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Molecular-scale investigation of the oxidation behavior of chromia-forming alloys in high-temperature CO₂

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Current and future power systems require chromia-forming alloys compatible with high-temperature CO₂. Important questions concerning the mechanisms of oxidation and carburization remain unanswered. Herein we shed light onto these processes by studying the very initial stages of oxidation of Fe22Cr and Fe22Ni22Cr model alloys. Ambient-pressure X-ray photoelectron spectroscopy enabled in situ analysis of the oxidizing surface under 1 mbar of flowing CO₂ at temperatures up to 530 °C, while postexposure analyses revealed the structure and composition of the oxidized surface at the near-atomic scale. We found that gas purity played a critical role in the kinetics of the reaction, where high purity CO₂ promoted the deposition of carbon and the selective oxidation of Cr. In contrast, no carbon deposition occurred in low purity CO₂ and Fe oxidation ensued, thus highlighting the critical role of impurities in defining the early oxidation pathway of the alloy. The Cr-rich oxide formed on Fe22Cr in high purity CO₂ was both thicker and more permeable to carbon compared to that formed on Fe22Ni22Cr, where carbon transport appeared to occur by atomic diffusion through the oxide. Alternatively, the Fe-rich oxide formed in low purity CO₂ suggested carbon transport by molecular CO₂.

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INTRODUCTION

Current and future power systems require structural alloys that resist corrosion in CO₂ at high temperatures (nominally >500 °C)¹. For example, CO₂ gas-cooled nuclear reactors have relied on a variety of steels as construction materials since the 1960s². Future power plants based on the oxy-combustion of fossil fuels—a process which enables efficient CO₂ capture—would require structural alloys capable of surviving contact with flue gases containing high concentrations of CO₂³. Likewise, future power systems that utilize an indirectly heated supercritical CO₂ Brayton cycle require alloys compatible with high-temperature CO₂⁴.

From a thermodynamic perspective, high-temperature CO₂ is significantly oxidizing to all metals present in a structural alloy. Therefore, oxidation resistance is required, which is often achieved by including high levels of chromium in the alloy. Ideally, high-temperature exposure results in selective oxidation of Cr to form a protective (slow-growing) Cr-rich oxide (chromia) scale on the surface of the alloy. Fe–Cr alloys (e.g., ferritic and martensitic steels) and Fe–Ni–Cr alloys (e.g., austenitic steels) are among the most frequently employed materials due to a favorable combination of high-temperature strength and cost².

The oxidation behavior of Fe–Cr and Fe–Ni–Cr based steels in high-temperature CO₂ has been studied for many years². An interesting and surprising outcome of this work is that CO₂ is generally more corrosive (producing higher oxidation rates) to steels than pure O₂ or air, despite that CO₂ has a much lower oxygen activity—the driving force for oxidation. For example, ferritic–martensitic steels that contain Cr contents between 9 and 12 wt% form slow-growing chromia scales in air, whereas fast-growing Fe-rich oxide scales form in CO₂^{3,5}. Even Fe–Cr and Fe–Ni–Cr based alloys with high (≥20 wt%) Cr levels can suffer from increased attack in CO₂ compared to air⁶. Furthermore, the

chromia scales formed on Fe–Ni–Cr alloys are generally less susceptible to failure in CO₂ than equivalent Fe–Cr alloys containing the same Cr content^{2,7,8}. This implies a difference in the nature of the oxide scales formed on these materials, the details of which are currently unclear. Another important consideration is impurities present in the CO₂ gas. In particular, small (ppm) levels of oxygen have proven detrimental to the oxidation performance of a variety of chromia-forming alloys in high-temperature CO₂^{9–12}. Again, the mechanism behind this behavior is not well understood.

One limitation that has partially hindered our understanding of high-temperature alloy oxidation processes, both in CO₂ and in other environments, is the ex situ nature of the analysis. That is, we apply microscopic and/or spectroscopic techniques to characterize the oxidized surface, after the reaction has occurred. While this approach certainly offers a wealth of information, some mechanistic details simply cannot be revealed in this way. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) is a relatively new technique that offers the opportunity to bridge this gap—particularly for understanding chemical processes at the oxide/gas interface. Specifically, the technique enables analysis of the composition and chemical environment (e.g., oxidation state) of elements in the near-surface regions (<5 nm) of a material at relatively high pressures of >25 mbar. This is over ten orders of magnitude higher than the typical operating pressure during XPS analysis. When combined with sample heating, AP-XPS can be used to study the surface reactions of materials at elevated temperatures in situ. As such, AP-XPS has been used over the last decade to produce tremendous understanding in the fields of catalysis, electrochemistry, environmental science, and many others, under more realistic experimental conditions^{13–17}. However, despite what appears to be an obvious area of research that

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Fig. 1 AP-XPS spectra of Fe²²Cr exposed to high purity CO₂. **a** Fe 2p_{3/2}. **b** Cr 2p_{3/2}. **c** O 1s. **d** C 1s.

can benefit from this technique, there are very limited reports on the use of AP-XPS to study the high-temperature oxidation/corrosion of structural materials¹⁸.

A second limitation to our current understanding of high-temperature oxidation processes is that experiments have generally focused on relatively long exposures. Often at these stages of reaction the alloy has reached a steady-state condition, controlled, for example, by diffusion of ions through the oxide layer¹. These long-term experiments are of obvious technological interest, since a primary goal is usually to estimate the very long service lifetime of the alloy (often >20 years), and longer experimental results improve the possibility of successful prediction. Much less work has focused on understanding the initial, transient stages of oxidation, where the alloy has not yet reached a steady state. The lack of experimental understanding on this topic can be mostly attributed to, until recently, a lack of instrumentation capable of analyzing the small (nm scale) variations that arise in the material at these early stages. Still, understanding these initial stages of oxidation is of fundamental interest, and can also yield important mechanistic understanding that is relevant to the long-term oxidation behavior of the alloy.

In this study, we have applied various advanced characterization techniques to shed light onto some of the fundamental processes that control alloy oxidation in high-temperature CO₂. We used AP-XPS to study the surface of Fe–Cr and Fe–Ni–Cr based model alloys in situ during exposure to 1 mbar of flowing CO₂ at temperatures up to 530 °C, while postexposure transmission electron microscopy (TEM) and atom probe tomography (APT) provided complementary analysis of the structure and composition of the oxidized surface at the near-atomic scale. Together, these analyses reveal an extraordinary level of detail into the behavior of chromia-forming alloys during the very initial stages of oxidation in high-temperature CO₂.

RESULTS

AP-XPS analysis in high purity CO₂

Figure 1 presents AP-XPS results for Fe₂₂Cr during exposure to 1 mbar of flowing, high purity (99.999%) CO₂ at temperatures ranging from room temperature (RT) to 530 °C. The elements of interest were tracked during the exposure by collecting high-resolution photoelectron spectra for the Fe 2p_{3/2}, Cr 2p_{3/2}, O 1s,

and C 1s core levels. The RT spectrum for Fe (bottom of Fig. 1a) reveals two primary peaks, which are located at electron binding energy (BE) of approximately 707 and 710 eV. These peaks correspond to Fe in the metallic state (Fe⁰) and Fe in an oxidized state (Fe^{X+}), respectively¹⁹. Similarly, the RT spectrum in Fig. 1b reveals peaks corresponding to both metallic and oxidized Cr. In fact, the photoelectron spectra for Fe, Cr, and Ni cations present in many compounds are complex and consist not of one, but of several overlapping peaks arising from multiplet splitting¹⁹. A consequence is that, while it is possible in principle to differentiate between the oxides of a particular metal (e.g., Fe₂O₃ vs Fe₃O₄), in practice many of these oxides exhibit only very minor differences in the shape and position of the corresponding metal spectrum, which makes unambiguous phase determination difficult or impossible depending on signal quality and spectral resolution. Indeed, this type of detailed peak fitting was beyond the scope of our current study, where measurements were taken at ambient pressures (limiting signal) and with emphasis on timely acquisition to capture dynamic processes (limiting collection times and resolution). For the purposes of this study, it is sufficient to recognize that the metal existed either in the metallic state, M⁰, or as an oxide, M^{X+}, where M = Fe, Cr, or Ni.

