In Situ Study of High Temperature Oxidation of Alloys Using Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Why Supercritical CO_2 Power Cycles?

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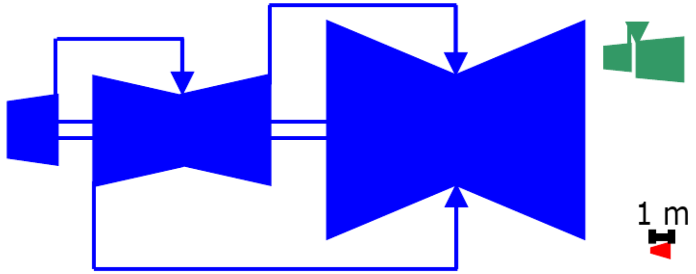
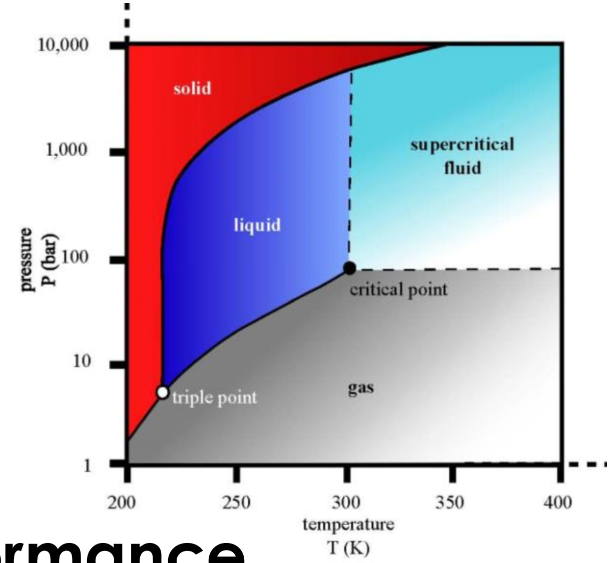
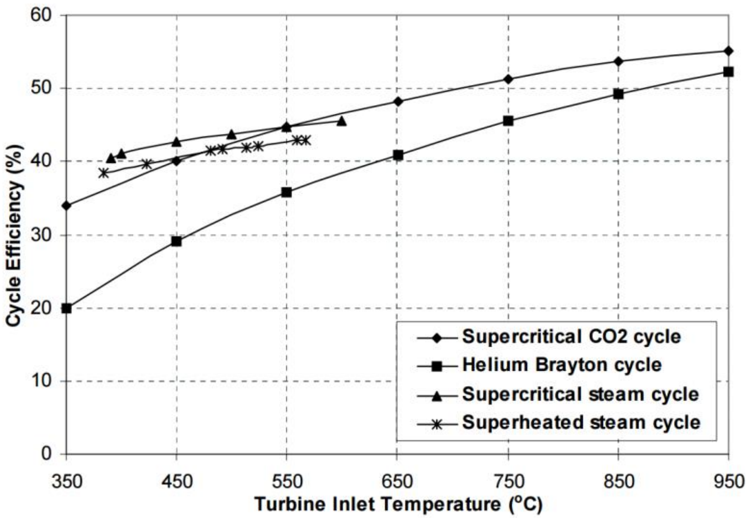
Efficient and Sustainable Power Production

Properties of sCO_2 Cycles	Impact
No phase change (Brayton Cycle)	Higher efficiency
Recompression near liquid densities	Higher efficiency
High heat recuperation	Higher efficiency
Compact turbo machinery	Lower capital cost
Simple configurations	Lower capital cost
Dry/reduced water cooling	Lower environmental impact
Storage ready CO_2 in direct cycles	Lower environmental impact



S. A. Wright, "OVERVIEW OF SUPERCRITICAL CO2 POWER CYCLE DEVELOPMENT AT SANDIA NATIONAL LABORATORIES," in *2011 University Turbine Systems Research Workshop*, Columbus, Ohio, 2011.



