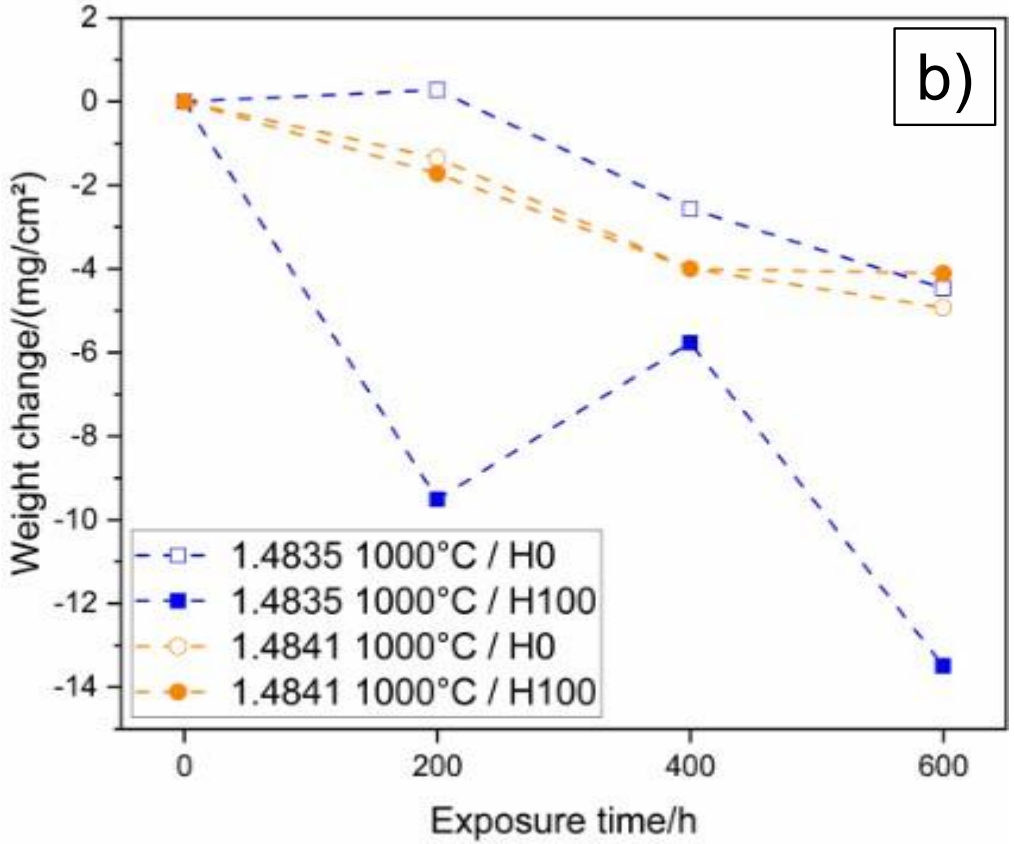
* Dimensions in mm

Preparation routine:

1. Machining of round bar material with a diameter of 12 mm to final dimensions
2. Polishing step for Rz 3.2, bare surface without oxides

