MATERIALS REQUIREMENTS FOR SCO2 (OXIDATION / CARBURIZATION)

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FORSCHUNGSZENTRUM JÜLICH GMBH

COMPASsCO2 Second Stakeholders Workshop

Next generation advanced materials for particle/supercritical CO_2 heat exchangers

Hybrid- physical venue: Hotel Anker, Kolpingstraße7, 97828 Marktheidenfeld, Germany
Online: Zoom

September 25th, 2023
11h00 – 15h00 CET
No registration fees

Overview of activities in COMPASsCO2 / WP4

Oxidation and corrosion behavior - test program shared between FZJ, CIEMAT and CVR.

Testing in lab. air or CO_2 (technical or high-purity gas) between 600°C and 900°C

Test methods:

- thermogravimetry experiments (FZJ)
- discontinuous testing (CIEMAT)
- cyclic oxidation (FZJ)
- high-pressure autoclave tests in supercritical CO_2 (CVR)

Post-exposure analytical studies:

- optical metallography,
- SEM / EDX (surface and cross-section analysis)
- GD-OES (FZJ)
- XPS (CIEMAT)

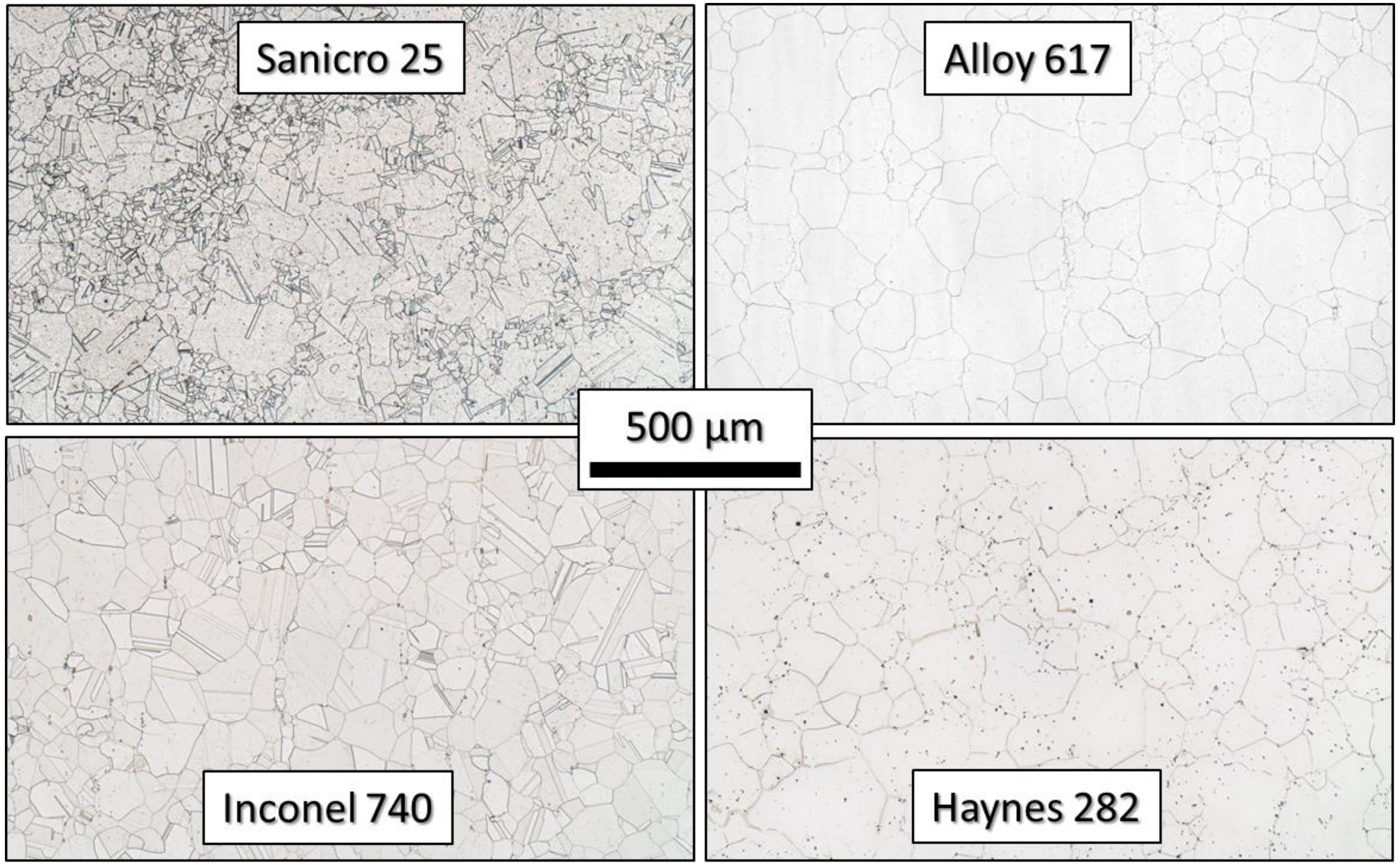
Studied candidate materials

Chemical compositions of studied materials (ICP-OES and combustion analysis of C, N)

