

Assessment of a High-Throughput Methodology for the Study of Alloy Oxidation using $Al_x Fe_v Ni_{1-x-v}$ Composition Gradient Thin Films

Matthew A. Payne,^{†,‡} James B. Miller,^{†,‡} Martin E. Oliveros,[§] Geronimo Perez,[§] Cristol P. Gouvea,[§] Bráulio S. Archanjo,[§] Carlos A. Achete,[§] and Andrew J. Gellman^{*,†,‡,#}

[†]Department of Chemical Engineering and [#]W.E. Scott Institute for Energy Innovation, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

[‡]DOE – National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, Pennsylvania 15236, United States

[§]Divisão de Metrologia de Materiais, Instituto Nacional de Metrologia, Qualidade e Tecnologia, Av. Nossa Senhora das Graças 50, 25250-020 Duque de Caxias, Rio de Janeiro, Brasil

ABSTRACT: The high-temperature oxidation of multicomponent metal alloys exhibits complex dependencies on composition, which are not fully understood for many systems. Combinatorial screening of the oxidation of many different compositions of a given alloy offers an ideal means for gaining fundamental insights into such systems. We have previously developed a highthroughput methodology for studying $Al_xFe_vNi_{1-x-v}$ alloy oxidation using ~100 nm thick composition spread alloy films (CSAFs). In this work, we critically assess two aspects of this methodology: the sensitivity of CSAF oxidation behavior to variations in $Al_xFe_yNi_{1-x-y}$ composition and the differences



between the oxidation behavior of ~100 nm thick CSAFs and that of bulk $Al_xFe_yNi_{1-x-y}$ alloys. This was done by focusing specifically on Al_xFe_{1-x} and Al_xNi_{1-x} oxidation in dry air at 427 °C. Transitions between phenomenologically distinguishable types of oxidation behavior are found to occur over CSAF compositional ranges of <2 at. %. The oxidation of $Al_{x}Fe_{1-x}$ CSAFs is found to be very similar to that of bulk Al_xFe_{1-x} alloys, but some minor differences between CSAF and bulk behavior are observed for Al_xNi_{1-x} oxidation. On the basis of our assessment, high-throughput studies of CSAF oxidation appear to be an effective method for gaining fundamental insights into the composition dependence of the oxidation of bulk alloys.

KEYWORDS: Al-Fe-Ni, oxidation, Al_2O_3 passivation, thin films, materials libraries, high-throughput screening

INTRODUCTION

The development and improvement of metal alloys that can survive for long periods of time in harsh oxidizing environments is important in many technological applications. The most common method for imparting oxidation resistance to an alloy is by the addition of a component that preferentially forms a passivating oxide scale (i.e., continuous protective layer) at or near the surface upon initial exposure to the oxidizing environment.¹⁻³ In certain high-temperature environments (most notably those containing H_2O vapor), only Al_2O_3 scales can offer suitable protection, so Al must be included as a component in any oxidation-resistant alloy.^{2,3} The Al content of an alloy must exceed a "critical Al concentration", N_{Al}^* , for a passivating Al₂O₃ scale to be established in an oxidizing environment; alloys with subcritical Al concentrations instead form nonprotective, subsurface Al₂O₃ precipitates that allow ongoing oxidation of the other metal components.^{2,4-8} Because increasing the Al content is detrimental to the mechanical properties of many alloys, $^{2,7,9-12}$ it is often desirable to design an alloy such that the Al concentration exceeds $N_{\rm Al}^*$ by as little possible, thereby achieving the optimal balance of physical durability and oxidation resistance. However, the oxidation of

multicomponent alloys is kinetically complex, depending on both alloy composition and the physical environment,^{2,3} which makes it difficult to predict the value of N_{Al}^* for arbitrary systems. Furthermore, it is impractical to identify N_{AI}^* empirically across large, multicomponent composition spaces by individually preparing and testing the oxidation behavior of many single-composition alloy samples. It appears that these considerations should make combinatorial screening an ideal approach for studying alloy passivation by Al₂O₃ scale formation. However, despite the recent proliferation of combinatorial and high-throughput methods applied to a wide variety of other problems in materials science,¹³ we are aware of only a handful of studies by other authors^{12,14–16} that have attempted to apply such methods to the study of Al-alloy oxidation.

We have recently published two studies in which we introduced and applied a high-throughput methodology for characterizing oxidation across continuous alloy composition

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Figure 1. Summary of a previous study of $Al_xFe_yNi_{1-x-y}$ CSAF oxidation in dry air at 427 °C.¹⁷ (a) Idealized composition distribution for a full-range $Al_xFe_yNi_{1-x-y}$ CSAF. (b) Photograph of an $Al_xFe_yNi_{1-x-y}$ CSAF annealed in UHV for 2 h at 427 °C prior to oxidation. The location of the ternary composition area is shown. (c) Photograph of an $Al_xFe_yNi_{1-x-y}$ CSAF that has been exposed to dry air at 427 °C for 4 h. The color variations across the surface reflect differences in oxidation behavior. Four regions exhibiting unique oxidation phenomenology (represented schematically around the photograph) were identified in real space. The $Al_xFe_yNi_{1-x-y}$ composition across the CSAF surface is indicated by the overlaid mesh.

space using $Al_xFe_yNi_{1-x-y}$ (subscripts designate atomic fractions) composition spread alloy films (CSAFs).^{17,1} Al_xFe_yNi_{1-x-y} was chosen as a model system for our studies because these are three of the primary metal components included in superalloys designed for both mechanical integrity and Al_2O_3 scale formation at high temperatures.^{10,10} However, because of limitations in the attainable CSAF thickness, the temperature of the oxidizing environments in our studies was limited to 427 °C, much lower than the 600-1200 °C typically considered for practical applications of alloys that form Al_2O_3 scales.^{4,6,10,11,19–23} Thus, it is important to realize that the oxidation that we observe is very transient (i.e., early stage) compared to that normally studied in these alloys. Accepting this limitation, the purpose of the work reported herein was to critically assess other aspects of our highthroughput methodology to better understand the significance of the results.

