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High-throughput characterization of early oxidation across $Al_xFe_yNi_{1-x-y}$ composition space



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ABSTRACT

Improving our fundamental understanding of the oxidation of multicomponent alumina-forming alloys is crucial to their ongoing development. In this work, high-throughput methods were developed to study oxidation of $Al_xFe_yNi_{1-x-y}$ alloys in dry air at 427 °C using composition spread alloy films as combinatorial libraries ($x = 0 \rightarrow 1, y = 0 \rightarrow [1-x]$). The results divide the $Al_xFe_yNi_{1-x-y}$ composition space into four regions of phenomenologically distinct oxidation behaviour. The boundary defining the critical Al concentration, N_{AI}^* (x, y), for establishment of a passivating Al_2O_3 scale was determined across the entire continuous $Al_xFe_yNi_{1-x-y}$ composition space.

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1. Introduction

1.1. Internal vs. external oxidation and N_{Al}^* in alumina-forming alloys

Metal alloys are ubiquitous in modern technology, with applications in areas ranging from structural materials to electronics, catalysis, and more. Properly designed alloys can achieve otherwise-unattainable combinations of mechanical, chemical, and economic characteristics that are superior to those of any of their pure elemental components. An alloy's functional properties arise from interactions among its component species and with the local operating environment, and can vary drastically with atomic composition (i.e. atomic fraction of each component). When this is the case, composition optimization becomes an integral part of alloy design. Oxidation-resistant alloys are an important example of alloys for which key properties are highly dependent on composition [1,2]. Many next-generation structural applications of alloys require continuing development and improvement of their oxidation resistance for use in high-temperature environments. Selection of alloy composition is often critical to achieving the desired combination of mechanical properties and oxidation resistance in thermochemically harsh environments [1–3].

tially forms a continuous alumina (Al₂O₃) layer or "scale" at or near its surface, creating a diffusion barrier that "passivates" the underlying material against further oxidation, greatly retarding bulk oxidation [3-7]. Passivation of an alloy surface by oxide scale formation is referred to as "external oxidation", while progressive oxidation of the bulk is known as "internal oxidation" [2,7–12]. Provided that a sufficiently dense and adherent scale is maintained, Al₂O₃ can remain stable and protective in oxidizing environments at temperatures >1280 °C [1–4,6,13]. The α -phase of Al₂O₃ is the most desirable and protective, but is only formed significantly at temperatures >950 °C by the conversion of more rapidly growing, pseudo-stable Al₂O₃ structures [4,14,15]. A minimum "critical Al concentration", N_{Al}^* , is required in an alloy for initial establishment of a continuous Al₂O₃ scale; for sub-critical Al concentrations, discontinuous Al₂O₃ is formed, leaving diffusion paths that allow continuing oxidation of the bulk [2,6,8,12,13,16]. The value of N_{Al}^* is dictated by a balance between the rate of oxygen permeation into the alloy and the diffusion of Al to the alloy surface [8]. Design of alumina-forming alloys is complicated by the fact that increasing Al content tends to mechanically compromise alloys by increasing their brittleness [2,9,13,17-19]. For this reason, it is desirable in structural applications to use the lowest Al content possible, while still providing adequate oxidation resistance. Therefore, rational design of any multicomponent alumina

"Alumina formers" are a type of metal alloy widely developed for oxidation resistance in high-temperature applications. An alumina former is an alloy that, under operating conditions, preferen-





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former requires a thorough understanding of how N_{Al}^* varies across the viable composition space.

1.2. Development of AlFeNi-based alumina formers

Al, Fe, and Ni are three of the main components in many alumina-forming structural superalloys [7,17,20–23]. Cr is often included as a fourth major component because it lowers the N_{Al}^* needed for establishment of an Al₂O₃ scale by what is termed a "third-element effect" [1–3,6,7,20,21]. In many oxidation-resistant alloys that do not contain Al (such as traditional stainless steels), Cr is incorporated to allow protective Cr₂O₃ scale formation, but these materials exhibit oxidation resistance at >900 °C that is inferior to that of the alumina formers. This is particularly true in environments containing both H₂O and O₂ due to the formation of volatile Cr-oxyhydroxides and the resulting evaporation of the scale [1–3,5,7,17,20,24,25].

