

CORROSION PERFORMANCE OF FERRITIC STEEL FOR SOFC INTERCONNECT APPLICATIONS

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ABSTRACT

Ferritic stainless steels have been identified as potential candidates for interconnects in planar-type solid oxide fuel cells (SOFC) operating below 800°C. Crofer 22 APU was selected for this study. It was studied under simulated SOFC-interconnect dual environment conditions with humidified air on one side of the sample and humidified hydrogen on the other side at 750°C.

The surfaces of the oxidized samples were studied by scanning electron microscopy (SEM) equipped with microanalytical capabilities. X-ray diffraction (XRD) analysis was also used in this study.

INTRODUCTION

Planar solid oxide fuel cells (PSOFCs) are an emerging power generation technology that produces electricity and heat by electrochemically combining a gaseous fuel and oxidizing gas via an ion-conducting electrolyte.¹ The gaseous fuel could be in the form of H₂, CH₄, or CO/H₂ and the oxidizing gas could be in the form of oxygen or air. During operation, oxygen ions (O²⁻) formed during the reduction reaction at the cathode move through an ion-conducting electrolyte to the anode to participate in the oxidation reaction along with hydrogen to form water. During the oxidation reaction, electrons are released and used in an outer circuit. An example of a SOFC single unit² is shown in Figure 1.

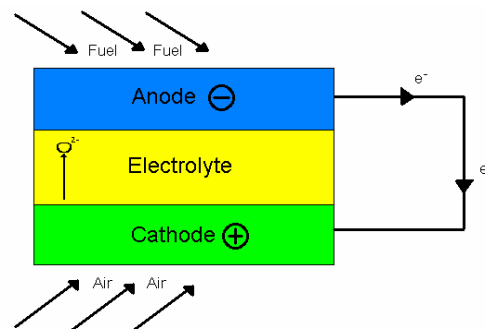


Figure. 1. Schematic diagram of a single unit of a solid oxide fuel cell showing the generation of useful power.

The open circuit voltage of this type of the cell is approximately 1 V. To generate higher voltages, these cells are connected through a conductive interconnect or a bipolar separator as shown in Figure 2.

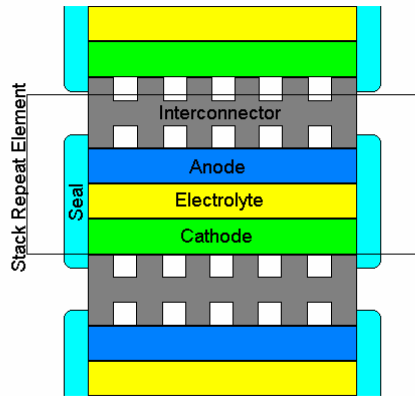


Figure. 2. Schematic diagram of a planar solid oxide fuel cell (PSOFC) stack.

The interconnect serves as a gas separator to prevent mixing of the fuel (anode) and air (cathode) and provides electrical connection between individual cells. Therefore, it must be durable and functional in the anodic and cathodic gases, while providing electrical connection in series with the fuel cell components of a PSOFC stack.

Significant progress has been made in reducing the operating temperature of the PSOFC stack from $\sim 1000^{\circ}\text{C}$ to below 800°C .³ This decrease in operating temperature allows the use of metallic materials for the interconnect components. There are several advantages of using metals over currently used ceramic materials based on doped LaCrO_3 : 1) achievement of gas tightness between fuel and air gases, 2) ease of handling, which lowers fabrication cost, and 3) high electronic and thermal conductivity, which increases the cell performance.⁴

During operation at 800°C , the p_{O_2} is usually at 0.21 atm at the cathode and approximately 10^{-21} atm at the anode for the hydrogen fuel containing 3% H_2O . Therefore, a potential metallic candidate undergoes oxidation in both the anodic (fuel) and cathodic (air) environments. Oxide scale formation takes place on the metallic material surface as a result of the material reacting with the fuel and atmospheric gases.^{5,6}

Chromium sesquioxide-forming metallic materials appear to be the most promising candidates since they show relatively low electrical resistance, high corrosion resistance, and suitable thermal expansion behavior.^{7,8} High chromium ferritic steels appear to be promising candidates to fulfill the technical and economical requirements among commercial Cr_2O_3 - forming alloys.

