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High-Throughput Screening Across Quaternary Alloy Composition Space: Oxidation of $(Al_xFe_vNi_{1-x-v})_{\sim 0.8}Cr_{\sim 0.2}$

Matthew A. Payne,[†] James B. Miller,[†] and Andrew J. Gellman^{*,†,‡}

[†]Carnegie Mellon University, Department of Chemical Engineering, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

[‡]Carnegie Mellon University, W.E. Scott Institute for Energy Innovation, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213, United States

ABSTRACT: Composition spread alloy films (CSAFs) are commonly used as libraries for high-throughput screening of composition-property relationships in multicomponent materials science. Because lateral gradients afford two degrees of freedom, an n-component CSAF can, in principle, contain any composition range falling on a continuous two-dimensional surface through an (n - 1)-dimensional composition space. However, depending on the complexity of the CSAF gradients, characterizing and graphically representing this composition range may not be straightforward when $n \ge 4$. The standard approach for combinatorial studies performed using quaternary



or higher-order CSAFs has been to use fixed stoichiometric ratios of one or more components to force the composition range to fall on some well-defined plane in the composition space. In this work, we explore the synthesis of quaternary Al-Fe-Ni-Cr CSAFs with a rotatable shadow mask CSAF deposition tool, in which none of the component ratios are fixed. On the basis of the unique gradient geometry produced by the tool, we show that the continuous quaternary composition range of the CSAF can be rigorously represented using a set of two-dimensional "pseudoternary" composition diagrams. We then perform a case study of $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ oxidation in dry air at 427 °C to demonstrate how such CSAFs can be used to screen an alloy property across a continuous two-dimensional subspace of a quaternary composition space. We identify a continuous boundary through the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ subspace at which the oxygen uptake into the CSAF between 1 and 16 h oxidation time increases abruptly with decreasing Al content. The results are compared to a previous study of the oxidation of $Al_x Fe_v Ni_{1-x-v}$ CSAFs in dry air at 427 °C.

KEYWORDS: composition gradient films, quaternary materials libraries, high-throughput screening, Al-Fe-Ni-Cr, oxidation

INTRODUCTION

Composition spread alloy films (CSAFs), that is, alloy thin films with continuous, lateral gradients in elemental composition (Figure 1), are a well-established platform for combinatorial materials research.¹ The coupling of CSAFs with rapid, spatially resolved analysis techniques facilitates high-throughput screening of composition-property relationships. In recent years, CSAF-based methods have been applied to study an increasingly wide variety of problems in materials science.² Due to the continuous nature of their composition gradients, CSAFs offer certain advantages over inkjet-printed combinatorial arrays³⁻⁵ and other alternative types of high-throughput libraries. However, the majority of the work that has been done with CSAFs has been limited to binary or ternary alloys; examples of studies involving quaternary or higher-order CSAFs⁶⁻¹² are far less common. In addition, in all but one¹² of these studies, at least some of the components are incorporated into the CSAFs in fixed ratios (most often as stoichiometric oxides). This approach reduces the degrees of freedom in the prepared composition range (making it easier to present and interpret the results of high-throughput measurements made across the CSAFs), but

also constrains the regions of composition space that can be accessed. For example, a quaternary CSAF of elements A-B-C-D created using A, B, and CD as base components can only access compositions with a C:D ratio of 1, i.e. $A_x B_y (CD)_{1-x-y}$ (subscripts designate atomic fractions) where $(0 \le x \le 1, 0 \le y \le [1 - x])$. The work reported herein explores the preparation and characterization of quaternary CSAFs for a more general case in which none of the alloy components are incorporated in fixed ratios. Specifically, we investigate the preparation of $(Al_x Fe_y Ni_{1-x-y})_{1-z} Cr_z$ CSAFs using a rotatable shadow mask (RSM) CSAF deposition tool¹³ developed previously in our group. We then perform a case study of the oxidation of these CSAFs to demonstrate how such a sample can be used to investigate alloy properties across a continuously defined region of quaternary composition space.

Al and Cr are often used as minor components in Fe/ Ni-based alloys to provide protection against corrosion in hightemperature oxidizing environments. If the Al content of an alloy

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Figure 1. Schematic depictions of (a) a ternary CSAF containing all possible compositions of $A_x B_y C_{1-x-y}$ and (b) a quaternary CSAF containing all possible relative compositions of $A_x B_y C_{1-x-y}$ where *z*, the atomic fraction of component D, is constant.

meets or exceeds some "critical Al concentration", N_{Ab}^* then a passivating Al₂O₃ layer or "scale" is established near its surface, greatly slowing the rate of further oxidation relative to that of an alloy with a subcritical Al content which does not form a passivating scale.^{14–19} Cr is frequently included in alloys that are designed to form passivating Al_2O_3 scales because Cr is known to lower the value of N_{AL}^* ^{16,17,20–24} which is desirable for improving various mechanical properties of the alloy.^{15,16,25-28} Highthroughput study of alloy oxidation using a CSAF library can enable determination of a continuous N_{Al}^* boundary through multicomponent composition space, separating composition regions which form a passivating Al₂O₃ scale from those that do not. Our case study seeks to identify an $N_{\rm Al}^*$ boundary for a specific $(Al_x Fe_y Ni_{1-x-y})_{1-z} Cr_z CSAF$ oxidized in dry air at 427 °C, and compare it to the $N_{\rm Al}^*$ boundary that we have measured previously²⁵ for ternary $Al_x Fe_y Ni_{1-x-y}$ CSAFs in the same environment.

