Oxidation behavior of Fe- and Ni-base alloys in supercritical CO_2 and related environments

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Introduction

Heat engine power cycles, using a working fluid of supercritical carbon dioxide (sCO_2), have the potential for high thermodynamic efficiencies when configured as a (indirect) recompression Brayton cycle.

Two aspects of the oxidation behavior of alloys were compared between several indirect- and direct-cycle related environments.

- The critical Cr content needed in Ni alloys to achieve a compact and protective chromia scale.
- The effect of surface finish on the oxidation behavior of Grade 91 ferritic-martensitic steel.

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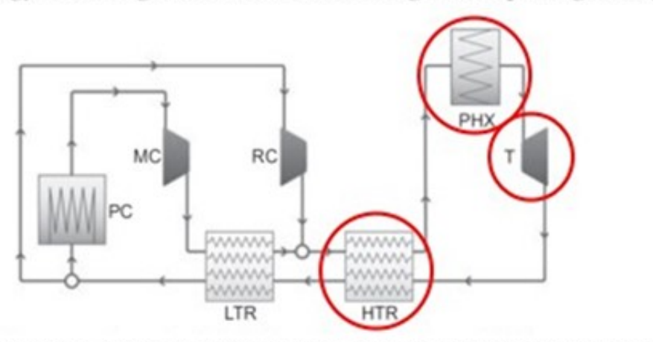
  - The split recuperator allows a portion of the high pressure sCO_2 to bypass the LTR to balance its heat duty and improve efficiency
  - For Fossil Energy applications, consideration must be given to use the significant thermal energy remaining in the combustion flue gas after passing through the PHX



High Temperature Components
T as high as 760°C
P as high as 350 bar
Essentially pure sCO_2

HTR high-temperature recuperator, LTR low-temperature recuperator, MC main compressor, PC primary cooler, PHX primary heat exchanger, RC recycle compressor, T turbine

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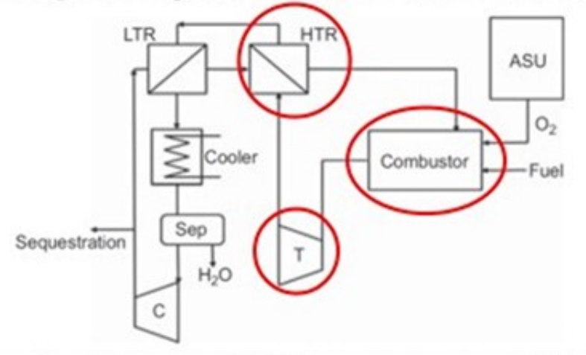
  - Higher turbine inlet temperatures and thus higher efficiencies
  - High pressure sCO_2 output allows for CO_2 transport and sequestration
  - Working fluid not pure CO_2, but contains other combustion products including H_2O



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Test	Gas composition	Gas Notes	Alloys	T, °C	P, bar	Flow rate at T/P, cm/min
sCO_2	CO_2	99.999% CO_2	Ni-xCr 91	700 550	200 200	0.8 0.7
aCO_2	CO_2	99.999% CO_2	Ni-xCr 91	700 550	1 1	25 25
DF4	CO_2+4%H_2O+1%O_2	Deionized H_2O	Ni-xCr	750	1	25
DF4S	CO_2+4%H_2O+1%O_2+0.1%SO_2	Deionized H_2O	Ni-xCr	750	1	25
sH_2O	H_2O	Deaerated deionized H_2O	Ni-xCr	700	200	2
Air	Laboratory air	Some H_2O present from relative humidity	Ni-xCr 91	700 550	1 1	0 0

Model Alloys

- Model alloys were produced using commercial production type techniques
- Not as pure as many model alloy studies, but with typical impurity levels found in commercial alloys
- Made in ingots large enough for normal wrought processing such as forging and rolling to allow for microstructures found in commercial alloys