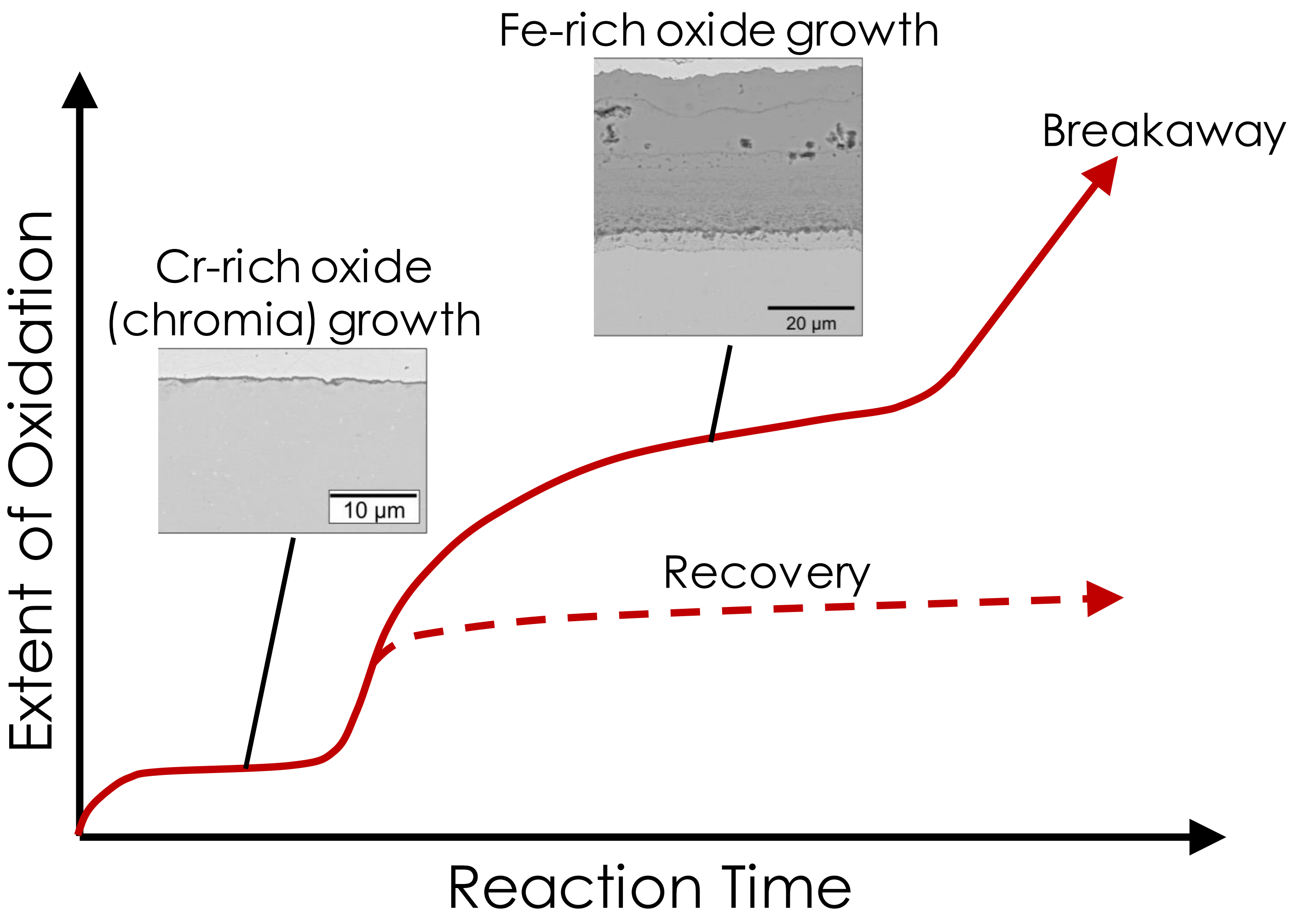


M. J. Driscoll, "Optimized, Competitive Supercritical-CO2 Cycle GFR for Gen IV Service," MIT-GFR-045, 2008.

Understanding alloy oxidation performance in CO_2 is crucial to enabling this technology

Oxidation Regimes of Fe-Cr Alloys in Hot CO_2

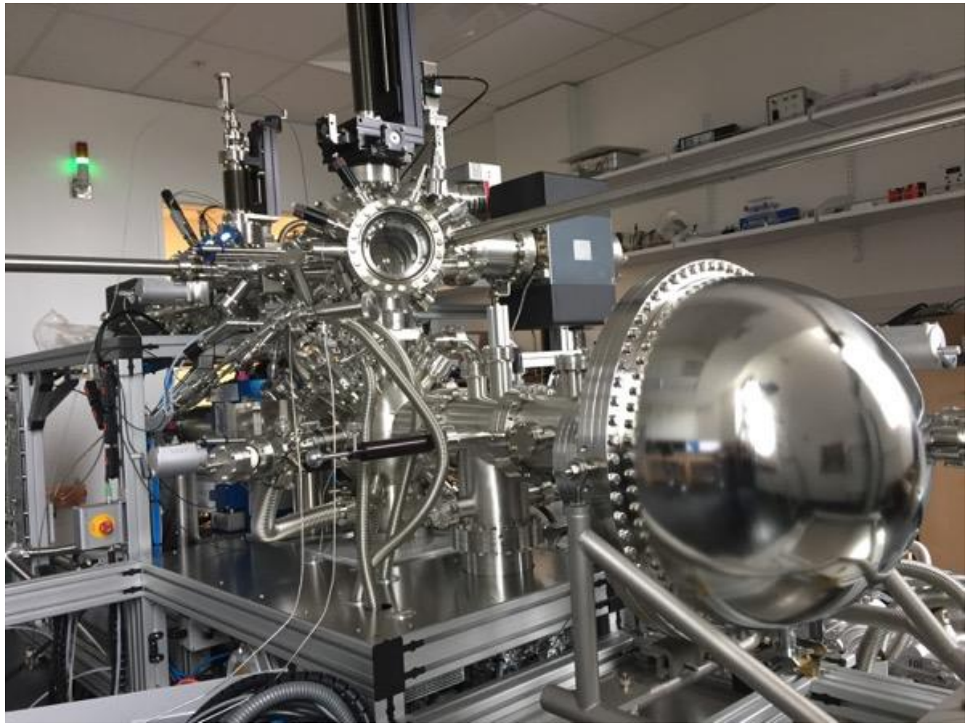
Understanding Early-Stage Processes to Predict Long-Term Performance



- Chromia forming Fe-based and Ni-based alloys are leading candidates for sCO_2 power cycles due to combination of creep strength and (potentially) oxidation resistance at the conditions of interest.
- Understanding factors that affect the formation and stability of chromia scales is critical.

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

A Surface-Sensitive Technique to Study Interfacial Reactions In Situ



AP-XPS at Oregon State University

Materials: Fe22Cr and Fe22Ni22Cr model alloys (wt%).

Sample prep: Alloys were polished using colloidal silica and cleaned to remove most of the carbon surface contamination with minimal change to the native oxide layer.

Exposure conditions: 0.1 to 1 mbar of flowing high purity (99.999%) CO_2 or low purity (99.9%) CO_2 at temperatures up to 530 °C.

This allowed in situ measurements during the very initial stages of oxidation in high temperature CO_2.