Alloy	Fe	Ni	Co	Cr	Al	Mo	Ti	Mn	Si	C	Other
Sanicro 25	41.5	24.2	1.50	23.4	0.03	0.23	0.03	0.56	0.19	0.084	Cu 2.93, Nb 0.5 W 3.47, N 0.28
Alloy 617	1.03	51.9	11.9	22.1	1.16	9.0	0.39	0.09	0.32	0.076	W 0.32
IN740	0.15	48.0	21.4	25.2	1.35	0.53	1.49	0.30	0.18	0.048	Nb 1.5, Ce 0.12
Haynes 282	0.61	52.5	10.1	18.6	1.50	8.7	2.15	0.05	0.25	0.070	Ce 0.17
P92	84.6	0.34	0.017	9.37	-	0.38	-	0.57	0.22	0.150	W 1.74, V 0.22

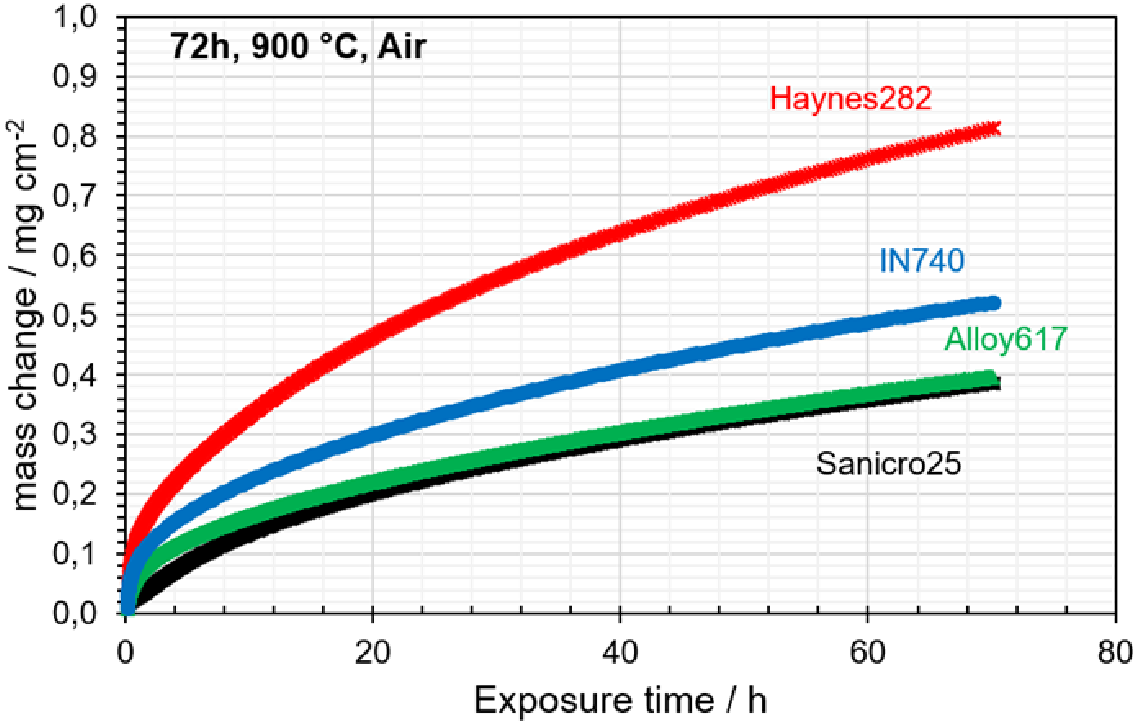
Studied candidate materials

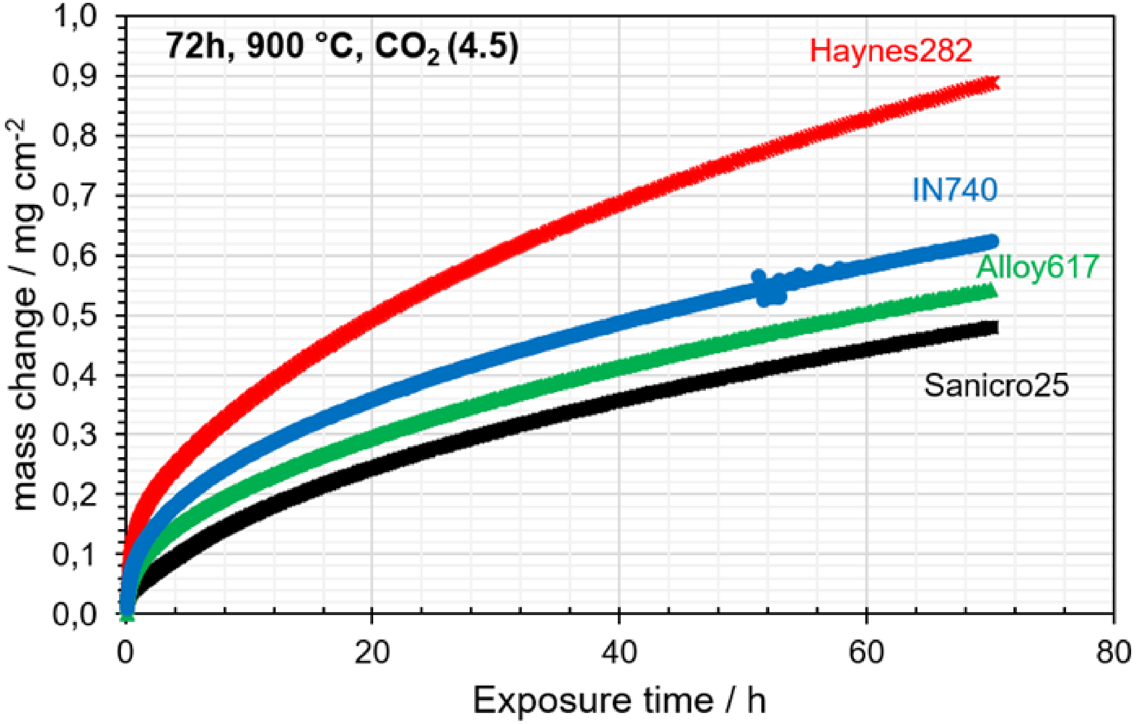
Etched optical metallographic cross-sections of as-received alloys



Oxidation Tests

Thermogravimetry data at 900°C (atmospheric pressure)

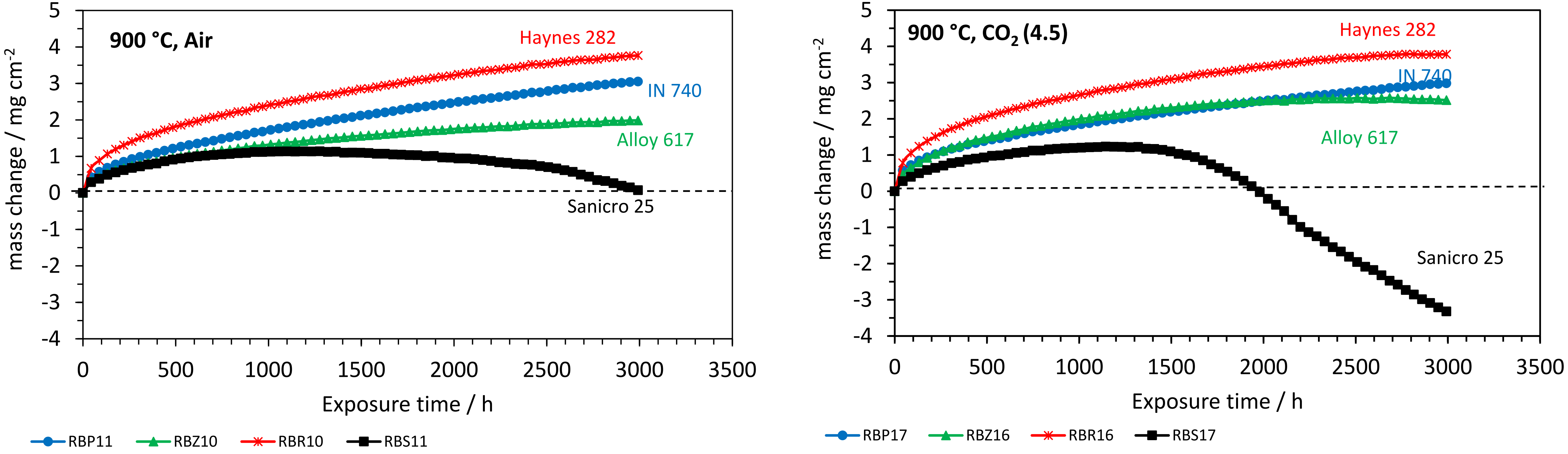




- Slightly higher mass changes in synth. air and CO_2
- Same ranking of alloys in terms of mass change in both test gases