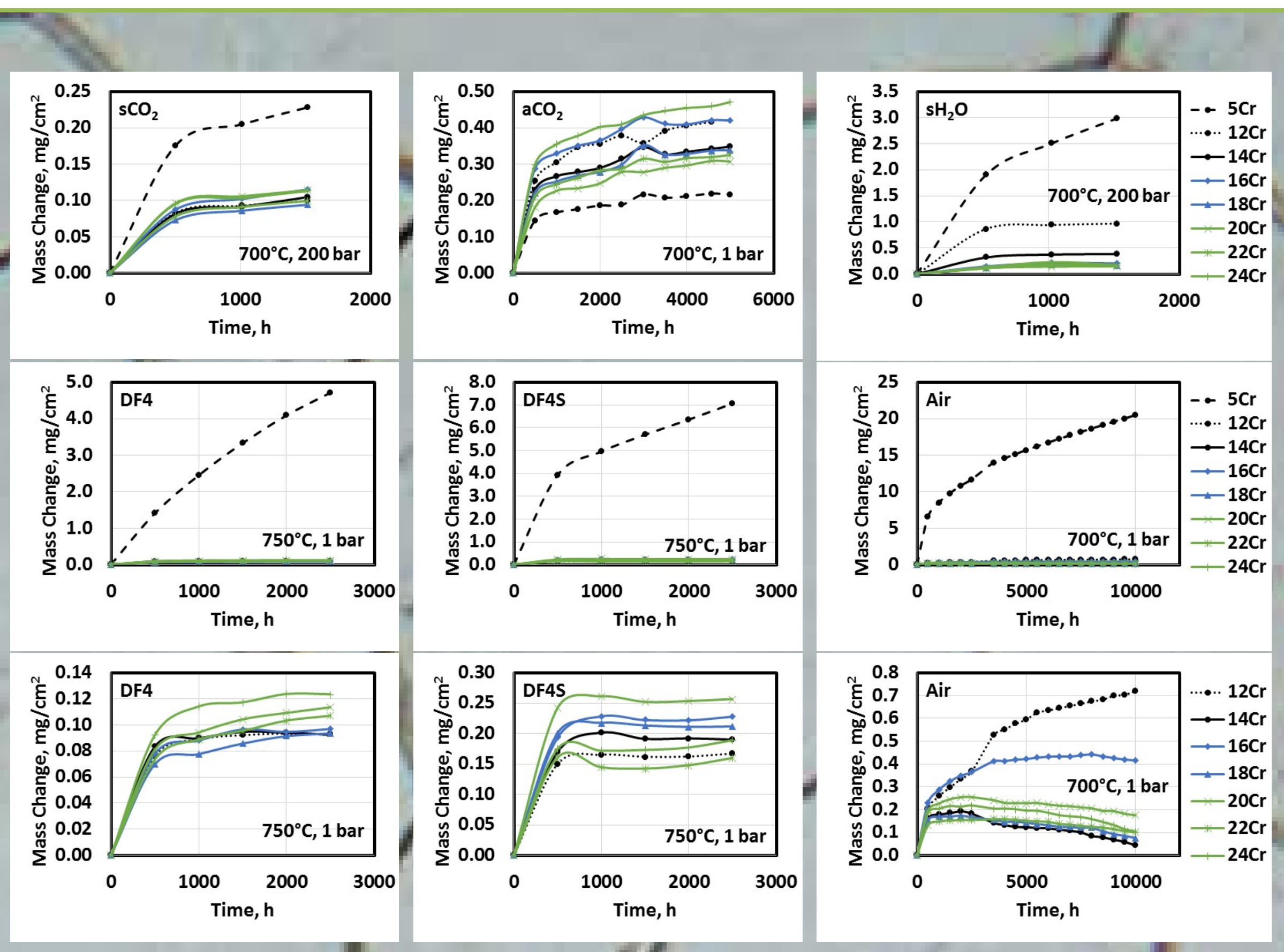
Masteralloy Ingot
178.6 lb

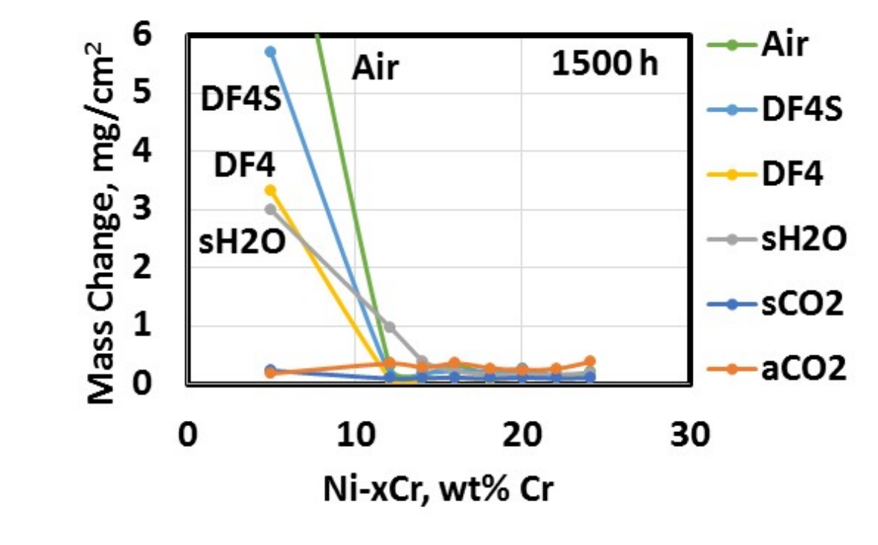
ESR Slag
CaF_2
30% CaO
30% Al_2O_3

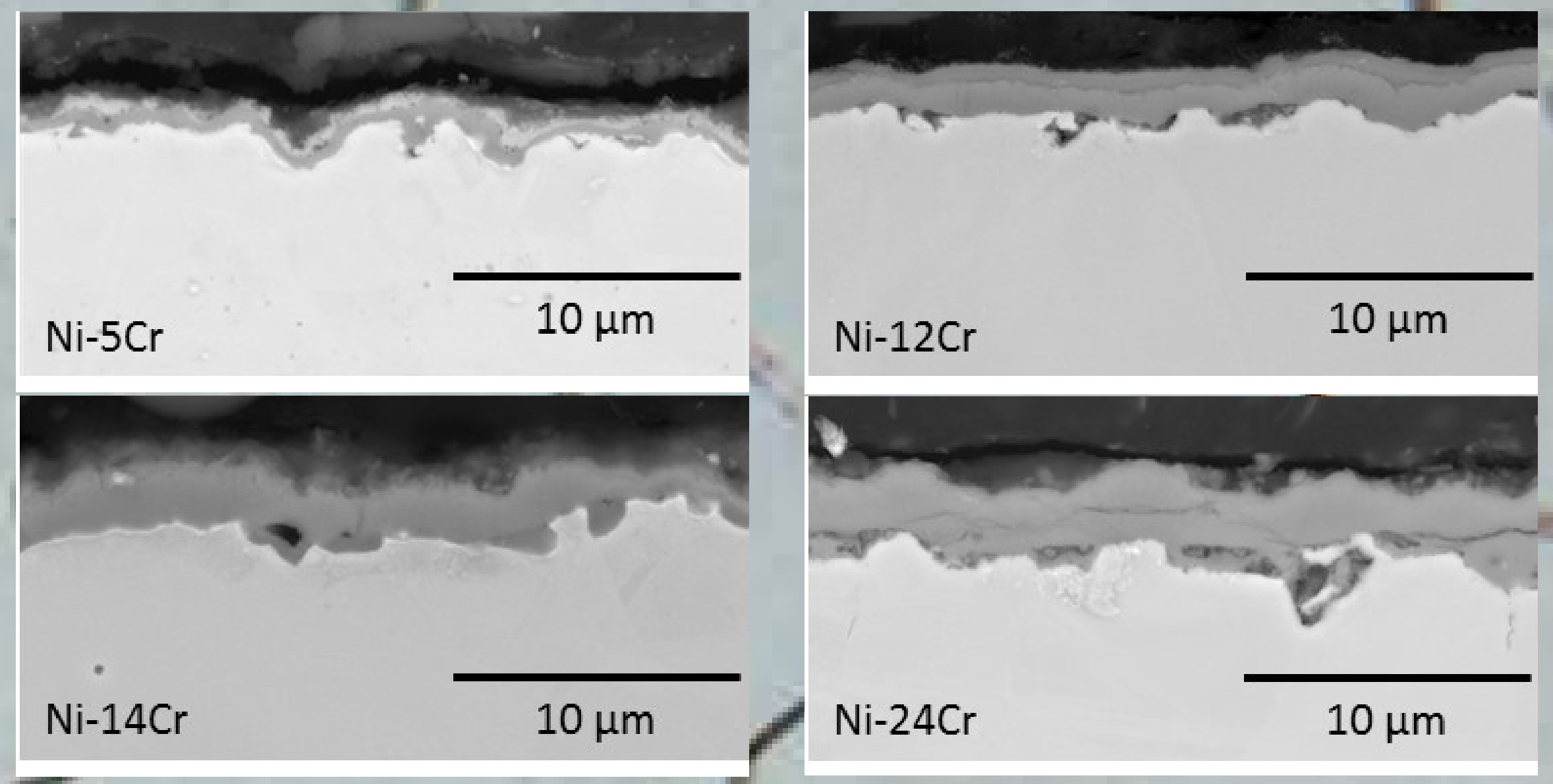
- Commercial purity feed stocks
- Binary master alloys of NiCr and Fe-Cr made by VIM+ESR to reduce O and S levels
- Final alloys made with VIM by combining the master alloy with Ni, Fe, and/or Si (or sometimes hot top material from a previous melt)
- Wrought processing
  - Computationally optimized homogenization heat treatment
  - Machined to remove surface defects
  - Wrapped in SS foil and preheated for 3 h
  - Upset forged
  - Forged flattened
  - Step forged and squared in multiple operations to 1.25"
  - Hot rolled to final size, ~0.1"

