Hydrogen-assisted Corrosion of Stainless Steels in Dual Atmosphere Exposure Conditions

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Problem Definition: Stainless steels, used as interconnects and balance-of-plant components in SOFC power generation systems, experience aggressive corrosion when exposed simultaneously to a “dual atmosphere” comprising of an oxidizing and a reducing gas atmosphere. This corrosion, manifested as epitaxial outwardly-growing iron oxide of platelet and whisker-type morphology on the oxidizing gas-exposed side, is particular to the dual atmosphere condition, as a stainless steel exposed to a single oxidizing atmosphere does not show nearly the extent of corrosion or metal loss. The dual atmosphere exposure condition, particularly, the presence of hydrogen on the reducing gas side of the steel, is hypothesized to accelerate the “breakaway” oxidation of iron. Although hydrogen readily diffuses into the stainless steel at elevated temperatures, the affect it has on the increase of breakaway oxidation is not well understood. Mechanisms involving thermodynamic and diffusional driving forces will be discussed with respect to the dual atmosphere condition. Experimental data revealing the extent of oxidation for certain stainless steels exposed to dual and single atmospheres for relatively short exposure times up to 800℃ are presented.

Technical Background: A “dual atmosphere” exposure of oxidizing and reducing gas is caused by the gaseous species required for efficient SOFC function. Interconnects separate these gases within the stack to ensure the anode is properly fed with fuel gas and the cathode fed with an oxidant. The two gases should not mix, which highlights the main function of the interconnect. The two gaseous species are also preheated and delivered to the stack from an outside, balance-of-plant system. When metal alloys are used for interconnects and BoP materials, they subsequently are exposed to dual atmosphere. At SOFC operating temperature, the alloys exhibit anomalous, localized corrosion as a result of dual atmosphere exposure (i.e. this phenomenon does not occur in air). Presented below are observational findings which describe this dual atmosphere corrosion