Key findings from one of our studies¹⁷ of $Al_xFe_yNi_{1-x-y}$ CSAF oxidation in dry air at 427 °C are presented in Figure 1. The CSAFs used in that study were created^{17,24} with a triangular composition gradient geometry, as shown schematically in Figure 1(a), to continuously span the full range of all possible $Al_x Fe_y Ni_{1-x-y}$ compositions $(x = 0 \rightarrow 1, y = 0 \rightarrow 1)$ [1 - x]). The photograph in Figure 1(b) shows the appearance of one of these $Al_xFe_yNi_{1-x-y}$ CSAFs after deposition, annealing at 427 °C for 2 h in ultrahigh vacuum (UHV), and brief exposure to ambient air at room temperature. The CSAF is ~100 nm thick and deposited on the $14 \times 14 \text{ mm}^2$ face of a polished Mo substrate. During the study, CSAFs like that shown in Figure 1(b) were exposed to dry air at 427 °C, resulting in simultaneous oxidation across the entire $Al_xFe_yNi_{1-x-y}$ composition space. Figure 1(c) shows a photograph of one of the CSAFs at the end of this exposure with the overlaid mesh indicating the $Al_xFe_yNi_{1-x-y}$ composition across the surface.¹⁷ The different discolorations visible across the CSAF surface in Figure 1(c) reflect the diverse oxidation

responses of different $Al_xFe_yNi_{1-x-y}$ compositions. Continuous boundaries (open circles) can be identified by optical and/or scanning electron microscopy (SEM) imaging of the oxidized $Al_{x}Fe_{y}Ni_{1-x-y}$ CSAFs. On the basis of spatially resolved analyses by energy-dispersive X-ray spectroscopy (EDX), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) depth profiling, we concluded from our previous work¹⁷ that these boundaries subdivide the composition space into four regions exhibiting phenomenologically different oxidation behaviors. The schematics around the photograph in Figure 1(c) represent the cross sections through the oxidized film that we associate with these four types of behavior. Regions 1, 2, and 3 are passivated by a continuous Al_2O_3 scale established exclusively at the surface (region 1) or in the subsurface beneath trace Fe/Ni/mixed oxides or variable-thickness α - Fe_2O_3 (regions 2 and 3). Region 4 compositions were unable to establish a protective Al₂O₃ scale at any depth; thus, the boundary of region 4 in $Al_xFe_yNi_{1-x-y}$ composition space represents the trajectory of N_{Al}^* for oxidation in dry air at 427 °C, as measured using the CSAF.

The goal of the work reported herein is to critically assess our CSAF methodology as previously applied to the study of $Al_xFe_yNi_{1-x-y}$ oxidation at 427 °C.^{17,18} Specifically, we investigate two aspects of practical interest: (1) the widths in composition of the transition boundaries between the different types of oxidation behavior and (2) the extent to which CSAF oxidation behavior is representative of the behavior of bulk alloys exposed to identical oxidizing conditions. In the interest of simplicity, we explore these aspects by focusing specifically on the binary Al_xFe_{1-x} and Al_xNi_{1-x} areas of $Al_xFe_yNi_{1-x-y}$ CSAFs oxidized in dry air at 427 °C.

RESULTS AND DISCUSSION

1. Assessing the "Sharpness" of Transitions in Oxidation Behavior on CSAFs. Our previous $study^{17}$



Figure 2. C_0 (top row) measured across the Al_xFe_{1-x} and Al_xNi_{1-x} binary regions of two Al_xFe_yNi_{1-x-y} CSAFs after $t_{ox} = 0$, 1, and 4 h in dry air at 427 °C and ΔC_0 (bottom two rows) measured in the time periods 0–1 h and 1–4 h. The data points from one CSAF are plotted as circles, whereas those from the other are plotted as diamonds. The maximum C_0 or ΔC_0 for each plot is scaled relative to the arbitrary maximum on the plot in the upper left; each tick mark on the vertical axes represents 5% of this maximum value. The vertical dashed lines represent the composition-space boundaries between the four regions exhibiting phenomenologically different types of oxidation behavior.

identified four different composition-space regions on oxidized (427 °C in dry air) $Al_xFe_yNi_{1-x-y}$ CSAFs that correlate with the results of EDX, Raman, and XPS analyses. The schematic depictions of oxide cross sections shown for the CSAF in Figure 1(c) illustrate the key, qualitative differences between regions detected with these analysis methods. However, it is not clear based on our previous work how "sharp" the transitions between the regions are, i.e., what change in the CSAF composition is needed to induce a well-defined transition from one behavior to the next. The width of the oxidation transitions on CSAFs dictates the precision with which important boundaries such as N_{Al}^{*} can be identified.

Of the analyses we have performed on oxidized $Al_xFe_yNi_{1-x-y}$ CSAFs, EDX allows the highest density sampling of different locations/compositions. As described in our previous work,^{17,18} EDX measurements can be used to estimate the total oxygen content, C_0 , of the CSAF, i.e., the total amount of oxygen present in the film cross section at any laterally resolved location. We have identified the $Al_xFe_yNi_{1-x-y}$ composition regions that are passivated on CSAFs by analyzing oxygen-uptake kinetics from measurements of $C_0(x, y)$ versus time of exposure to the oxidizing environment, $t_{ox}^{17,18}$

Figure 2 shows C_0 measured across the $Al_x Fe_{1-x}$ (left column) and $Al_x Ni_{1-x}$ (right column) binary regions of $Al_x Fe_y Ni_{1-x-y}$ CSAFs oxidized in dry air at 427 °C. The plots in the top row show total C_0 measured at $t_{0x} = 0$, 1, and 4 h, and the plots in the middle and bottom rows show the change

in C_0 , ΔC_0 , in the two intervening time periods. The full scale for C_0 or ΔC_0 on each plot is defined relative to the arbitrary maximum value in the upper-left plot. The data shown in Figure 2 were collected from two different CSAFs; points measured from one sample are plotted as circles, and those measured from the other are plotted as diamonds. The two data sets demonstrate remarkable reproducibility between the two different CSAFs. The vertical dashed lines in each plot mark the composition boundaries in regions 1-4 (see Figure 1(c)) corresponding to real-space features observed in optical or SEM images of the CSAFs. It is evident from Figure 2 that these boundaries correlate well with transitions in how C_O and/ or ΔC_0 change as a function of $Al_x Fe_{1-x}$ or $Al_x Ni_{1-x}$ composition. Of particular note is that $\Delta C_{\rm O} \cong 0$ from $t_{\rm ox} = 1$ to 4 h (bottom row) in regions 1-3, indicating that these compositions were passivated against further oxidation after some $t_{ox} \leq 1$ h. We attribute the small ΔC_0 from $t_{ox} = 0-1$ h (middle row) in regions 2 and 3 to initial growth of trace Fe or Ni oxides at the alloy surface before a passivating Al₂O₃ scale was established in the subsurface. Region 4 compositions exhibit the highest values of $C_0(t_{ox} = 4 \text{ h})$ (top row) and have $\Delta C_{\rm O} > 0$ from $t_{\rm ox} = 1-4$ h (bottom row), indicating that passivation did not occur. The high density of the EDX measurements in Figure 2 reveal that reproducible changes in oxygen-uptake kinetics can be clearly resolved in composition space at the identified boundaries, apparently over a range of just a few at. % in alloy composition. Because these kinetics are

related to the local oxidation phenomenology (see Figure 1(c)), this demonstrates that well-defined transitions in oxidation behavior must be completed over similarly narrow composition ranges.

XPS depth profiling allows spatially resolved analysis of the cross-sectional distribution of metals and oxides in a CSAF and, thus, can be used to distinguish more subtle differences in oxidation behavior than is possible based solely on oxygenuptake kinetics. However, because of the time required to measure the depth profiles, the maximum number of locations that can be practically analyzed is much smaller than with EDX. Therefore, we have used XPS depth profiling to focus specifically on three of our proposed transitions in oxidation behavior in the binary regions of $Al_xFe_yNi_{1-x-y}$ CSAFs oxidized for $t_{ox} = 4$ h in dry air at 427 °C (see Figure 1(c)): region 1 to region 2 in Al_xFe_{1-x} region 3 to region 4 in Al_xFe_{1-x} and region 2 to region 4 in Al_xNi_{1-x} . In each case, a series of five depth profiles was measured along a line crossing the continuous boundary (identified visually or with SEM on an oxidized CSAF surface) proposed to correlate with a transition in oxidation behavior.