Alloy	Ni wt%	Cr wt%	Al wt%	Si wt%	Mn wt%	Co wt%	Ti wt%	Fe wt%	Cu wt%	C ppm	N ppm	O ppm	S ppm
91	0.14	8.46	0.01	.036	0.44			Bal	0.16	1000	545		20
Ni5Cr	Bal	5.00	0.02	<0.01	0.02	0.03	0.01	<0.01	0.01	38	8	6	3
Ni12Cr	Bal	12.08	0.01	<0.01	0.01	0.12	<0.01	<0.01	<0.01	233	26	62	13
Ni14Cr	Bal	14.09	0.02	<0.01	<0.01	0.14	<0.01	<0.01	<0.01	311	29	15	7
Ni16Cr	Bal	16.04	0.02	<0.01	<0.01	0.22	0.01	0.02	<0.01	226	43	65	15
Ni18Cr	Bal	18.13	0.04	<0.01	<0.01	0.25	<0.01	0.02	0.01	270	50	17	8
Ni20Cr	Bal	20.08	0.03	<0.01	<0.01	0.26	<0.01	0.05	0.01	228	72	44	12
Ni22Cr	Bal	22.10	0.05	<0.01	<0.01	0.39	<0.01	0.16	<0.01	149	88	27	12
Ni24Cr	Bal	24.06	0.03	<0.01	<0.01	0.31	<0.01	0.12	0.01	119	96	38	16