RESULTS AND DISCUSSION

Quaternary CSAFs. CSAFs are ideal for combinatorial mapping across composition space of any alloy property which can be rapidly measured at discrete locations across a surface. Lateral composition gradients afford up to two degrees of freedom in the composition range that can be generated in any given CSAF. In the case of a ternary alloy, $A_x B_y C_{1-x-y}$ this is sufficient to produce a continuous spread of all possible compositions $(x = 0 \rightarrow 1, y = 0 \rightarrow [1 - x])$ across a finite, two-dimensional (2D) region of physical space. For example, Figure 1(a) shows a schematic of a full-range $A_x B_y C_{1-x-y}$ CSAF with a triangular geometry resembling a ternary composition diagram. However, because the composition range of an *n*-component CSAF is constrained to a 2D surface in an (n - 1)dimensional composition space, it is not possible for a CSAF to continuously span the entire composition space of a quaternary or higher-order alloy. The simplest approach for using a CSAF

to study such alloys would instead be to prepare a specific plane of interest through the composition space. The schematic in Figure 1b shows an example of a CSAF containing a single plane through quaternary A–B–C–D composition space. In principle, by fixing the atomic fraction of D at a constant value, *z*, an $(A_xB_yC_{1-x-y})_{1-z}D_z$ CSAF could contain all possible *relative* compositions of $A_xB_yC_{1-x-y}$ ($x = 0 \rightarrow 1, y = 0 \rightarrow [1 - x]$) by using a gradient geometry that is otherwise identical to that shown for the ternary CSAF in Figure 1a.

To investigate practical aspects of working with quaternary CSAFs, we attempted to prepare a sample like that shown in Figure 1(b), with a constant z = 0.2, and where the components A-B-C-D were Al-Fe-Ni-Cr, respectively. The CSAF was prepared under ultrahigh vacuum (UHV) using the RSM-CSAF deposition tool developed previously in our group.¹³ Using this tool, the CSAF components are simultaneously deposited onto the $14 \times 14 \text{ mm}^2$ face of a Mo substrate, each from a separate e-beam evaporation source. The sources for Al, Fe, and Ni are partially masked, creating a line-of-sight shadowing effect which causes the incident flux of each component to vary from zero to a maximum value in three independent directions across the substrate. We have previously demonstrated the ability to use the RSM-CSAF deposition tool to prepare ~100 nm-thick $Al_xFe_yNi_{1-x-y}$ CSAFs with composition gradients closely resembling those shown in Figure 1a.^{29,30} In attempting to prepare a quaternary $(Al_xFe_yNi_{1-x-y})_{0.8}Cr_{0.2}$ CSAF, we used Al, Fe, and Ni evaporation procedures identical to those used for making the $Al_xFe_yNi_{1-x-y}$ CSAFs, while a fourth, unmasked source deposited a roughly uniform amount of Cr across the substrate with a flux that was \sim 25% of the maximum molar flux of the other components. After deposition, the CSAF was UHVannealed for 2 h at 427 $^{\circ}\mathrm{C}$ in the RSM-CSAF deposition tool and then transferred to a scanning electron microscope (SEM) for composition mapping using energy-dispersive X-ray spectroscopy (EDX). Spatially resolved measurements of CSAF composition were made across a 13×13 grid with 1 mm spacing, which was centered on the face of the substrate. Figure 2 shows contour plots of the relative Al, Fe, Ni, and Cr compositions of the CSAF as a function of real-space position based on these 169 discrete measurements. The measured Al, Fe, and Ni concentrations in the CSAF each vary from 0 to \sim 80 at. % across the region, but the measured Cr concentration varies from 9 to 25 at. %, revealing that the sample deviates measurably from an "ideal" $(Al_xFe_yNi_{1-x-y})_{0.8}Cr_{0.2}$ CSAF, for which the Cr concentration would be constant at 20 at. %. These observed variations in the Cr atomic fraction are not caused by nonuniform Cr deposition, but result from the specific nature of the gradients produced independently for each of the other components, as will be demonstrated by the following discussion regarding the modeling of the CSAF's composition distribution.

To better understand the composition gradients obtained in the quaternary CSAF, the data shown in Figure 2 was used to fit a composition distribution model (CDM) describing CSAF composition as a continuous function of real-space position. The functional form of the CDM is built upon that originally developed for ternary CSAFs and reported in the appendix of a previous study.²⁹ The CDM provides a quantitative basis for estimating composition continuously at all locations across the CSAF from a set of discrete measurements, and is based on simplifying assumptions regarding the evaporative flux profiles produced by the RSM-CSAF deposition tool. Specifically, for each CSAF component, *i*, the CDM describes the relative molar amount of *i* per unit surface area, A_i accumulated across the



Figure 2. Real-space contour plots of the relative Al, Fe, Ni, and Cr concentrations in the quaternary CSAF as measured with EDX. The contours are fit based on discrete measurements made with 1 mm spacing on a regular grid.

