EARLY CAREER SCHOLARS IN MATERIALS SCIENCE

Corrosion of nickel and nickel–phosphorous-coated AISI 430 in dry (Ar–3% H_2) and humid hydrogen (Ar–3% H_2 –3% H_2O) atmosphere

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The corrosion behavior of uncoated, nickel (Ni) and nickel–phosphorous (Ni–P)-coated AISI 430 alloy was investigated in Ar–3% H_2 and Ar–3% H_2 –3% H_2O atmosphere at 800 °C for 100 h. Microstructure, chemical composition, and reaction products were analyzed by scanning electron microscopy, energy-dispersive spectroscopy, and X-ray diffraction techniques. The corrosion extent of Ni–P-coated AISI 430 is higher than Ni-coated AISI 430. Oxidation promotes corrosion in the uncoated and coated alloy. The oxidation rate of Ni-coated alloy is the lowest in Ar–3% H_2 but Ni–P-coated alloy in Ar–3% H_2 –3% H_2O for initial 20 h. The oxidation rate of the Ni–P-coated sample is ~ 14 times higher in 20–100 h in Ar–3% H_2 –3% H_2O . External growth of Cr_2O_3 is observed for Ni-coated alloy in Ar–3% H_2 and for Ni–P-coated alloy in both the atmospheres. Inward growth of Cr_2O_3 by AISI 430 alloy consumption attributes to the lowest oxidation rate and the corrosion extent of Ni-coated sample in Ar–3% H_2 –3% H_2O .

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Introduction

Ferritic alloys containing 16–24 wt% chromium such as AISI 441 and Crofer 22 APU are used as interconnects to separate cathode and anode environments in solid oxide fuel (SOFC) stacks. The cathode environment contains moisture in atmospheric air. The anode environment contains water as a by-product and/or water in fuel gas stream (hydrocarbons). The ferritic alloys degrade during long-term SOFC operation at high temperatures (600–850 °C) despite excellent oxidation resistance primarily due to chromium evaporation [predominately $\text{CrO}_2(\text{OH})_2$], breakaway oxidation, and residual stress

in the presence of water vapor depending on its content and oxygen partial pressure [1, 2, 3, 4, 5].

Water vapor increases the oxidation rate of ferritic alloys and corrodes the oxide scale [6, 7, 8, 9, 10]. Fe_2O_3 , Fe_3O_4 , and Fe–Cr oxide spinels are commonly reported in the oxide scales in water vapor exposure while protective chromium oxide and/or Mn–Cr oxide spinels in a dry oxidizing environment. Inner Cr_2O_3 and outer MnCr_2O_4 layers were observed in Crofer 22 alloy in dry air exposure but with a presence of crack/gap between these oxide layers in humid air [11].

The oxidation rate of ferritic alloys slightly increases in humidified hydrogen compared with humidified air [9, 12,

13, 14]. Chromium content in the ferritic alloys influence the microstructure development in a cathode side in simulated dual atmosphere. For instance, the microstructure of Crofer 22 APU (23% Cr) showed Mn–Cr oxide spinel with a Cr_2O_3 sublayer when treated in humidified air but Mn–Cr–Fe spinel with a Cr_2O_3 sublayer in a cathode side for dual atmosphere. The microstructure of AISI 430 (17% Cr) showed Mn–Cr oxide spinel with a Cr_2O_3 sublayer when treated in humidified air but random distribution of Fe_2O_3 (hematite) in Mn–Cr–spinel matrix in a cathode side for dual atmosphere while no significant microstructure change in humidified hydrogen and an anode side for dual atmosphere.

Several oxide and metallic coatings have been reported to improve oxidation and corrosion resistance of ferritic alloys and mitigate chromium evaporation, the SOFC interconnects, in simulated environments. Only the coatings studied in the humidified hydrogen and/or dual environment are discussed for brevity. Ce and La coatings improve oxidation resistance of a Fe–22Cr alloy in humidified hydrogen by forming oxide and perovskite oxides [15]. Nd_2O_3 and Y_2O_3 coatings significantly decrease the oxidation rate of Crofer 22, while the effect of La_2O_3 coating is insignificant [14]. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ and Co_3O_4 coatings decrease the area-specific resistance (ASR) of AISI 441 by approximately eight times but decompose into La_2O_3 and MnO, and Co metal, respectively [16]. The literature reports suggest that suitable coatings can protect ferritic interconnect alloys from corrosion in humid hydrogen and dual atmosphere as well. Oxide coatings can potentially increase corrosion resistance in a simulated SOFC environment if the coating remains stable in reducing atmosphere in an anode side. For instance, Mn–Co spinel is commonly recommended as a robust coating for metallic interconnect to mitigate chromium evaporation in humidified air but it is unstable in hydrogen [17].