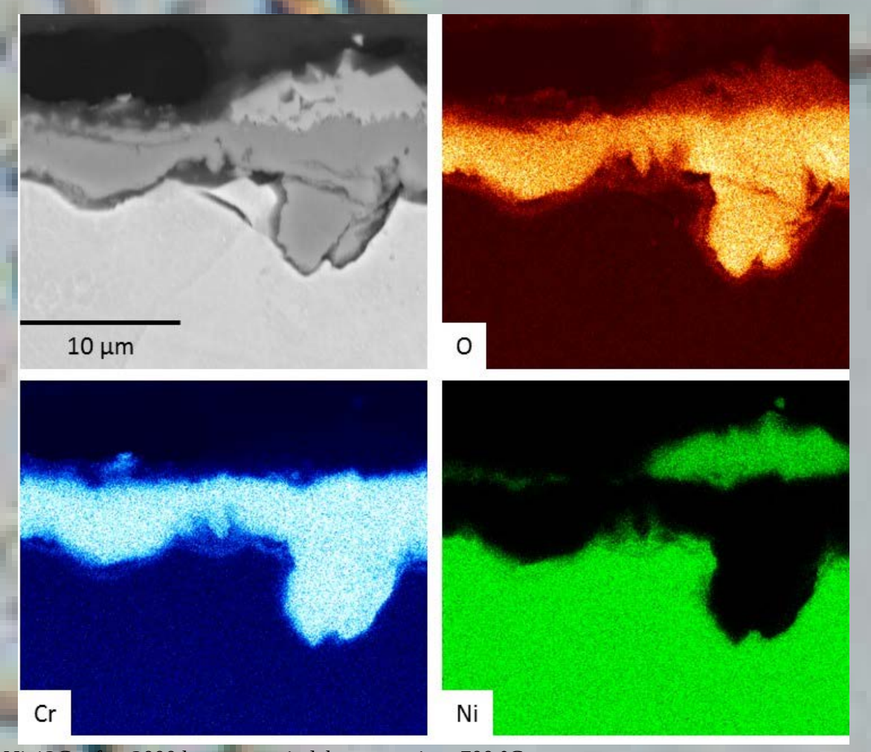
Critical Cr Content in Ni Alloys



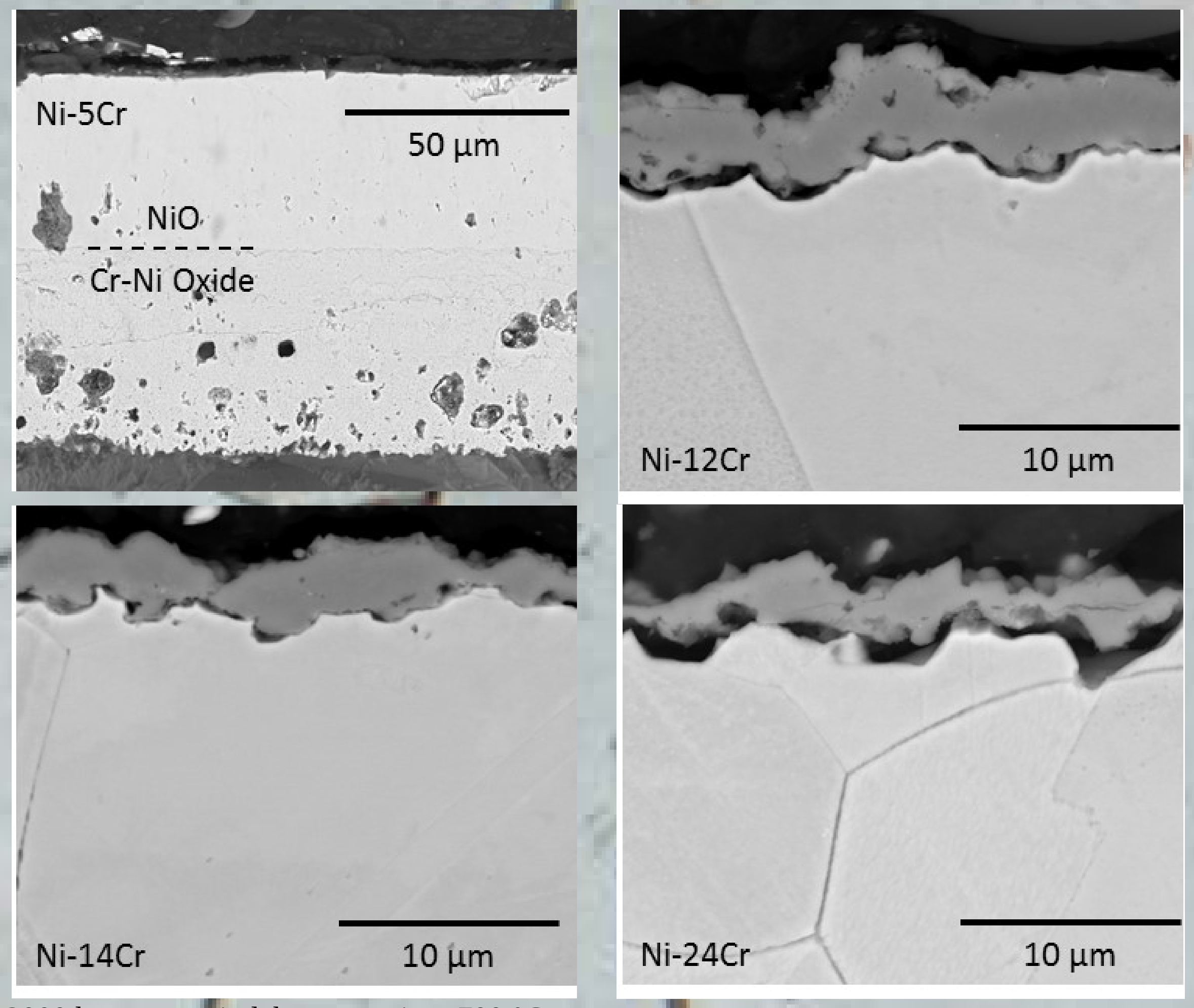




2000 h exposure in aCO_2 at 700 °C



Ni-12Cr after 2000 h exposure in laboratory air at 700 °C



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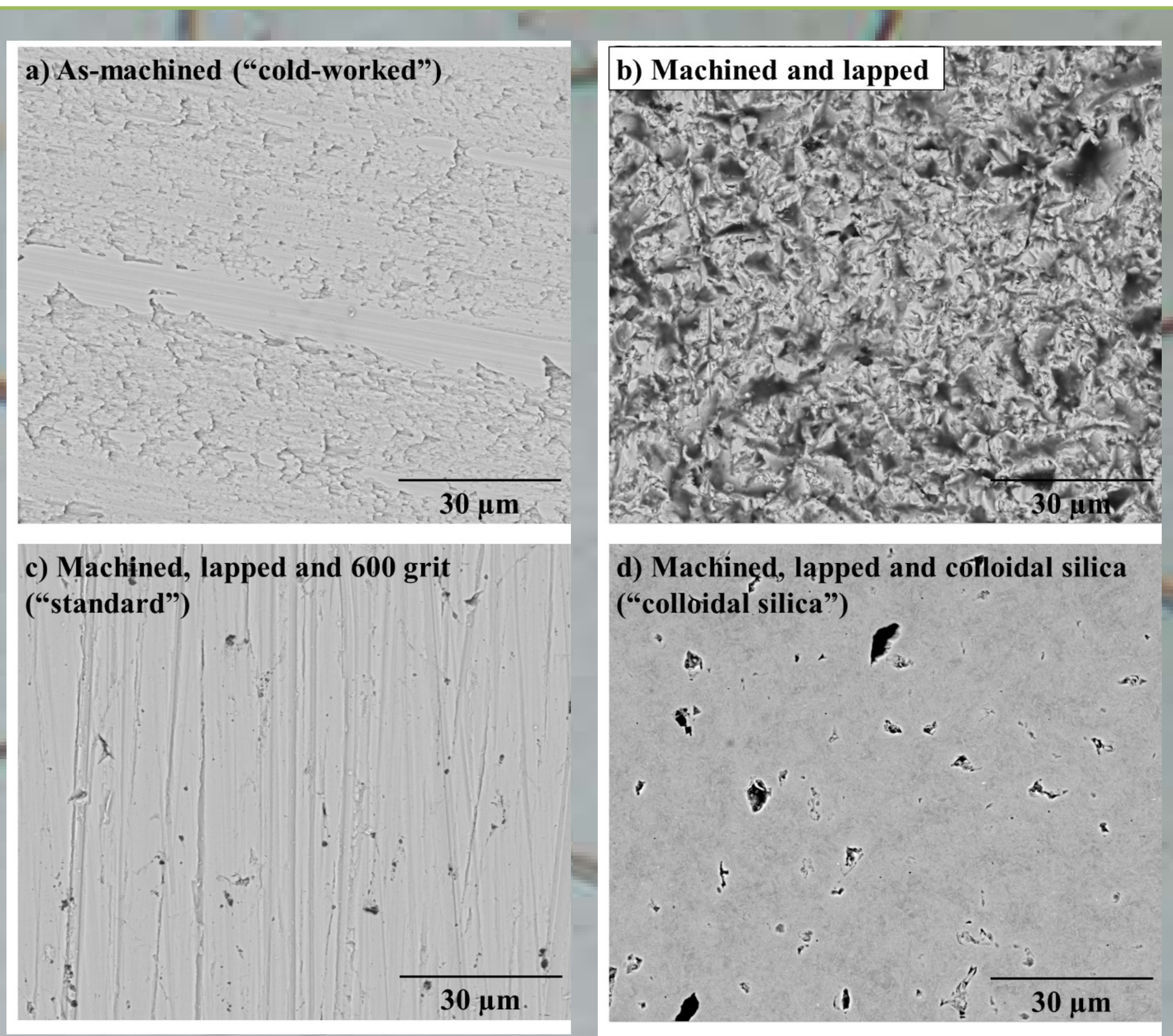
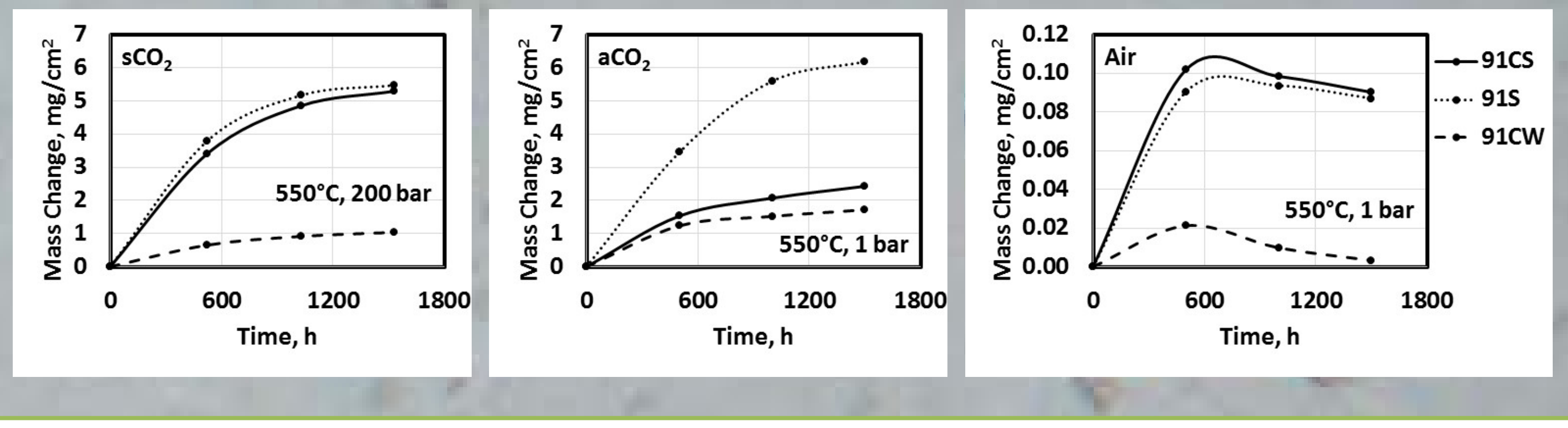
Surface Finish of Grade 91 Ferritc Steel