AlCrFeNi-based alloys constitute a class of superalloys that behave as alumina-forming austenitic stainless steels (AFASSs) in various environments at temperatures <900 °C [7,17,20,21]. Increasing the Fe content of an AlCrFeNi-based AFASS decreases raw-material cost and increases the melting point. However, Ni must be maintained at a high enough concentration to induce formation of a mechanically robust, austenitic (face-centred cubic) matrix structure [7,17,20,21]. Increasing the Fe, Al, and/or Cr content of the AFASS stabilizes a ferritic (body-centred cubic) matrix structure (observed at <912 °C in pure Fe), which causes brittleness at low temperatures and poor creep resistance at high temperatures [7,17,20,21]. As a consequence, increases in the Al and/or Cr content to improve oxidation resistance requires the replacement of some fraction of Fe with Ni in order to maintain mechanical integrity, which both makes the alloy more expensive and lowers its maximum operating temperature. Thus, as is the case with most alumina formers, accurate knowledge of the dependence of N_{Al}^* on composition is central to the design of AFASS alloys.

A significant limitation to determining optimum compositions of high-temperature AlCrFeNi-based alloys is that experimental studies of their properties have focused on single-composition samples [7,17,20,21,23]. Understanding of the influence of composition on oxidation behaviour has been achieved by cumbersome methods using large numbers of samples. Efforts to rigorously maximize the potential of these alloys must focus on development of materials models for accurate prediction of oxidation behaviour as a function of composition. Such models would be significantly improved by comprehensive experimental measurement of oxidation behaviour across continuous, multi-dimensional composition spaces, but this is prohibitively time consuming when using single-composition alloy samples.

1.3. High-throughput assessment of $Al_xFe_yNi_{1-x-y}$ oxidation

Experimental study of alloy properties across composition space traditionally requires preparation and characterization of a large set of discrete, single-composition samples. The time investment required for thorough exploration of a composition space quickly becomes impractical as either the number of components or the desired composition resolution increase. Measurement of properties in alloys can be greatly expedited through the use of composition spread alloy film (CSAF) sample libraries [26]. CSAFs are substrate-supported alloy films with continuous, lateral composition gradients. Since a ternary composition is specified by two, bounded degrees of freedom, an entire ternary composition space can, in principle, be contained on a finite, two-dimensional surface. CSAFs with properly positioned gradients can, therefore, serve as libraries containing all possible compositions of a ternary alloy, as shown in Fig. 1. When coupled with rapid, spatially



Fig. 1. Targeted spatial distribution of $Al_x Fe_y Ni_{1-x-y}$ CSAF compositions on the substrate surface. The central triangular region contains all ternary compositions and is surrounded by full-range binary and pure-component regions.

resolved characterization techniques, CSAFs allow measurement of composition-property relationships across the entire ternary composition space in a single experiment. Such combinatorial methods have been used increasingly for study of a diverse range of problems in materials science [15,19,26–29].

We have used $Al_xFe_yNi_{1-x-y}$ (subscripts designate atomic fractions) CSAF libraries to develop an experimental methodology for high-throughput assessment of oxidative passivation across alloy composition spaces. Basic oxidation behaviour relevant to AFASS alloys and other alumina formers of interest can be observed in the ternary $Al_xFe_yNi_{1-x-y}$ system. Of particular interest are the Al_xFe_yNi_{1-x-y} composition regions that establish a protective Al₂O₃ scale under a given set of oxidation conditions, i.e. the exposure history of an initially clean alloy to various temperatures and partial pressures of ambient O2 and/or other oxidizing species. Spatially resolved characterization of an oxidant-exposed $Al_xFe_yNi_{1-x-y}$ CSAF can reveal whether or not oxidation of a given composition has resulted in the establishment of a continuous Al₂O₃ passivation layer. Depending on alloy composition and the environment to which an alumina former is exposed, a passivating Al₂O₃ scale may develop either at the surface or in the subsurface beneath one or more layers of other oxides [2-4,6,8-10,12,17,18,22,30-33]. Once a continuous Al₂O₃ layer is established, further oxidation by scale thickening occurs with a slow parabolic growth rate [2,6,15]. Using AlNi alloys, Pettit showed that a second critical Al concentration, N_{Al}^{**} , is required for an alloy to supply sufficient Al to maintain this slow parabolic growth and ensure long-term scale stability, but his findings suggest that N_{AI}^{**} is only greater than N_{Al}^* at temperatures >630 °C [34].