substrate as the height of a simple geometric surface above the plane of the substrate. For shadow-masked components, we have shown previously¹³ that A_i is well approximated by a "linear wedge", like that shown in Figure 3. Uniquely describing a linear wedge relative to the plane of the substrate requires 4 geometric parameters. We define these parameters based on the orthogonal (x,y) coordinate system used in Figure 2 as h_i , w_i , α_i , and θ_i . The geometric significance of each parameter is shown in Figure 3: h_i (unitless) is the maximum height of the wedge, w_i (mm) is the width of the wedge, α_i (mm) defines the wedge position as the intersection of the zero-flux edge with the *x*-axis, and θ_i (degrees) describes the wedge orientation as the angle of rotation of the zero-flux edge with respect to the *x*-axis. Given these definitions, $A_i(x,y)$ can be calculated for any specified values of h_i , w_i , α_i , and θ_i as

$$A_{i}(x, y) = \begin{cases} \begin{pmatrix} h_{i}, & y < Y_{m,i} \\ h_{i} \left(\frac{y - Y_{0,i}}{Y_{m,i} - Y_{0,i}} \right), & Y_{m,i} \le y \le Y_{0,i}, & \cos \theta_{i} < 0 \\ 0, & y > Y_{0,i} \\ \\ \begin{cases} 0, & y < Y_{0,i} \\ h_{i} \left(\frac{y - Y_{0,i}}{Y_{m,i} - Y_{0,i}} \right), & Y_{0,i} \le y \le Y_{m,i}, & \cos \theta_{i} > 0 \\ \\ h_{i}, & y > Y_{m,i} \end{cases}$$
(1)

с .





Figure 3. Top: The "linear wedge" surface used in the CDM to describe $A_{Al}(x_i,y)$, $A_{Fe}(x_i,y)$, and $A_{Ni}(x_i,y)$ in terms of the parameters h_i , w_i , α_i , and θ_i . Bottom (left): Photograph of the quaternary CSAF with an overlaid grid of real-space coordinates across which the compositions used to fit the CDM were measured. Bottom (right): Graphical depiction of the best-fit CDM showing the wedge boundaries for $A_{Al}(x_i,y)$, $A_{Fe}(x_i,y)$, and $A_{Ni}(x_i,y)$. $A_{Cr}(x_i,y)$ is modeled as the plane passing through the three points labeled with the values of A_{Cr} .

where

$$Y_{0,i}(x) = (x - \alpha_i) \tan \theta_i$$
$$Y_{m,i}(x) = \frac{w_i}{\cos \theta_i} + (x - \alpha_i) \tan \theta_i$$

Since Al, Fe, and Ni were deposited from three independently shadow-masked evaporators, $A_{AI}(x,y)$, $A_{Fe}(x,y)$, and $A_{Ni}(x,y)$ were each defined according to eq 1 when fitting the CDM to the quaternary CSAF data in Figure 2. Conversely, the Cr was deposited from an unmasked evaporator to obtain a relatively uniform flux across the surface. However, we have shown previously¹³ that the A_i across a substrate of material deposited from an unmasked source actually varies slightly with an approximately planar trend (arising because the evaporators in the RSM-CSAF deposition tool are tilted at 15° relative to the substrate normal). For this reason, we fit $A_{Cr}(x,y)$ in the CDM as the height of a plane above the substrate surface, described by 3 geometric parameters. Relative to the orthogonal (x,y)coordinate system used in Figure 2, we defined these parameters as $A_{\rm Cr}(1,11)$, $A_{\rm Cr}(11,11)$, and $A_{\rm Cr}(6,1)$, that is, the values of $A_{\rm Cr}$ at three points on the substrate. For any specified values of $A_{Cr}(1,11)$, $A_{Cr}(11,11)$, and $A_{Cr}(6,1)$, $A_{Cr}(x,y)$ can then be calculated as

$$A_{\rm Cr}(x, y) = \frac{(x-1)a + (y-11)b + 100A_{\rm Cr}(1, 11)}{100}$$
(2)

where

$$a = 10(A_{Cr}(11, 11) - A_{Cr}(6, 1)) - 10(A_{Cr}(1, 11) - A_{Cr}(6, 1))$$

$$b = 5(A_{\rm Cr}(1, 11) - A_{\rm Cr}(6, 1)) + 5(A_{\rm Cr}(11, 11) - A_{\rm Cr}(6, 1))$$

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Having defined $A_i(x,y)$ for each of *j* total components, the mole fraction of each component in the CSAF, N_i , can be trivially calculated as

$$N_{i}(x, y) = \frac{A_{i}(x, y)}{\sum_{j} A_{j}(x, y)}$$
(3)

Defining $A_{AI}(x,y)$, $A_{Fe}(x,y)$, and $A_{Ni}(x,y)$ by eq 1 and $A_{Cr}(x,y)$ by eq 2, the values of 15 parameters are needed to evaluate $N_i(x,y)$ across the quaternary CSAF surface. A CDM was fit to the CSAF by performing a least-squares regression of N_i values predicted by the CDM, N_i^{CDM} (defined by eq 3), compared to the 676 discretely measured N_i values, N_i^{msrd} , corresponding to the data in Figure 2. The parameter values defining the best-fit CDM are shown in Table 1. A schematic visualization of the best-fit

 Table 1. Parameter Values Defining the Best-Fit CDM for the

 Quaternary CSAF

	$w_i (\mathrm{mm})$	h_i	$\alpha_i (\mathrm{mm})$	$\theta_i (\mathrm{deg})$
Al	7.6	1.00	908	179.38
Fe	6.2	0.69	5.1	63
Ni	4.9	0.54	5.7	299
	$A_i(1,11)$		$A_i(6,1)$	$A_i(11,11)$
Cr	0.21		0.19	0.18