This paper reports the oxidation performance of the commercial ferritic stainless steel Crofer 22 APU in moist hydrogen and moist air atmospheres and compares the different oxidativative effects of those two atmospheres.

EXPERIMENTAL

All experiments were carried out on commercial low coefficient of thermal expansion (CTE) commercial ferritic stainless, Crofer 22 APU, developed for SOFC applications by

Forschungszentrum Julich and commercialized by ThyssenKrupp VDM. Chemical compositions of the Crofer 22 APU samples used in this research study are shown in Table 1.

Table 1: Chemical Composition of Crofer 22 APU

Chemical I Composition (wt %)								
Fe	Cr	Mn	Ti	La	Al	Si	Cu	Ce
Bal.	22.3	0.53	0.055	0.10	0.0056	0.10	0.0046	0.0009

Corrosion experiments were carried out on flat samples in the shape of squares or discs. The square samples (25.4 mm x 25.4 mm x 0.5 mm) were exposed separately to fuel or moist air under isothermal conditions, i.e. a single environment. The discs (25.4 mm in diameter and 1 mm in thickness) were simultaneously exposed to fuel on one side and moist air on the other side, i.e., a dual environment. The simulated fuel was a mixture of H₂+3% H₂O and moist air was a mixture of air+3% H₂O.

The square samples were oxidized isothermally within the temperature range 750-800°C. Before each test, the samples were polished with 600 grit SiC paper and ultrasonically cleaned in acetone. In each single environment experiment, the samples were removed from the furnace, cooled, weighed, and reinserted into the furnace. The heating and cooling cycles were repeated several times during the exposure.

In the dual environment experiment, the samples were mounted onto a dual environment fixture (Figure 3) and installed inside the furnace.