Cobalt coating increases the oxidation rate despite Mn–Co spinel formation to inhibit oxygen ingress, but the spinel is unstable in humid hydrogen [15]. Nickel coating decreases the oxidation resistance by ~ 50 and the ASR by ~ 57 times of SUS 430 in humidified hydrogen [18]. Nickel-coated ($\sim 15\text{ }\mu\text{m}$ thick) AISI 441 corrodes in simulated dual atmosphere and forms oxide layer with porosity; metallic elements and gap between hematite and spinel layers in an air side and gap between iron oxide and nickel in a fuel side (H_2 – H_2O) were observed [19]. Nickel coating is also reported to mitigate chromium evaporation of SOFC interconnects in the air side [20, 21] and to improve oxidation resistance in humidified air [22, 23]. However, the microstructure of nickel-coated SOFC interconnect, the aim of our study, has not been detailed in humidified hydrogen and/or dual environment although interfacial microstructure plays a crucial role for long-term performance. For example, pores/voids and cracks at the oxide

scale can compromise thermo-mechanical integrity due to spallation of oxide scale. Ni–P coating, widely used for corrosion protection of steel, also improves the oxidation resistance of ferritic alloy in humidified air [24]. Significant porosity in the oxide scale is found for Ni–P-coated AISI 430 alloy [24] while negligible for nickel coating [22]. We have investigated the corrosion of $\sim 5\text{ }\mu\text{m}$ thick nickel and Ni–P-coated AISI 430 alloy, a commercial ferritic alloy with similar properties of specialized Crofer 22 APU and AISI 441, in dry (Ar –3% H_2) and humidified hydrogen (Ar –3% H_2 –3% H_2O) at 800 °C.

Results and Discussion

Oxidation behavior

Figure 1 shows the weight changes due to isothermal oxidation at 800 °C in dry hydrogen [Fig. 1(a)] and humid hydrogen [Fig. 1(b)] of uncoated, Ni-coated, and Ni–P-coated AISI 430 samples. The oxidation of all the samples follows parabolic rate law and weight gain decreases for the coated samples except for the Ni–P-coated sample in humid hydrogen. Weight gain is also lower in dry hydrogen, as expected, than in humid hydrogen. Weight gain for Ni–P-coated sample in Ar –3% H_2 –3% H_2O does not show clear parabolic nature; however, the trend suggests that more time is required.

The oxidation rate is determined by the following equation:

$$\left(\frac{\Delta w}{A}\right)^2 = k_p t, \quad (1)$$

where Δw is the weight change due to oxidation, A is the surface area, t is time for isothermal oxidation, and k_p is the oxidation rate ($\text{mg}^2/\text{cm}^4\text{ s}$).

The oxidation rates of the uncoated and coated samples are plotted in Figs. 1(c)–1(f). Oxidation rate in air–3% H_2O [22, 24] is also shown for comparison. Faster oxidation rate is observed in the initial 20 h except for the Ni–P-coated sample [Fig. 1(c)]. In initial 20 h, the oxidation rate is lower for the coated samples, Ni-coated sample being the lowest, than uncoated AISI 430. The oxidation rate decreases as the exposure environment changes from air–3% H_2O to Ar –3% H_2 –3% H_2O to Ar –3% H_2 . In the 20–100 h range [Fig. 1(e)], the oxidation rate of the Ni–P-coated sample is higher than AISI 430 in humid hydrogen. The oxidation rate of AISI 430 in dry hydrogen is higher than humid hydrogen.

Microstructure and X-Ray Diffractometer Analysis

AISI 430 in Ar –3% H_2

The surface morphology of AISI 430, isothermally treated in dry H_2 , in Fig. 2(a) shows two different layers—brighter

Figure 1: Oxidation behavior of AISI 430, Ni-coated AISI 430, and Ni-P-coated AISI 430 at 800 °C. (a) Weight change in Ar-3%H₂, (b) weight change in Ar-3%H₂-3%H₂O, (c) and (d) oxidation rate in initial 20 h, and (e) and (f) oxidation rate in 20–100 h. Oxidation rate in air-3%H₂O is given for comparison.

(marked as “1”) and a darker (marked as “2”). A higher magnification image in Fig. 2(b) reveals the microstructural difference between these two layers. Nodular-shaped bright phases in layer 1 and plate-like bright phases in layer 2 are scattered in a gray matrix. Qualitatively, the overall areal density

(phase fraction/mm²) of the gray and bright phases is higher in layer “2” than layer “1”.

The energy-dispersive spectrometer (EDS) spot analysis (not shown for brevity) reveals that the matrix in the brighter layer (“1”) contains lower Mn, Cr, and O and higher Fe than

Figure 2: SEM images of AISI 430 alloy surface corroded in Ar-3% H_2 at 800 °C for 100 h. (a) Low magnification and (b) high magnification. The dotted line indicates the boundary between brighter and darker layers. See the text.

the darker layer. The plate-like bright phases are Mn- and Cr-rich, while nodular bright phases are Fe-rich. The analyzed composition of the nodular and plate-like phases also includes elements in the matrix due to spatial resolution limit, causing ambiguity in distinguishing these phases. However, overall compositional analysis suggests the presence of Mn-Cr oxide spinel. Juxtaposition of EDS elemental maps (Supplementary Fig. S1) differentiates the matrix, nodular, and acicular phases. Overlapping of Cr-, Mn-, and O-maps supports Mn-Cr oxide spinel matrix and manganese oxide in the bright plate-like phases. Similarly, overlapping of Fe- and O-maps reveals iron oxide in the bright nodules and in the matrix.

X-ray diffractometer (XRD) analysis in Fig. 3(a) identifies $MnCr_2O_4$ (ICDD # 04-006-2565) and Fe_3O_4 (ICDD # 04-006-0425) spinel phases, consistent with the EDS analysis. It is noted that the Bragg's angle for Fe_3O_4 and $MnCr_2O_4$ diffraction planes overlaps. The smaller quantity of manganese oxide is beyond the XRD detection limit.