Figure 3 shows the results of the XPS depth profiling performed to investigate the transition from region 1 to region 2 in Al_xFe_{1-x} composition space. The SEM image (top) shows the portion of the oxidized CSAF surface where the depth profiles were later performed; the approximate areas sampled by the profiles are indicated by the circles labeled a-e. The continuous boundary between regions 1 and 2 is visible as a change in SEM contrast; region 1 appears lighter, whereas region 2 appears darker. Therefore, areas a and b fall entirely within region 2; areas d and e fall entirely within region 1, and area c spans both regions. The depth profiles obtained across areas a-e are presented in Figure 3(a-e), respectively; the labels indicate the composition of the CSAF at the center of each area as determined by EDX prior to high-temperature exposure (i.e., at $t_{ox} = 0$ h). The profiles plot the relative composition of elements in metallic or oxidized chemical states (determined using XPS) as a function of etching time with a rastered Ar⁺ beam, i.e., depth into the sample. Because the CSAFs are ~ 100 nm thick, ^{17,18} a length scale for depth into the sample can be approximated on the horizontal axes based on the time at which the Mo substrate appears, as shown in Figure 3(e). The profiles from Al_xFe_{1-x} region 1 (Figure 3(d,e)) show that a thin, continuous layer of oxidized Al was formed at the CSAF surface, whereas the rest of the cross section remained metallic and uniform in composition. The profiles from $Al_{x}Fe_{1-x}$ region 2 (Figure 3(a, b)) are very similar but show that the continuous layer of oxidized Al is present in the subsurface beneath trace Fe oxide at the surface (at greater depths, a small fraction of oxidized Al is also detected, but the Fe remains in a metallic state). The depth profiles contained entirely within regions 1 or 2 are consistent with the types of oxidation behavior proposed previously (see Figure 1(c)).¹⁷ The profiles indicate that a complete transition from region 1 to region 2 occurs over a composition window of $Al_{0.64}Fe_{0.36}$ to Al_{0.61}Fe_{0.39}. However, if the change in SEM contrast is indeed indicative of this phenomenological change in oxidation behavior, then the complete transition actually occurs within area c over a composition range of ~ 1 at. %.

The results of the XPS depth profiling across the N_{Al}^* boundary between regions 3 and 4 for Al_xFe_{1-x} are shown in Figure 4. The low-magnification SEM image (top) shows the approximate areas, labeled a–e, at which the five depth profiles



Figure 3. Line of XPS depth profiles performed on an $Al_x Fe_y Ni_{1-x-y}$ CSAF to investigate the transition between regions 1 and 2 for $Al_x Fe_{1-x}$ after $t_{ox} = 4$ h in dry air at 427 °C. The SEM image (top) shows the five areas, a–e, across which the depth profiles were performed. The boundary between regions 1 and 2 is visible based on the SEM contrast and passes through area c (region 1 appears lighter, and region 2 appears darker). (a–e) The depth profiles measured at the correspondingly labeled areas a–e. The label to the right of each plot is the CSAF composition at the center of the area at $t_{ox} = 0$ h. The plots show the relative composition of each detected element, *M*, in a metallic "M" or oxidized "M^(ox)" chemical state as a function of total Ar⁺ etch time. An approximate length scale is shown below the plot in e.

were later obtained on the oxidized ($t_{ox} = 4$ h) CSAF surface. In this case, the transition between regions is not visible by SEM contrast but is clearly evident visually (see Figure 1(c)). Areas d and e fall entirely within region 3, whereas areas a and b fall entirely within region 4. The visually identified boundary between regions 3 and 4 passes through area c. The profiles obtained across areas a—e are shown in Figure 4(a—e), respectively. Each profile is accompanied by an SEM image taken at the center of the measurement area prior to the depth profiling. The labels above these SEM images indicate the CSAF composition at the center of each measurement area determined using EDX at $t_{ox} = 0$ h. The appearance of the profiles from region 3 (Figure 4(d, e)) is consistent with the proposed passivation behavior shown in Figure 1(c).¹⁷ Given sufficient variations in the thickness of the surface α -Fe₂O₃,



Figure 4. Line of XPS depth profiles performed on an $Al_xFe_yNi_{1-x-y}$ CSAF to investigate the transition between regions 3 and 4 for Al_xFe_{1-x} after $t_{ox} = 4$ h in dry air at 427 °C. The topmost SEM image shows the five areas, a–e, across which the depth profiles were performed. The boundary between regions 3 and 4 is not visible based on the SEM contrast but passes through area c. (a–e) The depth profiles measured at the correspondingly labeled areas a–e, and SEM images taken at the center of the areas prior to obtaining the depth profiles. The label above each SEM image is the CSAF composition at the center of the area at $t_{ox} = 0$ h. The plots show the relative composition of each detected element, M, in a metallic "M" or oxidized "M^(ox)" chemical state as a function of total Ar⁺ etch time. An approximate length scale is shown below the plot in e.

uniform Ar^+ etching would not simultaneously expose the continuous, passivating Al_2O_3 layer in the subsurface. Thus, XPS depth profiling of such a cross section would be expected to reveal subsurface enrichment of Al oxide, but never to 100% for any given etch time, consistent with the profiles in Figure 4(e,d). In contrast, the profiles from region 4 (Figure 4(a, b)) show extensive formation of Fe oxide and no sign of Al oxide enrichment at any depth, indicating that the CSAF is not passivated. The CSAF surface in region 4 exhibits significant roughening as a result of the oxidation, as evident from the

SEM images in Figure 4(a,b). As a result, the transition from the CSAF to the Mo substrate appears more gradual in these profiles (etching of thinner areas revealed the Mo substrate much earlier than thicker areas). The profile in Figure 4(c) is consistent with an average of the profiles from the two different regions, arising from simultaneous sampling of the two different oxide cross sections present within area c. The set of profiles in Figure 4 suggest that a well-defined transition from region 3 to region 4 behavior occurs abruptly in Al_xFe_{1-x} composition space near $Al_{0.19}Fe_{0.81}$ as a result of a change in alloy composition of a few at. % at most.