In this work, Al_xFe_yNi_{1-x-y} CSAFs spanning all of ternary composition space $(x = 0 \rightarrow 1, y = 0 \rightarrow [1-x])$ were deposited across $14 \times 14 \text{ mm}^2$ polycrystalline Mo substrates and used for highthroughput, oxidation-characterization experiments. The targeted composition spread geometry is shown in Fig. 1. Our CSAF deposition capabilities limit their thickness to <200 nm. Therefore, we have focused on the early oxidation mechanisms occurring in CSAFs exposed to dry air for <4 h at 427 °C (relatively mild conditions for alumina formers). The goal was to locate the boundaries between composition regions that exhibit different internal and external oxidation behaviour, particularly the boundary defining the critical Al content for establishment of a passivating Al_2O_3 scale, $N_{Al}^*(x, y)$. To accomplish this, we developed a novel methodology for high-throughput oxidation studies on CSAFs. Characterization of Al_xFe_yNi_{1-x-y} CSAF composition gradients was performed in a scanning electron microscope (SEM) by automated composition mapping using energy-dispersive X-ray spectroscopy (EDX). For CSAFs exposed to dry air at 427 °C, visual analyses of oxidationinduced colour changes on their surfaces were sufficient to identify

oxidation behaviour boundaries in real space, which were converted to boundaries in composition space based on the EDX composition mapping. Additional EDX measurements were used to measure oxygen uptake across the CSAFs following exposure to dry air at 427 °C. Raman spectroscopy was used to identify oxide phases formed in different regions of a CSAF. Finally, X-ray photoelectron spectroscopy (XPS) depth profiles were performed at select locations (i.e. compositions) on a CSAF to elucidate specific oxidation behaviour by providing information on the cross-sectional composition of metallic and oxidized components. The combination of these techniques allows a single $Al_xFe_yNi_{1-x-y}$ CSAF to be used for comprehensive characterization of early oxidation behaviour across a ternary composition space for a given set of oxidation conditions. We find that, after 4 h of exposure to dry air at 427 °C, $Al_xFe_yNi_{1-x-y}$ composition space can be subdivided into four regions exhibiting different types of oxidation behaviour: (1) surface passivation by exclusive Al_2O_3 scale formation: (2) passivation by formation of a continuous subsurface Al_2O_3 scale; (3) passivation by a subsurface Al₂O₃ scale beneath a variable-thickness Fe₂O₃ surface layer; and finally, (4) a region that exhibits internal oxidation.

2. Experimental method

2.1. Rotatable shadow mask deposition tool for $Al_xFe_yNi_{1-x-y}$ CSAF preparation

A rotatable shadow mask (RSM) CSAF deposition tool, developed in our laboratory and described in detail elsewhere, was used to prepare full ternary $Al_xFe_yNi_{1-x-y}$ CSAFs [35]. The RSM-CSAF deposition tool incorporates four confocal e-beam evaporators that may be used to co-deposit up to four elemental components simultaneously by physical vapour deposition, with atomic-level mixing. Rotatable, semi-circular shadow masks are positioned between each evaporator and the deposition substrate. The source-masksubstrate geometry results in shadowing of the flux arriving at the substrate from each evaporator and the creation of a linear deposition-rate gradient across an \sim 7 mm band varving from zero at one edge to a maximum rate at the other. The direction of the gradient for a given component is controlled by the orientation of its shadow mask. Using three masks oriented at 120° from one another with appropriate evaporator alignment, the RSM-CSAF deposition tool allows us to create a full ternary CSAF that spans all of composition space on a single, compact substrate.