XPS is an extremely surface-sensitive technique (the escape depth of photoelectrons is generally <5 nm)²⁰. As such, the RT Fe 2p_{3/2} and Cr 2p_{3/2} spectra in Fig. 1a, b indicate that a thin native oxide layer covered the sample surface prior to exposure. That is, the native oxide layer contained both Fe and Cr (reflected by Fe^{X+} and Cr^{X+} peaks), while Fe⁰ and Cr⁰ peaks arose from the underlying metallic substrate. The O 1s spectrum in Fig. 1c confirms that oxygen was likewise present at the surface at RT, where the largest peak (BE ≈ 530.5 eV) corresponds to metal–oxygen (M–O) bonding from the native oxide layer described above¹⁹. Two additional peaks were required to fit the high BE portion of the O 1s spectrum. The peak near 532 eV is attributed primarily to carbon–oxygen bonding^{21–23}. Contributions in this region may also arise from OH (hydroxyl) groups^{21–23} present in the native oxide, however these OH groups were largely removed during a preheating step in ultrahigh vacuum (UHV) prior to the CO₂ exposure (see “Methods” section below). Finally, the peak near 533 eV is attributed to H₂O and possibly additional carbon–oxygen bonding^{24,25}. The RT spectrum in Fig. 1c shows an example of this fitting procedure, while Table 1 provides

Table 1. O 1s peak fitting results (% area) for samples exposed to high purity (99.999%) CO₂.

		C=O	C–O, –OH	M–O
Fe22Cr	RT	3	19	78
	200 °C	4	22	74
	400 °C	2	9	89
	530 °C	1	5	95
Fe22Ni22Cr	RT	4	18	77
	200 °C	4	21	75
	400 °C	5	19	77
	530 °C	3	16	81

Table 2. C 1s peak fitting results (% area) for samples exposed to high purity (99.999%) CO₂.

		O–C=O	C=O	C–O–C	sp ³ C–C	sp ² C–C
Fe22Cr	RT	8	10	6	56	19
	200 °C	9	10	19	52	9
	400 °C	3	2	5	26	63
	530 °C	1	2	5	13	79
Fe22Ni22Cr	RT	7	5	19	65	4
	200 °C	5	8	18	69	0
	400 °C	0	1	4	38	57
	530 °C	2	2	6	11	79

a summary of the fitting results for each alloy and temperature during the exposures in high purity CO₂. In short, the high BE O 1s peaks shown in Fig. 1c arose primarily from a thin layer of hydrocarbon-rich contamination present on the outermost surface of the sample (immediately above the native oxide layer). Similar contamination is present on virtually any surface exposed to atmospheric air. The C 1s spectrum in Fig. 1d confirms this carbon-rich layer, where several peaks exist.

Due to the importance of carbon for interpreting the results, we analyzed the C 1s spectra in detail. First, while the other spectra were normalized to the maximum of the main peak (and therefore have arbitrary intensities), the C 1s spectra were normalized to the background intensity at the low BE side of the spectra. This facilitates comparison of the intensity of the C 1s spectra, and therefore the amount of carbon on the surface of the sample, at different exposure temperatures. Second, we performed detailed peak fitting of the C 1s spectra for both alloys exposed to high purity CO₂. The RT spectrum in Fig. 1d shows an example of this fitting procedure, while Table 2 provides a summary of the fitting results for each alloy and temperature. The C 1s spectra required five peaks to achieve an adequate fit. The three highest BE peaks at 289.7, 288.6, and 286.8 eV correspond to carbon bonded to oxygen in various configurations, consistent with our interpretation of the O 1s spectrum described above²⁵. The two lowest BE peaks both correspond to C–C bonding, where the peak at 285.5 eV is characteristic of carbon atoms in an sp³ type (nondirectional) bonding configuration, while the peak at 284.6 eV is characteristic of sp² type (directional) bonding²⁶. The existence of all five of these peaks at RT is consistent with a surface layer of hydrocarbon contamination, as described above. In short, prior to exposure, the Fe22Cr sample consisted of the metallic substrate, covered by a layer of native oxide, and with an outermost layer of carbon-rich contamination. This type of surface is representative of an actual structural alloy upon first exposure to a high-temperature service environment.

Figure 1 shows no change in any of the spectra upon heating to 200 °C. Note that, from a thermodynamic perspective, CO₂ is significantly oxidizing to all metals of interest in this study. For example, the most noble of the metals (Ni) requires a partial pressure of O₂ (pO₂) on the order of 10^{−21} mbar (10^{−24} atm) to oxidize at the maximum temperature used in this study (530 °C), while even lower values of pO₂ are required to stabilize the oxide at lower temperatures. In comparison, the pO₂ in equilibrium with 1 mbar (10^{−3} atm) of pure CO₂ at 530 °C is on the order of 10^{−9} mbar (10^{−12} atm). Therefore, the pO₂ of the gas (even when ignoring the inevitable presence of O₂ impurities at ppm levels) was over ten orders of magnitude higher than what was required to stabilize the oxides. Hence, 200 °C was not enough to overcome the kinetic barrier to ionic diffusion through the native oxide layer, and therefore no further oxide growth occurred up to this temperature.

Further heating to 400 °C induced changes in the spectra for all elements. Figure 1b shows that the relative amount of Cr^{X+} to Cr⁰ increased slightly, suggesting that Cr had begun to participate in the oxidation process. Alternatively, the relative amount of Fe^{X+} to Fe⁰ decreased compared to the lower temperatures. This surprising result indicates that some of the Fe that existed as an oxide was in fact reduced to the metallic state, despite that the CO₂ environment was significantly oxidizing to Fe as described above. Meanwhile, all peaks corresponding to carbon–oxygen bonding in Fig. 1c, d decreased at 400 °C. This points to the desorption and/or decomposition of most of the hydrocarbon contamination that existed on the sample surface prior to exposure. As a result, the O 1s spectrum (Fig. 1c) at 400 °C consists primarily of the M–O peak, corresponding to oxygen that was present in the oxide layer. Finally, the C 1s spectrum (Fig. 1d) is dominated by C–C bonding, with ≈26% of the carbon atoms exhibiting sp³ configuration and ≈63% sp² configuration (Table 2). This ratio of sp³ to sp² bonding is approximately consistent with amorphous carbon²⁶.

Figure 1b reveals that upon heating to the maximum temperature of 530 °C, virtually all the measured Cr existed in the oxidized state (Cr^{X+}), indicating growth of the oxide layer. Remarkably, a significant portion of the detected Fe (Fig. 1a) remained in the metallic state at this temperature. Hence, exposure of Fe22Cr to high purity CO₂ resulted in the enrichment of Cr in the oxide layer beginning at the very initial stages of oxidation. The persistence of Fe⁰ up to and including the maximum exposure temperature of 530 °C likely arose from a nonuniform oxide thickness. Visual inspection of the sample after the exposure revealed a reflective but discolored surface, consistent with the existence of a thin oxide layer. Furthermore, the extent of discoloration was different among different grains, implying a difference in oxide thickness. Therefore, it is likely that for at least a portion of the analyzed area, the oxide layer remained thin enough to detect the underlying metallic substrate. As such, the decrease in the relative amount of Fe^{X+} to Fe⁰ described above likely reflects an exchange reaction at the oxide/alloy interface, whereby Fe oxide was reduced in favor of Cr oxidation. This in turn was captured by the XPS measurements by contributions to the overall spectra from the regions that had retained a sufficiently thin oxide layer.

Figure 1d reveals that the two peaks due to C–C bonding (i.e., pure carbon) remained at 530 °C. In fact, the intensity increased relative to the lower temperatures, indicating a larger quantity of carbon on the sample surface. This is despite that carbon is not thermodynamically stable in contact with pure CO₂, where the reaction $C + CO_2 = 2CO$ is favored at this temperature. These points provide evidence that this carbon layer was not simply remnants of surface contamination present prior to exposure (i.e., thermal decomposition of hydrocarbons), but originated from the CO₂ itself. Similar C 1s spectra arise from coke formation (carbon deposition) on metal surfaces in high-temperature CO₂-rich gases

Fig. 2 AP-XPS spectra of Fe22Ni22Cr exposed to high purity CO₂. **a** Fe 2p_{3/2}. **b** Cr 2p_{3/2}. **c** Ni 2p_{3/2}. **d** O 1s. **e** C 1s.

with high carbon activity, such as during CO₂-reforming of methane^{27,28}. Close inspection of the 530 °C spectrum in Fig. 1d also reveals that the position of the peak due to C–C bonding shifted to lower BE. This is consistent with a higher fraction of sp² bonding, as shown in Table 2. This increase in sp² (directional) type bonding hints at the onset of crystallization of amorphous carbon to graphite, which is known to occur at temperatures near 500 °C²⁹. The absence of any peak in the C 1s spectrum with a BE between 281.5 and 283.5 eV confirms no metal carbide formation³⁰, consistent with thermodynamic predictions. Finally, the O 1s spectrum at 530 °C in Fig. 1c is dominated by the M–O peak at BE of ≈531 eV, consistent with oxygen that was present primarily as a metal oxide.