The thermodynamic data of probable oxides in the studied atmospheres, determined from HSC Chemistry 9.0, are plotted in Fig. 4. Assuming 1 ppm H_2O presence, Cr_2O_3 is found to be in equilibrium with Ar-3% H_2 at 800 °C and remains stable at lower temperature. MnO is also stable. Accordingly, Cr_2O_3 is abundant and little MnO is present. In humid atmosphere, Cr_2O_3 forms by inward diffusion of oxygen from H_2O [9, 10, 25, 26]. Hydrogen, however, favors outward Cr^{3+} diffusion

plausibly by cleaning faster diffusion paths [5] despite Cr_2O_3 being an n -type oxide in the pO_2 [27] ($\sim 10^{-27}$ atm. at 800 °C) corresponding to Ar-3% H_2 -1 ppm H_2O . Mn^{2+} diffuses faster than Fe^{n+} and Cr^{3+} into Cr_2O_3 [28] and forms $MnCr_2O_4$ spinel. Faster hydrogen diffusion through the alloy potentially favors higher inward flux of oxygen [9]. Accordingly, local oxygen pressure may increase sufficiently to form Fe_3O_4 .

AISI 430 in Ar-3% H_2 -3% H_2O

The surface morphology of AISI 430, isothermally treated in Ar-3% H_2 -3% H_2O , in Fig. 5(a) shows porous as well as dense grains ($1.51 \pm 0.25 \mu m$) and sporadic needle-shaped phases. The compositions of both the porous and dense grains are the same (45 ± 5 Fe, 2 ± 0 Cr, and 53 ± 5 O). The needle-shaped phases are Mn- and Cr-rich (52 ± 0 Fe, 4 ± 1 Cr, 3 ± 1 Mn, and 41 ± 2 O) compared with the grains, indicating Mn-Cr oxide spinel.

The cross-sectional scanning electron microscopic (SEM) image is shown in Fig. 5(b). The porosities in the surface morphology is observed as the groove-like feature (marked with black arrow). The EDS elemental composition analysis (Supplementary Table S1) distinguishes the prominent features. Fe- and Cr-enriched dark spots (67 ± 1 Cr and 33 ± 0 Fe) in the AISI 430 (marked as "1") likely be $FeCr_2$ intermetallic compound. An Si- and O-enriched thin dark layer (marked as "2") indicates SiO_2 presence. Cr-, Mn-, and O-enriched dense layer "3" corroborates to Mn-Cr oxide spinel. The elemental analysis suggests Fe-Cr oxide spinel in a porous layer "4" and Fe_3O_4 spinel in a dense layer "5". Pores are scattered in layer "5". A crack/gap is observed between layers "4" and "5".

EDS spot analysis of the corroded AISI 430 is also consistent with the elemental maps (Supplementary Fig. S2) and line scan profile (Supplementary Fig. S3) as well. Juxtaposition of Si- and O-maps is consistent with SiO_2 presence in layer "2". Juxtaposition of Mn-, Cr-, and O-maps along with faded Fe map supports Mn-Cr oxide spinel in layer "3", while overlapping Fe-, Cr-, and O-maps support Fe-Cr oxide spinel in layer

Figure 3: XRD plots of samples at 800 °C for 100 h in (a) Ar-3% H_2 and (b) Ar-3% H_2 -3% H_2O . See the text.

Figure 4: Oxygen partial pressure in Ar-3%H₂ (assuming 1 ppm H₂O presence) and Ar-3%H₂-3%H₂O, and the thermodynamic equilibrium of compounds.

“4”. Similarly, overlapping Fe- and O-maps supports Fe₃O₄ presence in layer “5”.

MnCr₂O₄ (ICDD # 04-006-2565), Cr_{1.7}Fe_{1.3}O₄ (ICDD # 04-005-8771), and Fe₃O₄ (ICDD # 04-005-5733) compounds are confirmed from XRD analysis [Fig. 3(b)], which substantiates the EDS analysis. It is noted that the Bragg's angle for Fe₃O₄ and MnCr₂O₄ diffraction planes overlaps.

Corrosion of AISI 430 in humid hydrogen is discussed as follows. First, oxygen at the AISI 430 surface (S) forms by dissociative adsorption of H₂O according to [5]

Cr₂O₃ forms by internal oxidation but no external growth and subsequent protective layer since oxygen from H₂O diffuses inward from solid/gas interface. Iron oxide forms and reacts with Cr₂O₃ to form Cr_{1.7}Fe_{1.3}O₄ spinel. Second, Fe²⁺ diffusion through Fe-Cr oxide spinel is faster than Cr³⁺ [29]. Accordingly, iron oxide (Fe₃O₄) grows by outward Fe²⁺

Figure 5: SEM images of AISI 430 alloy corroded in Ar-3%H₂-3%H₂O at 800 °C for 100 h. (a) Surface and (b) cross-section. The dotted lines indicate the boundaries between different oxide layers. See the text. Nickel in the outermost layer electrodeposited on a corroded sample to avoid spallation during metallographic sample preparation.

diffusion, which is in equilibrium with Ar-3%H₂-3%H₂O (Fig. 4). Mn²⁺ from the substrate diffuses into Cr₂O₃ to form MnCr₂O₄. Third, dissociative adsorption of H₂O at the internal surface (surface defects such as cavity, pores, and cracks) continues to provide oxygen and hydrogen as well. In addition, hydrogen ingress from H₂O [25] and H₂ [30] gas has been reported for alloys and oxides. Faster diffusion of H₂ enhances oxygen transport through alloys and oxides [9]. Difference in the outward cations and inward oxygen ion through lattice generates vacancies, which coalesces into pores in the oxide layer. Pore/void formation in the grains at outermost Fe₃O₄ scale/gas interfaces perhaps due to evaporation of iron oxide in the form of Fe(OH)₂ (vapor pressure: 5.5 × 10⁻⁹ atm. at 800 °C as calculated from HSC Chemistry 9.0).