Cyclic oxidation tests

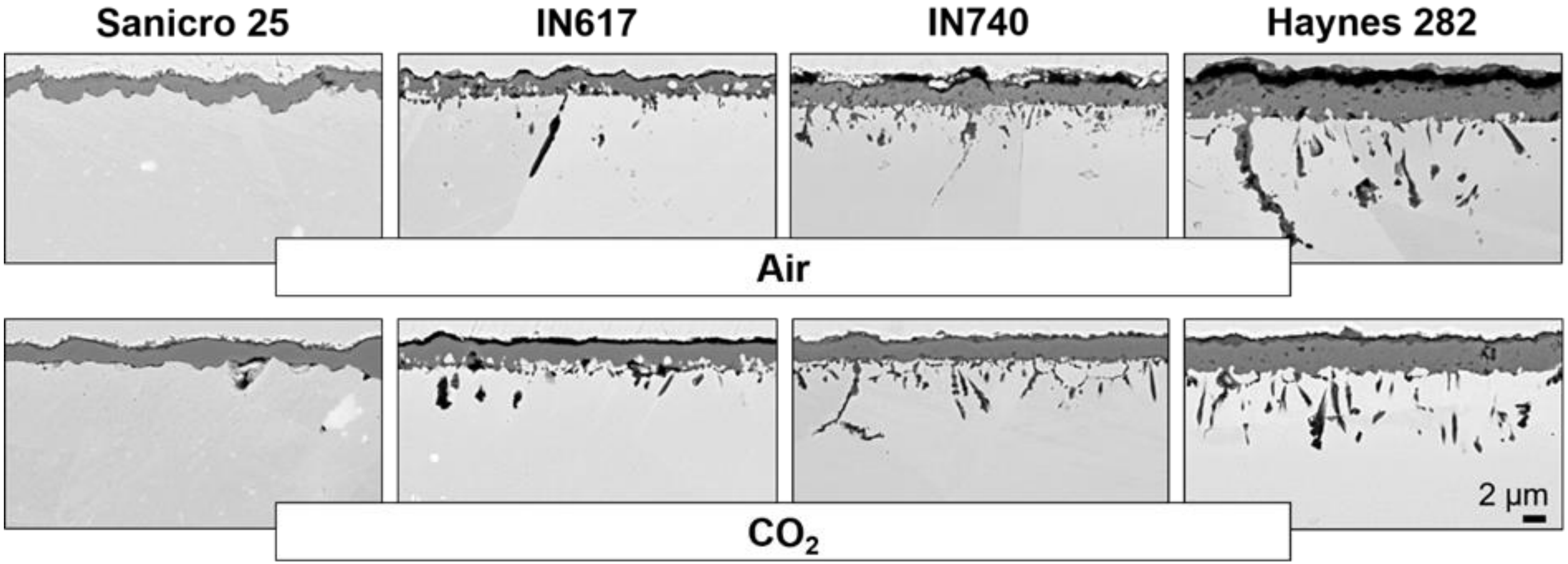
Mass change (exposure at 900 °C in air or CO_2 (4.5) – 11h heat. / 0.5h cool.)



- More extensive scale spallation from Sanicro25 in spite of low scale growth rate
- Increased tendency to scale spallation in CO_2 compared to air (for Sanicro 25 and Alloy 617)

Oxidation Tests

SEM cross-sections after 72 hours at 900°C (atmospheric pressure)



- Good agreement between mass changes and cross-section analysis
- Mass change is correlated with scale thickness and extent of internal oxidation (similar in air and CO_2)

Effect of alloy composition

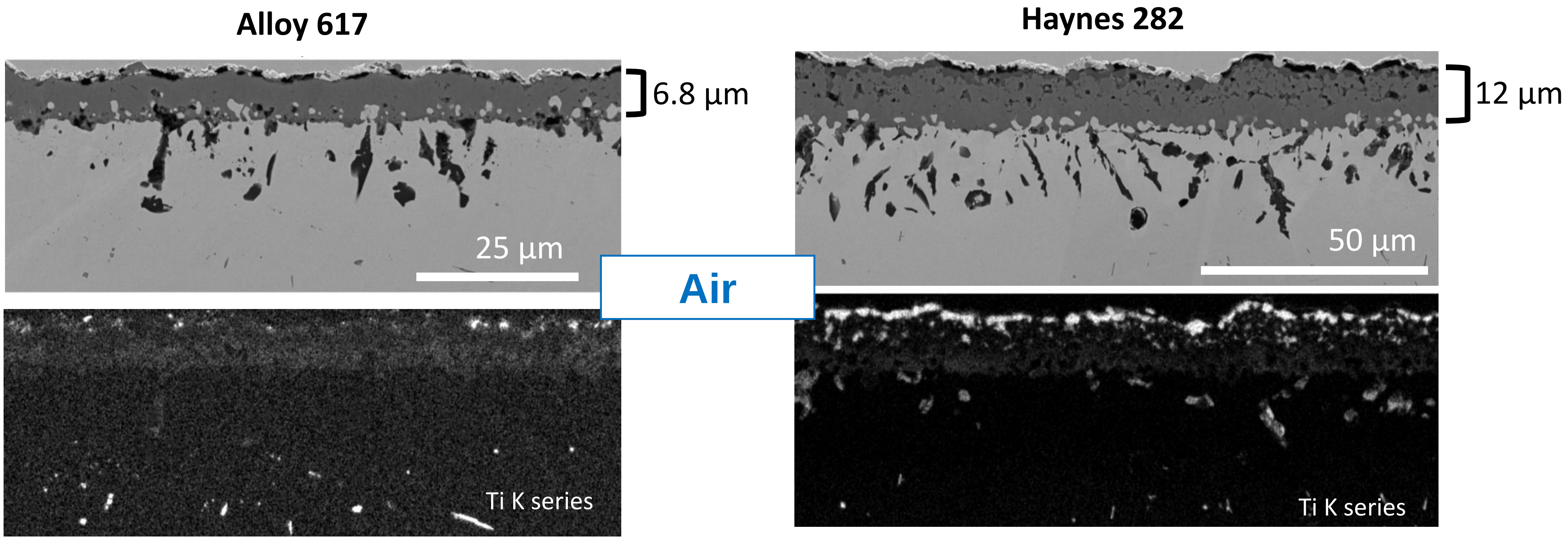
Materials compositions / wt% measured with ICP-OES