Figure 2 presents analogous AP-XPS results for the Fe22Ni22Cr sample exposed to 1 mbar of flowing, high purity CO₂ from RT to 530 °C. High-resolution spectra for the Fe 2p_{3/2}, Cr 2p_{3/2}, O 1s, and C 1s regions are shown, similar to the Fe22Cr sample (Fig. 1). In addition, Ni was tracked via the Ni 2p_{3/2} region, as shown in Fig. 2c. Unlike for Fe and Cr, the metallic form of Ni (Ni⁰) produces a main peak and satellite feature that are significantly separated in

BE. The major Ni⁰ peak exists at BE of ≈853 eV, while a minor, broad Ni⁰ satellite peak exists at BE of ≈859 eV. Meanwhile, Ni present as an oxide (Ni^{X+}) produces peaks intermediate to these two values, positioned at a BE of ≈856 eV. Therefore, the RT spectrum in Fig. 2c indicates no measurable amount of Ni oxide in the native oxide layer, where essentially all detected Ni corresponds to Ni⁰ that originated from the underlying metallic substrate. The RT spectra for the other elements in Fig. 2 reveal that the starting state for Fe22Ni22Cr was largely the same as for the Fe22Cr sample (Fig. 1). That is, the sample was covered by a native oxide of similar thickness (based on the ratio of oxidized peaks to metal peaks), which contained similar amounts of both Fe and Cr, and with an outermost layer of hydrocarbon contamination.

The Fe22Ni22Cr sample behaved almost identically to the Fe22Cr sample upon heating in 1 mbar of flowing high purity CO₂, which can be summarized by the following primary observations at each temperature: (1) essentially no change occurred at 200 °C, (2) heating to 400 °C largely eliminated the peaks corresponding to carbon–oxygen bonding that arose from surface contamination

Fig. 3 AP-XPS spectra of Fe22Cr exposed to low purity CO₂. **a** Fe 2p_{3/2}. **b** Cr 2p_{3/2}. **c** O 1s. **d** C 1s.

(Fig. 2d, e) and again resulted in the surprising effect of converting a significant quantity of oxidized Fe to the metallic state, at odds with thermodynamic predictions, and (3) heating to 530 °C resulted in the significant oxidation of Cr (and minimal oxidation of Fe), while the amount of surface carbon increased slightly and consisted of a larger fraction of sp² type C–C bonding. Finally, Fig. 2c shows that Ni participated only minimally in the oxidation process and remained primarily in the metallic state, where the Ni⁰ signal likely arose from the underlying alloy. Thus, the persistence of Ni⁰ peaks for all temperatures suggests that the oxide layer remained thin enough to detect the underlying metallic substrate, at least for a portion of the analyzed area.

AP-XPS analysis in low purity CO₂

Figures 1 and 2 presented AP-XPS results for alloys exposed to high purity (99.999%) CO₂ to a maximum temperature of 530 °C. The same alloys were also exposed to low purity (99.9%) CO₂ at slightly lower pressure (0.1 mbar) and a maximum temperature ranging from 407 to 427 °C. Figure 3 shows AP-XPS results for Fe22Cr from one such exposure to low purity CO₂. Comparison between Fig. 3 and Fig. 1 reveals essentially no difference for any of the spectra at RT and at 200 °C. Alternatively, heating to 400 °C resulted in drastically different behavior. In particular, Fig. 3a indicates that significant oxidation of Fe occurred in low purity CO₂. This is in stark contrast with results in high purity CO₂ (Fig. 1), where no oxidation occurred and some of the oxidized Fe was in fact reduced to the metallic state. Figure 3b shows that some Cr was also present in the oxide at 400 °C, while the lack of any metallic (Fe⁰ or Cr⁰) peaks shows that the oxide layer had grown to sufficient thickness for the entire analyzed area that the underlying metal was no longer detected. This is contrary to the exposure in high purity CO₂ (Fig. 1), where this did not occur despite a much higher exposure temperature (530 °C).

As with the exposure to high purity CO₂ (Fig. 1), Figs. 3c and 4d show that peaks corresponding to carbon–oxygen bonding decreased considerably at 400 °C, indicating the desorption and/or decomposition of hydrocarbon contamination. This again resulted in predominantly C–C bonding at 400 °C, indicative of pure carbon present on the oxide surface. However, unlike the case of high purity CO₂ (Fig. 1d) where the carbon layer increased with increasing time and temperature, the carbon was much less

stable in low purity CO₂ (Fig. 3d). Indeed, the intensity of the C–C peak decreased considerably at the highest temperature (407 °C), despite that this temperature was significantly lower than the highest temperature in high purity CO₂ (530 °C). Thus, while the layer of pure carbon was stable and grew over time in high purity CO₂, it was unstable and decreased with increasing temperature and time in low purity CO₂.

For brevity, analogous AP-XPS analysis of Fe22Ni22Cr in low purity CO₂ is shown in Supplementary Fig. 2. The Fe22Ni22Cr sample showed virtually identical behavior to the Fe22Cr sample described above.

Postexposure characterization

After completion of the AP-XPS experiments, we characterized the samples, with an emphasis on exposures in high purity CO₂, to further understand the oxidized surfaces. Figure 4 shows high-resolution TEM (HRTEM) images of a typical region of the Fe22Cr sample exposed to high purity CO₂. From top to bottom, the image in Fig. 4a shows the organometallic Pt layer used to protect the sample during the FIB lift-out process, the oxides formed during the exposure, and the alloy substrate. Figure 4a illustrates that the oxide has a duplex structure, with a continuous inner layer and a nodule-like outer layer, which appeared to grow inward and outward relative to the original metal surface, respectively. The higher magnification image in Fig. 4b shows that both the inner and outer layers are crystalline. The fast Fourier transform (FFT) pattern of the inner oxide layer indicated that it exhibited a cubic structure with a lattice constant of $a = 8.24 \text{ \AA}$, consistent with Fe_{3–x}Cr_xO₄³¹. The formation of this cubic structure during the initial stages of oxide growth is consistent with prior studies of Fe–Cr ferritic (BCC) alloys, and is expected for epitaxial reasons³². Indeed, the inner oxide showed an orientation relationship with the underlying metal according to $[001]_{\text{BCC-Alloy}} // [112]_{\text{Fe}_{3-x}\text{Cr}_x\text{O}_4}$, $(110)_{\text{BCC-Alloy}} // (220)_{\text{Fe}_{3-x}\text{Cr}_x\text{O}_4}$, implying that the oxide nucleated on the (110) plane of the BCC alloy surface³². The structure of the outer oxide was less clear. Some grains exhibited similar M₃O₄ structure as found for the inner oxide layer. For example, the FFT in Fig. 4c, which corresponds to the region indicated in Fig. 4b, suggests cubic structure with a lattice constant of $a = 8.45 \text{ \AA}$. However, other grains in the outer oxide layer, which also exhibited a cubic structure, showed significantly

Fig. 4 Cross-sectional TEM analysis of Fe22Cr after AP-XPS in high purity CO₂. **a**, **b** HRTEM images of the oxidized surface at low and high magnifications. **c**, **d** FFT patterns of outer and inner oxide layers corresponding to the regions indicated by red boxes in **b**.

different lattice parameters. We were unable to identify these phases by cross-referencing with the available crystallography database.