$pCO_2 = 10^{-3}$ bar

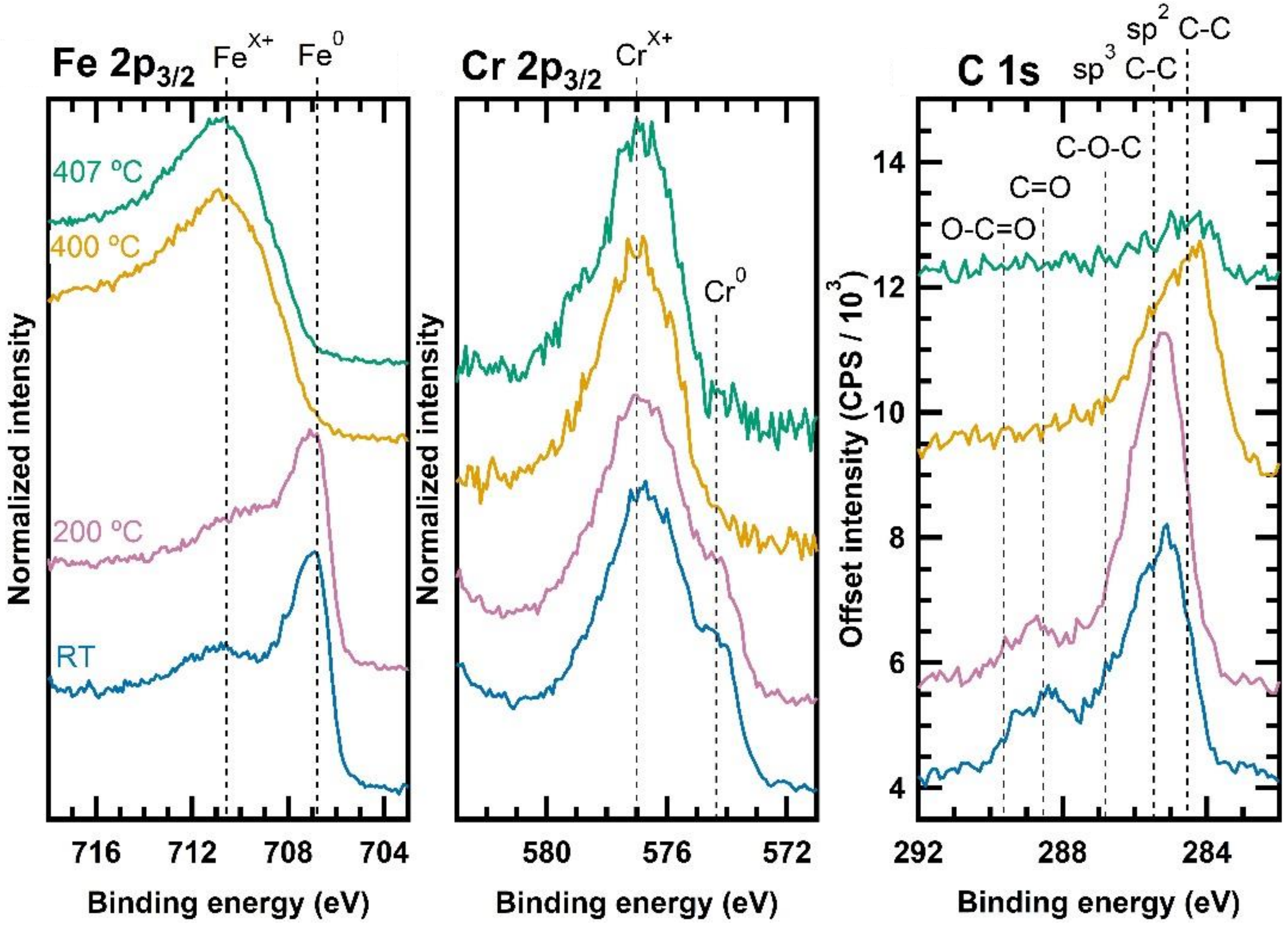
↕

$pO_2 \approx 10^{-12}$ bar

Equilibrium reaction	pO_2 (bar)
$2Ni + O_2 = 2NiO$	10^{-23}
$1/2Fe + O_2 = 1/2Fe3O_4$	10^{-27}
$2/3Cr + O_2 = 2/3Cr_2O_3$	10^{-40}

Significant Fe Oxidation in Low Purity CO_2

AP-XPS of Fe22Cr in Low Purity (99.9%) CO_2



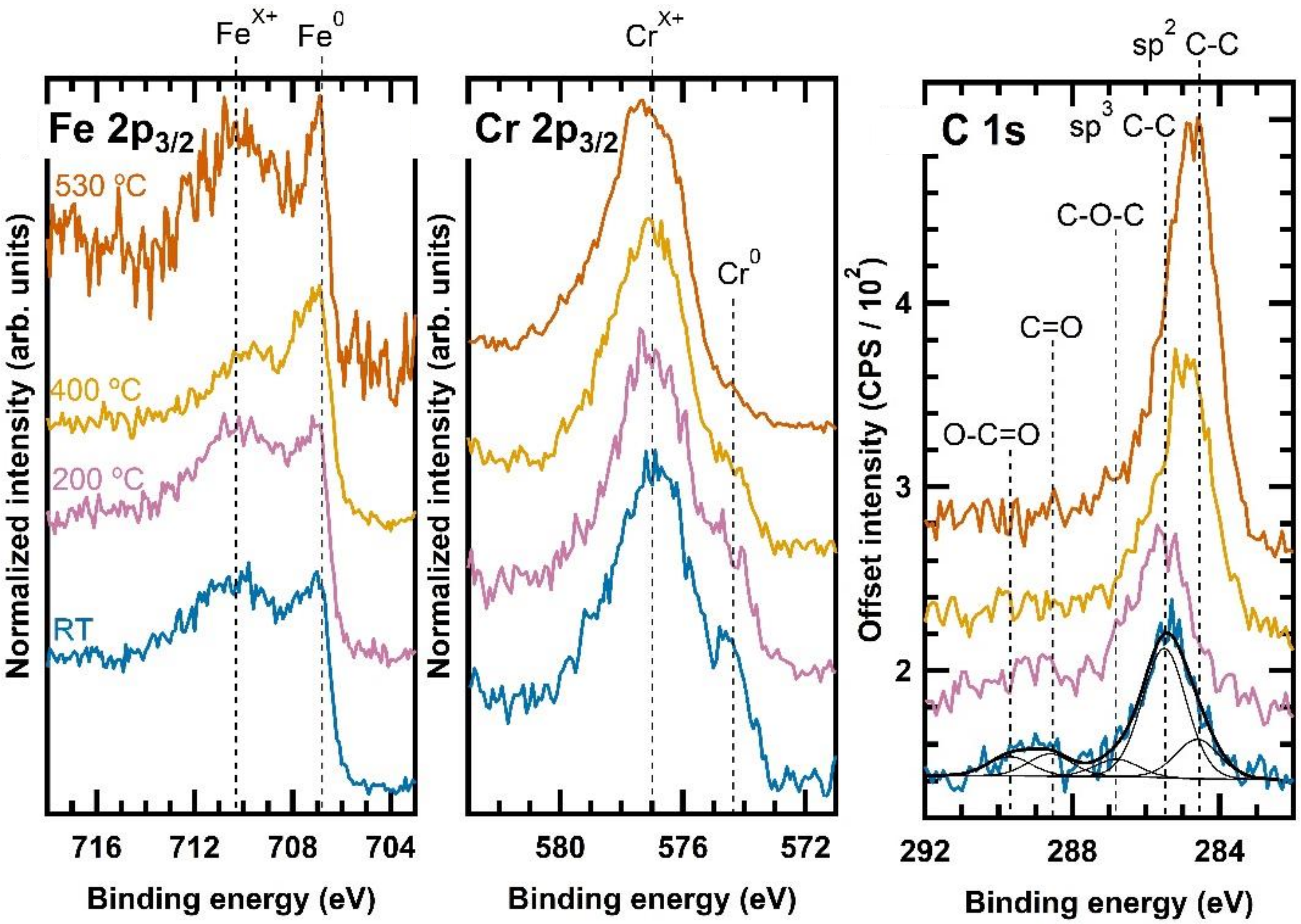
- Significant oxidation of both Fe and Cr, i.e., transient oxidation.
- Surface carbon is unstable and decreases with temperature and time.

$$CO_2 + C = 2CO$$

- This is the "expected" behavior of an Fe-Cr alloy in high temperature CO_2.