	Fe	Ni	Co	Cr	Al	Mn	Si	Nb	Ti	Mo
Sanicro 25	42.6	25.4	1.5	22.3	0.03	0.5	0.2	0.5	-	-
617B	1.2	54.6	11.9	22.3	1	0.04	0.05	-	0.4	8.2
740	0.1	49.7	20.6	24.5	1.4	0.3	0.2	1.5	1.4	-
282	0.2	57.1	10.6	19.6	1.6	0.02	0.04	-	2.2	8.6

- *The extent of internal oxidation increases with increasing alloy Al content*

Cyclic oxidation exposure: Ti incorporaton into scale

1000 h at 900 °C in air – 11h heat. / 0.5h cool



- *Scale growth rate correlates with alloy Ti-content – scale thickness increases with increasing alloy Ti content*
- *Qulitatively similar results obtained in CO_2*

Cyclic oxidation exposure

Mechanism of Ti-effect

Commercial materials compositions / wt%

	Fe	Ni	Co	Cr	Al	Mn	Si	Nb	Ti	Mo
Sanicro 25	42.6	25.4	1.5	22.3	0.03	0.5	0.2	0.5	-	-
617B	1.2	54.6	11.9	22.3	1	0.04	0.05	-	0.4	8.2
740	0.1	49.7	20.6	24.5	1.4	0.3	0.2	1.5	1.4	-
282	0.2	57.1	10.6	19.6	1.6	0.02	0.04	-	2.2	8.6

- *Scale thickness increases with increasing alloy Ti content*
- *Ti is known to cause so-called p-type doping effect*
- *Ti^{4+} substitutes Cr^{3+}; Ti^{4+} can be considered to enter the chromia lattice according to reaction:*

$$3TiO_2 \rightarrow 3Ti^{\cdot}_{Cr} + V'''_{Cr} + 6O^{x}_{O}$$

- *Vacancies lead to faster cationic diffusion transport through the scale*

S. Cruchley et al./Corrosion Science *75* (2013) *58–66*

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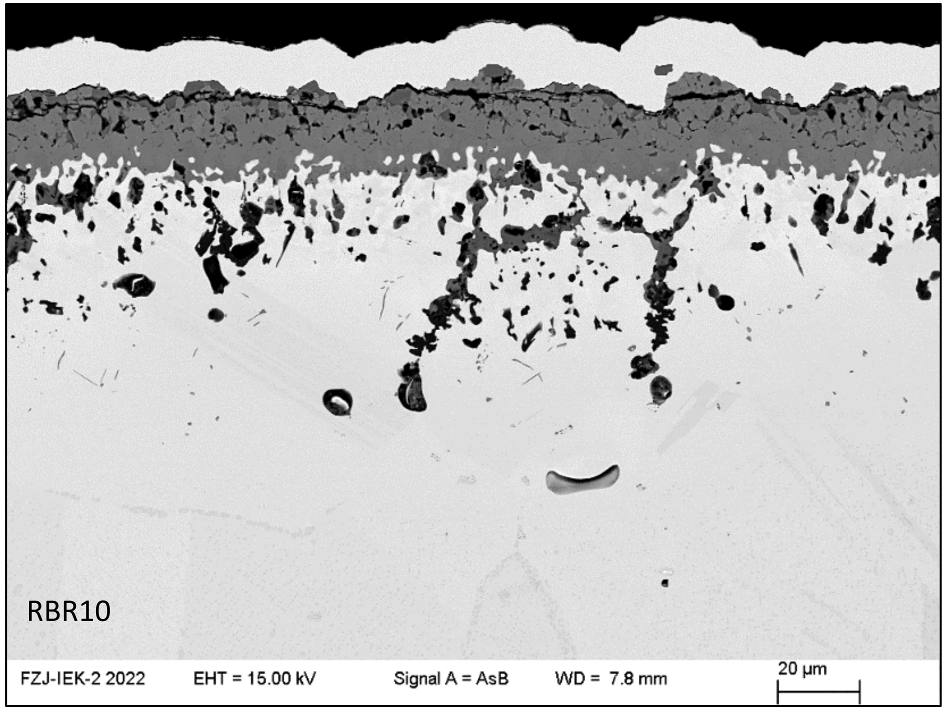
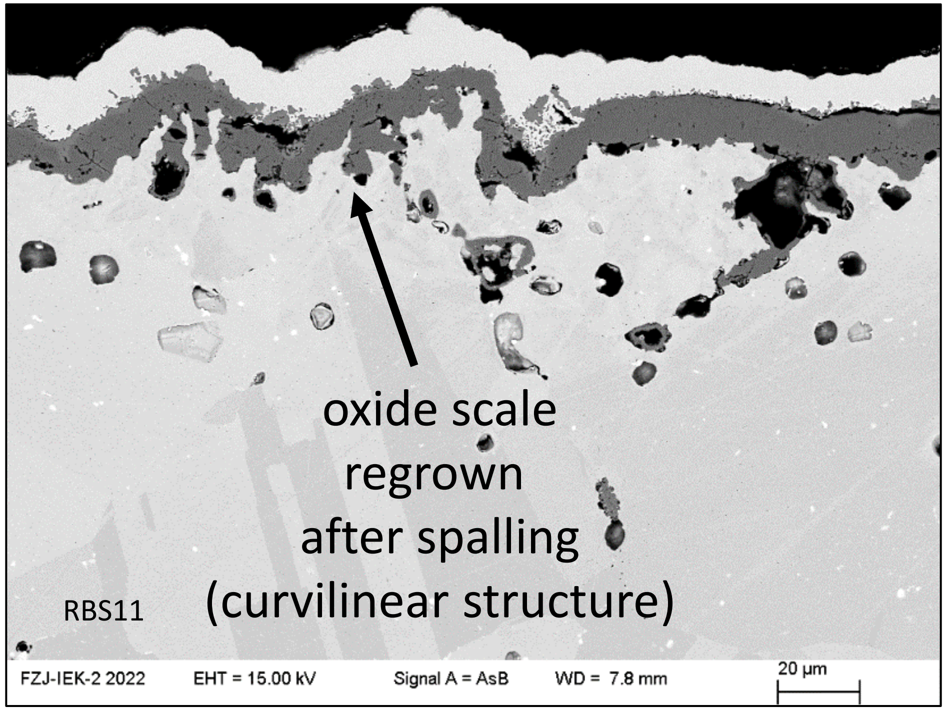
Effect of alloy composition on scale adherence