CDM is shown in Figure 3 next to a photograph of the CSAF, on which the (x,y) coordinate system and the grid of 169 points at which N_i^{msrd} values were obtained are superimposed. The accuracy of the CDM fit to the CSAF composition can be assessed by comparing the values of N_i^{CDM} and N_i^{msrd} on a point-by-point basis. Figure 4 presents histograms of the difference in these two values for each component at the 169 locations analyzed on the CSAF. These histograms provide an indication of how accurately the best-fit CDM represents the actual CSAF composition distribution (as would be measured with EDX) within the bounds of the analyzed grid: 49% of the N_i^{msrd} values agree with N_i^{CDM} to within ± 0.5 at. %, 83% agree to within ± 1.5 at. %, and 95% agree to within ± 2.5 at. %. As we discuss in previous work,²⁹ the absolute accuracy with which EDX can be used to determine CSAF composition is likely no better than ± 2 at. %. Based on the histograms in Figure 4, the CDM appears to be adequate for describing the local composition to within ± 2 at. % across the vast majority of the CSAF.

Accepting the best-fit CDM (defined by the parameter values in Table 1 and shown schematically in Figure 3) as sufficiently accurate, it can be used to assess the nature of the composition gradients obtained in the quaternary CSAF, and how they differ from an "ideal" $(Al_xFe_yNi_{1-x-y})_{0.8}Cr_{0.2}$ CSAF with a geometry like that shown in Figure 1b. A photograph of the CSAF with an overlay of the A_{Al} , A_{Fe} , and A_{Ni} "wedge" boundaries defined by the CDM is shown in the upper left of Figure 5. The dashed lines represent the edges at which A_i reaches zero, while the solid lines represent the edges at which A_i reaches a constant maximum value (see Figure 3). Recalling that Cr is present across the entire substrate, these boundaries reveal which components are present in different regions of the CSAF. The triangular region bounded by the three dashed lines is the Al-Fe-Ni-Cr quaternary region, as shown in the upper right of Figure 5. The CSAF also contains Al-Fe-Cr, Fe-Ni-Cr, and Al-Ni-Cr ternary regions, as well as Fe-Cr, Ni-Cr, and Al-Cr binary regions. The Al-Fe-Ni-Cr region is divided into four subregions, across each of which the gradient of A_i is constant for each component.



Figure 4. Histograms for each alloy component showing the difference between the compositions predicted by the best-fit CDM and the measured compositions used for the fitting. The numbers above each bar indicate the number of points (from a total of 169) falling within the range indicated on the horizontal axis.

As a result, the composition range contained within any one of the subregions falls on a single plane through the three-dimensional (3D) quaternary composition space. All compositions lying on such a plane can be described as a linearly weighted average of three fixed (binary and/or ternary) compositions. This allows the composition range of each subregion to be represented using a "pseudoternary" composition diagram, where the axes indicate the weighting fraction of these three fixed compositions rather than pure component fractions, as in standard ternary composition diagrams. The gradients of $A_{AI}(x,y)$, $A_{Fe}(x,y)$, and $A_{Ni}(x,y)$ change upon crossing the solid lines along which their maxima are reached. Thus, the segments of these lines falling within the Al-Fe-Ni-Cr quaternary region delineate an intersection of two planes through the 3D quaternary composition space, each of which must be represented using a different pseudoternary composition diagram. Four pseudoternary diagrams are required to represent the range of compositions present in the quaternary region of the CSAF in Figure 5. Compositions from the remaining binary or ternary regions can simply be plotted on standard ternary composition diagrams.

The points shown on the CSAF in the upper left of Figure 5 fall on a regular grid (0.5 mm spacing) from which data were collected for the study of Al–Fe–Ni–Cr oxidation presented in the following section. The CSAF composition at each point can be plotted on at least one of the seven diagrams shown in the bottom of Figure 5. Four of these are pseudoternary composition diagrams describing the composition range of the Al–Fe–Ni–Cr quaternary region, while the remaining three are standard ternary composition diagrams describing all possible compositions for which one of the component fractions has reached $N_i = 0$. The points on the diagrams and their corresponding points on the



Figure 5. Top (left): A regularly spaced grid on the quaternary CSAF surface (photographed) relative to the CDM-defined wedge boundaries for $A_{AI}(x,y)$, $A_{Fe}(x,y)$, and $A_{NI}(x,y)$. Top (right): The components contained in different regions of the CSAF, as determined based on the wedge boundaries. **Bottom:** The set of 7 different composition diagrams (4 pseudoternary, 3 ternary) required to rigorously represent all of the CSAF compositions predicted by the CDM at the points shown on the grid at top left. Corresponding sets of points are indicated with matching symbols.