Nickel-coated AISI 430 in Ar-3%H₂

The surface morphology of Ni-coated AISI 430, isothermally treated in Ar-3%H₂, is shown in Fig. 6(a). A dense layer with well-faceted grains and almost uniformly distributed pores is observed. Higher magnification images show the microstructure in the pore regions and brighter phases at grain boundaries in the dense layer. In the porous regions,

Figure 6: SEM images of Ni-coated AISI 430 alloy corroded in Ar-3%H₂ at 800 °C for 100 h. (a) Surface, (b) lower magnification cross-section, and (c) higher magnification cross-section. See the text for markings in the images. Ni-Cu in the outermost layer electrodeposited on a corroded sample to avoid spallation during metallographic sample preparation.

bright nodular and plate-like/acicular phases are distributed in a gray matrix. FeNi in the dense layer, Cr_2O_3 and/or Mn–Cr oxide spinel in a gray matrix, Mn–Cr oxide spinel in the acicular phase, and Cr_2O_3 in the nodules are present according to EDS spot analysis. However, EDS spatial resolution limits the accuracy of this analysis.

The cross-sectional SEM image is shown in Figs. 6(b) and 6(c). A gray layer, discontinuous bright phases, and dark spots are observed. The dark spots (marked as “1”) are SiO_2 . The gray layer (marked as “2”) contains 15 ± 3 Fe, 28 ± 2 Cr, 7 ± 1 Mn, 3 ± 1 Ni, 2 ± 1 Si, and 39 ± 2 O, suggesting Mn–Cr oxide spinel. The bright phases (spot “3”) inside the gray layer contains 56 ± 2 Fe, 11 ± 1 Cr, 28 ± 3 Ni, and 4 ± 1 O. The outermost gray layer (layer “4”) contains 11 ± 3 Fe, 35 ± 3 Cr, 1 ± 0 Mn, 5 ± 2 Ni, and 47 ± 2 O, suggesting Mn-doped Cr_2O_3 . The bright spots (spot “5”) in the outermost layer contains 44 ± 8 Fe, 5 ± 3 Cr, 42 ± 3 Ni, and 9 ± 2 O. Cracks in the oxide layer, specifically adjacent to the layer “3”, are prominent.

EDS spot analysis of the corroded AISI 430 is also consistent with the elemental maps of (Supplementary Fig. S2) and line scan profile (Supplementary Fig. S4). Overlapping of humps in the Si and O concentration profile, complimented by overlapping maps, confirms that the dark spots are SiO_2 . SiO_2 is also observed in the gray layer due to epoxy resin penetration in cracks during sample preparation for SEM analysis. Mn, Cr, and O concentrations increase with a simultaneous decrease of Fe in the gray layer, consistent with subsequent elemental maps, supporting Mn–Cr oxide spinel. Fe and Ni concentrations increase in the bright phases (spots “3” and “5”) along with a simultaneous decrease in Mn and Cr, and negligible O supports FeNi presence, consistent with corresponding elemental maps. Nickel diffusion into the AISI 430 to $\sim 37 \mu\text{m}$ is also consistent with nickel elemental map, which contributes to the bright interaction layer in the low magnification SEM image [Fig. 6(b)].

Cr_2O_3 (ICDD # 04-008-6181), MnCr_2O_4 (ICDD # 04-006-2565), and $\text{Fe}_{0.5}\text{Ni}_{0.5}$ (ICDD # 04-006-6296) compounds are confirmed from XRD analysis [Fig. 3(a)]. $\text{Fe}_{0.5}\text{Ni}_{0.5}$ formation by elemental interdiffusion of Fe and Ni induces residual strain, evident from the shift in Bragg’s diffraction angle corresponding to $2\theta \sim 44.5^\circ$ for AISI 430, towards the left side, perhaps generating the cracks.

Nickel-coated AISI 430 in Ar–3% H_2 –3% H_2O

The surface morphology of Ni-coated AISI 430, isothermally treated in Ar–3% H_2 –3% H_2O , is shown in Fig. 7(a). Well-faceted grains (marked as “1”), pores at grain boundaries, and scattered bright phases and sporadic dark grains at grain boundaries are observed. The composition of the faceted grains

Figure 7: SEM images of Ni-coated AISI 430 alloy corroded in Ar–3% H_2 –3% H_2O at 800 °C for 100 h. (a) Surface and (b) cross-section. See the text. Nickel in the outermost layer electrodeposited on a corroded sample to avoid spallation during metallographic sample preparation.

(34 ± 1 Fe, 1 ± 1 Cr, and 65 ± 2 Ni) corroborates to the solid solution of AISI 430 and Ni. The bright spots (marked as “2”) consist of 27 ± 2 Fe, 4 ± 1 Cr, 2 ± 1 Mn, 43 ± 2 Ni, and 24 ± 2 O, indicating oxide phases, likely Mn–Cr-oxide spinel or iron oxide. The composition of dark grains, marked as “3”, 18 ± 1 Fe, 1 ± 0 Cr, 7 ± 1 Mn, 31 ± 4 Ni, and 42 ± 4 O, suggests MnO_x phase. The sporadic oxide phases form due to localized oxygen variation.