SEM after 3000h exposure at 900 °C in air

Haynes 282



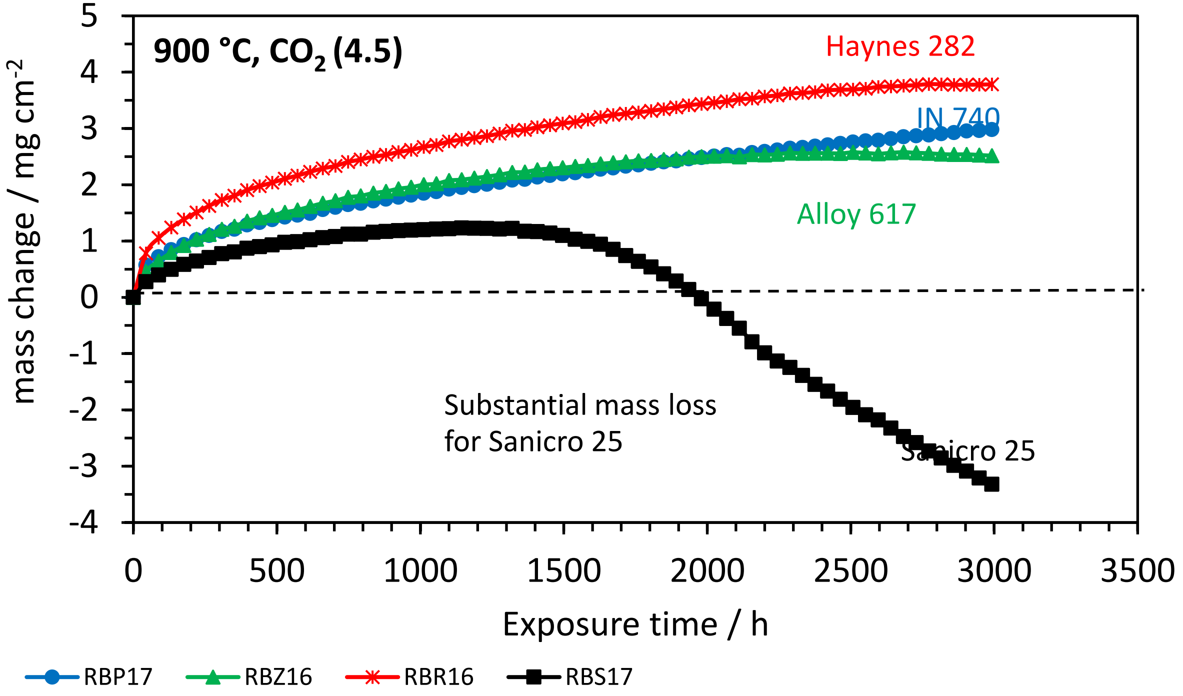
Sanicro 25



- Oxide scale remained adherent on Haynes 282 after 3000 h cyclic oxidation
- Observations in agreement with mass change data (next slide)

Cyclic oxidation exposure

Mass change (exposure at 900 °C in air or CO_2 (4.5) – 11h heat. / 0.5h cool.)