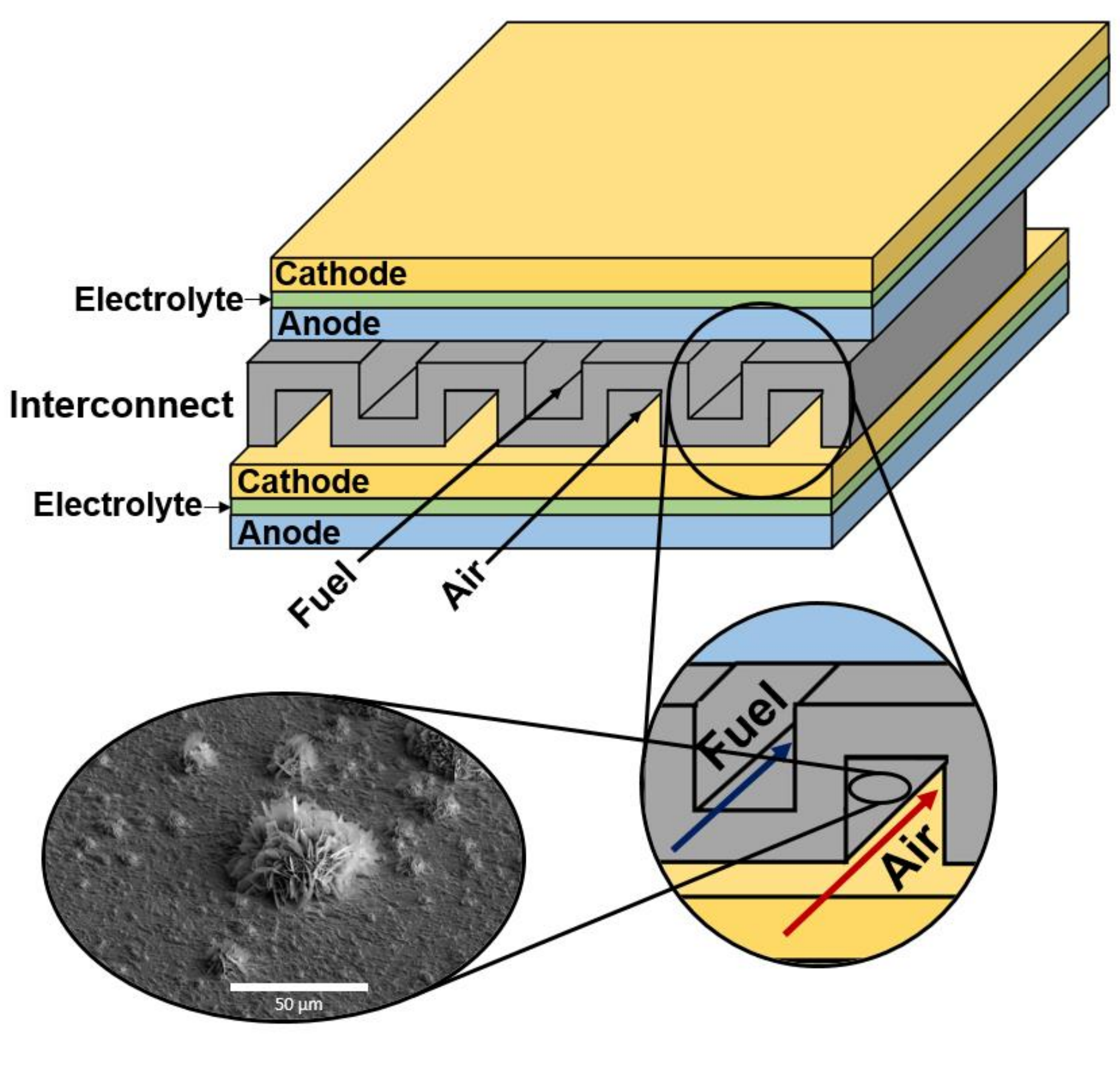