The cross-sectional SEM image is shown in Fig. 7(b). Dark spots (marked as “1”) adjacent to the substrate and a gray layer (marked “2”) followed by a bright layer (marked as “3”) with scattered gray spots (marked as “4”) are observed. EDS spot analysis (Supplementary Table S2) provides the composition of the distinct phases marked in Fig. 7(b). The dark spots (“1”) are SiO_2 , the gray layer (“2”) as well as the gray spots (“4”) are MnCr_2O_4 spinel, and bright layer (“3”) is the solid solution of AISI 430 and Ni (Fe–Ni solid solution).

EDS spot analysis of the corroded AISI 430 is also consistent with the elemental maps of (Supplementary Fig. S2) and line scan profile (Supplementary Fig. S5). Overlapping Si- and O- elemental maps confirms SiO_2 presence. Juxtaposition of Mn-, Cr-, and O-maps supports Mn–Cr oxide spinel presence in the gray layer (“2”) and spots (“4”), consistent with the increase in the concentration of Mn, Cr, and O with a simultaneous decrease of Fe in the corresponding concentration profile. Similarly, Fe–Ni solid solution is supported by overlapping Fe- and Ni-maps corresponding to the bright layer (“3”), consistent with the concentration profile. Nickel diffusion into the AISI 430 to $\sim 8 \mu\text{m}$ is consistent with nickel map.

MnCr_2O_4 (ICDD # 04-006-2565) and FeNi_3 (ICDD # 00-004-8417) intermetallic compounds are confirmed from XRD analysis [Fig. 3(b)]. The Fe and Ni ratio in EDS spot analysis, which corresponds to FeNi_2 , suggests the coexistence of Fe–Ni solid solution and FeNi_3 intermetallic compound in the bright layer “3”. It is also noted that, unlike in Ar–3% H_2 , FeNi_3 formation is associated with little shift in Bragg’s diffraction angle, corresponding to $2\theta \sim 44.5^\circ$ for AISI 430, indicating negligible residual strain.

The effect of dry and humid hydrogen on the corrosion of sulfamate sample can be elucidated by comparing respective microstructural analyses. Diffusivity of nickel ($D_{\text{Ni into Fe}}$) into b.c.c. α -iron is $5.26 \times 10^{-12} \text{ cm}^2/\text{s}$ [31], and diffusivities of iron ($D_{\text{Fe into Ni}}$) and chromium into nickel ($D_{\text{Cr into Ni}}$) are, respectively, $1.84 \times 10^{-13} \text{ cm}^2/\text{s}$ [32] and $1.26 \times 10^{-10} \text{ cm}^2/\text{s}$ [33] at $\sim 800^\circ\text{C}$. Atomic interdiffusion of elements, driven by chemical potential gradient, across the AISI 430/Ni interface results in the outermost NiFe layer. Higher $D_{\text{Ni into Fe}}$ than $D_{\text{Fe into Ni}}$ justifies nickel penetration into the AISI 430 alloy. Lower concentration Cr in AISI 430 as well as high stability of Cr_2O_3 perhaps limit chromium diffusion into nickel despite $D_{\text{Cr into Ni}} > D_{\text{Fe into Ni}}$. For the sample treated in Ar-3% H_2 , the noncontinuous Ni-Fe top layer is likely due to the lattice expansion-induced strain and localized strain related to hydrogen segregation preferably at grain boundaries [34] and subsequent spallation. Consequently, AISI 430 exposes to Ar-3% H_2 and corrodes. Cr_2O_3 , in equilibrium with Ar-3% H_2 (Fig. 4), readily forms. Mn diffuses into the Cr_2O_3 to form MnCr_2O_4 as discussed for AISI 430 alloy. The oxide layers, one (MnCr_2O_4) adjacent to the alloy and another (Mn-doped Cr_2O_3) at/near the coating/gas interface, are observed. Hydrogen favors outward cationic diffusion plausibly by cleaning paths for faster diffusion [35]. *Ab initio* modeling, supported by experimental results, shows faster chromium diffusion than iron and nickel into nickel, and Fe-Cr and Fe-Ni alloys [36]. Outward chromium diffusion, supported by its lower concentration in the AISI 430 (Supplementary Fig. S4) adjacent to the oxide scale, through the FeNi layer results in the outmost Cr_2O_3 layer. Hydrogen and oxygen from H_2O also diffuse inward through defects (pores and cracks), grain boundary, and vacancies in the coating and Cr_2O_3 . The diffusivity of hydrogen in nickel ($\sim 5.89 \times 10^{-5} \text{ cm}^2/\text{s}$) [37] is much higher than that of oxygen ($\sim 10^{-9} \text{ cm}^2/\text{s}$) [38, 39]. Faster hydrogen diffusion potentially favors higher inward flux of oxygen [9]. Inward oxygen diffusion initiates and continues Cr_2O_3 formation at the alloy/coating interface.