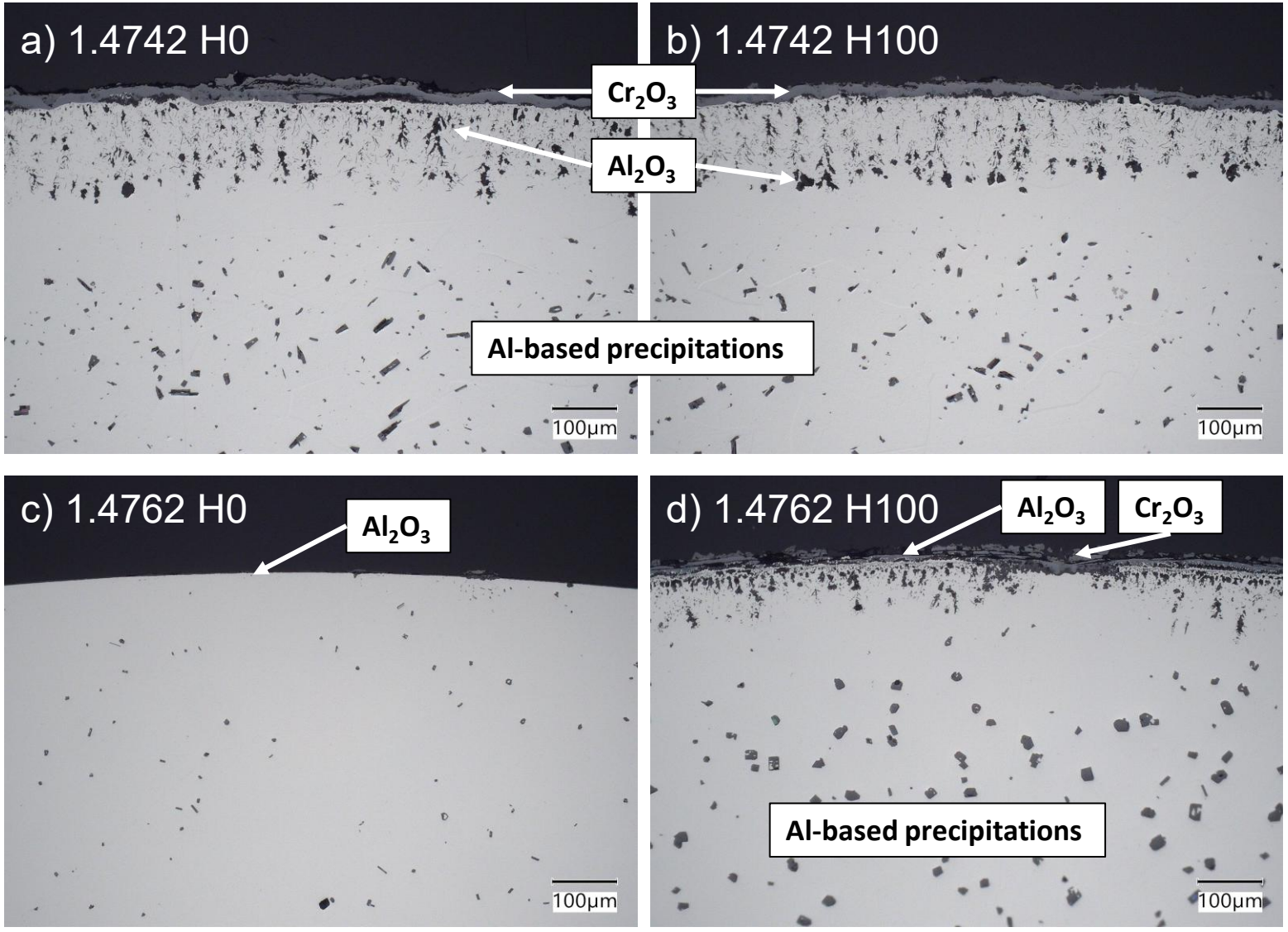
Results of Long-term exposure tests – gravimetric measurements





- Surface-related weight changes in the materials, measured on round bar samples after 200/400/600 h
- Weight increase for ferritic samples and weight decrease observed for austenitic samples
- Remarkably low mass increase over 600 h for 1.4762 in the 100% H_2 scenario