Figure 5 shows the results of the XPS depth profiling performed to investigate the transition upon crossing the $N_{\rm Al}^*$ boundary between regions 2 and 4 in Al_xNi_{1-x} composition space (region 3 behavior specifically involves the growth of α - Fe_2O_3 and therefore does not occur in binary Al_rNi_{1-r}). The low-magnification SEM image (top) shows the areas, labeled a-e, across which the five profiles were later performed. The boundary between regions 2 and 4 is visually obvious in optical images of oxidized CSAFs (see Figure 1(c)) and can also be discerned by SEM contrast; region 2 appears darker, whereas region 4 appears lighter. Thus, areas a and b are entirely within region 4; areas d and e are entirely within region 2, and area c spans both regions. Plots of the profiles obtained at areas a-e are shown in Figure 5(a-e), respectively. The EDX-measured composition at $t_{ox} = 0$ h and a higher-magnification SEM image from the center of each area (taken prior to the depth profiling) are also shown. It is evident from Figure 5 that an abrupt transition in oxidation phenomenology occurs around the composition Al_{0.29}Ni_{0.71}. The profiles from region 2 (Figure 5(d,e)) exhibit clear evidence of continuous oxidized Al in the subsurface beneath trace Ni oxide, consistent with the behavior we have proposed for this region (see Figure 1(c)).¹⁷ The profiles from region 4 (Figure 5(a,b)) appear to show partial subsurface enrichment of oxidized Al, but based on previous EDX measurements of oxygen-uptake kinetics at similar locations on other $Al_xFe_yNi_{1-x-y}$ CSAFs, this enrichment is not believed to correspond to the formation of a passivating Al_2O_3 scale in the subsurface.^{17,18} The higher-magnification SEM images appear to show that the surface has become roughened and/or pitted in region 4 as a result of the oxidation, likely explaining the small amount of Mo detected at short etch times in the profiles in Figure 5(a,b). It appears from Figure 5 that a complete transition from region 2 to region 4 in Al_xNi_{1-x} composition space occurs over ~ 1 at. % and that the appearance of the profile in Figure 5(c) is an average of the profiles from these two regions.

The results presented in Figures 2-5 indicate that phenomenologically definable transitions in the oxidation behavior of the CSAFs occur abruptly in Al_xFe_{1-x} and Al_xNi_{1-x} composition space upon crossing the continuous boundaries that were identified optically or with SEM. Although not explicitly investigated in this study, we expect that the same is true for the continuations of these boundaries through the $Al_xFe_yNi_{1-x-y}$ region of the CSAFs, as shown in Figure 1(c).¹⁷ For the specific boundaries that we have investigated, it appears that well-defined transitions in oxidation behavior occur completely over a composition range of $\sim 1-2$ at. %. However, it should be noted that the absolute accuracy with which we are able to determine CSAF composition (e.g., along the identified boundaries or at the depth profile locations) is limited by the accuracy of our EDX-based composition measurements (discussed in our previous work¹⁷) and is likely no better



Figure 5. Line of XPS depth profiles performed on an $Al_x Fe_y Ni_{1-x-y}$ CSAF to investigate the transition between regions 2 and 4 for $Al_x Ni_{1-x}$ after $t_{ox} = 4$ h in dry air at 427 °C. The topmost SEM image shows the five areas, a–e, across which the depth profiles were performed. The boundary between regions 2 and 4 is visible based on the SEM contrast and passes through area c (region 2 appears darker, and region 4 appears lighter). (a–e) The depth profiles measured at the correspondingly labeled areas a–e, and SEM images taken at the center of the areas prior to obtaining the depth profiles. The label above each SEM image is the CSAF composition at the center of the area at $t_{ox} = 0$ h. The plots show the relative composition of each detected element, *M*, in a metallic "M" or oxidized "M^(ox)" chemical state as a function of total Ar⁺ etch time. An approximate length scale is shown below the plot in e.

than ± 2 at. %. Thus, the actual $Al_xFe_yNi_{1-x-y}$ CSAF compositions at which the identified transitions in oxidation behavior occur may systematically differ from those reported within this degree of uncertainty.

2. Comparing Oxidation Behavior of CSAFs with That of Bulk Alloys. The other aspect of our high-throughput oxidation studies^{17,18} that we consider in this work is comparison of CSAF oxidation to that of single-composition bulk alloys exposed to identical oxidizing environments. It is

important to emphasize that the subject of our studies has been a very specific and unique system, namely, ~100 nm-thick Al_xFe_yNi_{1-x-y} films that were annealed in UHV at 427 °C, exposed briefly to ambient air at room temperature, and then oxidized at 427 °C for up to 4 h. There are two principal reasons why Al_xFe_yNi_{1-x-y} bulk alloys might exhibit oxidation behavior different from that of ~100 nm-thick CSAFs. First, the microstructure of the CSAFs is likely to be significantly different from that of bulk alloys, and this difference might influence oxidation processes (e.g., if oxygen and/or metal transport along grain boundaries plays an important role). Second, if oxide formation proceeds across enough of the CSAF cross section, preferential depletion of one or more of the component metals from the portion of the film that is not yet oxidized could cause a non-negligible change in its composition, which might alter subsequent oxidation processes. In contrast, a bulk alloy represents an essentially infinite reservoir of metals at constant composition.

Six bulk alloys (four different binary Al_xFe_{1-x} compositions and two different binary Al_xNi_{1-x} compositions) were prepared for comparison with $Al_x Fe_y Ni_{1-x-y}$ CSAFs. The specific compositions were chosen based on the results of our CSAF oxidation study 17 (see Figure 1(c)) with one each corresponding to regions 1–4 in Al_xFe_{1-x} and regions 2 and 4 in Al_xNi_{1-x} . The surfaces of these bulk alloys were polished and characterized before and after oxidation in dry air at 427 °C. Figure 6 shows backscattered electron (BSE) SEM images of each of the alloys after both $t_{ox} = 0$ h (left column) and $t_{ox} = 4$ h (right column). The compositions reported in Figure 6 were measured by performing EDX on the alloys at $t_{ox} = 0$ h. The "average" compositions were determined from scans taken across $\sim 700 \times 500 \,\mu\text{m}^2$ areas centered at the imaged locations. It can be seen from the BSE-SEM contrast that four of the alloys (Figure 6(a,b,e,f)) partitioned into two distinct phases. EDX point scans (~0.5 × 0.5 μ m² spot) were used to measure the compositions of the "light" and "dark" phases visible in each case; the results are shown below the average compositions. The phase compositions were found to be measurably different in all four of the two-phase alloys with the Al-rich phases appearing darker. The images of the other two alloys (Figure 6(c,d) do not appear to show any evidence of phase separation, revealing only shallow scratches that remain after polishing.

BSE-SEM images of identical locations on the alloys taken after $t_{ox} = 0$ h or $t_{ox} = 4$ h were indistinguishable from one another with the exception of $Al_{0.10}Fe_{0.90}$, which became noticeably roughened as a result of oxidation. Thus, to provide an additional example of the characteristic appearance of each surface, the $t_{ox} = 4$ h images shown in Figure 6 are from different locations on their respective alloys than the $t_{ox} = 0$ h images. The fact that BSE-SEM imaging reveals no change in the two-phase alloys as a result of the oxidation indicates that the microstructure (presumably formed when the alloys were cast) was not significantly affected by the oxidation. This is unsurprising given that the characteristic dimensions of the phase domains are large compared to the thickness of the various oxide layers formed in the ~100 nm-thick $Al_xFe_yNi_{1-x-y}$ CSAFs exposed to dry air at 427 °C (see Figure 1(c)).¹⁷ However, it further suggests that the oxidation processes under these conditions are likely to occur independently on each phase, i.e., that the two phase domains are unlikely to interact significantly while oxidizing and, therefore, may behave differently due to their differing compositions.