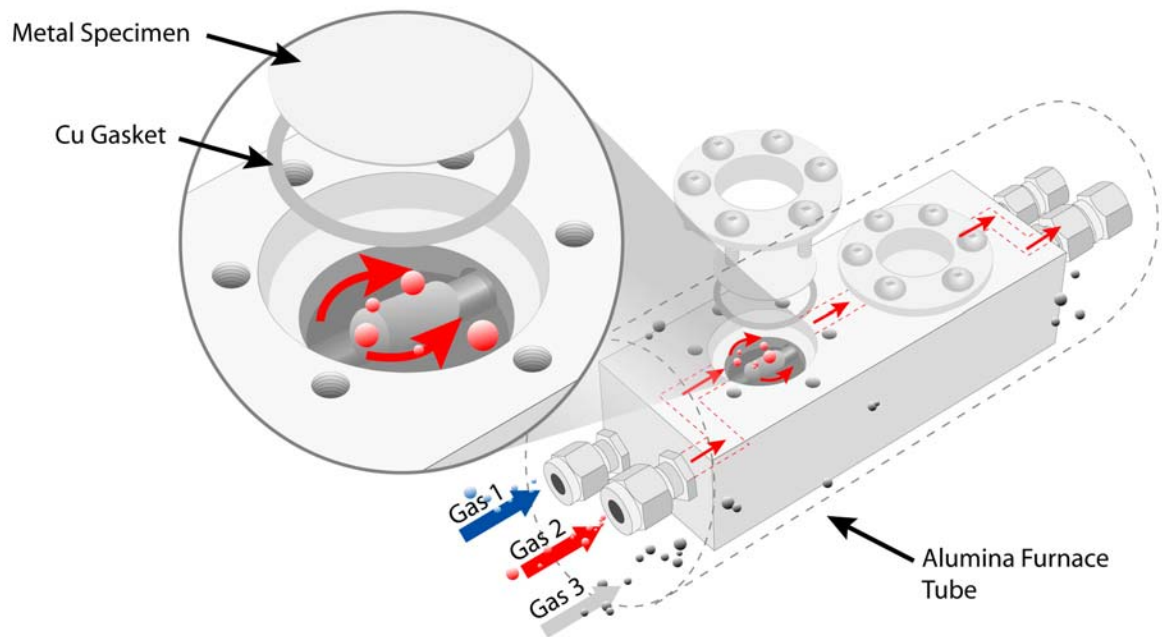


Figure 3. Experimental setup for flat samples in dual environments.

The samples were simultaneously exposed to the H₂+3% H₂O/ air+3% H₂O dual environment, with H₂+3% H₂O on one side and air+3% H₂O air on the other side (Figure 1: Gas 1 and Gas 3) for 200 h at 750°C. Also, in the same experiment a set of samples were simultaneously exposed to a single environment consisting of air+3%H₂O on both sides of each sample. (Figure 1: Gas 2 and Gas 3).

The post-oxidation surface investigations involved the use of the X-ray diffraction (XRD) to identify possible phases present in