Alloy 91 with four different surface finishes. (a), (c), and (d) show the surfaces of samples 91CW, 91S, and 91CS, respectively



Summary

The oxidation responses of Ni-xCr model alloys (where x varied from 5 to 24 wt%) were compared in six high temperature environments.

- The Ni-5Cr alloy in pure CO_2 environments (sCO_2 and aCO_2) was at least somewhat protective, while it was unprotective in the other environments.
- When H_2O or O_2 was part of the gas phase, a transition to protective kinetics occurred somewhere between 5-12Cr in DF4, DF4S and air, and at 14Cr in sH_2O.
- The oxygen activity in sCO_2 and sH_2O were similar, so H_2O was more aggressive than CO_2 for the Ni-5Cr alloy.

The ability to remain protective at low Cr values indicates that nickel base superalloys may be resilient to damage that exposes near-surface alloy that is depleted Cr—especially in pure CO_2.

- The oxidation responses of ferritic steel Grade 91, with three different surface finishes, were compared in three different environments at 550 °C.
- The mass gains in air were much lower than in CO_2 environments.
- The benefits of near surface cold work were observed—the samples with the most cold work had the smallest mass gains in all three environments.
- This indicates that surface enhancements to induce more residual stress, such as shot peening, may be of benefit for 9-12Cr ferritic-martensitic steels in sCO_2.

Acknowledgements

This work was performed in support of the US Department of Energy's Fossil Energy Crosscutting Technology and Advanced Turbine Research Programs. The Research was executed through NETL Research and Innovation Center's Advanced Alloy Development Field Work Proposal. Research performed by AECOM Staff was conducted under the RES contract DE-FE-0004000.

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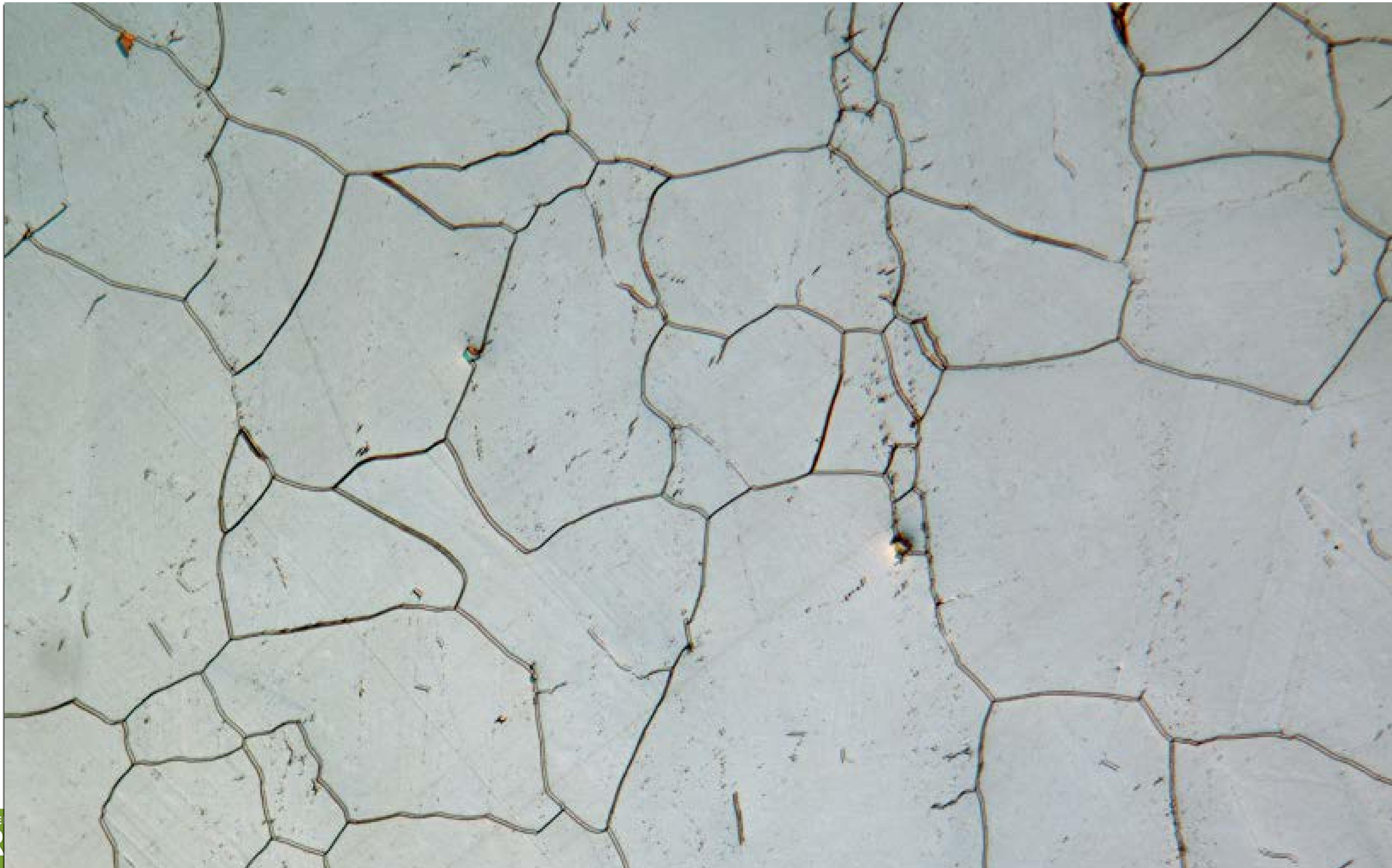