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Figure 6. BSE-SEM images of the bulk $Al_x Fe_{1-x}$ (a-d) and $Al_x Ni_{1-x}$ (e and f) samples taken after $t_{ox} = 0$ h (left column) and $t_{ox} = 4$ h (right column) in dry air at 427 °C. The compositions were measured at $t_{ox} = 0$ h. The average compositions were measured using ~700 × 500 μm^2 EDX area scans, whereas the individual phase compositions were measured with ~0.5 × 0.5 μm^2 "point" scans. Each pair of images shown in (a-f) were taken at different locations on their respective sample. Except for d, images taken at the same location on any of the samples after $t_{ox} = 0$ or 4 h were indistinguishable.

For the differences in the microstructure of our CSAFs and the bulk alloys to be investigated, an unoxidized $(t_{ox} = 0 h)$ Al_xFe_yNi_{1-x-y} CSAF prepared at Carnegie Mellon University was sent to the National Institute of Metrology, Quality and Technology of Brazil (Inmetro) for additional characterization using transmission electron microscopy (TEM). Cross sections of the CSAF/substrate were cut from six different locations using a focused ion beam (FIB) and analyzed by TEM. Figure 7 provides a summary of important results collected from one of these locations at which the CSAF composition was measured to be Al_{0.58}Fe_{0.42} during the initial characterization at Carnegie Mellon University. Figure 7(a) shows a cross-sectional view of the CSAF/substrate layering in an image collected by scanning transmission electron microscopy (STEM) with annular darkfield detection (the Mo is the substrate, and the Pt is a protective layer deposited as part of the FIB cutting procedure). Figure 7(b) is a TEM bright-field image, providing a highermagnification view of the CSAF layer. Figure 7(c) shows the diffraction pattern from the region imaged in Figure 7(b). The CSAF is polycrystalline, as revealed by the diffraction rings. Finally, Figure 7(d) is a TEM dark-field image of the same region shown in Figure 7(b) produced by selectively filtering for the (011) Bragg diffraction feature circled in Figure 7(c).

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Figure 7. Summary of FIB-TEM analyses performed on an $Al_xFe_yNi_{1-x-y}$ CSAF ($t_{ox} = 0$ h) at a location where the composition is $\sim Al_{0.58}Fe_{0.42}$. (a) STEM annular dark-field image showing the layering of the CSAF on the Mo substrate. The Pt layer was deposited on the surface of the CSAF for protection prior to the FIB cross sectioning. (b) TEM bright-field image showing a magnified view of the CSAF layer. (c) The diffraction pattern corresponding to the region imaged in b. The pattern is comprised of rings, indicating that the CSAF is polycrystalline. (d) TEM dark-field image of the same view field shown in b, filtered for the (011) Bragg diffraction feature circled in c. The image shows that columnar grains were formed in the CSAF.

The image in Figure 7(d) reveals that the CSAF has a columnar grain structure.

EDX and high-resolution transmission electron microscopy (HRTEM) were also used to analyze the sample (not shown in Figure 7). EDX measurements averaged across large areas of the CSAF cross section were consistent with the expected composition of $Al_{0.58}Fe_{0.42}$. On the basis of the STEM/TEM imaging (e.g., Figure 7(a,b,d)), the thickness of the CSAF at this location was determined to be 152 ± 3 nm. STEM imaging coupled with EDX elemental mapping revealed that any intermixing of the Mo substrate with the CSAF was limited to an interface region of ~4 nm in thickness. TEM dark-field imaging (e.g., Figure 7(d)) showed that the CSAF consists of columnar grains with lengths of 82 \pm 30 nm and widths of 20 \pm 5 nm. It is not clear whether these grains exhibit the same separation into two phases with the Al_{0.51}Fe_{0.49} and Al_{0.65}Fe_{0.35} compositions observed in the bulk Al_{0.56}Fe_{0.44} sample (Figure 6(b)). Fast Fourier transforms of HRTEM images and selected area diffraction patterns did confirm that the phase of some of the grains in the $Al_{0.58}Fe_{0.42}$ CSAF is cubic AlFe $Pm\overline{3}m$ (space group 221), consistent with the $Al_{0.51}Fe_{0.49}$ stoichiometry. However, a second phase consistent with the Al_{0.65}Fe_{0.35} stoichiometry could not be identified conclusively.

FIB-TEM analyses similar to those discussed for $Al_{0.58}Fe_{0.42}$ above were performed at five other locations with expected CSAF compositions (based on the initial characterization) of $Al_{0.32}Fe_{0.64}Ni_{0.04}$, $Al_{0.30}Fe_{0.45}Ni_{0.25}$, $Al_{0.10}Fe_{0.21}Ni_{0.69}$,

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Al_{0.09}Fe_{0.09}Ni_{0.82}, and Al_{0.06}Fe_{0.04}Ni_{0.90}. STEM/TEM imaging revealed that the CSAF thicknesses at these locations were 123 \pm 5, 125 \pm 2, 76 \pm 4, 60 \pm 3, and 53 \pm 7 nm, respectively, decreasing as the Ni fraction in the film increased. Despite these thickness differences, the composition as determined by EDX measurements across large areas of the CSAF cross section was similar to the expected composition at all of the locations. A similar grain structure to that visible in Figure 7(d)was observed at the Al_{0.32}Fe_{0.64}Ni_{0.04} and Al_{0.30}Fe_{0.45}Ni_{0.25} locations (where the CSAF thickness was >120 nm), whereas the structure at the more Ni-rich locations (where the CSAF thickness was <80 nm) consisted of much smaller grains with characteristic length and width dimensions on the order of ~ 10 nm. The presence of a multiphase equilibrium could not be conclusively proven with HRTEM at any of the sampled locations on the CSAF. However, it is worth noting that previous work at Carnegie Mellon University has shown directly using electron backscatter diffraction that ~100 nmthick Cu_xPd_{1-x} CSAFs exhibit multiphase equilibria consistent with the bulk Cu_xPd_{1-x} phase diagram.²⁵

The results in Figures 6 and 7 show that, before exposure to dry air at 427 °C ($t_{ox} = 0$ h), the microstructures of the bulk alloys and the CSAFs differ substantially. To investigate the potential effects of these differences on the oxidation process, we used XPS depth profiling to compare the oxide cross sections developed on each bulk alloy after $t_{ox} = 4$ h with those developed at CSAF locations with similar compositions; the results are shown in Figure 8. The bulk alloy profiles were measured across ~0.13 mm² circular areas and are labeled with the average composition of each bulk sample determined by EDX (see Figure 6). The CSAF profiles were measured across ~0.03 mm² circular areas (spanning a total range of ~2 at. % in the composition gradients) and are labeled with the composition at the center of each area as determined with EDX at $t_{ox} = 0$ h. Identical Ar⁺ etch conditions and time steps were used for all of the profiles in Figure 8; thus, the length scales of all the horizontal (i.e., depth) axes should be roughly equivalent and are approximated based on the appearance of the Mo substrate in the Al_{0.66}Fe_{0.34} CSAF profile.