The FeNi_3 intermetallic top layer is continuous for the sample isothermally treated in humid hydrogen. The pores at the grain boundaries, typical in final stage sintering, evolve during sintering of nickel coating. Oxygen in humid hydrogen generates more vacancies in nickel [40]. Probable relaxation of lattice strain in excess vacancies is supported by negligible shift in Bragg's diffraction angle in the XRD plot [Fig. 3(b)]. Accordingly, bare AISI 430 is not exposed, and cracks are absent at the interface, contrary to Ar-3% H_2 . Inward oxygen diffusion through grain boundary pores and vacancies leads to Cr_2O_3 formation and growth by internal oxidation, understood from no change in chromium concentration in the AISI 430 substrate adjacent to the oxide layer (Supplementary Fig. S5).

Ni-P-coated AISI 430 in Ar-3% H_2

The surface morphology of Ni-P-coated AISI 430, isothermally treated in Ar-3% H_2 , is shown in Fig. 8(a). Gray, dark, and bright phases and scattered pores are observed. The composition of the gray phases is 21 ± 2 Fe, 15 ± 4 Cr, 6 ± 1 P, and 57 ± 4 O. The dark spots consist of 21 ± 1 Fe, 5 ± 1 Cr, 2 ± 1 Ni, 11 ± 2 P, and 61 ± 3 O. The composition of bright grains is 17 ± 1 Fe, 11 ± 1 Cr, 7 ± 1 P, and 65 ± 2 O.

The cross-sectional SEM image is shown in Fig. 8(b). Light gray spots in the substrate (marked as "1"), dark gray layer (marked as "3"), and bright layer (marked as "4") are observed. Cracks are observed at the interface between the substrate and gray spots (marked as "2"), layers "5" and "6" interface, and in layer "3" adjacent to bright phases (marked as "4"). Supplementary Table S3 provides the composition, obtained from EDS spot analysis, of the possible phases. Light gray spots in the substrate ("1") are likely metal phosphide although elemental composition does not confirm the type of metal phosphide. Dark gray spots "2" and layer "6" are of similar composition, corroborating to Cr_2O_3 . Gray layer "3" is likely Mn-doped Cr_2O_3 . The bright phases are NiFe_2 (marked as "4"). Layer "6" is likely Fe-P oxide. Spots "7" are likely Cr_2O_3 .

EDS spot analysis of the corroded AISI 430 is also consistent with the elemental maps of (Supplementary Fig. S2) and line scan profile (Supplementary Fig. S6). Juxtaposition of Cr and P elemental maps corresponding to the light gray spot "1" confirms chromium phosphide, in agreement with their concentration profile. Mn-doped Cr_2O_3 presence in the gray layer "3" is supported by overlapping Mn-, Cr-, and O-maps, in accord with the Mn, Cr, and O increase and simultaneous decrease of Fe in the concentration profile. Overlapping Fe and Ni maps corresponding to bright phase "4", consistent Fe and Ni concentration increase and simultaneous decrease of O, Mn, and Cr, supports NiFe_2 intermetallic compound formation. Overlapping Fe-, P-, and O-maps corresponding to layer/spot "6" confirms Fe-P oxide presence. Overlapping Cr- and O-maps confirms Cr_2O_3 in the spots "7". Nickel diffusion

Figure 8: SEM images of Ni-P-coated AISI 430 alloy corroded in Ar-3% H_2 at 800°C for 100 h. (a) Surface and (b) cross-section. See the text. Ni-Cu in the outermost layer electrodeposited on a corroded sample to avoid spallation during metallographic sample preparation.

into the AISI 430 to $\sim 36 \mu\text{m}$ is consistent with the nickel elemental map.

$\text{Fe}_3(\text{PO}_4)_2$ (ICDD # 04-011-5916), $\text{Fe}_{0.5}\text{Ni}_{0.5}$ (ICDD # 04-006-6296), and Cr_2O_3 (ICDD # 04-008-6181) are identified by XRD analysis [Fig. 3(a)], which compliments EDS analyzes. The low quantity of chromium phosphide is perhaps beyond the XRD detection limit.

Crystallization of amorphous Ni–P coating and dissociation, and diffusion of atoms/ions/gas molecules, attributes to the observed corrosion of Ni–P-coated AISI 430 in dry hydrogen. Plausible corrosion mechanism follows. First, amorphous Ni–P crystallizes into Ni_3P and Ni [41, 42]. Diffusion of phosphorus from amorphous fraction of Ni–P and Ni_xP diffuses into nickel through lattice and grain boundaries [43]. Volume shrinkage due to crystallization generates pores. Second, molecular H_2 and H_2O diffuses into the coating layer through the pores. Atomic interdiffusion across the coating and alloy interface leads to $\text{Fe}_{0.5}\text{Ni}_{0.5}$ formation, which may induce residual strain, similar to Ni-coated AISI 430 in Ar–3% H_2 and generates interfacial cracks. The formation of the outermost Cr_2O_3 follows the same mechanism aforementioned. Iron interacts with P and O to form $\text{Fe}_3(\text{PO}_4)_2$. Activation energy of P diffusion is the lowest among other elements in a Ni–Cr alloy [44]. Phosphorous diffusion through grain boundaries followed by precipitation at alloy grain boundaries [42] attributes to Cr–P formation.