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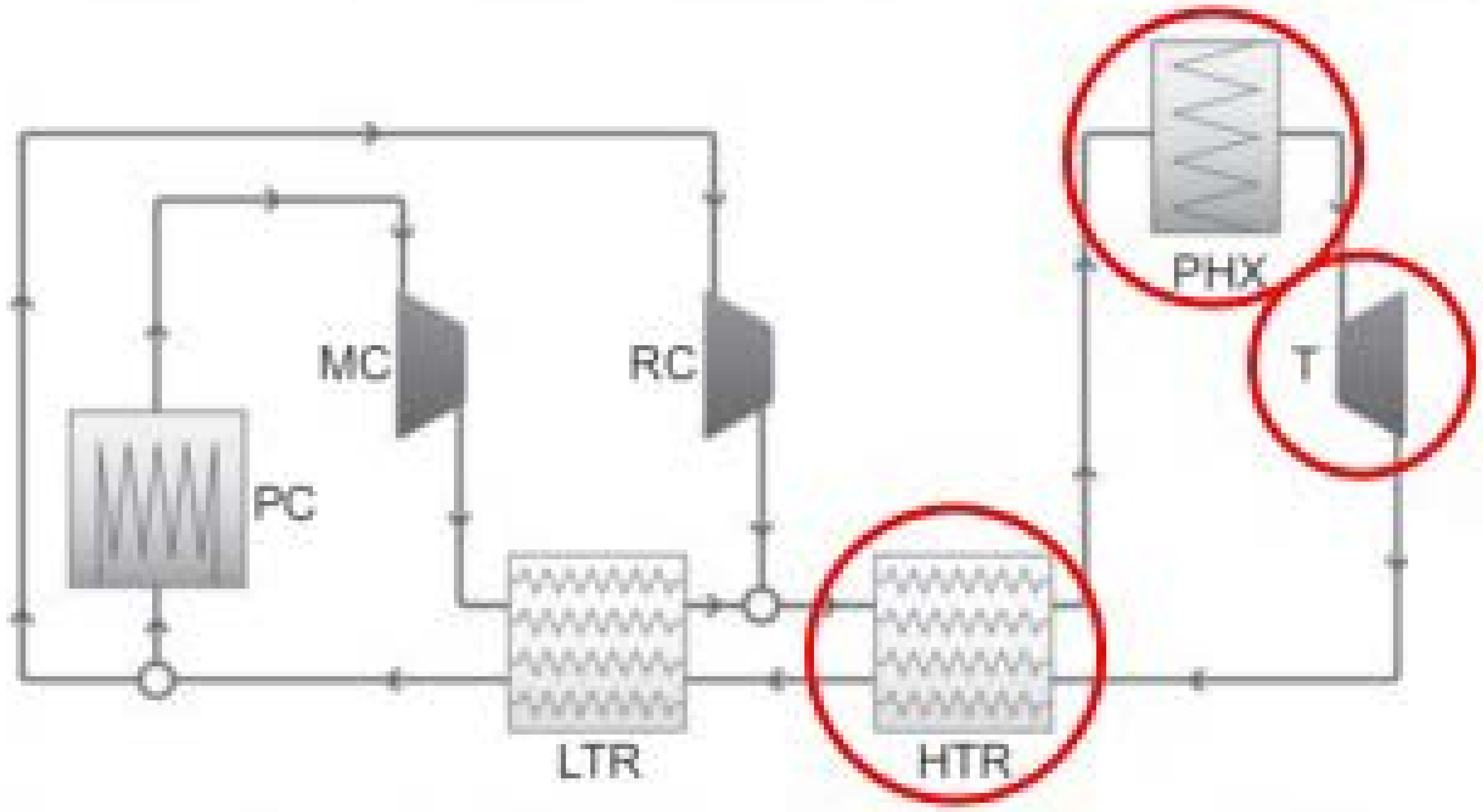

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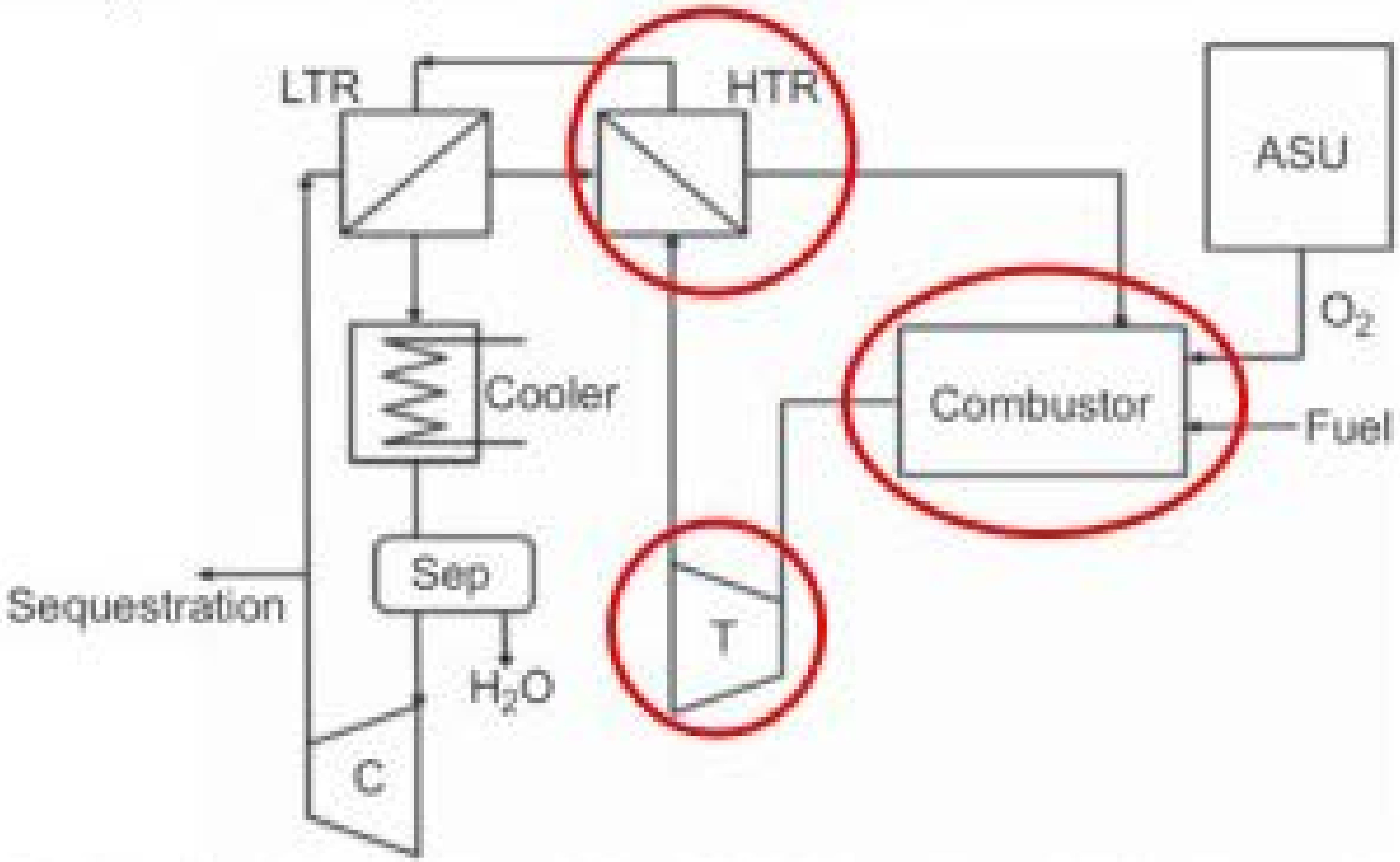