Results of Long-term exposure tests
Microscopically analysis of cross-sections



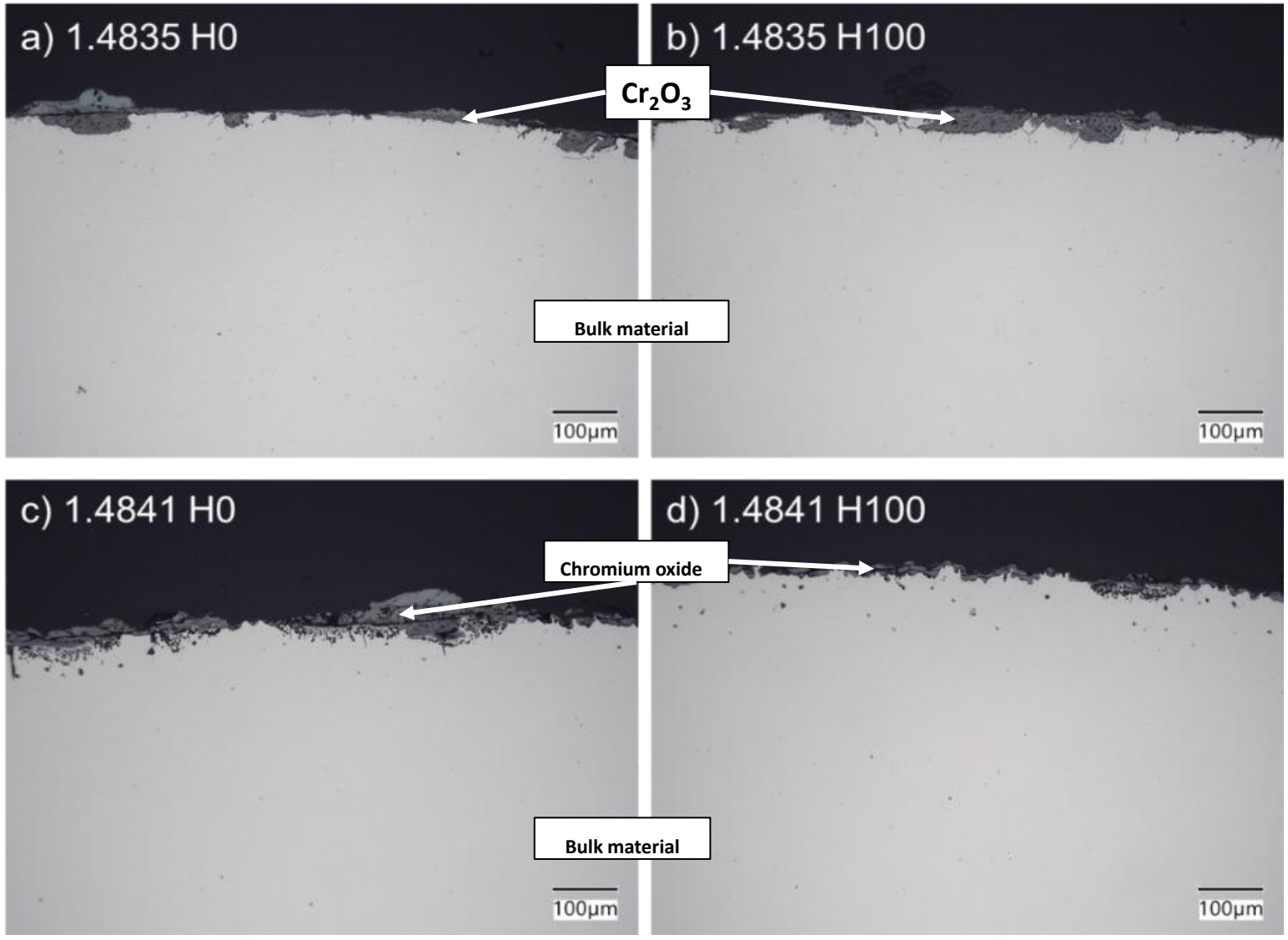
Ferritic heat-resistant steel: 1.4742

- Formation of an oxide boundary layer, LIBS analysis indicates Cr_2O_3
- Formation of an internal oxidation zone
- Chromium-depleted area
- Zone with large aluminum-based precipitates -> to be determined

Ferritic heat-resistant steel: 1.4762

- Differences in oxidation behavior
- H0 scenario shows only a very thin oxide layer (Al_2O_3, 2-5 µm)
- H100 case shows a thicker Cr_2O_3 oxide layer
- Residues of Al_2O_3 in the top layer