Selective Oxidation of Cr in High Purity CO_2

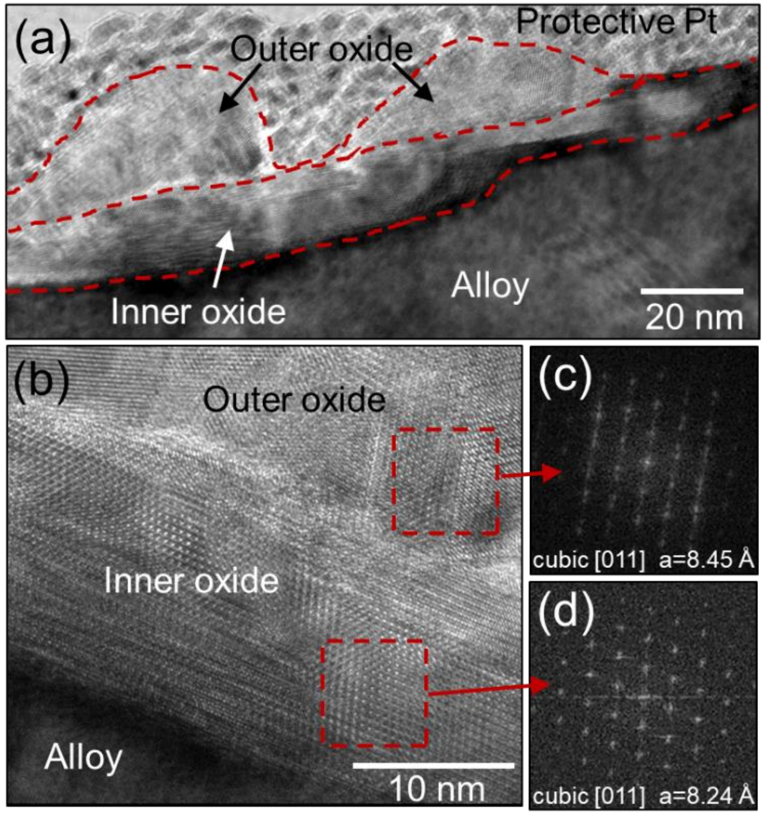
AP-XPS of Fe22Cr in High Purity (99.999%) CO_2



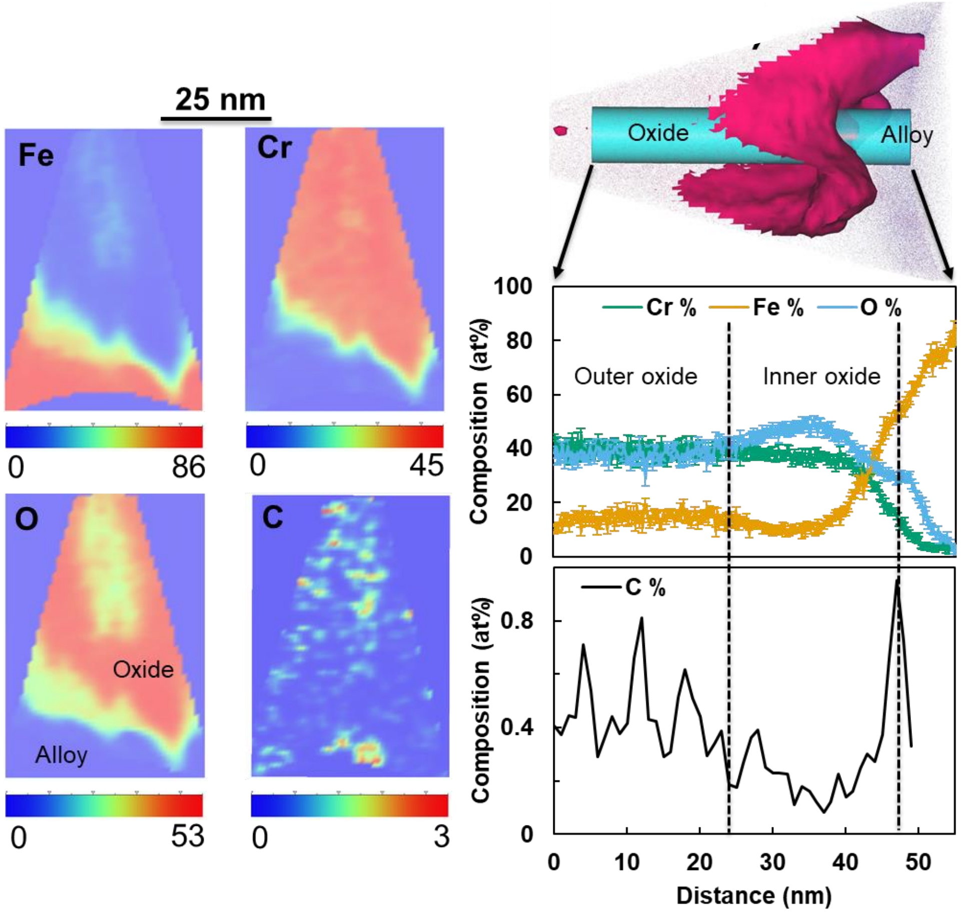
- Significant oxidation of Cr.
- Minimal oxidation of Fe.
- C signal increases and shifts to lower binding energy, which suggests deposition of pure carbon on the oxide surface.
- But C is not stable in pure CO_2?