CSAF are indicated with matching symbols. The complete set of diagrams is necessary to rigorously represent the full range of compositions contained in the quaternary CSAF according to the CDM (Figure 3). The four pseudoternary composition diagrams are sample-specific, and would change if any of the CDM parameters in Table 1 were changed. This complicates the comparison of property measurements made across any two quaternary CSAFs which are not precisely identical. However, based on the diagrams in Figure 5, the sample could be approximately described as an $(Al_xFe_vNi_{1-x-v})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF $(x = 0 \rightarrow 1, x = 0)$ $y = 0 \rightarrow [1 - x]$ for simplified comparison with similar CSAFs. Oxidation of Al-Fe-Ni-Cr. To demonstrate how the principles discussed in the previous section can be applied to the high-throughput screening of alloy properties across continuous quaternary composition space, we performed a simple case study of oxidation in dry air at 427 °C using the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF. This extends work we have done previously,²⁹⁻³¹ in which we characterized $Al_xFe_yNi_{1-x-y}$ CSAF oxidation in both dry and humid air at 427 °C. Our primary goal in those previous studies was to use CSAFs to identify the continuous $N_{\rm Al}^*$ boundary separating alloy compositions which form a passivating Al₂O₃ scale from those that do not. We determined whether different Al_xFe_yNi_{1-x-y} CSAF compositions established a passivating Al₂O₃ scale in

both dry and humid oxidizing environments by using EDX to monitor the total oxygen content, $C_{\rm O}$, of the CSAF cross section at different points across the CSAF as a function of total exposure time to the environment, $t_{\rm ox}^{29-31}$ For $t_{\rm ox} > 1$ h, compositions which had formed a passivating Al₂O₃ scale exhibited measurably lower changes in $C_{\rm O}$, $\Delta C_{\rm O}$, (i.e., oxygen uptake) with additional $t_{\rm ox}$ than those which were not passivated.²⁹⁻³¹

 $C_{\rm O}$ was measured across the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF for different values of t_{ox} in dry air at 427 °C on the grid shown in Figure 5. Figure 6 shows the ΔC_0 from $t_{ox} = 1$ to 16 h plotted using a color scale on the set of composition diagrams introduced in Figure 5. The data are displayed using continuous contours (fit based on measurements at the discrete compositions indicated by white points) on the four pseudoternary composition diagrams representing the quaternary region, while each point is individually color-coded in the three ternary composition diagrams. Figure 6 reveals an abrupt increase in ΔC_0 with decreasing $N_{\rm Al}$ across the entire range of compositions contained in the CSAF. In on our previous studies of $Al_xFe_yNi_{1-x-y}$ CSAF oxidation,²⁹⁻³¹ we showed that similar increases in $\Delta C_{
m O}$ occur upon crossing the $N_{
m Al}^*$ boundary between compositions which form a passivating Al₂O₃ scale and those that do not. We proceed assuming that this is also the case for oxidation of the $(Al_xFe_vNi_{1-x-v})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF in dry air at 427 °C, that is, for the data shown in Figure 6. We do not



Figure 6. EDX-measured oxygen uptake (ΔC_0 , arbitrary units) between t_{ox} = 1 and 16 h in dry air at 427 °C as a function of the (Al_xFe_yNi_{1-x-y})_{~0.8}Cr_{~0.2} CSAF composition. The pseudoternary diagrams show continuous contours fit to the discrete measurements made at the white points, while each point is individually color-coded in the ternary diagrams.

attempt to further verify this, as referring nonspecifically to the boundary along which the observed increase in $\Delta C_{\rm O}$ occurs as " $N_{\rm Al}^*$ " provides a suitable basis for all subsequent discussion of the present case study, regardless of its physical significance.

Given the spacing of the discrete points at which ΔC_0 was measured, it is difficult to propose a precise trajectory of $N_{\rm Al}^*$ through the diagrams based solely on the data in Figure 6. A key finding from our previous studies 2^{29-31} was that the discoloration patterns developed on Al_xFe_yNi_{1-x-y} CSAFs as a result of their oxidation in dry and humid air at 427 °C reveal the real-space trajectory of N_{Al}^* across their surfaces, that is, abrupt changes in the thickness or chemical composition of the surface oxide at $N_{\rm Al}^*$ were found to correlate with an obvious change in optical appearance. As simple visual analysis could then be used to map the N_{A1}^* boundary precisely in real space on the Al_xFe_yNi_{1-x-y} CSAFs, the CDMs fit to those CSAFs could be used to estimate the continuous composition-space trajectory of $N_{\rm Al}^{*\,29,30}$ Here, we consider whether N_{Al}^* might similarly be visually identified on the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF. Figure 7(a) shows a photograph of an Al_xFe_vNi_{1-x-v} CSAF oxidized for 4 h in dry air at 427 °C in one of our previous studies,²⁹ with the location of the ternary composition region (see Figure 1(a)) marked for reference. The abrupt change in surface discoloration indicated by the solid white line was found to correlate with N_{Ab}^* as determined by X-ray photoemission depth profiling and EDX measurements of Co and ΔC_0^{29} Figure 7(b) shows the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF after oxidation for 16 h in dry air at 427 °C with the location of the quaternary region marked for reference (see Figure 5). Many aspects of the appearances of the two oxidized CSAFs in Figure 7 are significantly different. The rate at which the visual appearance of the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF changed with increasing t_{ox}



Figure 7. (a) Photograph of an Al_xFe_yNi_{1-x-y} CSAF exposed to dry air at 427 °C for t_{ox} = 4 h.²⁹ The real-space trajectory of N_{Al}^{*} can be visually identified based on the discoloration of the surface, as shown. (b) Photograph of the (Al_xFe_yNi_{1-x-y})_{~0.8}Cr_{~0.2} CSAF exposed to dry air at 427 °C for t_{ox} = 16 h. Significantly more discoloration occurred as the result of oxidation near the top of the CSAF (at low values of N_{Al}) than across the remainder of its surface.

was found to be much slower than that of the Al_xFe_yNi_{1-x-y} CSAF (thus, a maximum t_{ox} of 16 h was used instead of 4 h). However, by t_{ox} = 16 h, the (Al_xFe_yNi_{1-x-y})_{~0.8}Cr_{~0.2} CSAF does appear to exhibit a well-defined boundary at which the surface discoloration increases abruptly with decreasing Al content, similar to the N^{*}_{Al} boundary on the Al_xFe_yNi_{1-x-y} CSAF for t_{ox} = 4 h.