The Al_{0.68}Fe_{0.32}, Al_{0.56}Fe_{0.44}, and Al_{0.28}Fe_{0.72} depth profiles from the bulk samples in Figure 8 are remarkably similar to the corresponding Al_{0.66}Fe_{0.34}, Al_{0.59}Fe_{0.41}, and Al_{0.26}Fe_{0.74} depth profiles from the CSAF. This suggests that the oxidation behavior in dry air at 427 °C observed for regions 1-3 in the Al_xFe_{1-x} section of the CSAF (see Figure 1(c)) is effectively the same as that of bulk alloys, despite both significant differences in microstructure (see Figures 6 and 7) and the much smaller amount of material available in the ~100 nm-thick CSAF. The $Al_{0.10}Fe_{0.90}$ (region 4) bulk profile required 6× more etch time than the other profiles to reach the depth at which the composition became uniform and metallic, indicating much more extensive Fe-oxide formation than on the other Al_rFe_{1-r} bulk samples. On the basis of the depth of oxide penetration revealed by the Al_{0.10}Fe_{0.90} bulk profile, it is unsurprising that the Al_{0.11}Fe_{0.89} CSAF profile shows essentially complete oxidation of the entire film cross section. Because of depletion of the metallic components, the Al_{0.11}Fe_{0.89} CSAF profile clearly cannot provide a representative picture of the oxide formation that occurs in bulk alloys with similar composition. However, it does plainly indicate that region 4 of the CSAF was not passivated by an Al₂O₃ scale, and simply making this distinction has been the primary goal of our previous studies.^{17,18}



Figure 8. XPS depth profiles measured on the bulk Al_xFe_{1-x} and Al_xNi_{1-x} samples compared with those measured at locations with similar compositions on an $Al_xFe_yNi_{1-x-y}$ CSAF (Mo substrate) both after $t_{ox} = 4$ h in dry air at 427 °C. The plots show the relative composition of each element, M, in a metallic "M" or oxidized "M^(ox)" chemical state as a function of total Ar^+ etch time. The labels above each profile are the CSAF or bulk composition measured with EDX at the profile location at $t_{ox} = 0$ h. Identical etch conditions were used for all of the profiles, so the depth increments corresponding to the tick marks on the horizontal axes should be roughly equivalent for all of the plots; an approximate length scale is shown below the $Al_{0.66}Fe_{0.34}$ and $Al_{0.11}Fe_{0.89}$ CSAF profiles. The $Al_{0.10}Fe_{0.90}$ bulk profile was measured using 6× more etch cycles than the other profiles and thus sampled ~6× further in total depth.

The $Al_x Ni_{1-x}$ bulk depth profiles in Figure 8 do not match their corresponding CSAF profiles as closely as the Al_xFe_{1-x} pairs. One possible interpretation of the Al_{0.31}Ni_{0.69} bulk profile is that it represents an average of two different types of behavior, where an Al₂O₃ scale is formed at the surface of the $Al_{0.38}Ni_{0.62}$ "dark" phase regions visible in Figure 6(e) and in the subsurface of the $Al_{0.28}Ni_{0.72}$ "light" phase regions. This explanation would be qualitatively consistent with the behavior identified individually for these compositions on the $Al_xFe_yNi_{1-x-y}$ CSAFs, as shown in Figure 1(c). It is very likely that the two phases oxidized essentially independently of one another in the bulk sample given the large characteristic dimensions of the phase domains relative to the thickness of the oxide layers that are formed. However, a sufficiently small grain size in a CSAF could allow significant lateral interactions between phases with differing compositions during oxidation, even if a similar two-phase equilibrium was formed. As mentioned previously in the discussion of the FIB-TEM results, Ni-rich locations on that particular $Al_xFe_yNi_{1-x-y}$ CSAF were comprised of very small grains with characteristic dimensions on the order of ~ 10 nm. Thus, it is possible that the differences between the $Al_{0.31}Ni_{0.69}$ bulk and the $Al_{0.31}Ni_{0.69}$ CSAF depth profiles in Figure 8 are related to differences in grain structure. A challenge in assessing the final pair of Al_xNi_{1-x} profiles at Al_{0.24}Ni_{0.76} (CSAF) and Al_{0.22}Ni_{0.78} (bulk) is that Ni oxidizes slowly in dry air at 427 °C. As a result, the presence or absence of a passivating Al₂O₃ scale cannot be discerned easily based on the amount of Ni oxide that was formed, as can be done based on the amount of Fe oxide formed in Al_xFe_{1-x} . With this in mind, the $Al_{0.22}Ni_{0.78}$ bulk depth profile in Figure 8 suggests strongly that no passivating Al₂O₃ scale was formed, as it reveals no subsurface enrichment of Al oxide. The location at which the Al_{0.24}Ni_{0.76} CSAF depth profile was measured became significantly roughened/pitted as a result of the oxidation (see Figure 5(a)), complicating its interpretation and making direct comparison with the Al_{0.22}Ni_{0.78} bulk profile difficult. However, we have concluded based on additional analyses in our previous studies^{17,18} that this region of the CSAF is not passivated by the formation of an Al₂O₃ scale.

SUMMARY AND OUTLOOK

By specifically focusing on Al_xFe_{1-x} and Al_xNi_{1-x} oxidation in dry air at 427 °C, we have investigated two aspects of a highthroughput methodology that we have developed to study oxidation using $Al_x Fe_y Ni_{1-x-y}$ CSAFs (see Figure 1).^{17,18} EDX measurements of oxygen-uptake kinetics (Figure 2) and XPS depth profiling (Figures 3, 4, and 5) showed that readily definable changes in the oxidation phenomenology of the CSAFs occur over composition ranges of $\sim 1-2$ at. % at boundaries between regions exhibiting different oxidation behaviors. The ability to identify these boundaries continuously in real space on the CSAF surface allows precise measurement of $Al_x Fe_y Ni_{1-x-y}$ compositions at which important transitions in oxidation behavior occur, including the N_{Al}^* boundary separating compositions, which form a passivating Al₂O₃ scale from those that do not. However, it is important to recognize that these results apply specifically to oxidation of ~100 nmthick Al_xFe_vNi_{1-x-v} films, which might differ from that of bulk alloys exposed to identical environments. Despite electron microscopy analyses (Figures 6 and 7) revealing significant differences in the microstructure of bulk and CSAF samples, XPS depth profiling (Figure 8) showed remarkable agreement between the metal/oxide cross sections developed in the Al_xFe_{1-x} region of a CSAF and those developed in bulk alloys. Conversely, there were notable differences in the metal/oxide cross sections developed in the Al_xNi_{1-x} region of the CSAF and those developed in bulk alloys. Thus, at least in certain cases, it appears that microstructural differences might lead to practical issues with extrapolating our high-throughput results to bulk alloy systems. This concern aside, our work still clearly demonstrates the potential value of applying high-throughput, CSAF-based methods to the study of oxidation in multicomponent alloys. Any issues related to differences in the oxidation behavior of CSAFs compared to bulk alloys could, in principle, be simply overcome given the ability to create sufficiently thick CSAFs. Additional component(s) could also be incorporated into the CSAFs to generate alloy libraries representing any plane through a quaternary or higher-order composition space. In this way, high-throughput methods similar to ours could be used to rapidly screen alloy oxidation in any given environment across continuous composition ranges of practical interest.