Results of Long-term exposure tests – microscopically analysis of cross-sections



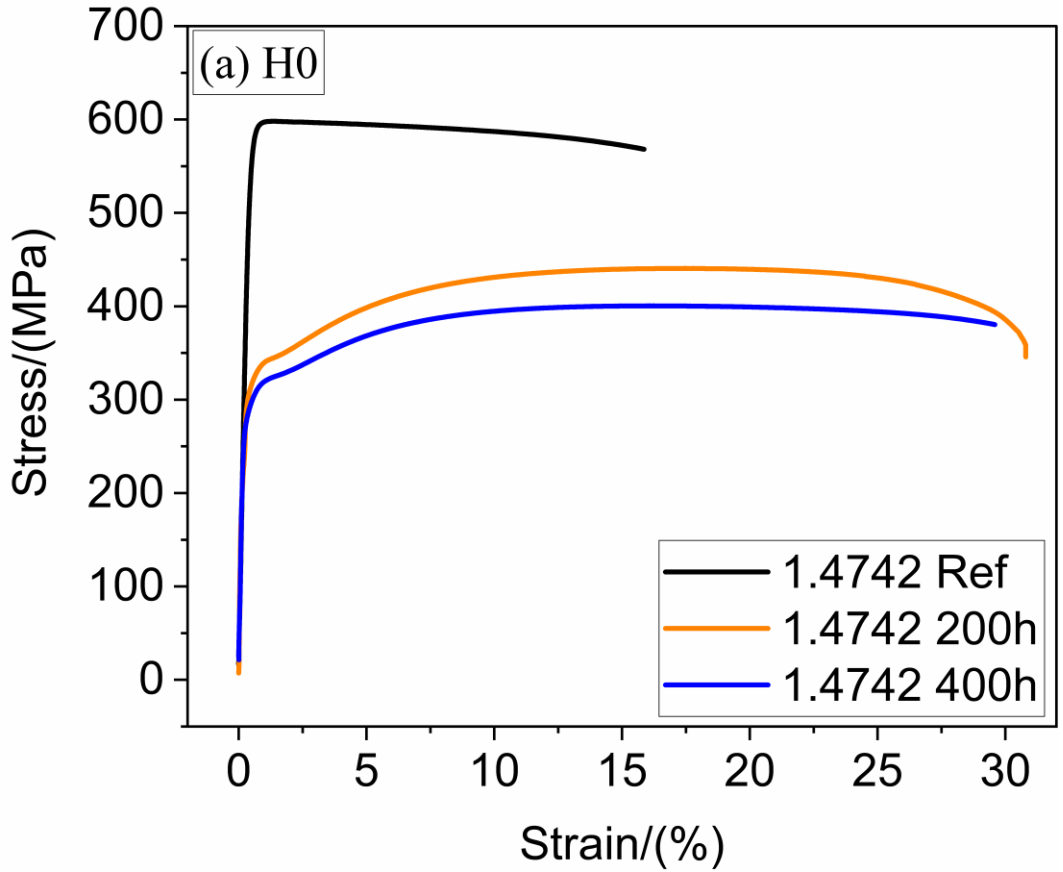
Austenitic heat-resistant steel: 1.4835

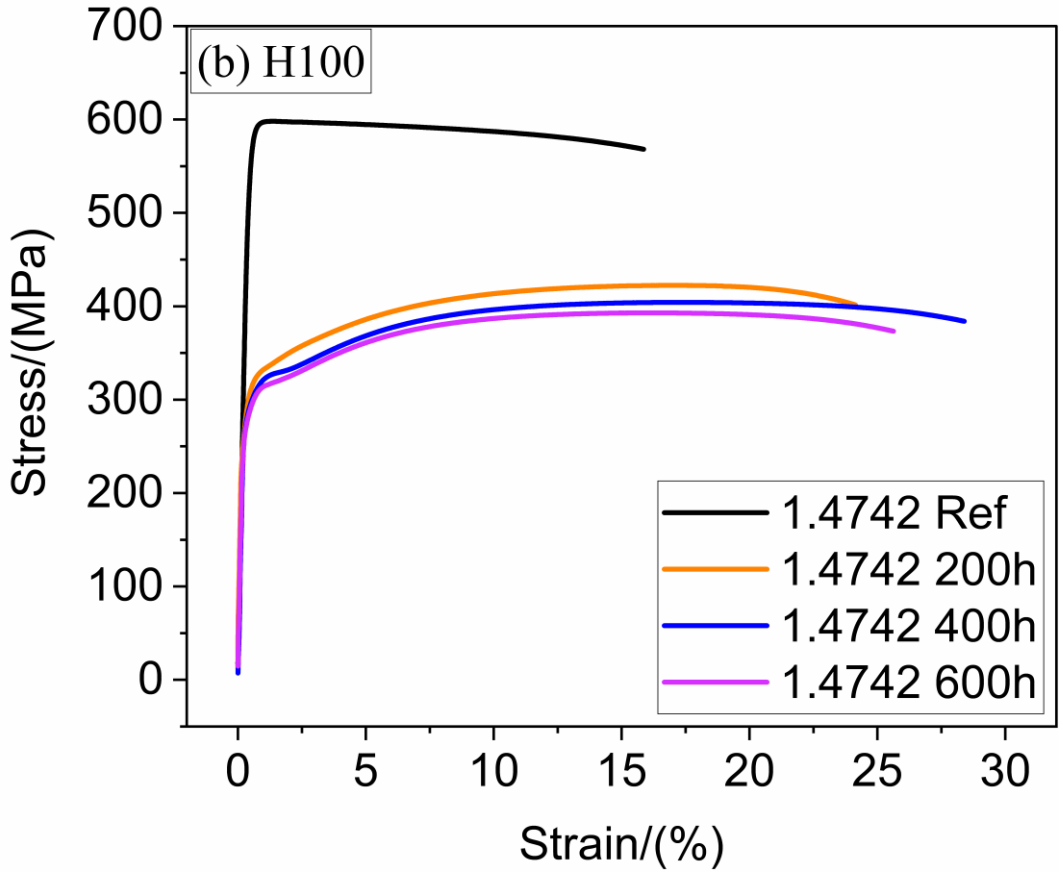
- Formation of a chromium oxide surface layer
- No internal oxidation zone
- No oxidic precipitates visible in the bulk material
- Formation of surface oxide flakes

Austenitic heat-resistant steel: 1.4841

- Formation of a chromium oxide surface layer
- Local formation of an internal oxidation zone based on Al_2O_3
- No oxidic precipitates visible in the bulk material below the boundary layer
- Formation of surface oxide flakes