To determine whether the abrupt change in surface discoloration of the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF visible in Figure 7b is correlated with N_{Ab}^* we used the CDM for the sample (Figure 3 and Table 1) to compare the composition-space trajectory of the visually observed boundary with the ΔC_0 data shown in Figure 6. The trajectory of the observed boundary across the quaternary region of the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF is shown as a dashed black line on the photograph in Figure 8a. The boundary



Figure 8. (a) The real-space boundary on the photograph at right was identified based on the discoloration of the oxidized ($t_{ox} = 16$ h in dry air at 427 °C) (Al_xFe_yNi_{1-x-y})_{~0.8}Cr_{~0.2} CSAF surface. The continuous composition-space trajectory of the boundary predicted by the CDM is shown in the three pseudoternary diagrams. Its clear correlation with an abrupt increase in oxygen uptake (ΔC_{O} , arbitrary units) upon decreasing the Al content suggests that this boundary is $N_{\rm Al}^{*}$. (b) A similar "kink" feature to that circled on the photograph of the oxidized (Al_x Fe_yNi_{1-x-y})_{~0.8}Cr_{~0.2} CSAF (left) was also observed on an (Al_x Fe_yNi_{1-x-y})_{~0.9}Cr_{~0.1} CSAF (right), indicating that it arises from a reproducible physical effect of alloy composition.

traverses three of the four planes through quaternary composition space. The composition-space trajectory of the boundary (as calculated with the CDM) is superimposed on the three pseudoternary composition plots in Figure 8a, showing the measured $\Delta C_{\rm O}$ from $t_{\rm ox}$ = 1 to 16 h across these planes. For

reference, the white square and triangle mark corresponding ends of the boundary on the photograph and the diagrams. The visually observable boundary correlates well with the abrupt increase in ΔC_0 and, therefore, does appear to reveal the trajectory of $N_{\rm Al}^*$ on the $(Al_x {\rm Fe}_y {\rm Ni}_{1-x-y})_{\sim 0.8} {\rm Cr}_{\sim 0.2}$ CSAF.

Because we can determine the real-space trajectory of boundaries on a CSAF with an accuracy of about ± 0.1 mm,²⁹ the visual analysis in Figure 8a allows the trajectory of $N_{\rm Al}^*$ to be determined much more precisely than is possible based only on the ΔC_0 data in Figure 6, which was measured with 0.5 mm spacing on the grid shown in Figure 5. For example, the point where $\Delta C_0 \cong 0$ at Al_{0.09}Fe_{0.59}Ni_{0.15}Cr_{0.17} = $[Al_{0.28}Fe_{0.56}Cr_{0.16}]_{0.32}[Fe_{0.77}Cr_{0.23}]_{0.07}[Fe_{0.59}Ni_{0.24}Cr_{0.17}]_{0.61} \ \text{ap-}$ pears to be an outlier in the lower right pseudoternary diagram in Figure 6, but in Figure 8a it clearly lies within an interesting "kink", where the value of N_{Al}^* abruptly decreases as the Ni-to-Fe ratio increases. The inherent advantage of high-throughput screening methods lies in their ability to reveal complex trends in composition-property relationships, like that represented by this kink. To qualitatively explore the reproducibility and relevance of the kink feature on the $(Al_xFe_vNi_{1-x-v})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF, we prepared a second CSAF with similar gradient geometry, but approximately half the Cr content. EDX composition mapping similar to that shown in Figure 2 confirmed that the second sample could be approximately described as an $(Al_xFe_yNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF. Photographs of the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF after exposure to dry air at 427 °C for t_{ox} = 16 h and the $(Al_xFe_yNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF after exposure to an identical environment for $t_{ox} = 4$ h are compared in Figure 8b. No significant changes in the discoloration of the $(Al_xFe_vNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF were observed between $t_{ox} = 1$ and 4 h (consistent with the behavior we have observed previously for Al_xFe_yNi_{1-x-y} CSAFs^{29,30}), so it was not oxidized beyond t_{ox} = 4 h. The final appearance of the oxidized $(Al_xFe_yNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF appears to be intermediate to that of the oxidized $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF and oxidized $Al_xFe_yNi_{1-x-y}$ CSAFs²⁹ (e.g., Figure 7a). A kink similar to that observed on the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF is also visible on the $(Al_xFe_yNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF; these features are circled on the images of the CSAFs in Figure 8b. It is not surprising that the feature is less pronounced on the $(Al_xFe_yNi_{1-x-y})_{\sim 0.9}Cr_{\sim 0.1}CSAF$ than on the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF, given that it is not observed at all on $Al_xFe_yNi_{1-x-y}$ CSAFs²⁹ (e.g., Figure 7a) and, therefore, must eventually disappear entirely as the Cr content decreases. That the kink appears on both samples in Figure 8b suggests that these features do, in fact, arise from a reproducible physical effect related to oxidation of $(Al_xFe_vNi_{1-x-v})_{1-z}Cr_z$ CSAFs in dry air at 427 °C, and is an interesting phenomenon revealed by our high-throughput approach.