the scale, scanning electron microscopy (SEM) to determine morphology of the oxide scales, and x-ray dispersive energy spectroscopy (EDS) to generate concentration profiles of the mounted and polished cross sections of the investigated materials.

RESULTS AND DISCUSSION

The results of the gravimetric experiments for Crofer 22 APU in H₂+3% H₂O at 750°C and in air+3% H₂O 800°C, plotted as (mass change/area)² versus oxidation time, are shown in Figure 4.

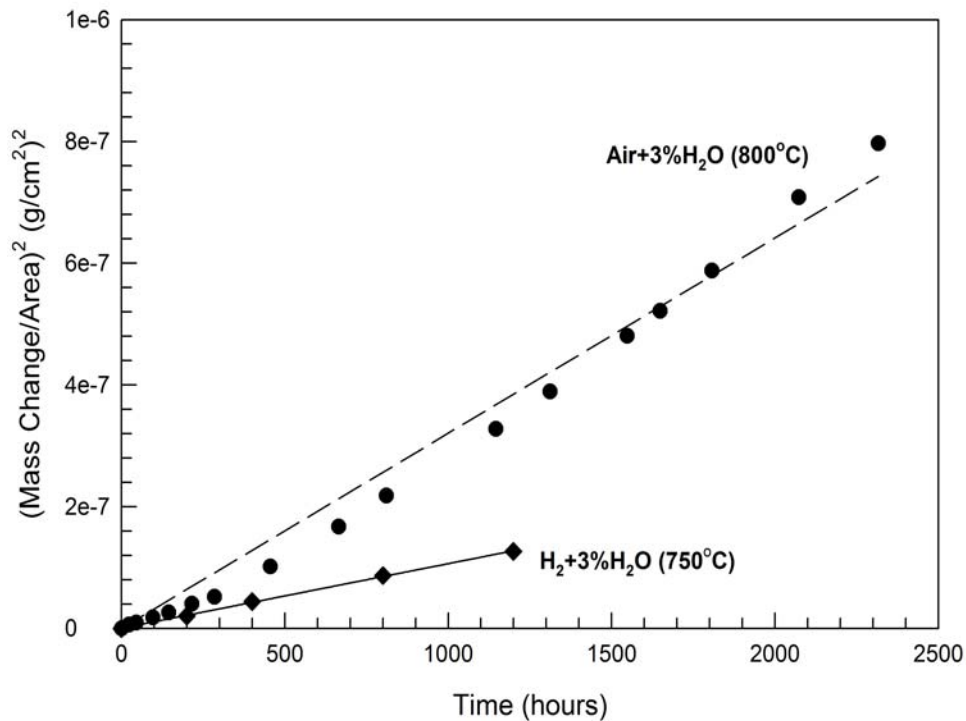


Figure 4: (Mass change/area)² versus oxidation time for Crofer 22APU oxidized in air+3% H₂O 800°C and H₂+3% H₂O at 750°C.