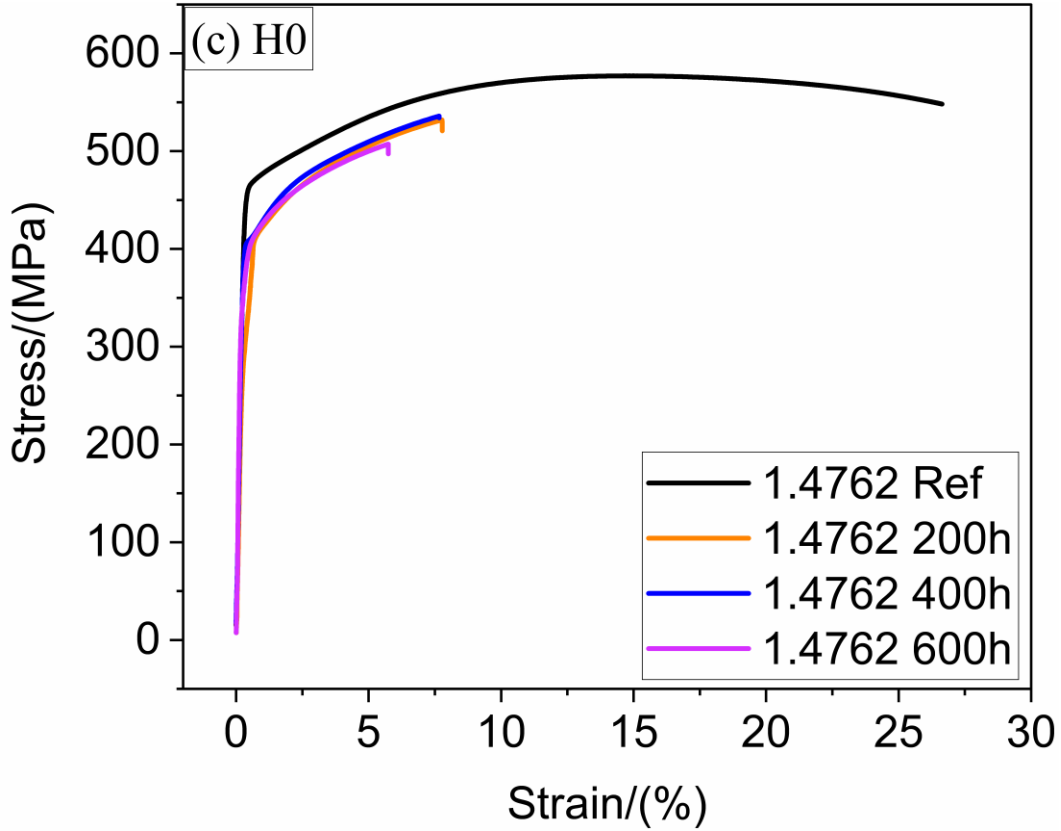
Results of Long-term exposure tests – tensile tests 1.4742

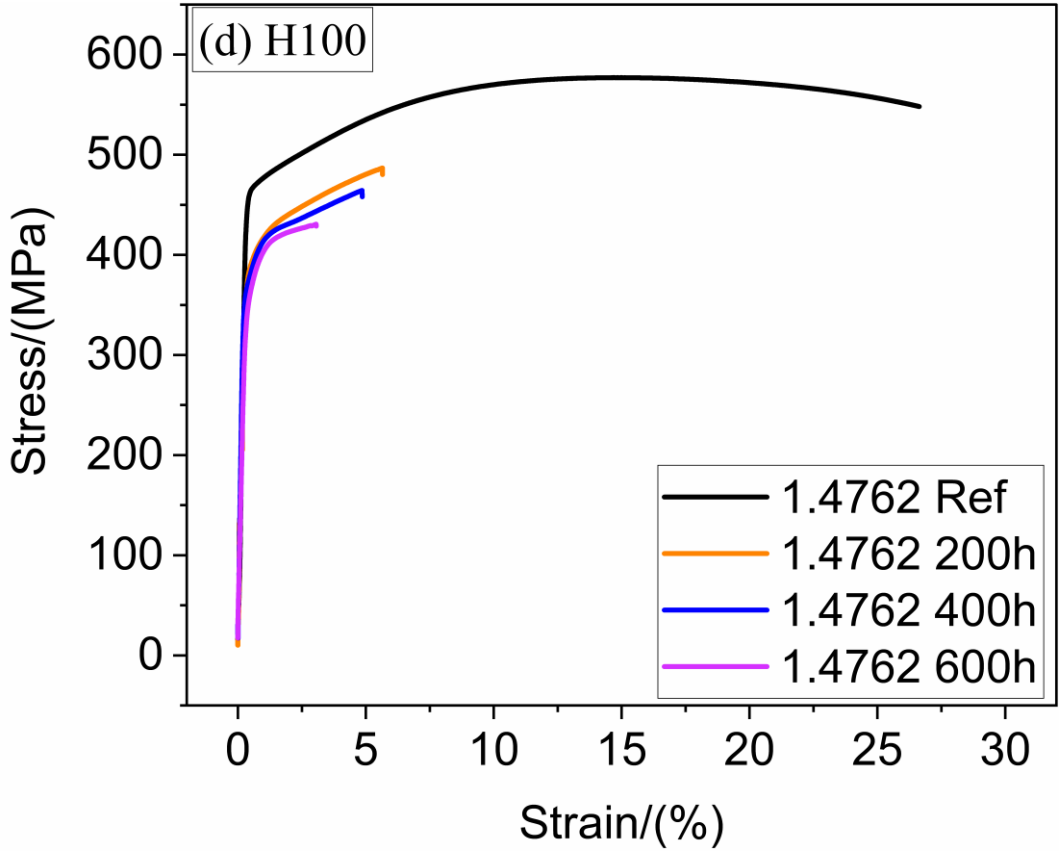




- Increase in elongation to failure for both atmospheres (more pronounced for H0 than for H100)
- Elongation to failure fluctuates, more pronounced for H100
- Yield strength reduced, but almost identical for both atmospheres