The boundary shown in the composition diagrams in Figure 8a is a rigorous 2D representation of a continuous trajectory of N_{Al}^{*} in dry air at 427 °C, which we have directly measured through the $(Al_xFe_yNi_{1-x-y})_{1-z}Cr_z$ composition space. However, the value of z can be regarded as being roughly constant for simplified comparison with the N_{Al}^{*} boundary that we have measured previously²⁹ for $Al_xFe_yNi_{1-x-y}$ CSAFs in the same environment. This allows values of N_{Al}^{*} as a function of the Fe-to-Ni ratio to be compared directly on CSAFs with and without the addition of ~20 at. % Cr (i.e., for $z \cong 0.2$ and z = 0). Figure 9 shows this comparison with N_{Al}^{*} plotted as a function of $N_{Fe}/(N_{Fe} + N_{Ni})$. The error bars represent the estimated uncertainty arising from the accuracy of our visual determination of the real-space coordinates lying along the N_{Al}^{*} boundaries. The actual values of



Figure 9. Comparison of N_{Al}^* in dry air at 427 °C across all Fe-to-Ni ratios in $Al_xFe_yNi_{1-x-y}$ and $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$, as determined by high-throughput CSAF experimentation. N_{Al}^* is significantly lower for $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ when $N_{Fe}/(N_{Fe} + N_{Ni}) \leq 0.85$.

 $N_{\rm Cr}$ along the $N_{\rm Cr} \cong 0.2$ boundary vary systematically between ~0.17 and ~0.23. By comparing the $N_{\rm Al}^*$ boundaries in Figure 9, it can be seen that the addition of ~20 at. % Cr to an $Al_x {\rm Fe}_y {\rm Ni}_{1-x-y}$ CSAF oxidized in dry air at 427 °C does not appear to significantly affect the value of $N_{\rm Al}^*$ when $N_{\rm Fe}/(N_{\rm Fe}+N_{\rm Ni}) > 0.85$. However, at $N_{\rm Fe}/(N_{\rm Fe}+N_{\rm Ni}) \cong 0.85$, the value of $N_{\rm Al}^*$ abruptly decreased in the $(Al_x {\rm Fe}_y {\rm Ni}_{1-x-y})_{\sim 0.8} {\rm Cr}_{\sim 0.2}$ CSAF and remained significantly lower than in the $Al_x {\rm Fe}_y {\rm Ni}_{1-x-y}$ CSAFs across the remainder of composition space. This abrupt decrease in the value of $N_{\rm Al}^*$ corresponds with the kink feature circled in Figure 8b. While this is an interesting observation, its physical origins are not further considered here, as the primary intent of the case study is simply to demonstrate methods for high-throughput screening of alloy properties across continuous quaternary composition spaces.

CONCLUSIONS

While the continuous composition range contained in a quaternary CSAF is, by definition, constrained to a 2D surface in the 3D composition space, the characterization and representation of this surface can pose a number of challenges. Provided a high degree of control over CSAF preparation, the ideal approach would be to prepare a quaternary CSAF spanning a composition range that falls on a plane through quaternary composition space and, therefore, can be represented by a single 2D composition diagram. This can be accomplished without coupling any of the CSAF components in a fixed ratio if the A_i (molar amount per unit surface area) gradient is constant for each component across the surface. For less ideal cases, a CSAF's composition distribution might still be modeled continuously across its surface, given a reasonable means of estimating $A_i(x,y)$ for each component. However, the ability to rigorously represent such model-predicted composition ranges using 2D diagrams can be complicated depending on the complexity of the function(s) describing $A_i(x,y)$. Well-characterized CSAFs can serve as ideal platforms for high-throughput screening of composition-property relationships across continuous quaternary alloy composition space, as demonstrated by our case study of oxidation using an $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF. In principle, many of the specific concepts discussed in this work could also be extended to studies using quinary or higher-order CSAFs.

EXPERIMENTAL PROCEDURES

Creation of (Al_xFe_yNi_{1-x-y})_{1-z}Cr_z CSAFs. The $(Al_xFe_yNi_{1-x-y})_{1-z}Cr_z$ CSAFs were created under UHV conditions at ~5 × 10⁻¹⁰ Torr with the RSM-CSAF deposition tool, which we have described elsewhere.¹³ Using the tool, the four