The plots are linear for the material studied in both environments, which are in agreement with the parabolic rate law of oxidation

$$(\Delta m/A)^2 = k_g t$$

where, Δm is mass change, A is the sample surface area, k_g is the parabolic rate constant determined from the gravimetric measurements, and t is the oxidation time. The values of k_g are shown in Table 2.

Table 2. Parabolic rate constants for Crofer 22 APU in single environments of air+3% H₂O and H₂+3% H₂O.

Environment	k_g (g ² /cm ⁴ h)
Air + 3% H ₂ O (800°C)	3.40E-10
H ₂ + 3%H ₂ O (750°C)	1.07E-10

Crofer in H₂+3% H₂O has a lower k_g value than in air+3% H₂O. This indicates that Crofer 22 APU has faster oxidation kinetics in air+3% H₂O than in H₂+3% H₂O.

The XRD results obtained for the material in humidified hydrogen and humidified air revealed the presence of a Cr₂O₃-like phase and a (Mn, Cr) spinel-like phase. An example of the XRD pattern for Crofer in air+3% H₂O after 2000 h exposure is shown in Figure 5.

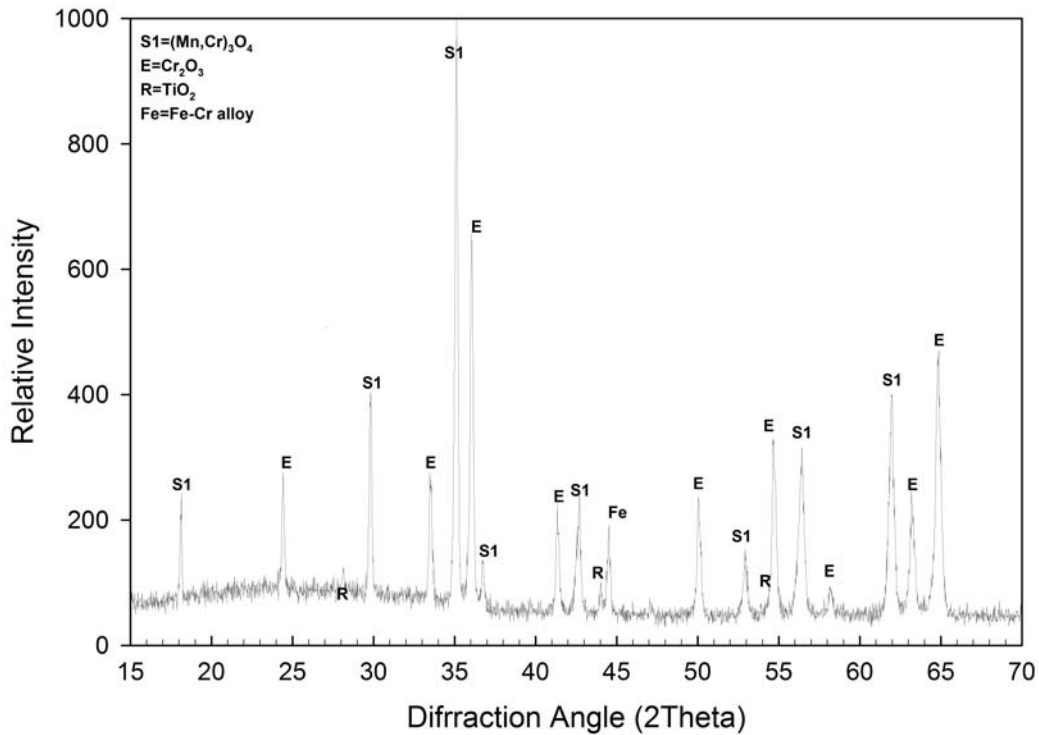


Figure 5. XRD pattern for Crofer 22 APU exposed to air+3% H₂O at 800 °C for 2000h.