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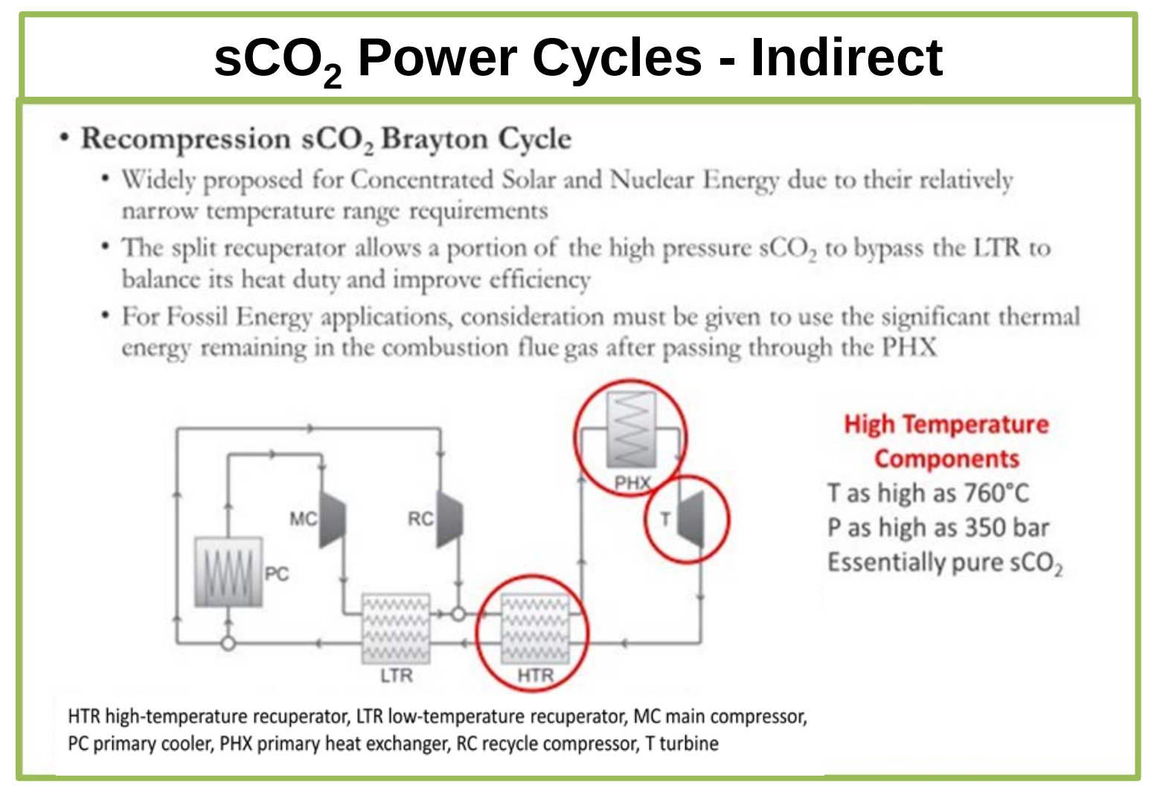

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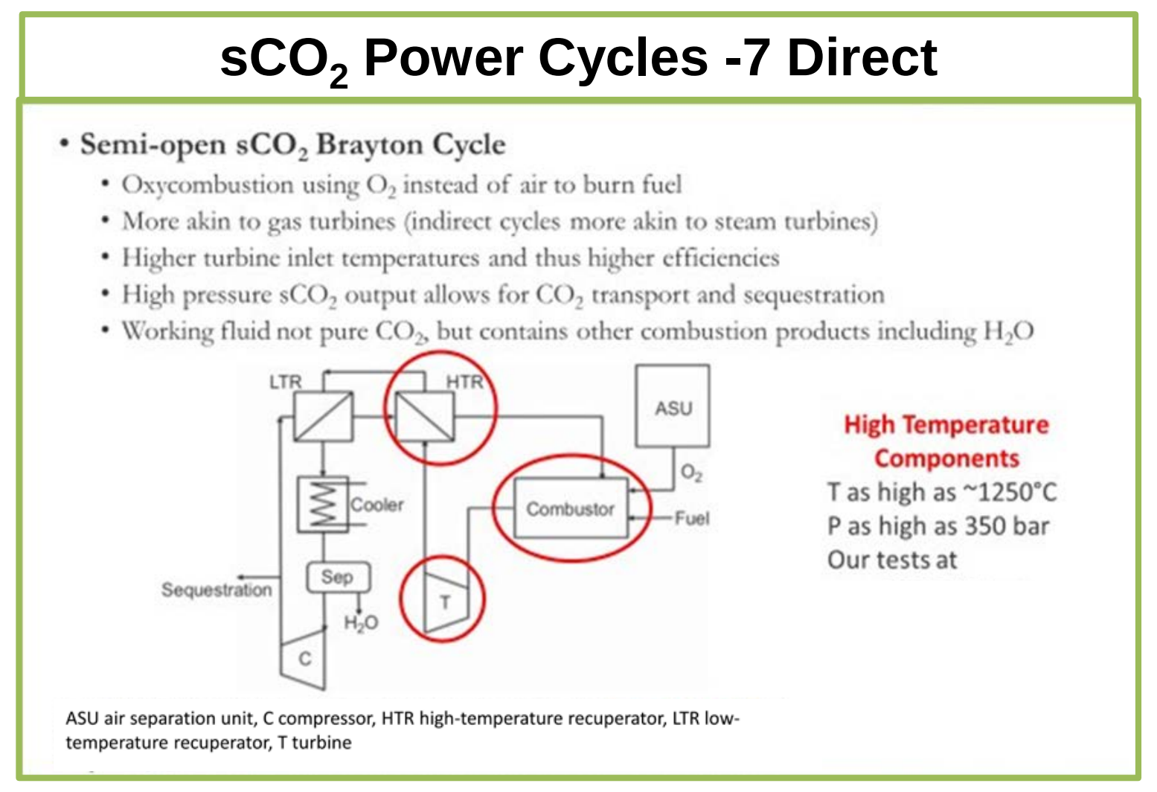