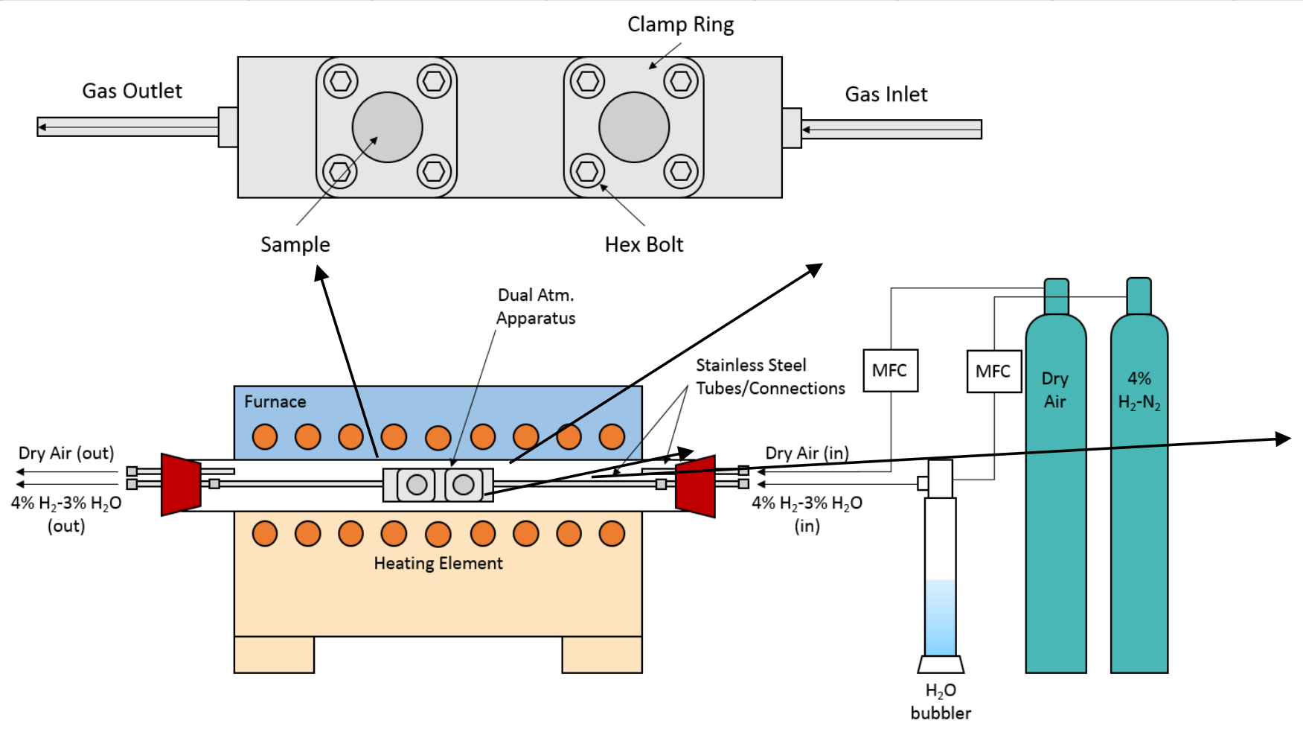