Also, literature data indicate formation of a thicker oxide scale on Crofer in air than in H₂-H₂O. This difference in scale thickness is caused by different p_{O2} in air (0.2 atm) and H₂-H₂O (10⁻²¹ atm).⁹

A significant difference in scale thickness was observed for Crofer exposed simultaneously to air+3% H₂O on one side and H₂+3%H₂O on the other side (dual environment). Figure 6 shows SEM cross sections of the scale formed on the Crofer sample in the dual environment with one surface oxidized in H₂+3% H₂O and the other surface in air+3% H₂O.

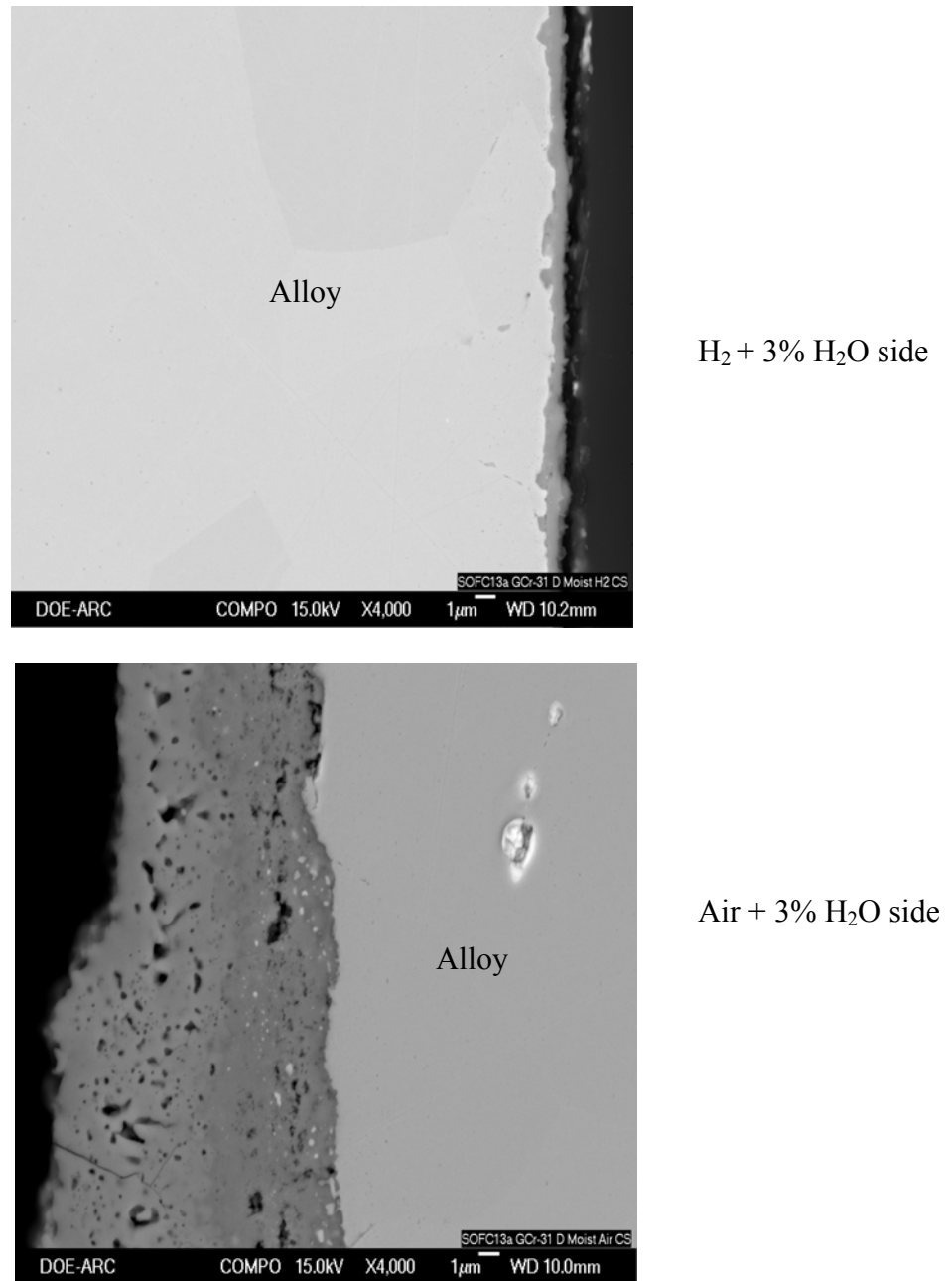


Figure 6. SEM (backscattered electron) cross-section micrographs of Crofer 22 APU after exposure to dual H₂+3% H₂O/ air+3% H₂O environment for 200h at 750°C.

Much thicker scale formed on the air side of the sample than on the hydrogen side. This indicates that the surface exposed to humidified air oxidized faster than the surface exposed to humidified hydrogen.

Figure 7 shows the elemental distribution of O, Cr, Mn, and Fe inside the scale formed in $H_2+3\% H_2O$ as determined by EDS.