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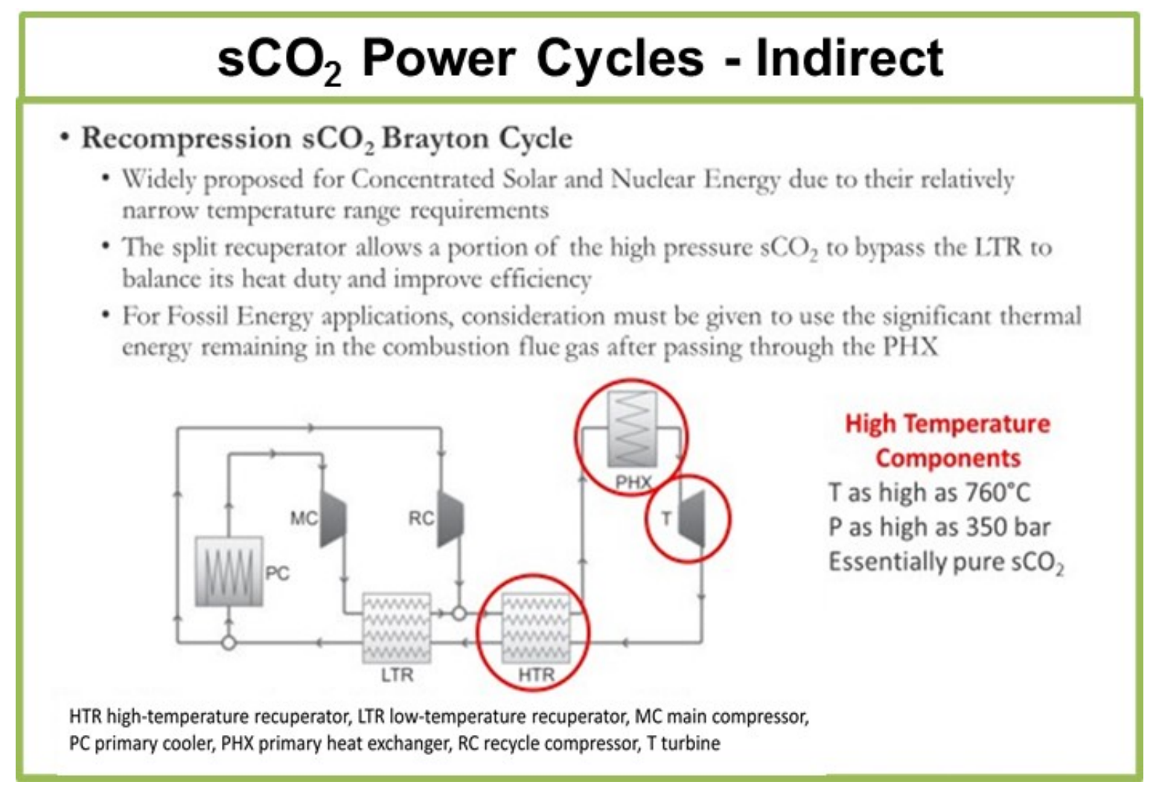

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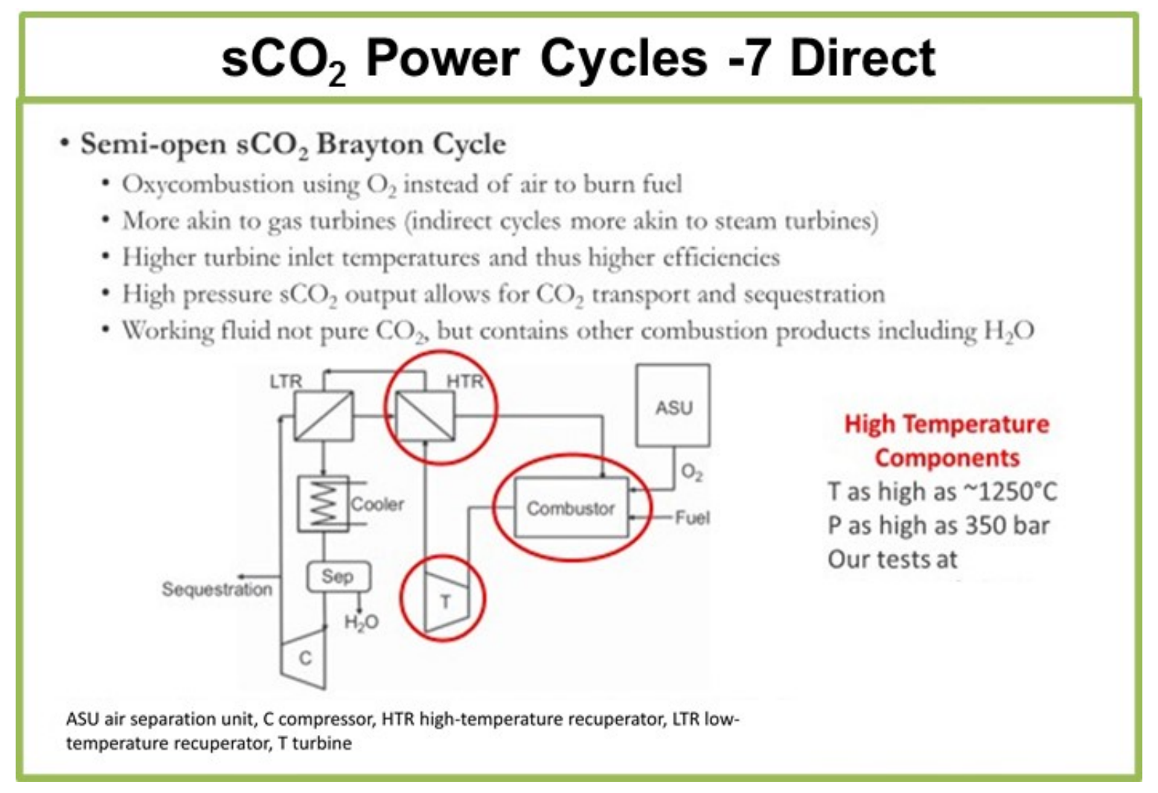

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