The RSM-CSAF deposition tool is housed in a stainless-steel, ultra-high vacuum (UHV) chamber. An XYZ-manipulator is used to position a sample holder designed for $14 \times 14 \times 2.5$ mm³ substrates at the focal point of the evaporation sources. The sample holder includes a resistive, ceramic heater capable of heating the substrate to \sim 630 °C. Temperature is monitored by a type-N thermocouple spot-welded to the side of the holder, on which the Mo substrates are mounted with a thermally conductive paste and held in place by set screws. The chamber is also equipped with a Varian ionization gauge for UHV pressure measurement, an RBD Instruments ion gun for sputter cleaning the substrate by Ar⁺ bombardment, an SRS RGA-200 mass spectrometer for analysis of trace gas species, and a Maxtek quartz crystal microbalance (QCM) for measurement of deposition fluxes. The chamber is evacuated by a turbomolecular pump and obtains a typical operating pressure of $\sim 10^{-7}$ Pa after bake-out and outgassing of filaments. For CSAF deposition, Mantis Deposition e-beam evaporators attached to the RSM-CSAF deposition tool are used to generate metal fluxes from an aperture in the water-cooled casing housing each evaporator.

For the studies described here, two $Al_xFe_yNi_{1-x-y}$ CSAFs were deposited on the $14 \times 14 \text{ mm}^2$ surfaces of 2.5 mm-thick, polycrys-talline-Mo substrates purchased from *SPAWR Industries* and polished to a root mean squared roughness <1.5 nm by *Valley Design*

Corp Operations. Before each CSAF deposition, the substrate was cleaned by gently swabbing the deposition surface with isopropyl alcohol and then loaded into the CSAF deposition chamber. The chamber was then evacuated and the substrate was annealed at 477 °C for 2 h prior to bake-out. Once the post-bake-out operating pressure was achieved, the deposition surface was sputtered by a defocused, 2 kV Ar⁺ beam (\sim 5 µA sample current) for 20 min to remove any oxide or adsorbed contaminants and the substrate was annealed at 477 °C for 1 h and allowed to cool to room temperature in UHV. Another 20 min of Ar⁺ sputtering was performed immediately preceding CSAF deposition. Appropriate e-beam evaporator power settings were determined by calibrating component fluxes using QCM measurements of deposition rate. The highest achievable deposition rate for Ni in regions of maximum flux was $\sim 0.2 \text{ nm/min}$ ($\sim 3 \times 10^{-9} \text{ mol/cm}^2/\text{min}$). Evaporator power settings for Al and Fe were chosen to yield molar deposition rates similar to that of the Ni. The $Al_xFe_yNi_{1-x-y}$ CSAFs were each deposited for 500 min, producing a film thickness of ~120 nm. Substrate temperature increased to ~50 °C during deposition due to radiative heating by the evaporation sources. Following deposition, the substrate was annealed in UHV for 2 h at 427 °C to crystallize the CSAF and then cooled to ambient temperature in UHV. The RSM-CSAF deposition chamber was then vented and the sample was transferred to a Tescan Vega3 SEM operated at ${\sim}10^{-2}\,\text{Pa}$ for composition gradient mapping using EDX. The only oxidizing environment experienced by the CSAF prior to its preliminary characterization was ambient air for the period of ~15 min required for its transfer from the deposition chamber into the SEM.