Ni–P-coated AISI 430 in Ar–3% H_2 –3% H_2O

The surface morphology of Ni–P-coated AISI 430, isothermally treated in Ar–3% H_2 –3% H_2O , is shown in Fig. 9(a). Large grains ($4.82 \pm 1.46 \mu\text{m}$) and smaller grains at the boundaries of the large grains are observed. Cracks are found in the large grains. The composition and O/Fe (~ 1.8) ratio suggest the coexistence of Fe_2O_3 and Fe_3O_4 in the large grains, and the Fe/O ratio of ~ 1.4 suggests Fe_3O_4 in the smaller grains. The coexistence of Fe_2O_3 and Fe_3O_4 perhaps contributes to the observed cracks due to their density difference.

The cross-sectional SEM images are shown in Figs. 9(b) and 9(c). Distinct features are marked. Pores in spots “2” and each layer, and crack in layer “6”, are observed. EDS spot analysis (Supplementary Table S4) provides the elemental

composition of the distinct phases. Light gray spots in the substrate (spots “1”) are likely metal phosphides, although elemental composition does not confirm the type of metal phosphide. Bright phases “5” are solid solution of AISI 430 and Ni. Dark gray spots “2” are Mn-doped Cr_2O_3 . Layer “4” is likely Cr_2O_3 . Layer “7” is likely Fe–Cr oxide spinel along with P presence. Layer “6” is likely to be Fe–P oxide. Layers “8” and “9” are iron oxide, while brighter layer “9” contains more iron.

EDS spot analysis of the corroded AISI 430 is also consistent with the elemental maps of (Supplementary Fig. S2) and line scan profile (Supplementary Fig. S7). Juxtaposition of Cr and P maps, consistent with increased P and Cr concentration, corresponding to the light gray spot 1 confirms Cr–P phase. Overlapping Mn, Cr, and O maps corresponding to the gray layer supports Mn-doped Cr_2O_3 , consistent with their concentration profile. Overlapping Fe and Ni maps, consistent with increased Fe and Ni concentration corresponding to bright phase “5”, supports Fe–Ni intermetallic compound. Overlapping Fe, P, and O maps, consistent with their increased concentration corresponding to layer “6”, confirms Fe–P oxide presence. Nickel diffusion into the AISI 430 to $\sim 40 \mu\text{m}$ is consistent with the nickel elemental map.

Fe_3O_4 (ICDD # 04-007-2412), Cr_2O_3 (ICDD # 04-008-6181), $\text{Cr}_{1.7}\text{Fe}_{1.3}\text{O}_4$ (ICDD # 04-005-8771), $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$ (ICDD # 04-006-8207), $\text{Fe}_3(\text{PO}_4)_2$ (ICDD # 04-011-5916), Cr_{12}P_7 (04-007-1024) are identified. It is noted that the Bragg’s angle for Cr_2O_3 and $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$, and $\text{Fe}_3(\text{PO}_4)_2$ and Cr_{12}P_7 , diffraction planes overlaps.

Plausible corrosion mechanism follows. Similar to the dry hydrogen, pores form in the coating due to the crystallization of amorphous Ni–P. H_2 and oxygen from H_2O diffuse into the coating through the pores, grain boundaries, and lattice defects. Simultaneously, iron diffuses into the coating and forms Fe–P oxide by reacting with P to form $\text{Fe}_3(\text{PO}_4)_2$. Iron and chromium diffuses through this oxide. Fe_3O_4 , equilibrium with humid hydrogen, readily forms. Iron oxide reacts with chromium to form $\text{Cr}_{1.7}\text{Fe}_{1.3}\text{O}_4$ and $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$. The inward diffusion of oxygen triggers Cr_2O_3 formation by internal oxidation. Iron continues to diffuse outward through $\text{Cr}_{1.7}\text{Fe}_{1.3}\text{O}_4$. Accordingly iron oxide, preferably Fe_3O_4 , forms. EDS analysis shows that Fe_3O_4 is oxygen-deficient, indicating oxygen vacancies, enhancing inward oxygen diffusion. Oxygen-deficient FeO

Figure 9: SEM images of Ni–P-coated AISI 430 alloy corroded in Ar–3% H_2 –3% H_2O at 800 °C for 100 h. (a) Surface, (b) lower magnification cross-section, and (c) higher magnification cross-section. See the text. Nickel in the outermost layer electrodeposited on a corroded sample to avoid spallation during metallographic sample preparation.

Figure 10: Schematic diagram to illustrate atomic/ionic/molecular diffusion direction, and reaction layers for the coated AISI alloys corroded at 800 °C for 100 h. (a) Ni-coated AISI 430 in Ar-3%H₂, (b) Ni-coated AISI 430 in Ar-3%H₂-3%H₂O, (c) Ni-P-coated AISI 430 in Ar-3%H₂, and (d) Ni-P-coated AISI 430 Ar-3%H₂-3%H₂O. SiO₂, Ni-diffusion zone in the AISI 430, and cracks and pores are not marked to avoid complexity. See the text for detail.

is also found, perhaps due to local oxygen variation. Volume change due to this phase transition causes crack in grains as seen in the surface morphology [Fig. 9(a)].