- Higher CTE of Sanicro 25 compared to Haynes 282
- Difference in the oxide microstructure, it is possible that Sanicro 25 has a higher module of elasticity resulting in more stress generation ín oxide upon cooling

Cyclic oxidation exposure

Mass change (exposure at 900 °C in air or CO_2 (4.5) – 11h heat. / 0.5h cool.)

Commercial materials compositions / wt%

	Fe	Ni	Co	Cr	Al	Mn	Si	Nb	Ti	Mo	Ce
Sanicro 25	42.6	25.4	1.5	22.3	0.03	0.5	0.2	0.5	-	-	<0.009
617B	1.2	54.6	11.9	22.3	1	0.04	0.05	-	0.4	8.2	0.028
740	0.1	49.7	20.6	24.5	1.4	0.3	0.2	1.5	1.4	-	0.122
282	0.2	57.1	10.6	19.6	1.6	0.02	0.04	-	2.2	8.6	0.17

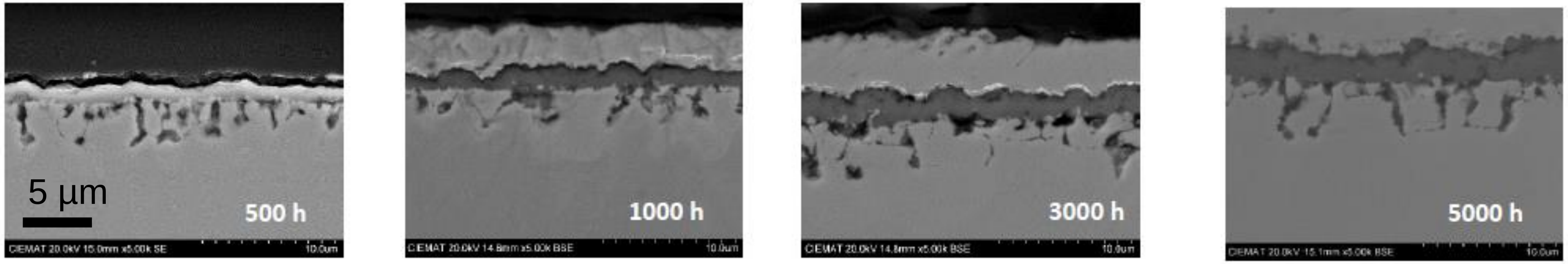
- Presence of minor Ce addition in alloy
- RE enhance oxidation resistance
- Act as a sulphur-getter, which prevents formation and oxide adherence loss

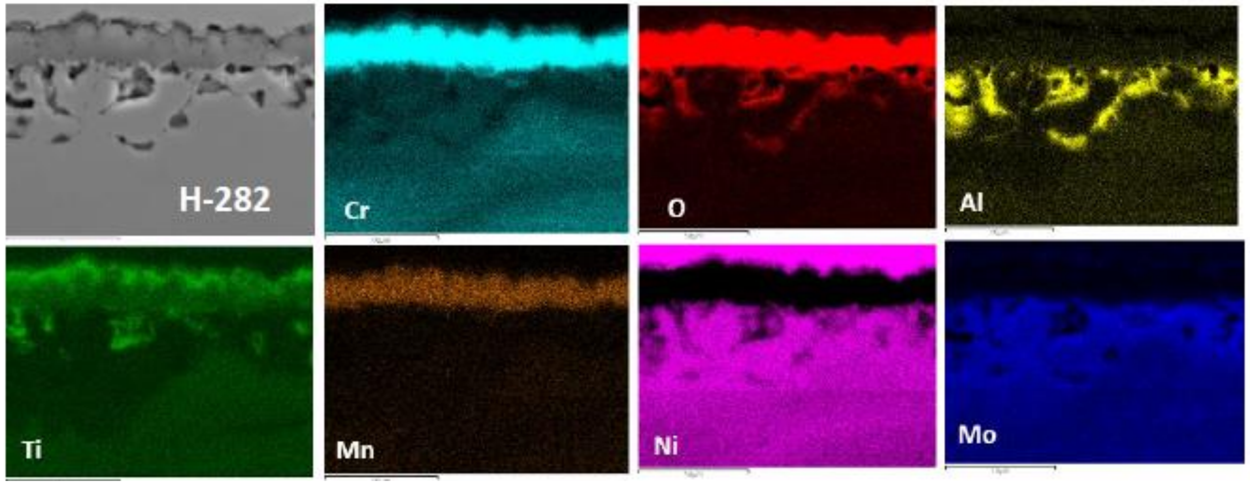
N.B. Ce was not specified in nominal compositions of studied alloys