Figure 5 shows a cross-sectional scanning TEM (STEM) image and corresponding energy-dispersive X-ray spectroscopy (EDS) maps of a typical region of the Fe22Cr sample. While it was not possible to differentiate the inner and outer oxide layer from the STEM images such as that shown in Fig. 5a, the interface could be inferred based on the nodule-type structure of the outer oxide layer, as revealed by the HRTEM images in Fig. 4a. This approximate interface, as well as the oxide surface and the oxide/alloy interface, are delineated by the white dashed lines in Fig. 5. The EDS maps in Fig. 5b–e indicate that both the inner and outer oxide layers are rich in Cr, while a relatively small amount of Fe is also distributed throughout both layers. A zone of Cr depletion that is ≈ 25 nm thick persists immediately below the oxide layer, consistent with the selective oxidation of Cr. Finally, Cr-rich particles appeared immediately below the Cr depletion zone (Fig. 5d), to a depth of ≈ 400 nm into the alloy. Both TEM and APT analyses confirmed these were α -Cr intermetallic precipitates, as shown in Supplementary Fig. 3. These particles are known to form in Cr-rich ferritic matrices at the temperatures used in this study, and therefore they are unrelated to the oxidation process³³. Their close proximity to the alloy surface likely reflects that they precipitated at dislocations caused by the mechanical action of the polishing surface finish, the so-called “cold-worked zone”. Figure 5f shows an EDS profile taken across the red line in Fig. 5a. Note that (1) the quantification was done without standards and (2) the spatial resolution of EDS is limited at this scale due to

scattering effects. Therefore, the results in Fig. 5f should not be considered quantitative. In addition, EDS is not a reliable method of measuring small levels of carbon. Despite these limitations, the profile confirms the presence of both Cr and Fe in the oxide layer and suggests the ratio of Fe/Cr is higher in the outer oxide layer compared to the inner oxide layer.

Due to the limitations described above, we further employed APT to characterize the oxide layer formed on Fe22Cr at the near-atomic scale. Figure 6 presents APT results of a specimen that captured the oxide/alloy interface. The two-dimensional compositional maps in Fig. 6a reveal that the oxide is enriched in Cr and contains some Fe, consistent with the EDS results in Fig. 5. In addition, local carbon enrichment as high as ≈ 3 at% decorates the entire oxide layer. To better visualize these composition variations, Fig. 6b presents a one-dimensional compositional profile estimated using a 10 nm cylindrical region of interest that spans from the surface of the oxide layer to ≈ 10 nm into the underlying alloy. Comparison of the compositional profiles from APT (Fig. 6b) and EDS (Fig. 5f) reveals a similar trend for Fe, where it reaches a minimum within the bottom half of the oxide layer. We may therefore infer the interface of the inner and outer oxide layer by correlating with the TEM results described above, which is indicated by the black dashed line in Fig. 6b. The APT results thus provide a quantitative composition of the inner and outer oxide layers. In particular, the Cr/Fe atomic fraction ranges from ≈ 3.5 to 3.8 throughout most of the outer and inner oxide layer, thus confirming significant Cr enrichment. Finally, C is distributed throughout the entire oxide, where it decreases from ≈ 1 to 0.2 at% from the top to bottom of the oxide layer. Quantification of the

Fig. 5 Cross-sectional STEM/EDS analysis of Fe22Cr after AP-XPS in high purity CO₂. **a** STEM image of the oxidized surface. **b–e** Corresponding EDS maps showing elements of interest. **f** EDS line profile taken along the red line shown in **a**.

entire APT specimen indicated that the outer oxide layer contained ≈ 0.76 at% carbon, while the inner oxide layer contained ≈ 0.31 at% carbon.

We performed analogous TEM and APT analyses on the Fe22Ni22Cr sample exposed to high purity CO₂ and Figs. 7–9 show the results. Figure 7a–f shows a cross-sectional STEM image and corresponding electron energy loss spectroscopy (EELS) maps of a representative area of the oxidized surface, where the red lines delineate the oxide layer. As seen in Fig. 7f, the oxide remained very thin (<5 nm) over portions of the surface. This presumably represents the native oxide layer, which therefore defines the original metal surface. Thus, unlike the Fe22Cr sample, the oxide formed on Fe22Ni22Cr grew exclusively inward relative to the original metal surface. This resulted in three distinct regions of inward-growing (inner) oxides in Fig. 7, which appeared to contain different levels of Fe, Cr, and Ni. For example, quantification of the EELS maps indicated the leftmost was exclusively Cr oxide, while the middle and rightmost showed varying levels of Cr, Fe, and Ni in the oxide. Interestingly, the rightmost inner oxide region contained a higher level of Cr (Fig. 7e) and O (Fig. 7f) near the top compared to the bottom of the inward-growing oxide. Furthermore, Fig. 7e reveals that some Cr depletion occurred beneath the inward-growing oxides in each case, while depletion of metallic Cr also occurred at the outermost surface of the sample, between the inward-growing oxides. These observations imply that Cr enrichment ensued during growth of the inward-growing oxides, which was apparently supported by diffusion both parallel and perpendicular to the sample surface. Internal Cr-rich oxides also precipitated within an ≈ 50 nm zone at the surface of the alloy, and were particularly concentrated at the bottom of this zone. This likely represented the cold-worked zone caused by the polishing surface finish, as described above³⁴.

We collected HRTEM images of the same region to correlate with the EELS analysis and Fig. 7g–k shows the results. Figure 7g

shows a bright-field TEM image of the same region as Fig. 7a, where the oxide is again delineated by the red lines. The dark regions within the cold-worked zone arise from diffraction contrast caused by the large number of structural defects (e.g., dislocations) in this zone. Figure 7h–k shows HRTEM images and associated FFT patterns of two of the inner oxide regions. The leftmost oxide is indexed to Cr₂O₃, consistent with the EELS results described above. The Cr₂O₃ showed an orientation relationship with the underlying alloy according to (002)_{FCC-Alloy}//(006)_{Cr2O3}. The FFT pattern of the middle inward-growing oxide (Fig. 7k) showed contributions from both the FCC matrix as well as Fe₃-xCr_xO₄, with no apparent orientation relationship. This suggests that this inward-growing oxide was smaller than the thickness of the TEM specimen, resulting in contributions from both the oxide and surrounding alloy matrix in the FFT pattern. Both the EELS and HRTEM results are consistent with the notion that the Fe22Ni22Cr alloy was in the process of selective oxidation of Cr, which occurred in the sequence: FCC alloy $\rightarrow$ Fe₃-xCr_xO₄ $\rightarrow$ Cr₂O₃.

Figure 7d above suggested that a thin (<5 nm) layer rich in carbon resided at the outermost surface, immediately below the protective Pt layer. While the AP-XPS results presented earlier did suggest the existence of pure carbon on the sample surface (Fig. 2e), it is difficult to determine whether the thin layer of carbon in Fig. 7d originated from the CO₂ exposure for two reasons: (1) a thin layer of carbon contamination covers any surface exposed to atmospheric air and (2) the protective (organometallic) Pt layer also contains carbon. However, significantly thicker (>20 nm) regions of carbon also formed occasionally, such as those shown in Fig. 8. The EELS maps in Fig. 8 confirm the outermost layer consisted of pure carbon, while inner oxides rich in Cr formed immediately beneath it. Thick carbon layers such as these cannot be explained by the two reasons described above. Therefore, this carbon layer almost certainly resulted from the CO₂ exposure. The carbon-rich layer is shown in more detail via HRTEM

Fig. 6 APT analysis of Fe22Cr after AP-XPS in high purity CO₂. **a** Two-dimensional atomic composition maps showing a 10-nm slice of an APT specimen that captured the oxide layer and underlying alloy. **b** One-dimensional compositional profile corresponding to a 10 nm diameter cylindrical region of interest across the oxide/alloy interface. Error bars represent the standard counting error as described in the “Methods” section.

images taken at progressively higher magnifications in Fig. 8g–i. The images show that it consists of an amorphous matrix decorated with small (<5 nm) crystallized grains, while Fig. 8i confirms the grains are graphite. This is fully consistent with our interpretation of the C 1s spectra described above. That is, pure carbon deposited on the sample surface when the oxidation process began at a temperature around 400 °C. Increasing to 530 °C initiated the onset of crystallization, which resulted in graphite nanoparticles and a corresponding change in the C 1s spectrum reflecting a higher fraction of sp² (directional) C–C bonding. Collectively, the AP-XPS and TEM results confirm that carbon was deposited on the surface of the oxide during exposure in high purity CO₂.