Overall, the corrosion extent of Ni-P-coated AISI 430 is higher than Ni-coated AISI 430 probably due to more reaction as understood from the microstructural analysis. In both dry and humid hydrogen atmosphere, corrosion occurs due to atomic and ionic transport of the alloy and coating constituents as well as atomic/molecular gaseous species (oxygen and hydrogen) from H₂O and H₂, driven by chemical potential gradient, as shown in the schematic diagram in Fig. 10. However, MnCr₂O₄ growth direction is opposite for dry and humid hydrogen for Ni-coated AISI 430. In Ar-3%H₂ atmosphere, Cr₂O₃ forms by internal oxidation and grows externally followed by outward Mn²⁺ and Cr³⁺ diffusion and the formation of MnCr₂O₄ and outward Cr₂O₃ layer as shown in Fig. 10(a). In Ar-3%H₂-3%H₂O, Cr₂O₃ forms by internal oxidation but grows inward by AISI 430 consumption. Mn²⁺ diffuses into Cr₂O₃ and forms MnCr₂O₄. Inward Cr₂O₃ growth perhaps acts as a diffusion barrier for outward cationic transport for Ni-coated AISI 430 [Fig. 10(b)]. For Ni-P-coated AISI 430, Cr₂O₃ forms by internal oxidation and grows externally in both Ar-3%H₂ and Ar-3%H₂-3%H₂O atmospheres [Figs. 10 (c) and 10(d)]. However, faster diffusion through Cr₂O₃, due to the absence of a continuous MnCr₂O₄ layer, attributes to higher extent of reaction in Ar-3%H₂-3%H₂O as seen by multilayered oxides [Fig. 10(d)]. A nickel-coated AISI 430 alloy, based on this study, may be considered for SOFC interconnect.

Ni-P coating cannot be used. Further investigation of corrosion behavior of the coated alloy in humid hydrogen as a function of water content, temperature, and time would be beneficial for better understanding the corrosion progression and mechanisms.

Conclusions

The corrosion behavior of uncoated and Ni- and Ni-P-coated AISI 430 alloy was investigated in dry (Ar-3%H₂) and humid (Ar-3%H₂-3%H₂O) hydrogen at 800 °C for 100 h. Qualitatively, higher corrosion is observed in humid hydrogen for uncoated AISI 430 alloy but in dry hydrogen for the Ni AISI 430. Ni-P-coated samples corrode more than Ni-coated samples. Corrosion occurs due to atomic and ionic transport of the alloy and coating constituents as well as atomic/molecular gaseous species from H₂O and H₂. Lattice strain due to atomic interdiffusion of Ni and Fe favors corrosion by crack formation in Ni-coated AISI 430 in Ar-3%H₂. Nickel diffuses only ~8 μm into AISI 430 alloy for Ni-coated sample in Ar-3%H₂-3%H₂O compared with 36–40 μm for the remaining samples in this study. Inward growth of Cr₂O₃ toward AISI 430 in Ar-3%H₂-3%H₂O likely attributes to limit outward cationic diffusion and inward nickel diffusion as well. Only oxides and phosphates are found in the reaction layer for Ni-P-coated AISI 430 corroded in Ar-3%H₂-3%H₂O unlike to the Ni_{0.5}Fe_{0.5}/FeNi₃ intermetallic layer for the other samples.

Experimental Methodology

2.54 cm × 2.54 cm × 0.06 cm AISI 430 coupons (MSC Industrial Supply Co. USA) were etched and cleaned. Nickel coating, 4.96 ± 0.28 μm thick, was electrochemically deposited on AISI 430 using sulfamate bath as described in another report [22, 23]. Another set of cleaned AISI 430 was coated with Ni-P, 5.24 ± 0.10 μm thick, by a proprietary electroless deposition method (Advanced Technical Finishing, Huntsville, Alabama, USA) in accordance to MIL-C-26074 Class 1.

Uncoated and Ni- and Ni-P-coated AISI 430 coupons were exposed in dry hydrogen (Ar-3%H₂) and humid hydrogen (Ar-3%H₂-~3%H₂O) gas in an atmosphere-controlled furnace (Lindberg: General Signal, Model #54233, Waterson, WI, USA) at 800 °C. The furnace was purged overnight with dry hydrogen prior to heating. The gas was passed through deionized water at room temperature to incorporate ~3% H₂O in the humid hydrogen. A 100 sccm flow rate of the gas was maintained. All the samples were isothermally treated for a cumulative 100 h. A 3 °C/min ramp rate was maintained during heating and cooling. The samples undergone at least five thermal cycles.

The corroded samples were weighed using an analytical balance (Mettler Toledo, Model AG245, Switzerland) to determine the extent of oxidation.

XRD (Siemens D500, KRISTALLOFLEX DACO-MP 710/710 H)) was used to confirm the deposition of nickel coating and identifying the crystalline compounds formed during oxidation. The samples were scanned in $20\text{--}80^\circ 2\theta$ range with 0.04° step size.

SEM (SEM, FEI Quantity 650 FEG) was used to analyze the surface morphology as well as interfacial microstructure of the dried and oxidized samples. EDS (AMETEK EDAX) attached to the SEM was used to determine the elemental composition. The samples were sectioned and polished to optical finish for investigating the interfacial microstructure. Compositional profile across the metal-coating interface was investigated using EDS line scan. EDS mapping complemented the elemental distribution and compositional profile.

The EDS spot analysis provides the compositional variation for different phases and/or layers although the spatial resolution ($>1\text{ }\mu\text{m}$) and fluorescence effect limits the accuracy of the quantitative analysis. EDS line scan analysis provides the information about interdiffusion of elements across the interface, and elemental mapping provides visual elemental distribution. These analyses complement each other and provide a better understanding of the elemental distribution. In this study, the compositions of the different phases analyzed by EDS are reported in atomic%.

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Supplementary material

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