CSAF components were codeposited onto a $14 \times 14 \text{ mm}^2$ polycrystalline-Mo substrate (2.5 mm thick, rms roughness <1.5 nm). The deposition faces of the substrates were initially sputtered for 20 min with a defocused, 2 kV Ar⁺ beam (~5 μ A sample current) to remove contaminants. The substrates were then annealed at 477 °C for 1 h, and cooled to room temperature. The Ar⁺ sputtering was repeated immediately before the CSAFs were deposited. To create the CSAFs, the Al, Fe, Ni, and Cr were deposited onto the substrate simultaneously, each from a separate e-beam evaporator (\geq 99.98% pure source material). Before deposition, a quartz crystal microbalance was used to measure the deposition rate from each source to determine appropriate power settings such that the Al, Fe, and Ni had approximately equal maximum molar deposition fluxes that were $\sim 4 \times$ and $\sim 9 \times$ greater than that of the Cr for the $(Al_{x}Fe_{v}Ni_{1-x-v})_{\sim 0.8}Cr_{\sim 0.2}$ and $(Al_{x}Fe_{v}Ni_{1-x-v})_{\sim 0.9}Cr_{\sim 0.1}$ CSAF, respectively. The wedge-like profiles of $A_{\rm Ab}$ $\dot{A}_{\rm Fe}$, and $A_{\rm Ni}$ across the CSAFs are created by partial, line-of-sight shadowing of the apertures of the Al, Fe, and Ni evaporators by independent, rotationally orientable shadow masks, which control the orientations of the wedges.¹³ The mask above the Cr evaporator was removed to obtain uniform A_{Cr} across the CSAFs. The alignments and mask orientations used for the Al, Fe, and Ni evaporators were identical to those previously used to create fullrange Al_xFe_vNi_{1-x-v} CSAFs.^{29,30} Each CSAF was deposited for 500 min, resulting in a total film thickness of ~100 nm (near the maximum achievable with the RSM-CSAF deposition tool). After deposition, the CSAFs were annealed at 427 °C for 2 h and cooled to room temperature in UHV. After the chamber was vented to atmosphere, the CSAFs were exposed for ~15 min to ambient air at room temperature while they were transferred to a Tescan Vega3 SEM for analysis of their composition distributions.

Composition Mapping of the CSAFs. Immediately following the deposition of each CSAF, spatial mapping of its composition distribution was performed in a Tescan Vega3 SEM operated at $\sim 1 \times 10^{-4}$ Torr. EDX spectra were collected using an Oxford Instruments X-max 80 mm² detector controlled by INCA Energy software. The detector was calibrated once hourly with pure Ni. Individual spectra were measured across $50 \times 50 \ \mu m^2$ areas of the surface with 1 mm spacing on a regular grid. The spectra were measured from 0 to 10 keV (10 eV binning, >350 000 total counts) at a working distance of 15 mm with the SEM beam operating at 13.52 kV. The CSAF compositions (as shown in Figure 2) were determined by processing the collected spectra using the Oxford Instruments software package INCA ThinFilmID, which was used to account for inhomogeneous layering within the electron beam interaction volume. The spectra were quantified under the assumption that the $(Al_xFe_yNi_{1-x-y})_{1-z}Cr_z$ CSAF forms a flat layer which is homogeneous and well-adhered to the Mo substrate (in previous work,³¹ we have shown this to be an accurate approximation for similar $Al_x Fe_v Ni_{1-x-v}$ CSAFs). The composition measurements were repeated three times at each location and averaged to reduce noise.

Oxidation of CSAFs. After initial analysis at $t_{ox} = 0$ h (deposited/annealed, ~15 min exposure to ambient atmosphere), each $(Al_xFe_yNi_{1-x-y})_{1-z}Cr_z$ CSAF was exposed in increments to dry air at 427 °C for a total time, t_{ox} . The exposures were performed in a tube furnace (quartz tube, ~2 cm in diameter and ~60 cm long), with one end open to atmosphere and the other end connected to a gas-introduction manifold. The furnace was preheated prior to each exposure such that its temperature

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was stable at 427 ± 1 °C while a continuous flow of ~1 slpm of dry air was applied through the tube using the manifold. The CSAF was loaded into the furnace in a ceramic boat (which was preheated with the furnace), such that only the bottom of the Mo substrate was in direct contact with the boat. The CSAF was removed from the furnace at the end of each incremental exposure, and the bottom of its substrate was placed in contact with aluminum foil to dissipate heat, cooling to room temperature in ~2 min.

EDX Measurement of C_0 in the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ **CSAF.** EDX measurements of C_0 (the total amount of oxygen present across the entire CSAF cross section) as a function of position across the $(Al_xFe_yNi_{1-x-y})_{\sim 0.8}Cr_{\sim 0.2}$ CSAF were made after $t_{ox} = 0$, 1, 4, and 16 h. The spectra used to derive C_0 were collected across 50 \times 50 μ m² areas of the CSAF surface centered at the points on the grid in Figure 5. In total, 344 different locations were sampled. The spectra used to derive C_0 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 30 kV. Arbitrary values for C_0 were calculated as the oxygen EDX signal scaled by the (much larger) Mo EDX signal from the substrate. As we have discussed in previous work,³⁰ the C_0 values calculated in this way are approximately proportional to the total amount of oxygen present across the entire CSAF cross section because the depth sensitivity of 30 kV EDX is much greater than the CSAF thickness. Three individual measurements of C_0 were made at each location for each t_{ox} and averaged to reduce noise. The data shown in Figures 6 and 8a are the $\Delta C_{\rm O}$ from $t_{ox} = 1$ to 16 h, that is, $C_O(t_{ox} = 16 \text{ h}) - C_O(t_{ox} = 1 \text{ h})$.

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.A.P., J.B.M., and A.J.G. conceived, designed, and carried out the experiments.

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Notes

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ABBREVIATIONS

CSAF, composition spread alloy film; RSM, rotatable shadow mask; 2D, two-dimensional; UHV, ultrahigh vacuum; SEM, scanning electron microscope; EDX, energy-dispersive X-ray spectroscopy; CDM, composition distribution model; 3D, three-dimensional

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