EXPERIMENTAL METHODS

Creation of $Al_xFe_vNi_{1-x-v}$ CSAFs. The $Al_xFe_vNi_{1-x-v}$ CSAFs were created using a rotatable shadow mask CSAF deposition tool, which we described previously.²⁴ The tool is housed in a stainless-steel UHV chamber with an operating pressure of $\sim 5 \times 10^{-10}$ Torr. The substrates used to support the CSAFs were polycrystalline-Mo blocks with dimensions 14 \times 14 \times 2.5 mm³. The CSAFs were created by evaporative deposition onto one of the $14 \times 14 \text{ mm}^2$ faces (rms roughness <1.5 nm) of the substrates. After loading a substrate into the UHV chamber, the deposition face was sputtered for 20 min with a defocused, 2 kV Ar⁺ beam (~5 μ A sample current) to remove contaminants. The substrate was then annealed at 477 °C for 1 h and allowed to cool to room temperature. Another cycle of Ar⁺ sputtering was performed immediately before the CSAF deposition. To create the CSAF, the Al, Fe, and Ni were simultaneously deposited onto the substrate, each from a separate e-beam evaporator loaded with \geq 99.98% pure source material. Prior to deposition, a guartz crystal microbalance was used to measure the deposition rates and determine the power required for each of the evaporators to achieve approximately equal molar deposition rates. The composition gradients in the CSAF arise from partial line-of-sight shadowing of each evaporator by a mask, which creates a gradient across the surface in the incident evaporative flux of each component.²⁴ Appropriate evaporator alignments and mask orientations have been previously determined to obtain full-range $Al_xFe_yNi_{1-x-y}$ CSAFs similar to that shown schematically in Figure 1(a).¹⁷ The deposition time for the CSAFs was 500 min, resulting in film thicknesses of ~ 100 nm (due to limitations of the e-beam evaporators, this is near the maximum achievable with the deposition tool). Immediately after deposition, each CSAF was annealed at 427 °C for 2 h and cooled to room temperature in UHV. The chamber was then vented to the atmosphere, and the CSAF was exposed to ambient air at room temperature for ~15 min while it was transferred to a Tescan Vega3 SEM system with an operating pressure of $\sim 1 \times 10^{-4}$ Torr.

Composition Mapping of $Al_xFe_yNi_{1-x-y}$ CSAFs. Immediately following the deposition of each $Al_x Fe_y Ni_{1-x-y} CSAF$, spatial mapping of the composition gradients was performed in the Tescan Vega3 SEM system using EDX measurements made with an Oxford Instruments X-max 80 mm² detector. The detector was controlled by INCA Energy software and calibrated hourly with a pure Ni standard. EDX spectra were collected across the CSAF surface from 50 \times 50 μ m² areas arranged in a square grid with 1 mm spacing. The spectra were measured from 0 to 10 keV (10 eV binning, >300,000 total counts) at a working distance of 15 mm with the SEM beam operating at 11.24 kV. The CSAF composition at each location was determined by processing the collected spectra using the Oxford Instruments software package INCA ThinFilmID, which was used to account for the layering of the sample within the electron beam interaction volume. The assumption used in quantifying the spectra was that the $Al_xFe_yNi_{1-x-y}$ CSAF forms a flat, homogeneous layer on the Mo substrate (on the basis of FIB-TEM results like those shown in Figure 7, this appears to be an accurate approximation). Three separate measurements of composition were made at each location and averaged to reduce noise. The discrete $Al_xFe_yNi_{1-x-y}$ compositions determined in this way at the points located on the square grid on each CSAF were used to parametrize a composition distribution model, which estimates CSAF composition as a continuous function of position on the surface. This model is used in determining the compositionspace trajectories of real-space boundaries observed on the CSAFs; its assumptions and functional form are described in the appendix of one of our previous studies.¹⁷

Oxidation of $Al_xFe_yNi_{1-x-y}$ CSAFs. After initial analyses of the $Al_x Fe_y Ni_{1-x-y}$ CSAFs were performed at $t_{ox} = 0$ h (deposited/annealed with ~15 min exposure to ambient air at room temperature), the CSAFs were incrementally exposed to dry air at 427 °C for total times of t_{ox} = 1, 2, and 4 h. The exposures were performed in a quartz tube (~2 cm in diameter and ~ 60 cm long) that was heated by a furnace with one end connected to a gas-introduction manifold and the other end open to the atmosphere. Prior to each exposure, the furnace was preheated until the temperature was stable at 427 \pm 1 °C, and the manifold was used to maintain a continuous flow of ~ 1 slpm of dry air through the tube. The CSAF was then loaded into a ceramic boat (which was preheated with the furnace) and quickly pushed to the center of the tube. Only the bottom of the Mo substrate was in direct contact with the boat. At the end of each exposure increment, the sample was removed from the furnace, and the bottom of the substrate was placed in contact with a sheet of aluminum foil to quickly dissipate heat, cooling the CSAF to room temperature in ~ 2 min. Various characterizations of the CSAF were then performed before proceeding with the next incremental exposure to dry air in the furnace.

EDX Measurement of C_0 in $Al_xFe_yNi_{1-x-y}$ CSAFs. EDX was used to measure C_0 (the total amount of oxygen present throughout the entire film cross section) as a function of composition across the $Al_xFe_yNi_{1-x-y}$ CSAFs after $t_{ox} = 0, 1, 2,$ and 4 h. Each individual spectrum used to derive C₀ was collected across a 50 \times 50 μ m² area of the CSAF surface. The locations of these areas were chosen (with guidance from the composition distribution model) to provide a dense sampling of the $Al_x Fe_y Ni_{1-x-y}$ composition space. In total, 71 different binary Al_xFe_{1-x} compositions and 59 different binary Al_xNi_{1-x} compositions were sampled across two different CSAFs (corresponding to the data presented in Figure 2). The spectra used to derive C_0 were measured from 0 to 10 keV (10 eV binning, >250,000 total counts) at a working distance of 15 mm with the SEM beam operating at 20 kV. An arbitrary value for $C_{\rm O}$ was calculated from the oxygen EDX signal scaled by the (much larger) Mo EDX signal from the substrate. As discussed in our previous work,¹⁷ the values of C_0 calculated in this way are approximately proportional to the total amount of oxygen present across the CSAF because the depth sensitivity of 20 kV EDX is much greater than the CSAF thickness. Three separate measurements of C_0 were made for each CSAF composition at each t_{ox} and averaged to reduce noise.