Visualizing the Oxidized Surface

Post-Exposure TEM and APT of Fe22Cr Exposed to High Purity CO_2

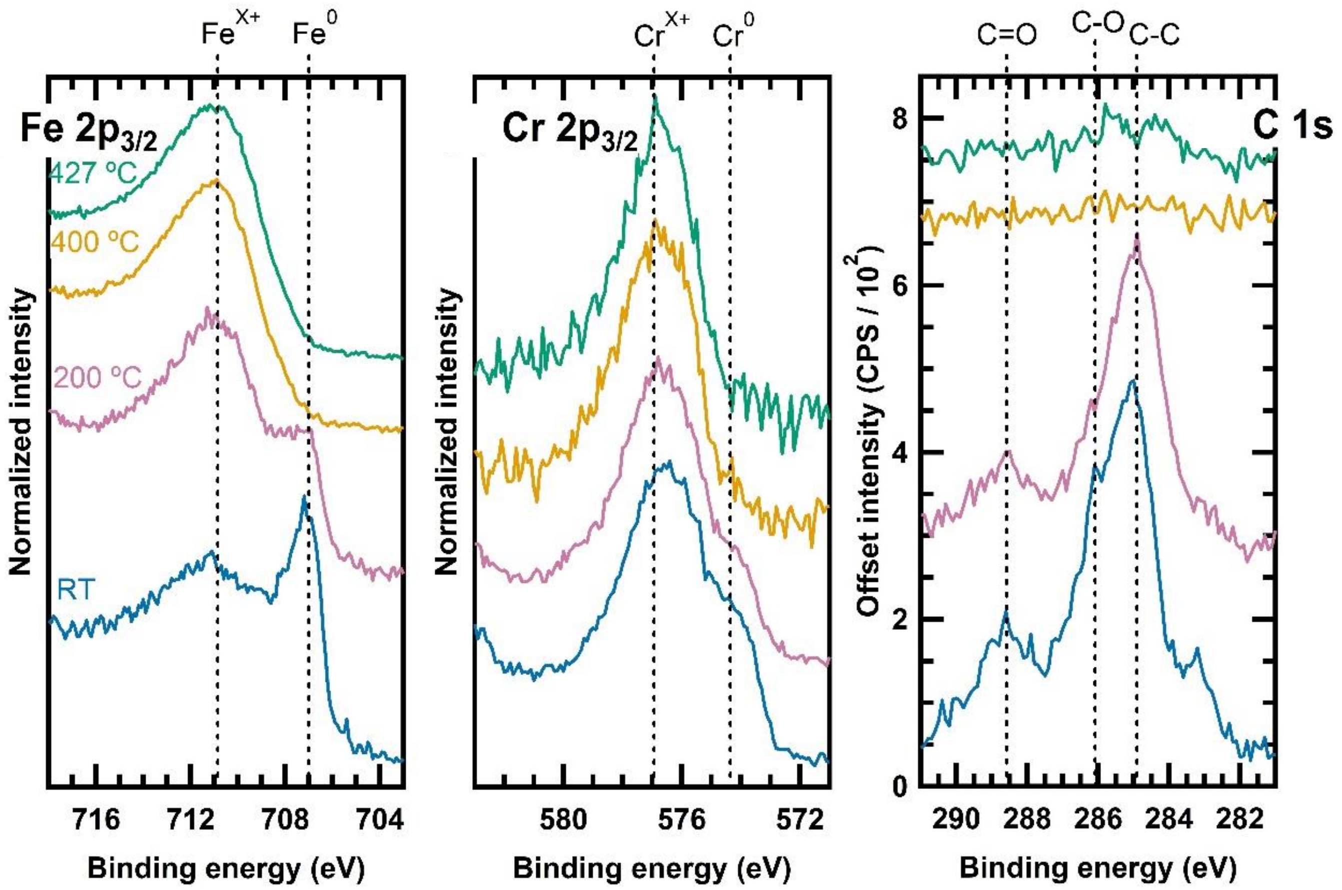


- Two-layer oxide consisting of M_3O_4 spinel structure.
- Oxide is Cr-rich, consistent with AP-XPS results.
- APT confirms carbon diffusion through the oxide layer.



Significant Fe Oxidation in Low Purity CO_2

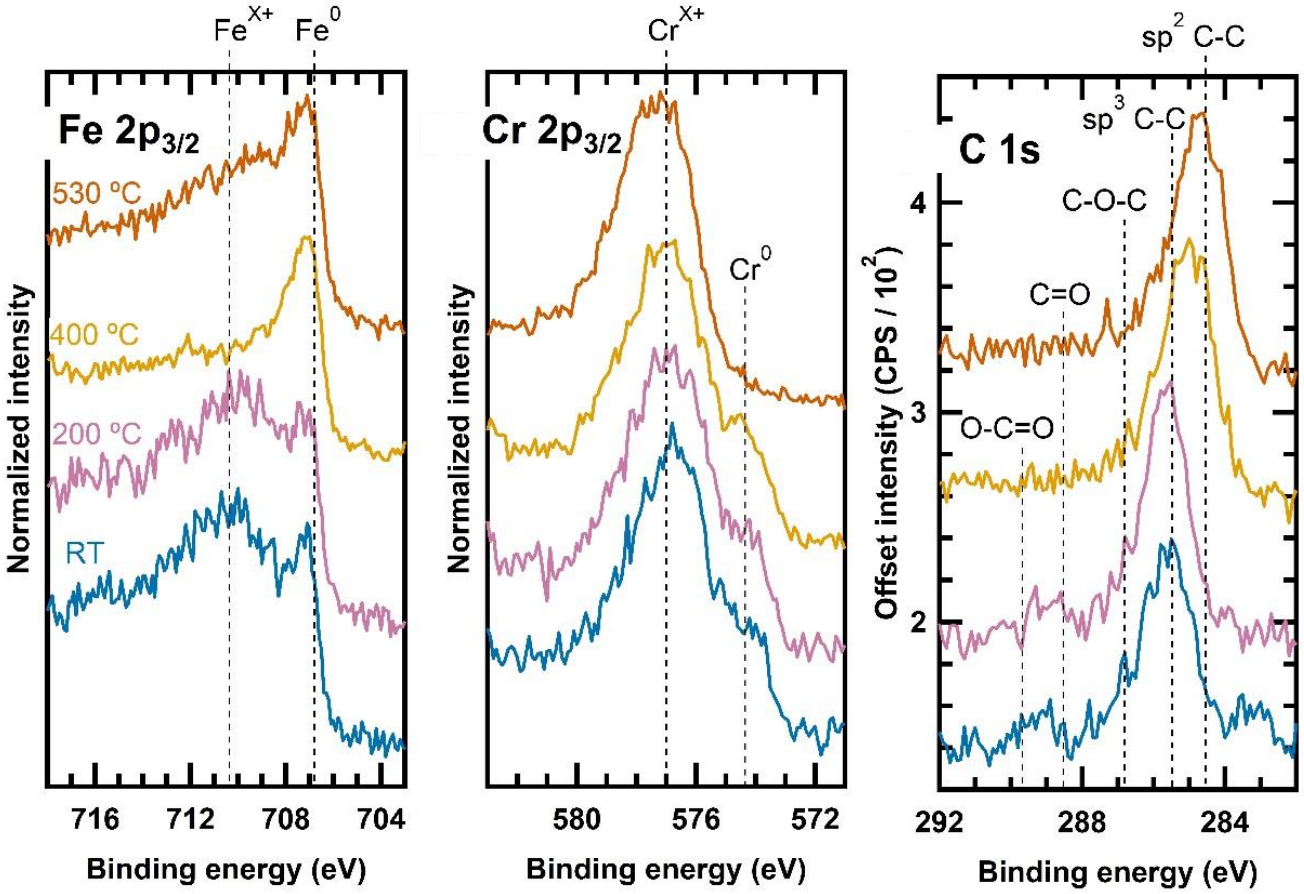
AP-XPS of Fe22Ni22Cr in Low Purity (99.9%) CO_2