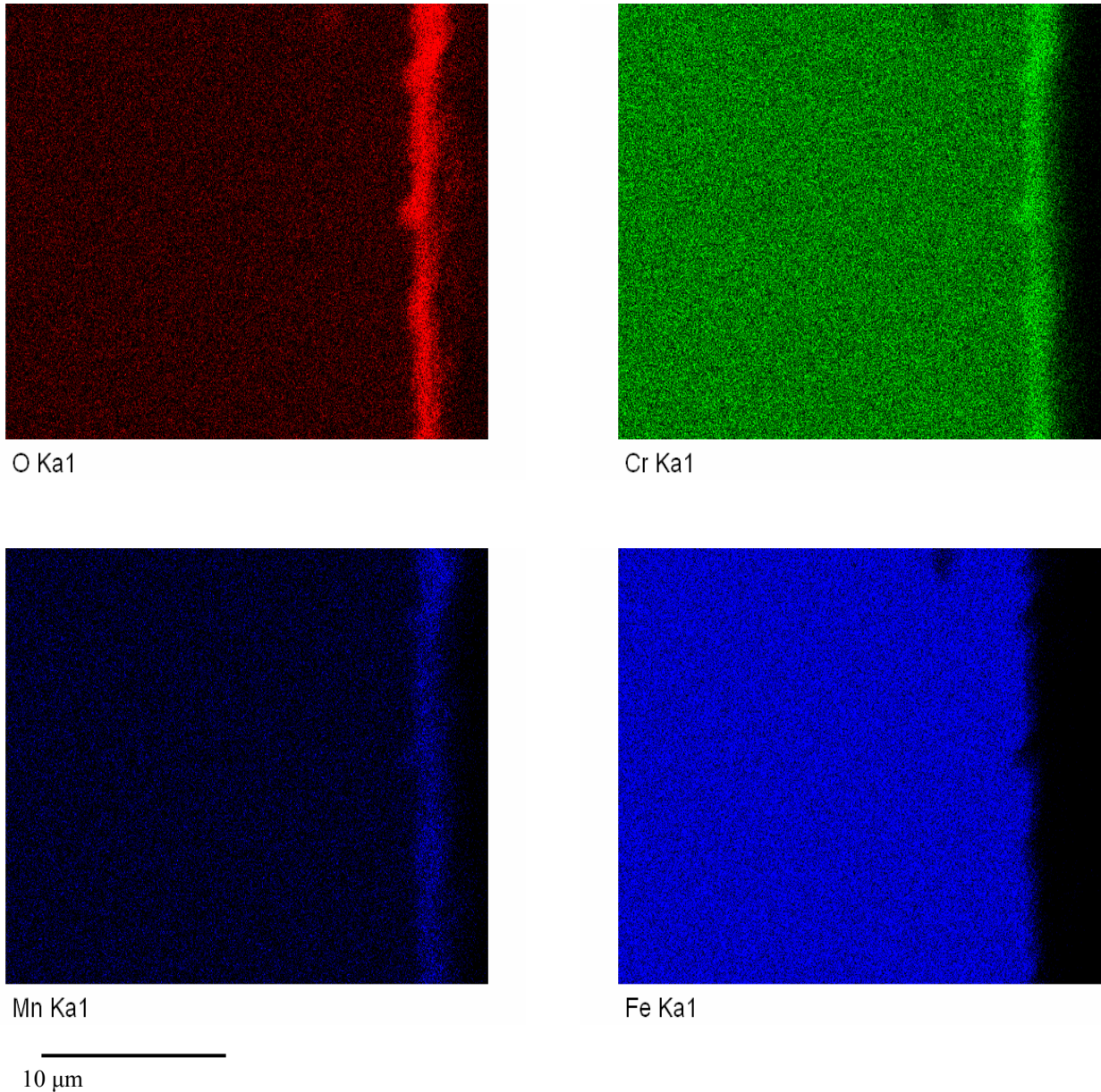


Figure 7. EDS maps of oxygen, chromium, manganese, and iron for scale formed on Crofer 22 APU during exposure to $H_2+3\% H_2O$ in dual $H_2+3\% H_2O/ air+3\% H_2O$ environment for 200h at $750^{\circ}C$.

Oxygen was found uniformly distributed inside the scale. The highest concentration of Cr was detected in the inner layer, and Mn along with Cr was detected in the outer layer. Fe was not

detected in this scale, however it was found in scale formed on the other side of the sample, which was exposed to air+3% H_2O , Figure 8.