Figure 9 presents analogous APT analysis of the Fe22Ni22Cr sample exposed to high purity CO₂. The two-dimensional compositional maps in Fig. 9a reveal a curved interface between the oxide and underlying alloy. Considering the TEM results (Figs. 7 and 8), the shape and thickness of the oxide suggests the APT specimen captured the edge of an inward-growing (inner) oxide region. The maps reveal a complex distribution of Fe, Cr, and Ni in the oxide. The carbon map shows a region of carbon enrichment near the outermost portion of the APT specimen, which likely corresponds to the carbon layer present on the sample surface described above. Alternatively, relatively little carbon is present within the oxide, in contrast to the Fe22Cr specimen (Fig. 6). The one-dimensional compositional profile in Fig. 9b illustrates these composition changes in more detail and suggests the oxide contains an approximately uniform Ni content of ≈10 at%, an Fe content that varies from 30–50 at% and Cr content that varies from ≈10 to 30 at%. Hence, this inner oxide region had not yet become significantly enriched in Cr. Finally, the carbon content

was high at the outermost surface as described above, whereas it was relatively low and nonuniform throughout the oxide, reaching levels as high as ≈0.6 at% and as low as 0 at%. Quantification of the entire APT specimen indicated that the oxide layer contained ≈0.21 at% carbon.

The above TEM and APT results enabled detailed visualization of the structure and composition of the oxidized surfaces at the near-atomic scale. As such, the analysis was necessarily confined to a very small portion of the samples. XPS sputter depth profiles were also collected to determine the composition of the oxidized surface as a function of depth at a much larger scale (≈100 μm diameter analysis area), as shown in Fig. 10. Note that each point in the profiles correspond to a photoelectron spectrum for that element, such as those shown in Figs. 1–3. Therefore, the XPS depth profiles contain information related to both the quantity (i.e., composition) and chemical state of each element. The approximate oxide/alloy interface, which is defined as the point where the height of the Cr⁰ peak exceeds that of the Cr^{x+} peak, is indicated by a vertical dashed line in each profile. The atomic compositions of Cr, O, Fe, and/or Ni are plotted on the left axis, while C is plotted on the right axis. Figure 10a reveals a composition profile for Fe22Cr exposed to high purity CO₂ that is largely consistent with the STEM/EDS and APT analyses (Figs. 5 and 6), where the oxide is ≈40 nm thick and is enriched in Cr. A large quantity of carbon is detected within the top ≈2 nm of the profile. This likely arose from the carbon layer left on the surface from the AP-XPS exposures as well as from contamination that settled on the surface upon exposure to atmospheric air. As with the APT results (Fig. 6), a relatively large quantity of carbon persists throughout the oxide layer, where it decreases monotonically from the oxide surface to the oxide/alloy interface.

Fig. 7 Cross-sectional TEM analysis of Fe₂₂Ni₂₂Cr after AP-XPS in high purity CO₂. **a** STEM reference image. **b–f** EELS mapping of the area indicated by the orange dashed line in **a**. **g** Bright-field TEM image of the same region used for EELS mapping. **h, j** HRTEM images of the regions indicated by orange dashed lines in **g**. **i, k** FFT patterns of the regions indicated by orange dashed lines in **h** and **j**. The oxide layer is delineated by the red lines.

Figure 10b shows the depth profile for Fe₂₂Ni₂₂Cr exposed to high purity CO₂. The slow decay in the oxygen trace is consistent with the noncontinuous, exclusively inward-growing (inner) oxides revealed by TEM. The behavior of Fe and Ni is likewise consistent. That is, these elements were present at relatively large amounts within the “oxide layer” defined by the depth profile, however their respective photoelectron spectra (not shown) indicated that they both existed primarily in the metallic state (Fe⁰ and Ni⁰) from the very beginning of the profile. Hence, Fe and Ni signal arose primarily from the alloy substrate, at regions that had not yet formed inner oxides. Instead, the oxide was, on average, enriched in Cr. This is consistent with the TEM results, which showed that the inner oxides were in the process of becoming enriched in Cr. As with the Fe₂₂Cr sample, Fig. 10b indicates a significant amount of carbon within the top ≈2 nm of the sample. However, unlike the

Fe₂₂Cr sample, minimal carbon is observed in the inner oxides formed on Fe₂₂Ni₂₂Cr, where the carbon trace drops immediately to the noise level (≈1 at%) after the first 2 nm.

Figure 10a, b indicated significant carbon within the relatively thick oxide formed on Fe₂₂Cr in high purity CO₂, whereas there was little or none in the thinner and noncontinuous inner oxides formed on Fe₂₂Ni₂₂Cr. To show that this is not simply a consequence of the oxide being thicker for the Fe₂₂Cr sample, Fig. 10c compares the carbon profiles for the two alloys after normalizing to the thickness of the oxide layer, as defined above. Furthermore, Fig. 10d compares the C 1s spectra at a normalized oxide thickness of 0.25 (i.e., ¼ of the way through the oxide layer) for each alloy. Clearly, the oxide layer formed on Fe₂₂Cr contained a significant amount of carbon, whereas the oxide layers formed on Fe₂₂Ni₂₂Cr contained very little (below the detection limit).

Fig. 8 Cross-sectional TEM analysis of Fe22Ni22Cr after AP-XPS in high purity CO₂. **a** STEM reference image. **b–f** EELS mapping of the area indicated in **a** by the orange dashed line. **g–i** HRTEM images showing the carbon layer at increasing magnification. The oxide layer and carbon layer are both delineated by the red lines.

Finally, Fig. 10d shows that the position of the C 1s peak within the oxide layer of Fe22Cr (284.2 eV) is consistent with exclusively C–C bonding, indicative of atomic carbon.

XPS sputter depth profiles were also collected for both alloys after exposure to low purity CO₂, as shown in Fig. 10e–g. Both alloys exhibited a duplex oxide structure, with an outer layer of primarily Fe oxide and an inner layer containing both Fe and Cr. As with the high purity CO₂ exposures (Fig. 10a, b), significant carbon resided in the oxide formed on Fe22Cr, while little or none appeared in the oxide formed on Fe22Ni22Cr. However, unlike for high purity CO₂, the carbon present in Fe22Cr exposed to low purity CO₂ was clearly concentrated in the inner oxide layer. Figure 10g compares the C 1s spectra at a depth of 4.6 nm (approximately halfway through the oxide). The spectra confirm little or no carbon (below the detection limit) in the oxide formed on Fe22Ni22Cr. Meanwhile, the C 1s peak position within the oxide formed on Fe22Cr (283.5 eV) is notably lower than the one seen in the oxide formed in high purity CO₂ (284.2 eV). This peak position is consistent with C–Cr bonding, indicative of Cr-rich carbides³⁵.

DISCUSSION

We designed this work to simultaneously achieve, as closely as possible, two competing objectives: (1) closely simulate realistic conditions of an oxidizing alloy surface in a high-temperature CO₂ service environment and (2) enable analysis of the oxidizing sample at an unprecedented level of detail, to reveal mechanisms that have hereto been unobservable experimentally. We describe the full approach in the “Methods” section below, however certain

aspects of the experimental design warrant emphasis. We used a chemical mechanical polishing approach with 0.05 μm colloidal silica slurry to prepare the alloy surfaces used for all analyses. This produced a surface with extremely low roughness (<0.01 μm), while still retaining some structural defects near the alloy surface induced by the mechanical action of the polishing particles^{34,36}. This smooth surface facilitated accurate interpretation of the experimental results, for example, by limiting two-dimensional projection artifacts during TEM analysis and enabling distinction between the oxide layer and underlying alloy during sputter depth profiling. Meanwhile, near-surface structural defects are universally present for alloys commissioned for high-temperature service, and these defects play a critical role in the oxidation behavior of the alloy^{34,36}. Therefore, we avoided the more idealized (defect-free) surfaces that can be produced, for example, by electropolishing or sputtering and/or annealing under UHV prior to the exposure. Similarly, we adopted a cleaning procedure that combined an ultrasonic bath, UV ozone treatment, and modest heating under UHV to remove a significant quantity of the atmospheric carbon-containing contamination that settles on the sample, without significantly changing the native oxide layer that formed on the alloy surface upon exposure to ambient air. This enabled accurate interpretation of the fate of carbon associated with the reaction of CO₂, while still preserving the native oxide, which represents the critical first step in the oxidation pathway of the alloy. In short, while some degree of compromise was unavoidable, we adopted an approach that enabled analysis of the very initial stages of oxidation of a structural alloy at conditions that closely simulate what the alloy would experience upon exposure to a high-temperature CO₂ environment.