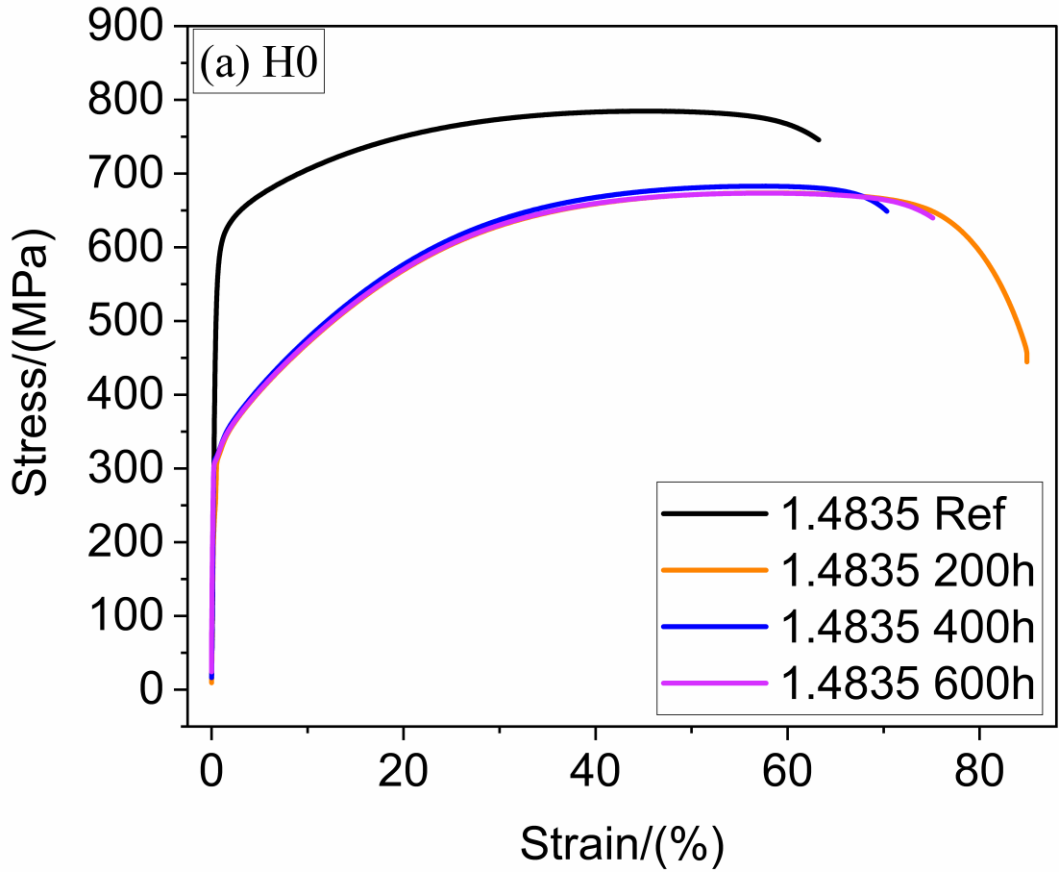
Results of Long-term exposure tests – tensile tests 1.4762