- Same behavior as Fe22Cr:
- Significant oxidation of both Fe and Cr.
- Surface carbon is unstable and decreases with temperature and time.
- Minimal participation of Ni (not shown).

Selective Oxidation of Cr in High Purity CO_2

AP-XPS of Fe22Ni22Cr in High Purity (99.999%) CO_2



- Same behavior as Fe22Cr:
- Significant oxidation of Cr.
- Minimal oxidation of Fe.
- C signal increases and shifts to lower binding energy, which suggests deposition of pure carbon on the oxide surface.

Visualizing the Oxidized Surface

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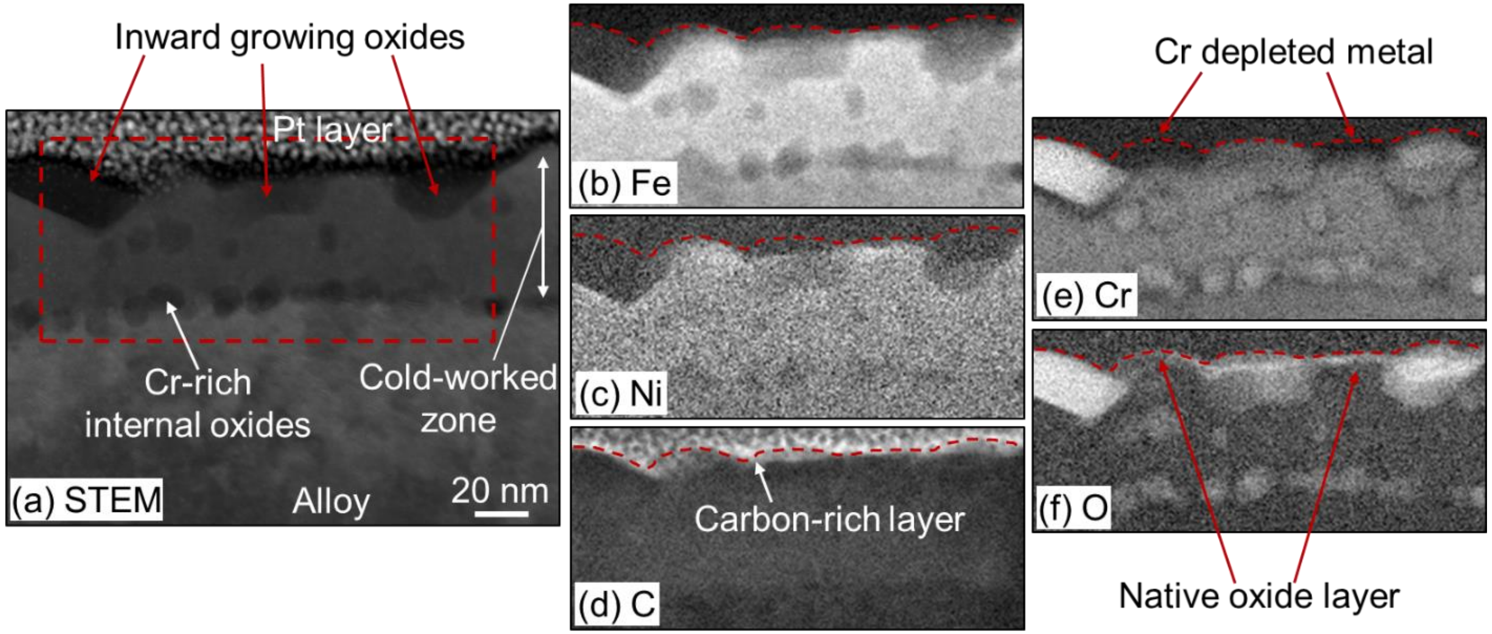
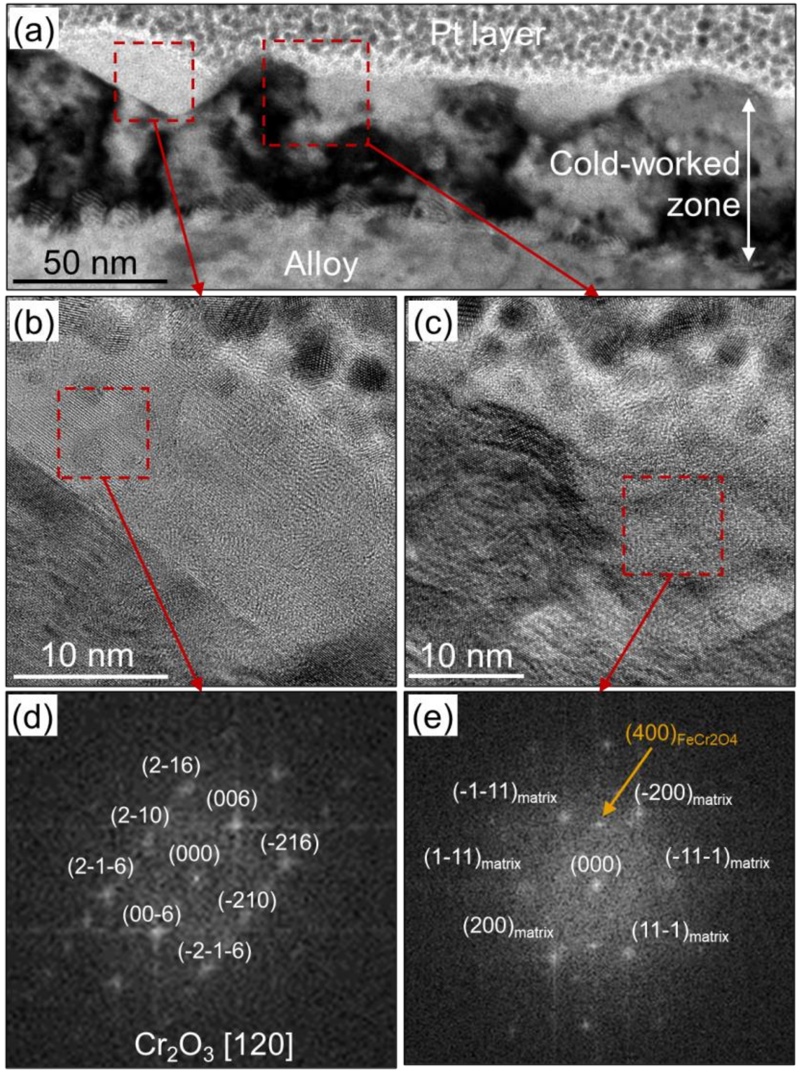
Post-Exposure TEM of Fe22Ni22Cr Exposed to High Purity CO_2