Fig. 9 APT analysis of Fe22Ni22Cr after AP-XPS in high purity CO₂. **a** Two-dimensional atomic composition maps of an APT specimen that captured the oxide layer and underlying alloy. **b** One-dimensional compositional profile corresponding to a 10 nm diameter cylindrical region of interest across the oxide/alloy interface. Error bars represent the standard counting error as described in the “Methods” section.

The AP-XPS results revealed that the very first stages of oxidation were radically affected by the CO₂ purity for both the Fe22Cr and Fe22Ni22Cr samples. That is, Fe-rich oxides formed in 99.9% CO₂, while Cr-rich oxides formed in 99.999% CO₂. The notion that impurities play an important role during the initial stages of oxidation in CO₂ is not surprising^{10–12,37}. In fact, prior investigations of the initial stages of oxidation in a 9Cr steel found a similar pattern of behavior to our current study⁹. That is, a Cr-rich oxide formed during the early stages of oxidation in high purity CO₂, whereas Fe-rich oxides formed in low purity CO₂. The authors of the earlier reports concluded that the more reactive O₂ molecules provided the oxygen that contributed to the first stages of oxide growth, where the more limited supply of O₂ in high purity CO₂ favored the preferential oxidation of Cr⁹. While our results are not inconsistent with this notion, they do reveal important additional details of this process.

The deposition of pure carbon on the surface of the growing oxide layer in high purity CO₂ was implied by AP-XPS (Figs. 1 and 2) and confirmed by postexposure TEM (Fig. 8). To understand this phenomenon, we consider the surface reactions governing the exposure. The most favorable reactions during the exposure are the oxidation of the metals (M = Cr, Fe, Ni) and of C by O₂ impurities in the CO₂ gas according to

where reaction of the metals is supported by ionic diffusion through the native (and subsequently growing) oxide layer. Hence, beginning from the first stage of the reaction at temperature between 200 and 400 °C, metals in the alloy and C

present initially as surface contamination competed for reaction with the limited supply of molecular oxygen present in the gas. The oxidation did not proceed by O₂ impurities alone, however, as there was evidence for deposition of carbon onto the sample surface, despite that reaction (2) is highly favored. This implies that CO₂ molecules also contributed to the oxidation process. The oxidation of the metals occurs by

while the oxidation of carbon by pure CO₂ is also predicted

The fate of CO produced by reactions (3) and (4) is one of four. First, it may desorb from the surface. Second, it may react with dissociated oxygen to revert back to CO₂

Third, it may further oxidize metal according to

Fourth, it may recombine with an additional CO molecule by the reverse of reaction (4). The last scenario would require the local accumulation of CO on the sample surface, since the forward reaction is predicted in pure CO₂, as described above. Either by scenario three, four, or both, carbon deposition occurred during the exposures. The stability of the carbon layer in high purity CO₂ therefore reflects a kinetic scenario arising from the sum of the rates of all the competing reactions described above. In short, the rate of removal of carbon was less than the rate that carbon was produced as a by-product of the metal oxidation process.

Fig. 10 XPS sputter depth profiles collected after AP-XPS experiments. **a, b** Depth profiles for samples exposed in high purity CO₂. **c** Atomic percentage of C as a function of the normalized thickness of the oxide layer. **d** C 1s spectra at a normalized oxide depth of 0.25. **e, f** Depth profiles for samples exposed in low purity CO₂. **g** C 1s spectra at a depth of 4.6 nm. The approximate oxide/alloy interface is indicated for each sample.

The deposition of solid carbon at the oxide/gas interface in high purity CO_2 has interesting implications for the subsequent oxidation behavior of the alloy. That is, the oxygen activity established at the oxide/carbon interface is very likely lower than the one that would otherwise exist at the oxide/gas interface in the absence of solid carbon. Therefore, we propose that this carbon layer played an important role in promoting the selective oxidation of Cr at these early stages, by producing a surface chemical environment that was not strongly oxidizing to Fe (or Ni) and therefore discouraged their outward diffusion. It is interesting to note that CO_2 is somewhat unusual in this way, where the species that is reduced in favor of metal oxidation (i.e., carbon) forms a solid phase at the conditions of interest, and can therefore accumulate on the surface as a by-product of the reaction. This is contrary to oxidation in most other oxidizing environments. In H_2O for example, hydrogen formed as a by-product of metal oxidation may simply desorb from the surface and be removed by the flowing gas, and therefore does not subsequently affect the oxygen activity at the oxide/gas interface. Hence, we believe the selective oxidation of Cr in high purity CO_2 did not occur solely due to the lower oxygen activity of the bulk gas (by virtue of the low O_2 impurity level), but was assisted also by the presence of carbon deposited as a by-product of the metal oxidation process.

At this early stage of the reaction, the selective oxidation process in high purity CO_2 manifested in different ways for the two alloys. For both alloys, the AP-XPS results showed that the ratio of Fe^0 to Fe^{x+} increased as the oxide began to grow (Figs. 1 and 2). This implies that oxidized Fe was chemically reduced either (1) at the surface of the oxide or (2) at the oxide/metal interface (at regions of the sample where the oxide layer remained thin enough to observe this interface). Because some Fe was observed in the outward-growing (outer) oxide layer in Fe22Cr, this suggests that the oxygen activity at the surface of the oxide was still somewhat oxidizing to Fe, inducing its outward diffusion (albeit at a rate lower than that of Cr). Furthermore, no evidence of clusters of metallic Fe in the oxide were found by APT, which may be expected if oxidized Fe were reduced at the surface of the growing oxide and then incorporated into it. Thus, the first scenario is unlikely. Instead, the TEM results showed clear evidence of depletion of metallic Cr in the substrate for both alloys. For Fe22Cr, which contained a relatively uniform inner oxide layer, the depletion occurred perpendicular to the surface. For Fe22Ni22Cr, evidence of Cr depletion is seen both parallel and perpendicular to the surface to support the Cr enrichment of the periodic, inward-growing oxides. In summary, the increase in the ratio of Fe^0 to Fe^{x+} for the alloys exposed to high purity CO_2 likely reflects a solid-state exchange reaction at the oxide/alloy interface, whereby Fe oxide was reduced in favor of Cr oxide, with Fe diffusing back into the alloy substrate.

In contrast to the scenario described above, the low purity CO_2 contained sufficient oxygen impurities that no carbon accumulation accompanied metal oxidation. This resulted in an oxygen activity at the surface that was closer to the one expected for the bulk gas, which was very oxidizing to all metals in the alloy, and therefore enabled significant outward diffusion of Fe.

Two important considerations from an application perspective are whether the carbon layer observed for the high purity CO_2 exposures herein persists for (i) higher pressures and (ii) longer durations. Regarding point (i), higher pressures imply higher oxygen activities, which may destabilize the carbon layer. This is especially true considering that industrial applications likely would use lower purity CO_2 for cost reasons. However, carbon deposition via reaction (6) and the reverse of reaction (4) (i.e., the Boudouard reaction) also becomes more favored by higher pressures. For instance, at 530 °C and a carbon activity equal to 1, the equilibrium CO/CO_2 ratio decreases from ≈ 10 at 1 mbar to ≈ 0.1 at 1 bar, and ≈ 0.01 at 200 bar. Hence, if the Boudouard reaction is a dominant form of carbon deposition, relatively little CO accumulation is

required at the surface of the sample, especially at the pressures expected in supercritical CO_2 (sCO_2) power generation systems. Furthermore, in closed-loop systems such as an indirect sCO_2 power cycle, metal oxidation would likely result in CO accumulation and therefore very low O_2 levels after prolonged operation. Thus, higher pressures and more realistic (closed-loop) environments would not necessarily discourage carbon deposition accompanying the oxidation process and may in fact favor it. Regarding point (ii), as the oxide layer thickens, the flux of metal ions to the surface will decrease. This would reduce competition for O_2 molecules such that reaction (2) may proceed more readily, while the rate of CO production by reaction (3) would also decrease. In short, at longer times the extent of the competitive reactions described above might be expected to destabilize carbon present on the oxide surface. Nevertheless, low levels of oxygen are known to negatively impact the oxidation performance of chromia-forming alloys in high-temperature CO_2 at higher pressures and longer times, particularly by prolonging the transient oxidation period prior to formation of a protective Cr-rich oxide scale^{10–12}. The results presented herein offer a possible explanation for this behavior.