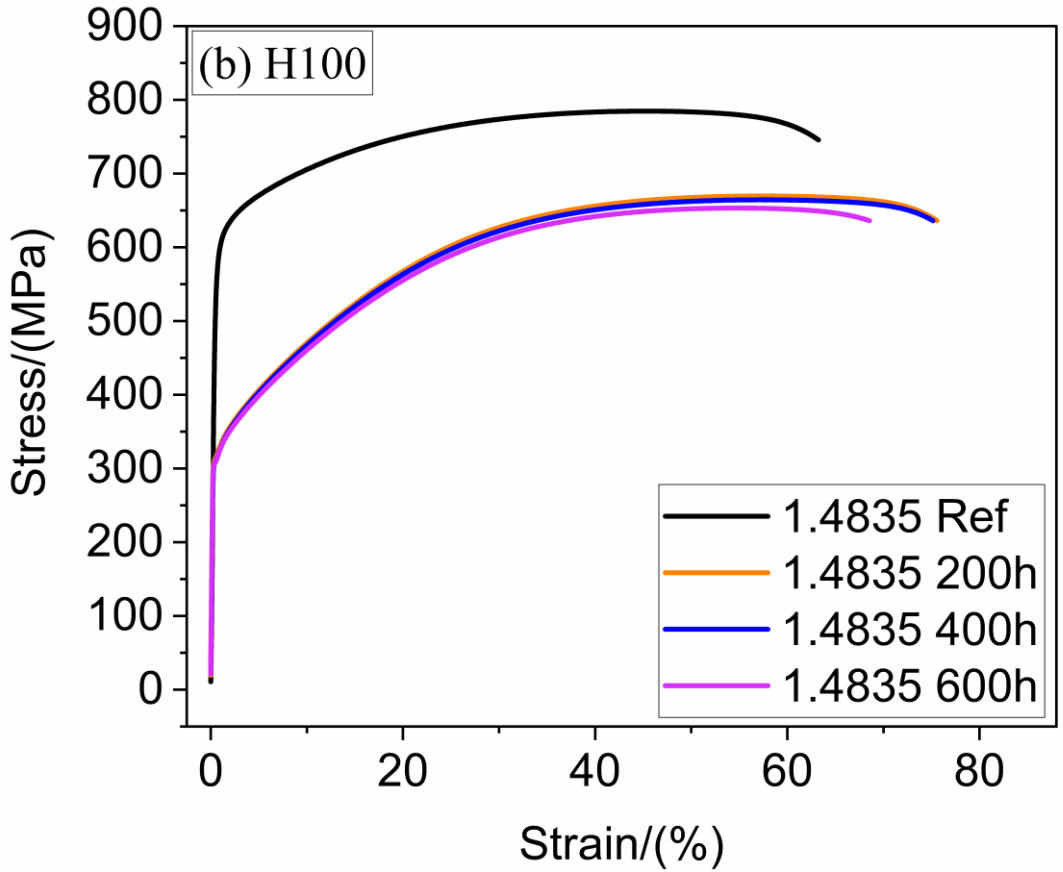




- Reduction of elongation to failure, yield and tensile strength, more pronounced in H100 than in H0
- Further investigations are being carried out to examine the specific corrosion behaviour of this material and the significant reduction in elongation to failure.

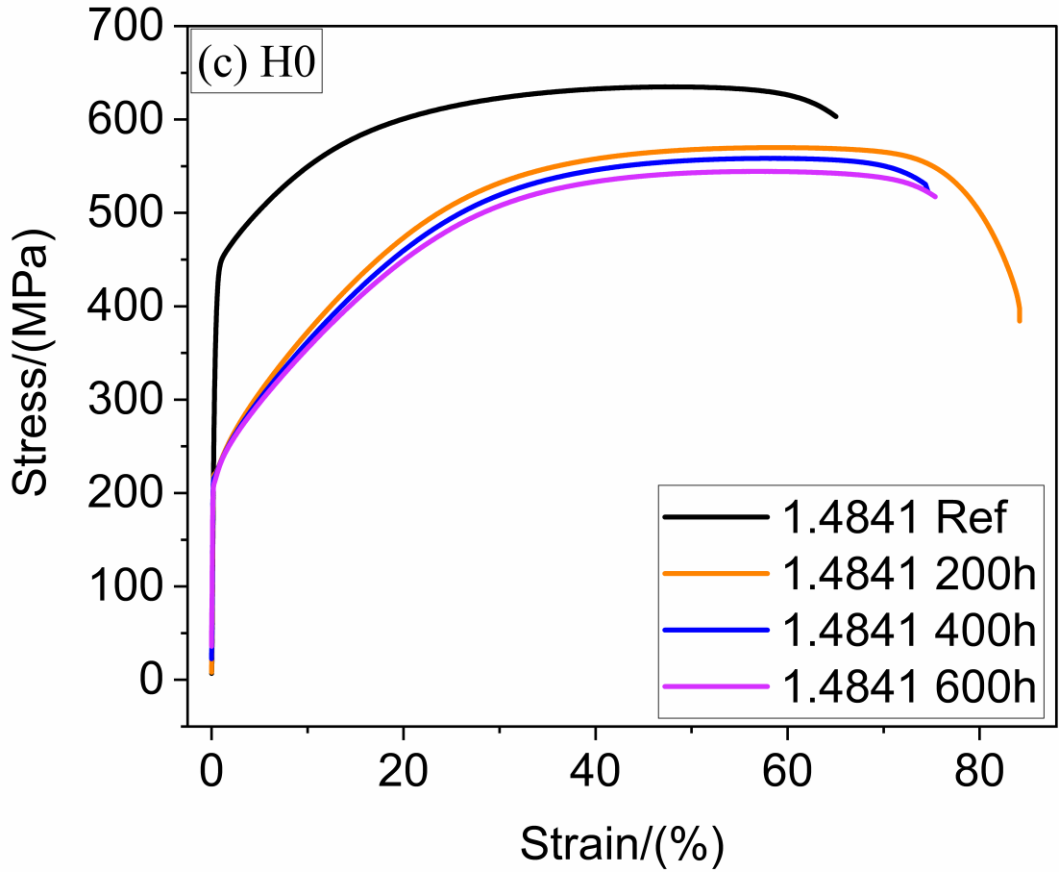
Results of Long-term exposure tests – tensile tests 1.4835