2.2. EDX mapping of composition gradient geometry on $Al_xFe_yNi_{1-x-y}$ CSAFs

Initial mapping of the $Al_xFe_yNi_{1-x-y}$ CSAF composition gradients was performed in the SEM by EDX using an Oxford Instruments Xmax 80 mm² detector. The samples were mounted on a computer-controlled stage allowing automated, high-throughput measurements. Using the software package INCA Energy, spectra were acquired from a 13×13 square grid of points spanning the $12 \times 12 \text{ mm}^2$ region in the middle of the $14 \times 14 \text{ mm}^2$ substrate (169 total points). A secondary electron image ($1000 \times magnifica$ tion) was captured at each location and inspected to ensure that no foreign debris or other abnormalities were present. EDX spectra were obtained from 0-10 keV (10 eV binning) by rastering the 11.24 kV SEM beam over a 50 \times 50 μ m² area centred on each grid point and measuring emitted X-rays for 40 s livetime while operating at \sim 45% detector deadtime. The 50 \times 50 μ m² size was chosen to minimize artefacts arising from any small defects or microstructures while still maintaining sufficient resolution in composition space (the concentration of each component in the CSAF changes by <1 at.% across 50 μ m). The CSAF thickness was \sim 120 nm, but the characterization depth of 11.24 kV EDX in Al, Fe, Ni, and Mo is >300 nm [36]. Thus, conventional quantification of the EDX spectra was inappropriate, as the accuracy of the algorithm built into INCA Energy is critically dependent on the assumption that the entire sampled volume is homogenous. In reality, the sampled volumes on the CSAFs consist of two distinct layers: a roughly homogenous $Al_x Fe_y Ni_{1-x-y}$ film on top of an effectively infinite thickness of Mo. The Oxford Instruments software package INCA ThinFilmID accounts for the effects of lavered samples and was used to quantify the EDX spectra obtained in INCA Energy to determine accurate CSAF compositions. Three separate EDX measurements of CSAF composition were made at each point and the results were averaged to reduce noise.

To predict CSAF composition as a continuous function of real-space location, the composition data from the initial characterization grid was fit to a simple model, based on the deposition geometry of the RSM-CSAF deposition tool [35]. This "composition distribution model" (CDM) assumes that each alloy component is deposited in real space as a "wedge" starting at zero thickness and increasing linearly across the width of an infinitely long band until a plateau value is achieved. Based on this assumption, the composition at all real-space locations on a ternary CSAF can be determined by specifying a location, orientation, gradient width, and relative maximum molar thickness of each of the three component wedges. A best-fit CDM was defined by the set of these parameters which minimized the sum of squared errors between the CDM-predicted composition and EDX-measured composition over all 169 measurement points. The best-fit CDM describes ternary alloy compositions across the entire surface of the CSAF. A more detailed description and the functional form of the CDM is provided in Appendix A.

2.3. Oxidation and visual analysis of $Al_xFe_yNi_{1-x-y}$ CSAFs

Elevated-temperature oxidation of the two $Al_xFe_yNi_{1-x-y}$ CSAFs was performed by placing the samples in a ceramic boat in the centre of a quartz tube furnace (\sim 60 cm long, 2 cm diameter) with one end open to atmosphere and the other end connected to a cylinder of lab-grade dry air. A regulator was used to apply a continuous flow of \sim 1 slpm of the dry air through the furnace. The furnace and boat were preheated to 427 °C with the air flowing. The CSAF samples were then positioned in the boat such that only the non-CSAF side of the substrate was in contact with the boat. It takes \sim 5 min for the temperature of a loaded CSAF to rise to within 20 °C of the furnace temperature. After total exposure times, t_{ox} , of 1, 2, and 4 h, the samples were removed from the furnace and the non-CSAF sides were placed in contact with aluminium foil to quickly dissipate heat, cooling them to near room temperature in ~ 2 min. The CSAFs were then photographed and loaded into the SEM for further characterization.

Composition-dependent changes in the surface colouration of $Al_xFe_yNi_{1-x-y}$ CSAFs occur during oxidation, and we have used visual analysis of this phenomenon as a tool to identify boundaries between regions exhibiting different oxidation behaviour. Using images of the oxidized CSAF surfaces after $t_{ox} = 4$ h, real-space locations of boundaries between visually distinct regions can be converted to composition space boundaries using the best-fit CDMs. Visual analysis, in combination with spectroscopic characterization techniques that revealed the phenomenological significance to visually identifiable regions, was used to determine continuous boundaries between regions of ternary composition space having different oxidation behaviour.