Postexposure TEM, APT, and XPS of samples exposed to high purity CO_2 indicated that Fe22Cr oxidized more extensively compared to Fe22Ni22Cr. In particular, the oxide formed on Fe22Cr grew both outward and inward relative to the original metal surface, while that formed on Fe22Ni22Cr grew inward only. Hence, the outward diffusion of Fe (and Ni) was completely suppressed for Fe22Ni22Cr. We are aware of six possible explanations for this difference in behavior:

- (1) The local chemical environment established on the surface was less oxidizing, which in principle could be caused by increased carbon deposition.
- (2) The native oxide was more protective.
- (3) The growing oxide contained a higher level of Cr.
- (4) The growing oxide exhibited a different crystal structure.
- (5) The different structure of the alloy substrate affected metal diffusion rates supporting the oxidation reaction.
- (6) The presence of Ni within the oxide limited outward diffusion.

The first option appears unlikely, considering more carbon deposition was observed for Fe22Cr (Fig. 1) compared to Fe22Ni22Cr (Fig. 2). The second option is likewise unlikely, considering that the native oxide layers contained similar levels of Fe and Cr (Figs. 1 and 2). The third and fourth options can also be dismissed: while some of the inward-growing oxides on Fe22Ni22Cr had fully converted to Cr_2O_3 , most exhibited the same (M_3O_4) structure as the inward-growing oxide formed on Fe22Cr, and at least some contained similar or higher levels of Fe, including the one captured by the APT specimen (Fig. 9). Finally, the fifth option is dismissed as some surface regions were not enriched in Cr, but nevertheless no outward oxide growth occurred (Fig. 7), implying that diffusion of Cr in the alloy was not a limiting factor. Hence, the most likely explanation for the decreased extent of oxidation for Fe22Ni22Cr appears to be the presence of Ni within the growing oxide, such as that observed by APT in Fig. 9. Decreased oxidation rates for increasing Ni has been demonstrated previously in Fe–Ni–Cr alloys, which has been attributed to slower diffusion in $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ oxides³⁸.

There is a driving force for carbon diffusion from the CO_2 environment into the metal once an oxide layer has formed, and the nature of this carburization process has significant implications for the stability of the growing oxide layer¹. Indeed, the Fe22Cr sample exposed to high purity CO_2 showed significant carbon in the oxide, which decreased monotonically from the oxide surface to the oxide/alloy interface, implying carbon diffusion into the material. Alternatively, Fe22Ni22Cr exposed to high purity CO_2 showed less carbon in the oxide, especially

Table 3. Compositions of alloys used in this study (at%).

	Fe	Ni	Cr	Co	Ti	Al	Cu	C	N	O	S
Fe22Cr	76.36	0.08	23.23	–	0.01	0.02	0.01	0.16	0.06	0.06	0.002
Fe22Ni22Cr	55.91	20.31	23.43	0.06	0.02	0.04	0.01	0.15	0.06	0.02	0.002

averaged over a relatively large surface area of the sample (Fig. 10a, b). As described above, both the crystal structure of the oxide and the amount of Cr within it were not significantly different between the alloys. Therefore, the decreased carbon transport again could be related to Ni in the oxide. Another possibility is that the carbon uptake in the Fe22Ni22Cr alloy accumulated immediately below the oxide, whereas it diffused into the bulk of the alloy for the case of Fe22Cr. This could effectively increase the carbon activity at the oxide/alloy interface and therefore reduce the driving force for carbon diffusion through the oxide. Some evidence of this is found in the APT results (Figs. 6 and 9). That is, the carbon content of the alloy immediately beneath the oxide grown on Fe22Cr (0.1 at%) is similar to the value expected for the bulk alloy (Table 3), whereas the carbon content beneath the oxide grown on Fe22Ni22Cr (1.0 at%) is higher than expected. Previous work has highlighted the effect of increasing alloy Ni content in decreasing carbon permeability in the alloy, which may explain this accumulation³⁹. Alternatively, it is possible this carbon accumulation is related to a decarburization process that may have occurred during the very first instances of exposure, prior to establishment of an oxide that served as an effective diffusion barrier to carbon⁴⁰. In short, Ni present in the oxide, the underlying alloy, or both, appeared to reduce the amount of carbon uptake by the alloy during the very first stages of exposure.

The mode of carbon transport through the oxide is a question of fundamental importance, both for alloy oxidation in CO₂ and other oxidizing-carburizing environments. Researchers have proposed that molecular diffusion of CO₂ along grain boundaries is the most likely mode of carbon transport in dense (porosity-free) Cr-rich oxide scales⁴¹, such as the oxides observed during the high purity CO₂ exposures herein. This theory is predicated in part by radiotracer studies done with bulk Fe and Cr oxides, which showed immeasurably small solubility of atomic carbon in the grain boundaries or the lattice of these oxides⁴². However, our results suggest that this conclusion is perhaps not readily extendable to the oxides grown on metals during an oxidation reaction, at least for the beginning stages of exposure. That is, the TEM results of Fe22Cr exposed to high purity CO₂ (Fig. 4) did not reveal any significant defects throughout the oxide (pores, cracks, etc.) other than grain boundaries. Meanwhile, the chemical state of the carbon present within the oxide from the XPS sputter depth profile (Fig. 10d) indicated exclusively C–C bonding, with no evidence of C–O bonding that would be expected for molecular CO₂. It remains possible that molecular CO₂ did exist within the oxide during the reaction, but that it decomposed at some point thereafter. Furthermore, it is difficult to rule out possible effects of Ar⁺ sputtering in modifying the chemical state of the detected carbon. Nevertheless, the results do indicate the presence of atomic carbon in the oxide layer during the time and conditions of the postexposure analysis, which raises the possibility that carbon transport occurred by atomic diffusion through the oxide layer. This transport may well have occurred along grain boundaries, considering the nonuniform distribution of carbon revealed by APT (Fig. 6). The supply of atomic carbon available to diffuse through the oxide is readily understood by the competing surface reactions described above.

The incorporation of significant carbon into the Cr-rich oxide layer on Fe22Cr beginning at the first stage of exposure in high purity CO₂ undoubtedly plays a role in the subsequent protective

behavior of the oxide. For example, carbon at the grain boundaries may weaken the strength of these interfaces, making the oxide more susceptible to cracking⁴¹. Likewise, carbon that accesses the underlying alloy will preferentially react with metallic Cr and therefore reduce the amount available to support selective oxidation. Regardless of the precise mechanism, the results point to the beneficial effect of Ni in slowing both oxidation and carburization in chromia-forming alloys, and therefore enabling formation of a more protective oxide scale, during the initial stages of exposure to high-temperature CO₂.

It is interesting to note that the oxide formed on Fe22Cr in low purity CO₂ (Fig. 10e) showed a duplex structure that is quite representative of much longer-term exposures of low-Cr steels (e.g., 9–12Cr steels) in CO₂, where selective oxidation of Cr likewise does not prevail². That is, the oxide consists of an outer layer of essentially pure Fe oxide and an inner layer of (Fe, Cr) oxide, where the interface of the inner and outer oxide represents the original metal surface. This proposed original metal surface, based on the above interpretation, is indicated for each alloy exposed to low purity CO₂ in Fig. 10e, f. Of particular note, it is generally accepted that the inner oxide layer grows by molecular diffusion of CO₂ through defects (such as nanopores) in the Fe-rich duplex oxide scale¹. This in turn liberates carbon at the oxide/alloy interface, which diffuses into the steel and reacts with metallic Cr to form Cr-rich carbides. Thus, in this proposed growth mechanism, carbon transport through the Fe-rich duplex oxide scale occurs by the molecular diffusion of CO₂. Figure 10e fully supports this growth mechanism and suggests that it may well prevail beginning at the very early stages of oxidation. That is, carbon is present in the oxide, but only within (and below) the inner oxide layer, while the chemical state of the carbon (Fig. 10g) is consistent with Cr-rich carbides. A likely explanation is that carbides formed in the alloy immediately below the oxide/alloy interface and were subsequently incorporated into the inward-growing, inner oxide layer. Hence, the source of carbon did not originate at the surface of the oxide, but rather at the oxide/alloy interface, as a by-product of metal oxidation by CO₂. This mode of carbon transport contrasts with the case of relatively defect-free, Cr-rich oxide scales such as those formed in high purity CO₂ described above, where the carbon diffusion profiles imply a source of carbon originating at the oxide surface. Interestingly, no carbon is observed throughout the oxide formed on Fe22Ni22Cr in low purity CO₂ (Fig. 10f), despite that it also formed an Fe-rich oxide. Once again, this points to the beneficial effect of Ni in limiting carburization of Fe–Cr based alloys in high-temperature CO₂.