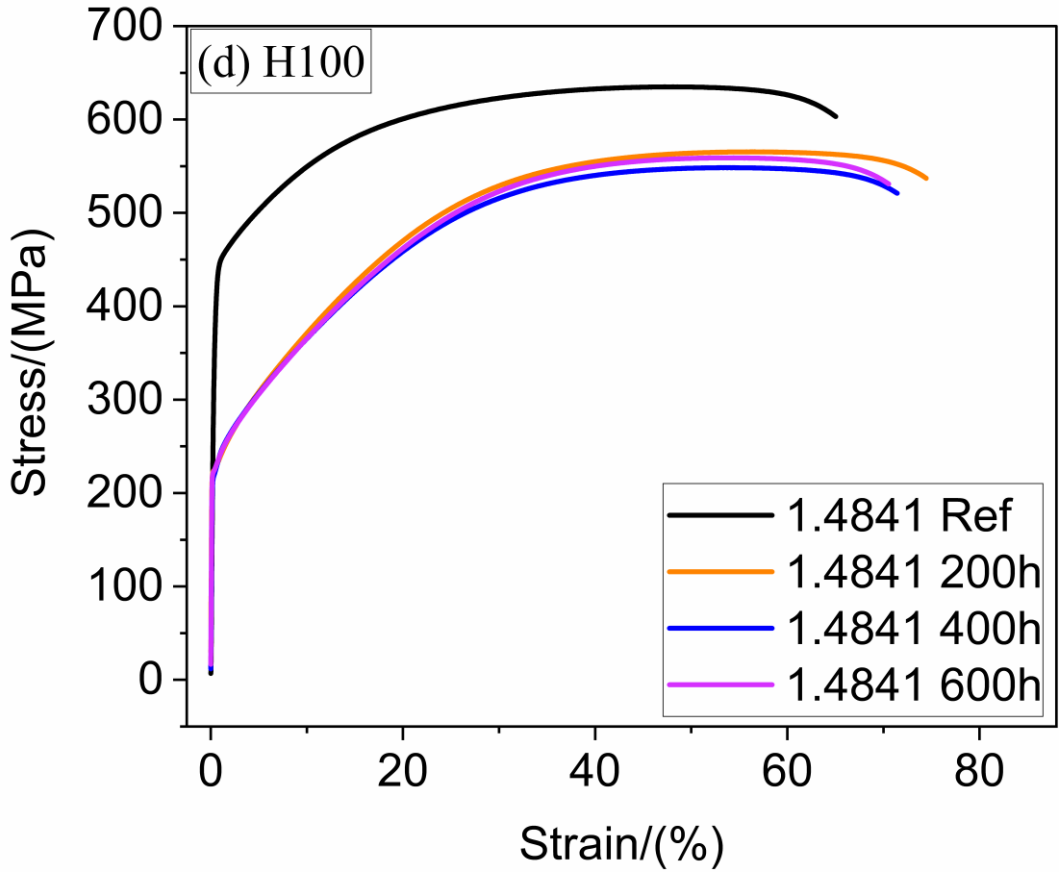




- Slight increase in elongation to failure for both atmospheres
- Reduction in yield strength and tensile strength remain the same for both atmospheres
- No significant influence of the hydrogen combustion atmosphere detected

Results of Long-term exposure tests – tensile tests 1.4841





- Slight increase in elongation to failure for both atmospheres
- Reduction in yield strength and tensile strength remain the same for both atmospheres
- No significant influence of the hydrogen combustion atmosphere detected

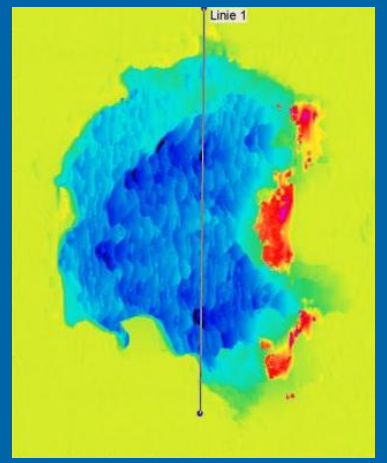
Summary and Conclusion

- Changes in the microstructure cause a decrease in tensile strength and yield strength.
- Ferrites in particular have shown microstructural changes deep into the sample, with the greatest corresponding decrease in strength.
- Embrittlement effects observed (elongation to failure decreases significantly for 1.4762), occurring in both the reference and pure H_2 combustion atmospheres
- Gravimetric investigations show differences in the corrosion behaviour of ferrites (oxidation = increase in mass) and austenite (oxidation + spalling of oxide flakes = decrease in mass

Good news:

Despite microstructural changes, the steels examined show no significantly greater degradation of mechanical properties after exposure to hydrogen combustion atmospheres compared to natural gas!

Thank you for your attention!



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