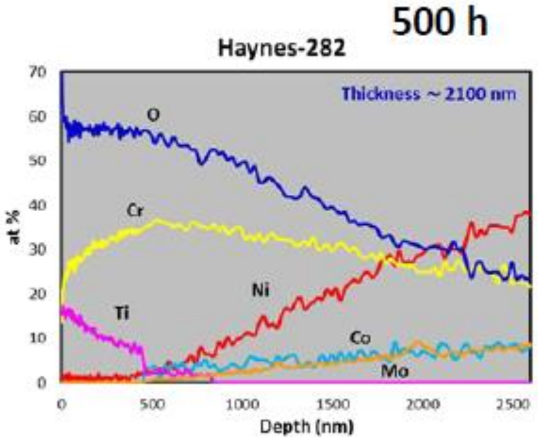
WP4 - 4.2 Internal wall corrosion tests

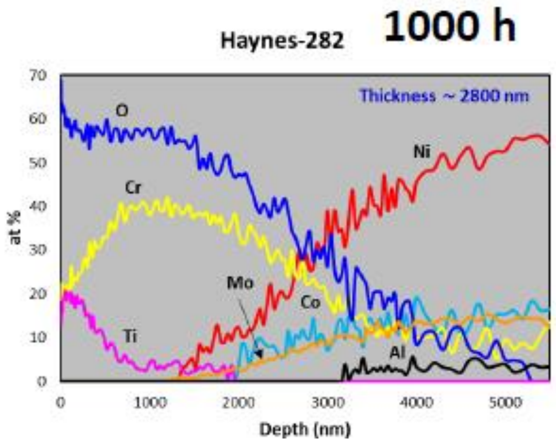
STATUS:

- Corrosion tests at 700°C: Metallographic examination of specimens at 700°C is finishing with the two CO_2 grades
  - Only minor corrosion attack at 700°C, Ti-incorporation into sale

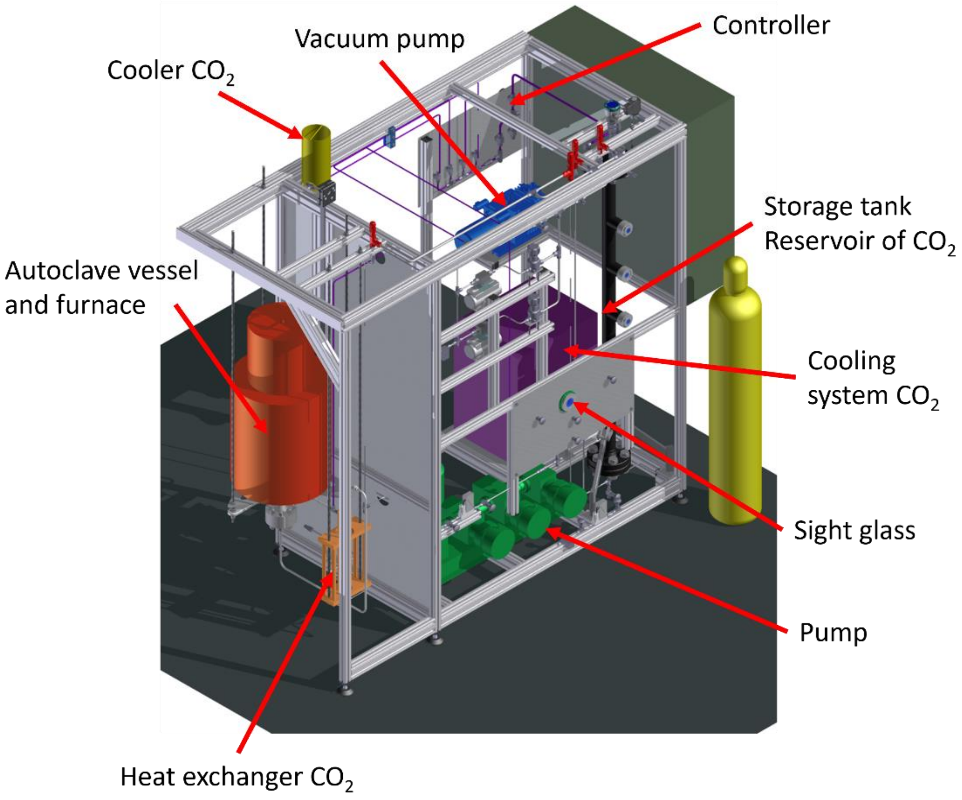








Assembly of the testing device - Supercritical CO_2 Autoclave (ScCAc)



sCO_2 autoclave for materials testing

Testing conditions:
Temperature 700° C
Pressure 120 bar
Gas purity: I.G. (99.995)

- Tests to be initiated in last quarter of 2023

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Conclusions and outlook

- Selected materials qualified for use in heat-exchangers under lab. air and CO_2
- Degradation rates of Ni-base alloys at 700°C in both environments very low
- Degradation rates at 900°C can be correlated with alloy contents of Ti and Al
- Minor additions of reactive element (Ce) appear to be important in determining long-term oxide scale resistance to spallation
- At atmospheric pressure no substantial increase in degradation in CO_2 compared to lab.air and no carburization observed
- During remaining project period testing under high-pressure (supercritical) CO_2 as well as that of new Cr-based materials (coatings) will be accomplished

This project has received funding from the European Union's Horizon 2020 Research and Innovation Action (RIA) under grant agreement No. **958418.**

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THANK YOU

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