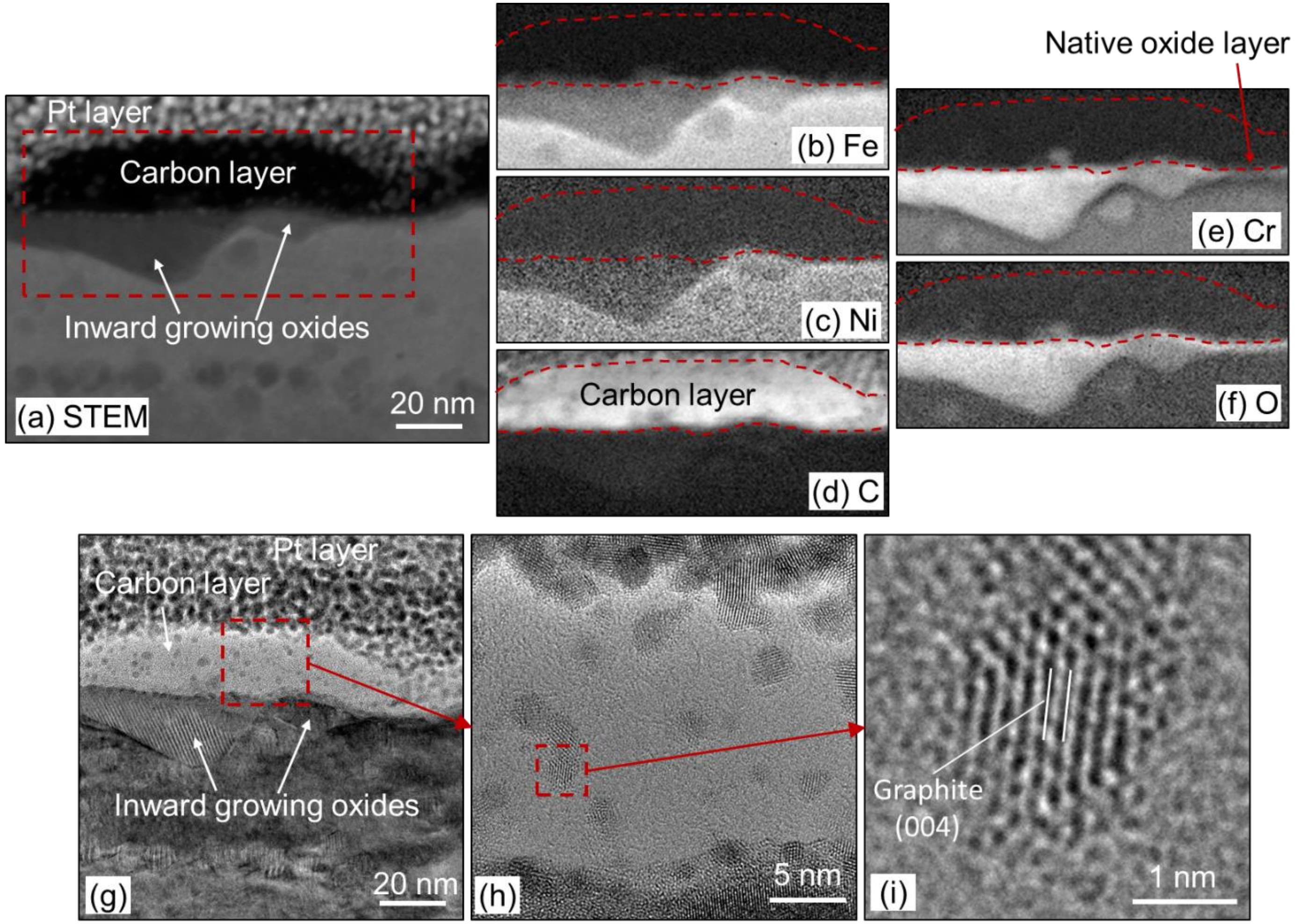




- Oxide is discontinuous and inward growing only.
- Oxide is Cr-rich, consistent with AP-XPS.
- Partial conversion from Cr-rich M_3O_4 to Cr_2O_3.
- Evidence of thin carbon layer on the oxide surface?