In conclusion, we developed a methodology to study the very first stages of alloy oxidation in high-temperature CO₂. A variety of techniques collectively captured the dynamic, nonequilibrium processes that ultimately controlled the oxidation behavior of Fe22Cr and Fe22Ni22Cr alloys at these early stages. In particular, we demonstrate the power of AP-XPS as a means to study high-temperature metal oxidation reactions in situ, by unveiling processes unobservable by virtually any other technique. In revealing fundamental mechanisms of oxidation at these early stages, we further shed light onto processes likely connected to the long-term degradation behavior of chromia-forming alloys in high-temperature CO₂. Specifically, CO₂ purity is critical for rapid establishment of a Cr-rich oxide scale. This appears to be related to carbon deposited on the oxide surface during reaction in high purity CO₂, which affects the local oxygen activity at this surface.

This carbon, in turn, can diffuse through the Cr-rich oxide beginning at the first instants of reaction, which may impair the long-term protectiveness of the oxide. Alloy Ni content both hinders outward oxide growth, promoting faster chromia formation, and limits carbon diffusion through the oxide, which may explain the increased resilience of chromia-forming alloys containing high levels of Ni to the unique oxidation concerns posed by high-temperature CO₂-rich environments. This work highlights the importance of considering early stage processes to understand the long-term stability of oxide scales formed on structural alloys in high-temperature environments.

METHODS

Alloy fabrication and sample preparation

Model alloys with compositions of Fe22Cr and Fe22Ni22Cr (22 indicating nominal content of the proceeding element wt%) were fabricated in a vacuum induction furnace using industrial-purity elemental input materials. For convenience interpreting the results of this paper, Table 3 shows the alloy compositions in at%. Metallic elements were measured by wavelength dispersive X-ray fluorescence spectroscopy and interstitial elements were measured by combustion analysis in a LECO system (CSLL45). The alloys were homogenized and hot worked (forging and rolling) into plates of ~13 mm thickness. Samples were machined from the alloy plates into dimensions of 8 mm × 8 mm × 2 mm. The sample faces were lapped using 17.5 µm alumina slurry to remove machining damage. The sample face used for all subsequent analysis was further polished to a mirror finish using 0.05 µm colloidal silica and a polishing pad. This type of finish resulted in area-averaged surface roughness values (S_a) on the order of 0.01 µm³⁶.

AP-XPS exposures

AP-XPS experiments were performed in a laboratory based SPECS system which is described in more detail elsewhere⁴³. Samples were ultrasonically cleaned in acetone followed by a UV ozone treatment prior to loading into the AP-XPS loadlock. The sample was then heated to a temperature of ~140 °C UHV (1.1 × 10⁻⁹ mbar). This was the maximum temperature that the sample could be heated to without significant changes in the 2p spectra of the metals (Cr, Fe, and/or Ni). Supplementary Fig. 1 shows the native oxide layer before and after this preheating step, which indicates that the main effects were to reduce the amount of hydroxyl groups and the amount of carbon-oxygen bonding. Collectively, the goal of this cleaning procedure was to reduce the amount of adventitious carbon-containing contamination on the sample surface, with little change to the native oxide layer.

After cooling to RT, the sample was exposed to the flowing reaction gas for the duration of the exposure. The gas consisted either of high purity (99.999%) CO₂ at a pressure of 1 mbar or low purity (99.9%) CO₂ at a pressure of 0.1 mbar. Supplementary Table 1 shows the maximum impurity contents of each gas, as provided by the manufacturer.

High-resolution spectra were collected for C 1s, O 1s, Cr 2p, Fe 2p, and/or Ni 2p core levels using monochromatized Al Kα radiation (hν = 1486.65 eV, 50 W, and 15 kV) and a pass energy of 35 eV. The spectrometer resolution at this pass energy, defined as the FWHM of the Ag 3d peak measured from a Ag calibration sample in 1 mbar of flowing N₂ at RT, was 0.65 eV. The instrument BE was calibrated by collecting Ag 3d spectra with three different pass energies, adjusting the slits to align all three spectra, then verifying the linearity with a Au/Cu sample. The X-ray beam diameter, which defines the area of analysis, was ~300 µm.

Spectra were first collected in flowing gas at RT. Then, the sample was heated stepwise, with the same spectra collected at various temperature increments, up to a maximum temperature of ~530 °C (high purity CO₂ exposure) or ~407–430 °C (low purity CO₂ exposure). The temperature was measured using a type-K thermocouple spot welded to the sample holder immediately adjacent to the sample. Each heating increment required between approximately 15 and 50 min, and the sample was then held at each temperature for ~35–45 min during data collection. The spectra were collected one at a time with a step size of 0.1 eV and averaged over multiple scans (two scans for Fe 2p, Cr 2p, Ni 2p, and O 1s, four scans for C 1s during low purity CO₂ exposure and six scans during high purity CO₂ exposure). Therefore, a given spectrum represents the average over the collection period for that element, which was ~18 min for Cr 2p, ~4 min for O 1s, ~7 min for Fe 2p, ~6 min for Cr 2p, and ~10 min for Ni 2p. The sample

was held at the maximum temperature for an additional 35–45 min (70–90 min total) during a second round of spectra acquisition (results in the paper show the second round of spectra, which were nearly identical to the first) before cooling to RT under continued gas flow.

CasaXPS software was used for peak fitting. For the O 1s spectra, all peak shapes were 30% Lorentzian and 70% Gaussian and had FWHM of 1.5 eV. The M–O peak position (530.5 eV) and the C–O, C=O, OH peak position (532.0 eV) were allowed to vary ±0.5 eV, while the H₂O peak position was fixed at 533.2 eV. For the C 1s spectra, a Lorentzian asymmetric line shape (LA(2,3,0)) with a FWHM of 1.2 eV was used to fit the sp² C–C peak, while all other peak shapes were 30% Lorentzian and 70% Gaussian and had FWHM of 1.4 eV. Peaks positions were fixed at 284.6 eV (sp² C–C), 285.5 eV (sp³ C–C), 286.8 eV (C–O–C), 288.6 eV (C=O), and 289.7 eV (O–C=O).

Postexposure analysis

After the AP-XPS exposures, the samples were removed from the system and further characterized using a variety of techniques. XPS depth profiles were collected on a PHI VersaProbe III. High-resolution spectra were collected for Fe 2p, Cr 2p, Ni 2p, O 1s, and C 1s core levels using a using monochromatic Al Kα radiation and a pass energy of 55 eV. The X-ray beam diameter, which defines the area of analysis, was ~100 µm. A 1 keV Ar⁺ ion beam was used for sputtering accompanied by Zalar rotation. This yielded a sputtering rate of 3.02 nm/min (calibrated to SiO₂). Approximate depths were calculated by assuming a sputter rate of Cr₂O₃ relative to SiO₂⁴⁴.

TEM and associated EDS analyses were performed using an FEI Titan 80-200 TEM equipped with four windowless silicon drift detectors. Additional TEM imaging and EELS analysis was performed using a separate FEI Titan 80-300 TEM equipped with a spherical aberration (Cs) corrector. A high-angle annular dark-field detector was using for STEM imaging. Specimens for TEM analysis were prepared using the focused ion beam lift-out method using an FEI Helios Nanolab SEM.

APT analysis was performed using a CAMECA LEAP 4000X HR in laser pulsing mode with 80–100 pJ laser energy and a pulse fraction of 20%. The specimen temperature was 40 K, while the detection rate was maintained at 0.005 atoms/pulse. Data were reconstructed and analyzed using the integrated visualization and analysis software, version 3.8.5 by CAMECA. Error bars for the one-dimensional composition profiles represent the standard counting error, σ, defined as $\sigma = \sqrt{(c_i(100 - c_i)/N_i)}$, where c_i is the local concentration of species i and N_i is the total number of atoms in the concentration measurement.

DATA AVAILABILITY

All relevant data that support this study are available from the corresponding author upon request.

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AUTHOR CONTRIBUTIONS

R.P.O. designed the study and wrote the manuscript. R.A., J.T.D. and G.S.H. performed the AP-XPS analysis. J.P.B. performed the XPS depth profiling. B.G. and A.D. performed the APT analysis. T.L. performed the TEM analysis. O.N.D. provided input during the study. All authors participated in discussion of the results and editing of the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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