Figure 1. Schematic of cell stack, highlighting gas flow separation function of the interconnect

Experimental: A high throughput experimental test set up has been assembled to examine up to 8 samples under single and dual atmosphere conditions

Test Specimen	Composition (wt. %)										
	Cr	Mo	Ni	Mn	Si	C	Ti/Nb	N/B	P	S	Fe
Steel 1	18.0	1.90	≤1.0	≤1.0	≤1.0	≤0.025	≤0.80	≤0.035/ -	≤0.04	≤0.03	bal.
Steel 2	20.0	-	8.0-10.5	≤2.0	≤0.75	≤0.08	-	≤0.1/ -	≤0.045	≤0.03	bal.



Test Matrix

Time: 10 - 500 h

Temperature: 500 – 800C °C

Alloys: Ferritic steels

Atmosphere:

Single: Dry air/Dry air

Dual: H_2-H2O-N_2 | Dry Air

Figure 2. Schematic of dual atmosphere test rig and overall test set-up for simulated dual atmosphere exposure

Observations: Morphological Changes

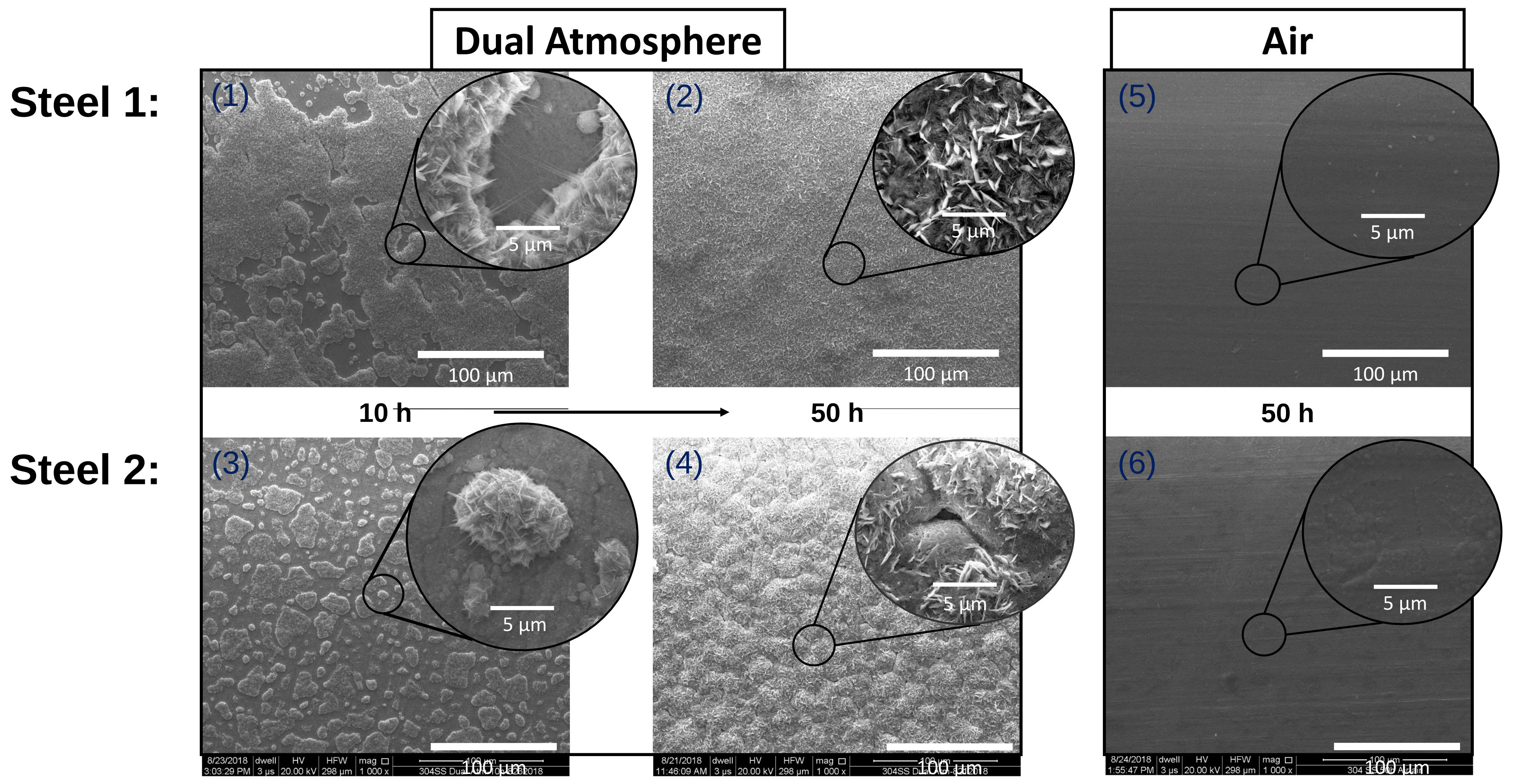


Figure 3. Scanning Electron Microscope (SEM) micrographs of Steel 1 exposed to dual atmosphere for 10 h (1) and 50 h (2), Steel 2 exposed to dual atmosphere for 10 h (3) and 50 h (4), Steel 1 exposed to air on both sides for 50 h (5), and Steel 2 exposed to air on both sides for 50 h (6)