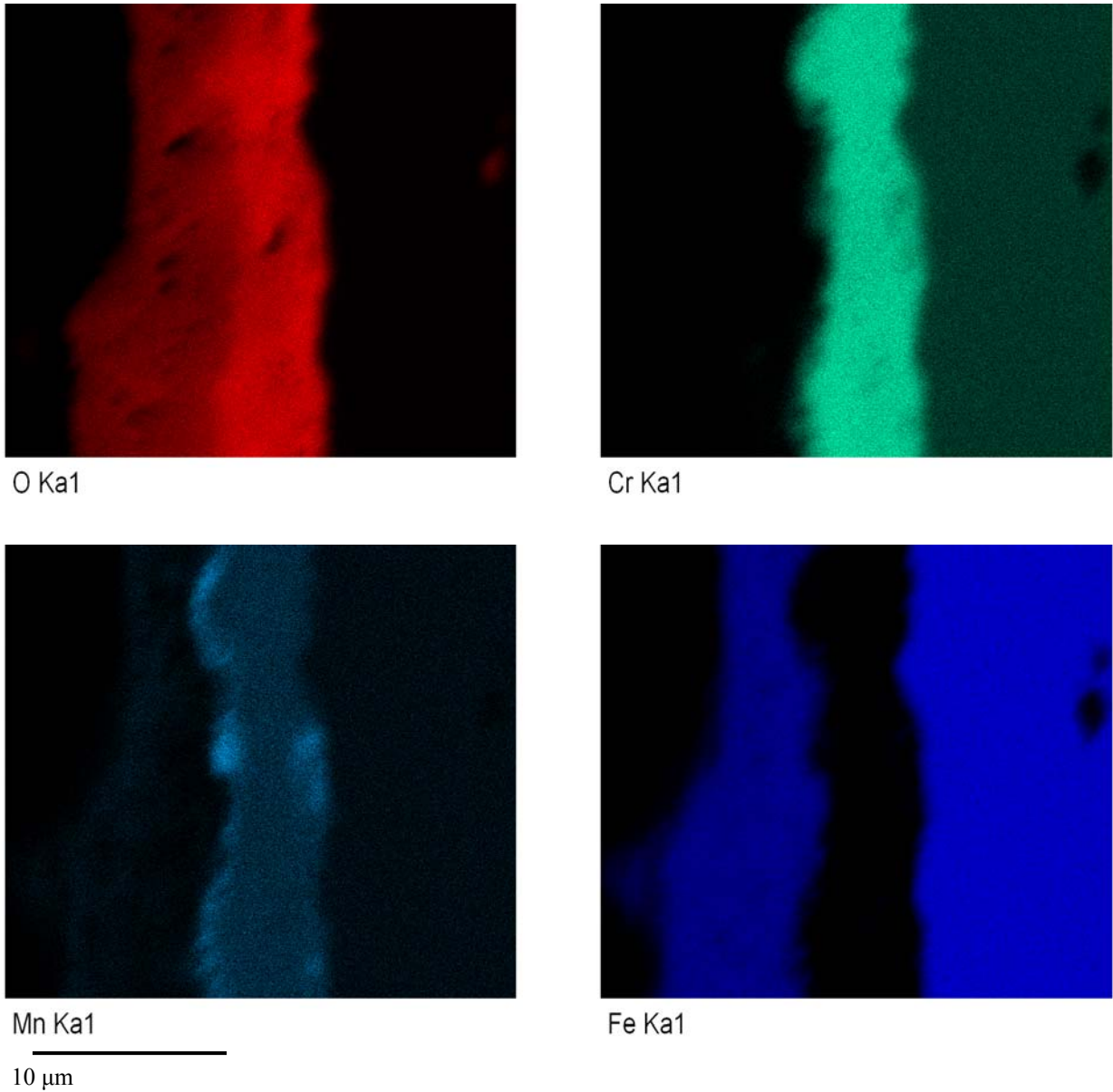


Figure 8. EDS maps of oxygen, chromium, manganese, and iron for scale formed on Crofer 22 APU during exposure to air+3% H_2O in dual H_2 +3% H_2O / air+3% H_2O environment for 200h at 750°C.

From Figure 8, it appears that oxygen is distributed uniformly inside the scale, chromium is present in the inner layer, iron is present in the outer layer, and Mn was detected between the Cr inner layer and the Fe outer layer. The presence of Fe in the scale as detected by XRD as a hematite like-phase on the air side in the dual environment indicates an atypical effect of moist hydrogen on the scale formation on the air side for ferritic steels which is in good agreement with literature data.¹⁰⁻¹³

CONCLUSIONS/ SUMMARY

Based on the kinetic results, Crofer 22 APU obeys the parabolic rate law of oxidation in $H_2+3\% H_2O$ at $750\text{ }^\circ\text{C}$ and in air + $3\% H_2O$ at $800\text{ }^\circ\text{C}$. A higher parabolic rate constant was determined for Crofer in air + $3\% H_2O$ and lower in $H_2+3\% H_2O$ indicating its higher oxidation rate in air.

The XRD results obtained for Crofer 22 APU in $H_2+3\% H_2O$ and air+ $3\% H_2O$ revealed the presence of Cr_2O_3 -like phase and (Mn, Cr) spinel-like phase.

In the $H_2+3\% H_2O/$ air+ $3\% H_2O$ dual environment, much thicker scale formed on the air+ $3\% H_2O$ side of the sample than on the $H_2+3\% H_2O$ side. This indicates that the surface exposed to humidified air oxidized faster than the surface exposed to humidified hydrogen.

A significant concentration of iron was detected only in the scale formed on the air side in the $H_2+3\% H_2O/$ air+ $3\% H_2O$ dual environment.

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