Confirmation of Carbon Deposition in High Purity CO_2

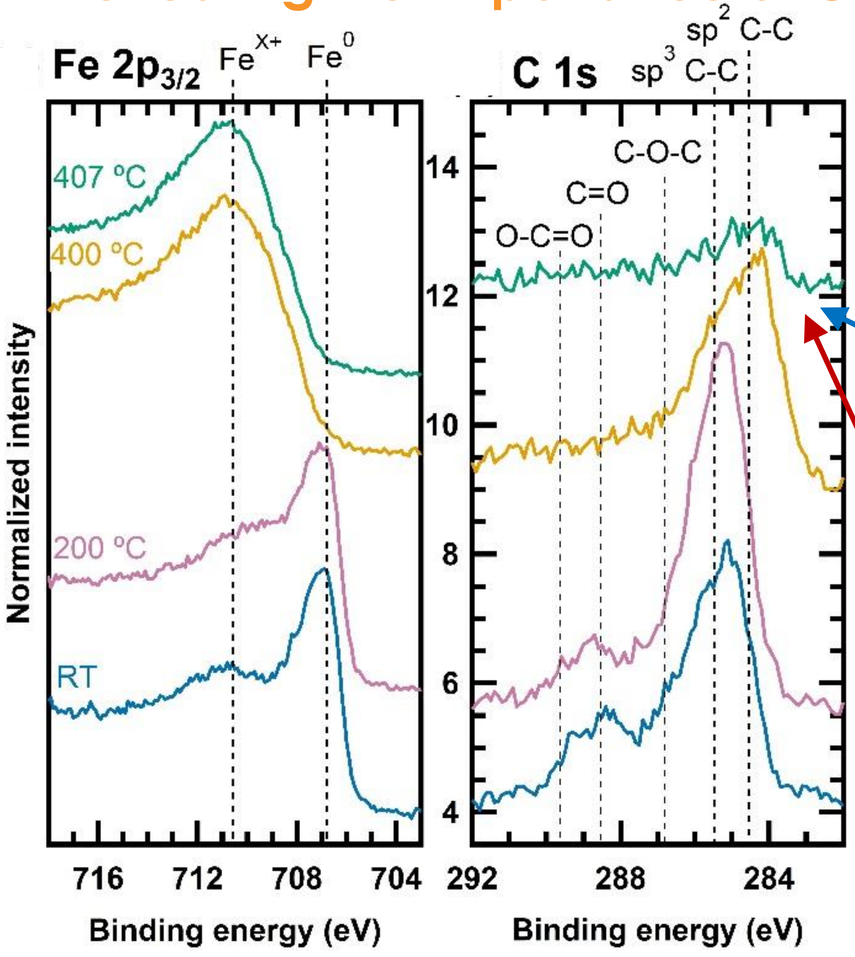
Post-Exposure TEM of Fe22Ni22Cr Exposed to High Purity CO_2



- Regions of significant carbon deposition found periodically across the sample surface.
- Graphite nanoparticles suggest the onset of crystallization, consistent with AP-XPS results.

Proposed Oxidation Mechanism

Revealing the Importance of CO_2 Purity on Competitive Surface Reactions



Low purity CO_2

Oxidation by CO_2

$$CO_2 + M = MO + CO$$

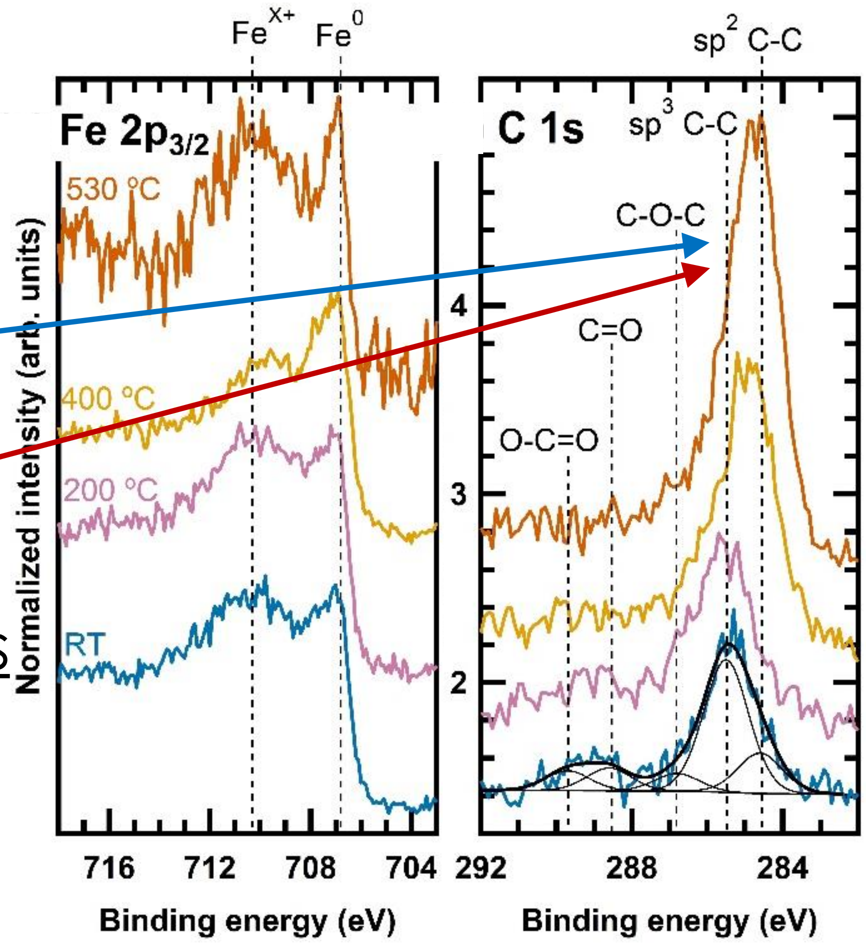
$$CO_2 + C = 2CO$$

$$CO + M = MO + C$$

Oxidation by O_2 impurities

$$O_2 + 2M = 2MO$$

$$O_2 + C = CO_2$$



High purity CO_2

Summary and Conclusions

Summary

- AP-XPS enabled in situ measurements of the first stages of oxidation of Fe22Cr and Fe22Ni22Cr alloys in high temperature CO_2.
- The competitive surface reactions driving metal oxidation result in deposition of carbon onto the oxide surface in high purity CO_2, thus revealing a gas/oxide interface that is far from local thermodynamic equilibrium.
- Surface carbon significantly reduces the oxygen activity at the oxide surface, promoting the selective oxidation of Cr.

Conclusions

- CO_2 purity is critical for quickly establishing a protective chromia scale.
- AP-XPS is powerful technique to study high temperature oxidation of alloys.

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