XRD: Compound Formation

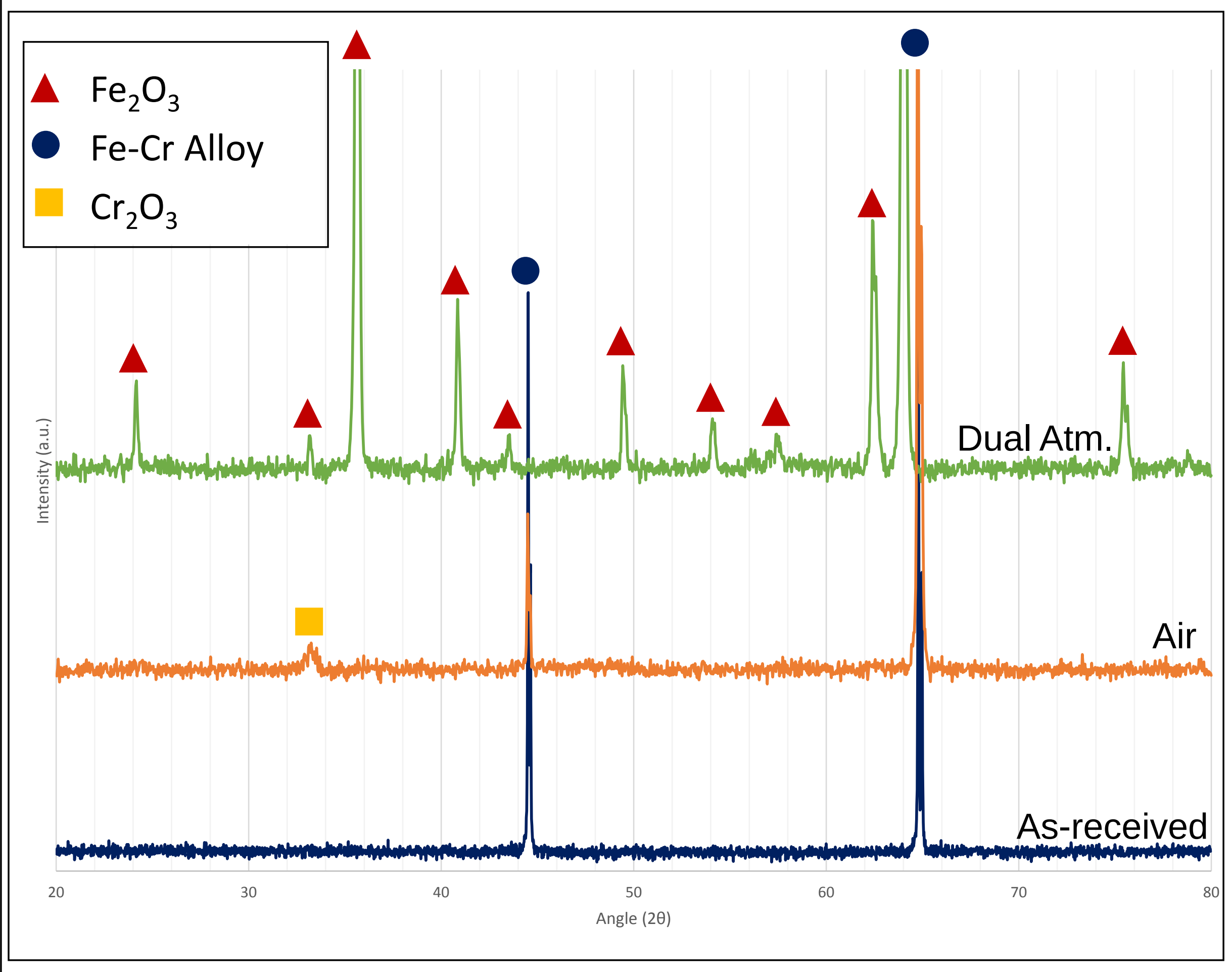