XPS Depth Profiling. The XPS depth profiling of both the $Al_xFe_yNi_{1-x-y}$ CSAFs and the bulk alloys was performed in a ThermoFisher ThetaProbe instrument with a hemispherical energy analyzer. The XPS measurements were made using monochromated Al K_{α} X-rays; an X-ray spot diameter of ~200 μ m was used for the profiles measured on the CSAFs, and a spot diameter of ~400 μ m was used for the profiles measured on the bulk alloys. During each set of XPS measurements, spectra were acquired across 10–14 eV ranges of binding energies containing the nonoverlapping Al 2s, Fe 2p_{1/2}, Ni 2p_{3/2}, and Mo 3p_{3/2} peaks. With the pass energy of the hemispherical analyzer held constant at 100 eV, the spectra were collected by scanning across each energy range in 0.05 eV

steps with 0.2 s dwell time per step. The sets of XPS measurements were alternated with uniform etching of the analysis area by a rastered Ar⁺ beam (3 kV, 1 μ A) in 65 identical cycles (except for the Al_{0.10}Fe_{0.90} bulk profile in Figure 8, for which 390 cycles were used) to obtain XPS data as a function of depth into the samples. It is possible to discern whether the monitored species were in a metallic or oxidized chemical state based on the position of the peaks in their XPS spectra; oxidized metals have their peak binding energies increased by $\sim 2-5$ eV over the binding energies of the metallic species. The spectra were processed using Thermo Avantage software to fit metallic and/or oxidized peaks to each of the spectra. The geometric parameters used to define each of the peaks and examples of fit spectra are provided in the appendix of one of our previous studies.¹⁸ The relative compositions of the elemental components were calculated by normalizing their total peak areas by Wagner sensitivity factors, and the metallicto-oxidized ratio for each species was assumed to be equal to the ratio of the area of the metallic peak to the area of the oxidized peak(s)

 Al_xFe_{1-x} and Al_xNi_{1-x} Bulk Sample Preparation and **Handling.** The six Al_xFe_{1-x} and Al_xNi_{1-x} bulk samples were cast as \sim 700 cm³ ingots at the United States Department of Energy National Energy Technology Laboratory facility in Albany, Oregon. Tokens with approximate dimensions of 7×7 \times 2.5 \rm{mm}^3 were cut from these ingots by wire electrical discharge machining. One $7 \times 7 \text{ mm}^2$ face of each token was then mechanically polished in a sequence of seven steps, first using 1200 grit sandpaper, then 9, 6, 3, and 1 μ m Buehler MetaDi Supreme Polycrystalline Diamond solutions, and finally 0.3 and 0.05 μ m Buehler Micropolish II Alumina compounds. The 9, 6, and 3 μ m solutions were applied using Buehler nylon pads, and the 1 μ m solution and Micropolish II Alumina compounds were applied using a Buehler microcloth. In between each step, the surface of the token was thoroughly rinsed with deionized water to remove any residual polishing material from the previous step. Visually, the surfaces of the tokens developed a mirror finish as a result of the polishing sequence. The tokens were then placed under UHV in the chamber housing the CSAF deposition tool, sputtered with a defocused 2 kV Ar⁺ beam (~1 μ A current per token) for ~20 min, and annealed for 2 h at 427 °C. Similar to the $Al_{x}Fe_{y}Ni_{1-x-y}$ CSAFs, the tokens were exposed to ambient air at room temperature for ~ 15 min as they were transferred to the Tescan Vega3 SEM system for initial $(t_{ox} = 0 h)$ characterization. The resulting roughness of the token surfaces was not quantified but can be qualitatively assessed based on the SEM images shown in Figure 6. After initial characterization, the tokens were oxidized in dry air at 427 °C for 4 h by the same procedures used for the $Al_xFe_yNi_{1-x-y}$ CSAFs.

SEM Imaging. All SEM imaging was performed in the Tescan Vega3 system at a working distance of 11 mm with the beam operating at 20 kV. The electron beam diameter was ~90 nm, and the scan rate was 1 ms per pixel. The SEM images of the $Al_xFe_yNi_{1-x-y}$ CSAF surfaces (Figures 3–5) were generated by secondary electron detection, whereas those of the bulk Al_xFe_{1-x} and Al_xNi_{1-x} alloy surfaces (Figure 6) were generated by BSE detection.

EDX of Bulk Alloy Samples. The compositions shown for the bulk Al_xFe_{1-x} and Al_xNi_{1-x} alloys in Figure 6 were determined from EDX spectra processed using the default quantification routine in the INCA Energy software. These spectra were measured from 0 to 10 keV (5 eV binning,

>200,000 total counts) at a working distance of 15 mm with the SEM beam operating at 20 kV. The "average" compositions were determined from spectra measured while rastering the beam over an \sim 700 × 500 μ m² area on the surface, whereas the compositions of the "light" and "dark" phases were determined from spectra acquired with the beam held stationary (sampling an ~0.5 × 0.5 μ m² area). Each of the compositions shown in Figure 6 is the average of five individual measurements.

FIB-TEM Analyses of $AI_xFe_yNi_{1-x-y}$ CSAF. The Al_xFe_yNi_{1-x-y} CSAF sent to Inmetro underwent the same preparation, UHV-annealing, handling, and initial characterization steps at Carnegie Mellon University as those used in the oxidation studies, except it was not exposed to dry air at 427 $^{\circ}$ C, i.e., $t_{ox} = 0$ h. The sample was shipped in a sealed container filled with Ar to minimize ambient air exposure while in transit, and, upon arrival at Inmetro, the sample was removed from this container under N2 in a glovebag attached to the microscope. Cross sections (~5 × 10 μ m²) of the CSAF/substrate were prepared by FIB using an FEI Nova NanoLab 600 and were analyzed by TEM in a Cs-corrected FEI Titan 80-300 (300 kV operating voltage) equipped with an X-FEG filament and monochromator. Conventional bright-field and dark-field TEM images were processed using DigitalMicrograph software. STEM images were acquired using a Gatan bright-field/annular dark-field detector with a camera length of 38 mm and a convergence semiangle of 27.3 mrad. EDX spectra used for chemical analyses were measured using an EDAX analyzer. EDX elemental maps were acquired by a drift-corrected STEM spectrum imaging experiment and processed using TIA software. A combination of measurements using HRTEM, selected area diffraction, nanobeam diffraction, and EDX were used to identify the Al Fe $Pm\overline{3}m$ phase in the Al_{0.58}Fe_{0.42} cross section of the CSAF.

AUTHOR INFORMATION

Corresponding Author

*E-mail: gellman@cmu.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. M.E.O., G.P., C.P.G., B.S.A., and C.A.A. performed the FIB-TEM analyses. M.A.P., J.B.M., and A.J.G. conceived, designed, and carried out the remainder of the experiments.

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Notes

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ABBREVIATIONS

CSAF, composition spread alloy film; UHV, ultrahigh vacuum; SEM, scanning electron microscopy; EDX, energy-dispersive Xray spectroscopy; XPS, X-ray photoelectron spectroscopy; BSE, backscattered electron; TEM, transmission electron microscopy; FIB, focused ion beam; STEM, scanning transmission electron microscopy; HRTEM, high-resolution transmission electron microscopy

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