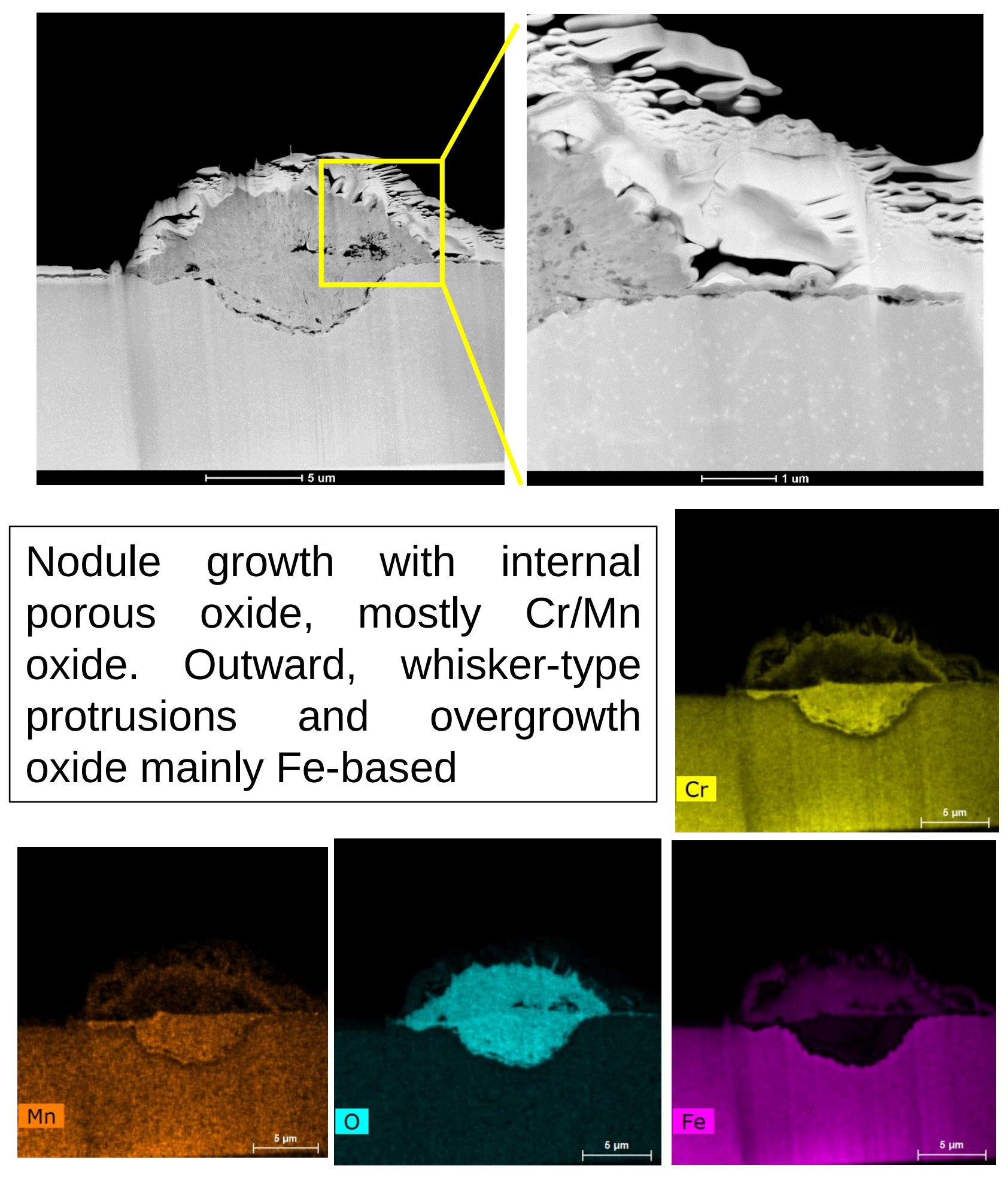


Figure 4. X-Ray Diffraction (XRD) pattern comparison for Steel 1 as-received, Steel 1 exposed to air on both sides for 50 h, and Steel 1 exposed to dual atmosphere for 50 h

TEM: X-Sectional Analysis



Nodule growth with internal porous oxide, mostly Cr/Mn oxide. Outward, whisker-type protrusions and overgrowth oxide mainly Fe-based

Figure 3. Transmission electron microscope (TEM) image of oxide nodule grown on a ferritic stainless steel after 50 h of dual atmosphere exposure

Discussion

Dual atmosphere exposure conditions lead to anomalous corrosion – local metal loss with buildup of iron oxide rich nodular scale

- Multiple cations are present in stainless steels, however, Fe preferentially oxidizes locally forming nodules and platelets
- Oxidation and nodular growth is time dependent – increasing in severity with time
- Samples exposed to dry air do not exhibit local metal loss and nodular growth
- Localized metal corrosion and nodular scale formation is hypothesized to be due to:
  - Transport of atomic H through metal and reaction with oxide at the metal-oxide interface
  - Development of redox H_2-H_2O atmosphere at/within metal oxide
  - Modification of metal oxide defect structure and accelerated transport of cations

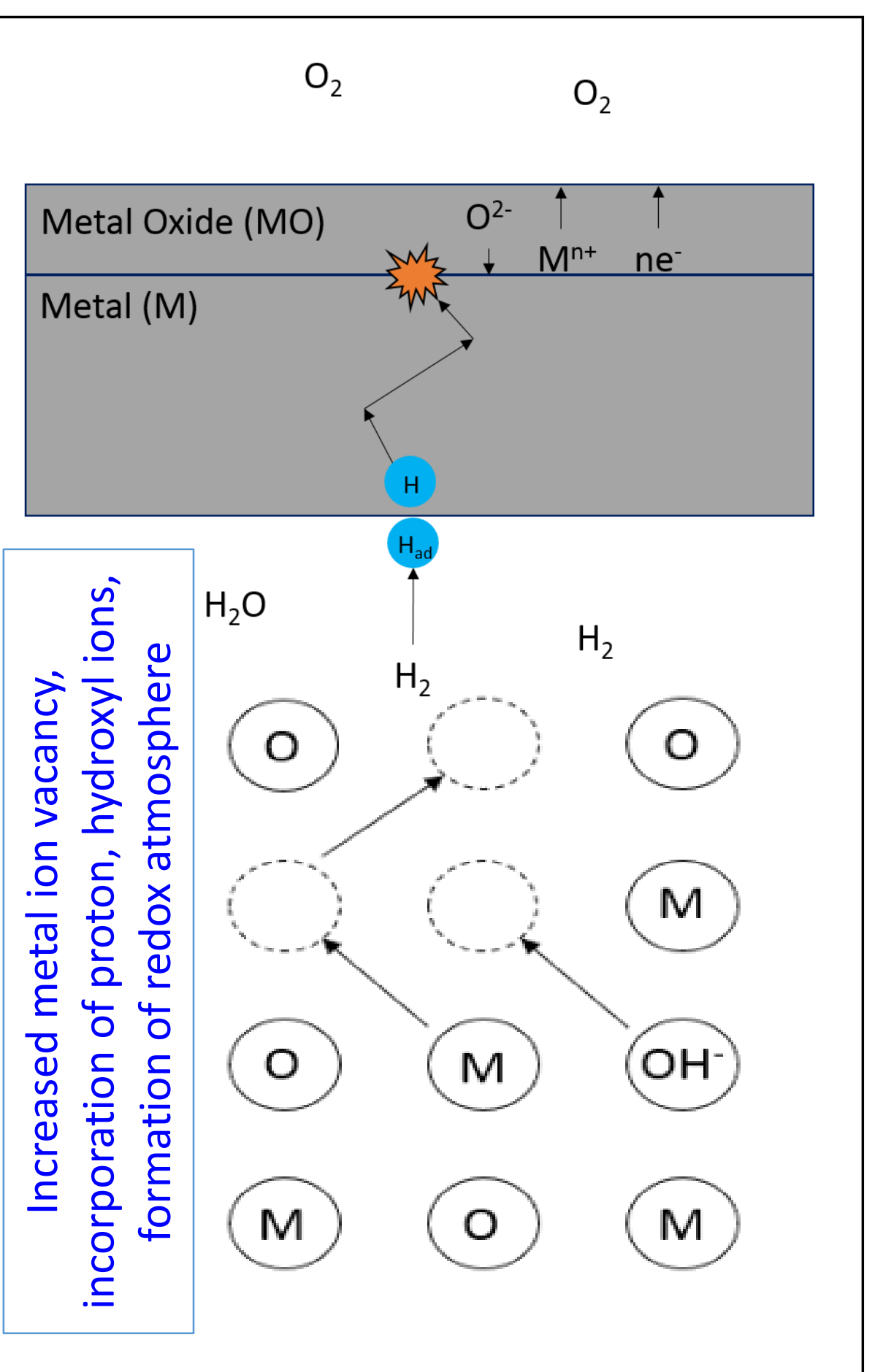


Figure 5. Schematic representation of diffusing species within stainless steel under dual atmosphere exposure conditions

Conclusions

- ➢ Breakdown of protective scale and localized metal loss is observed under dual atmosphere conditions
- ➢ The oxide overgrowth predominantly consists of Fe-oxide nodules. Inner oxide remains porous.
- ➢ Preferential growth of platelets and whiskers are observed.
- ➢ Mechanisms for accelerated oxide growth and iron oxide rich nodule formation is hypothesized to be due to modification of oxide defect structure, redox gas chemistry and preferential growth.

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