2.4. EDX, Raman, and XPS characterization of oxidized $Al_x Fe_y Ni_{1-x-y}$ CSAFs

Alloy oxidation kinetics are often studied by measuring weight gain per unit surface area of the alloy as a function of time using bulk, single-composition alloy samples [6,17,18,22,37]. Because spatially resolved gravimetric analysis of CSAFs is infeasible, a high-throughput, spatially resolved, EDX-based method was developed as an alternative for measuring oxygen uptake across the CSAFs. For an SEM accelerating voltage of 20 kV, the effective probing depths in Al, Fe, Ni, and Mo are all about an order of magnitude greater than the \sim 120 nm thickness of the CSAFs [36]. As a result. Mo accounts for >85% of the raw signal in the 20 kV EDX spectra obtained from the $Al_xFe_yNi_{1-x-y}$ CSAFs on Mo substrates. As will be shown later, the depth of oxygen penetration after t_{ox} = 4 h does not exceed the thickness of the CSAFs, even in the most heavily oxidized regions. Since the thickness of the layer containing Al, Fe, Ni, and oxygen is much smaller than the total sampled thickness, it is reasonable to assume that the oxygen EDX signal will scale linearly with the amount of oxygen present without significantly affecting the Mo signal and, therefore, that the total molar oxygen content at any point in the CSAF is proportional to the oxygen signal scaled by the Mo signal. Thus, the ratio of O-to-Mo EDX signals serves as a metric that is proportional to the total oxygen mass per unit surface area traditionally measured using gravimetric analysis of bulk alloy samples. Using this EDX-based method, the local oxygen content, $C_0(x, y)$, was measured quantitatively at $t_{ox} = 0, 1, 2, and 4 h$ across the two $Al_xFe_yNi_{1-x-y}$ CSAFs. The distribution of measurement points across each CSAF was chosen with guidance from the best-fit CDM to ensure a high-density sampling of most of ternary composition space. The CSAF compositions at the selected points were measured using the same EDX/ThinFilmID procedures as were used for the initial mapping of the CSAF composition gradients. After this initial measurement of the CSAF metal-component composition at each point using EDX at 11.24 kV, C_0 was determined at each point from additional EDX spectra obtained with the SEM accelerating voltage increased to 20 kV, as described above. After t_{ox} = 0, 1, 2, and 4 h, three independent measurements of C_0 were made at each location and averaged to reduce noise. In this way, oxygen uptake was determined with high resolution across $Al_xFe_yNi_{1-x-y}$ composition space.

A Raman spectrum was obtained at 61 locations across one of the oxidized CSAFs (t_{ox} = 4 h) to identify specific oxide phases present. A *Horiba-Jobin Yvon* LabRam HR Raman system, equipped with a 200 mW green laser (532 nm wavelength) which was filtered to ~50% intensity, was used for the measurements. The aperture size was 100 µm and an *Olympus* BX-30-LWD confocal microscope with a 50x long working distance objective was used for focusing, resulting in a beam diameter of ~30 µm at the surface. Initial calibration of the CCD detector was performed using Si. The Ramanshift spectrum in the range 100–1500 cm⁻¹ was obtained at each location on the CSAF by averaging ten consecutive 5 s acquisitions. A de-spike procedure was run on each spectrum using NGSLabSpec software. The resulting spectra indicated the presence of α -Fe₂O₃, NiO, and NiFe₂O₄ in various regions across the oxidized CSAF.

XPS depth profiling was used to determine the cross-sectional composition through the CSAF used for the Raman analysis at select sites of interest. XPS depth profiling is a destructive technique involving alternating cycles of XPS measurements and removal of surface material from the measurement site by Ar⁺ etching. This allows the composition of thin (\sim 1 nm) layers to be determined as a function of depth into a sample. The XPS studies were performed using a ThermoFisher ThetaProbe instrument with a hemispherical energy analyser and an X-ray spot size of 200 µm. Survey scans across a binding energy range of 100-1200 eV with a 0.25 eV step size, 0.2 s dwell time, and 200 eV pass energy were used to confirm that no unexpected chemical species were present on the CSAF. Subsequent scans used for quantification were obtained over 10-14 eV ranges around the non-overlapping Al 2s, Fe 2p_{1/2}, Ni 2p_{3/2}, and Mo 3p_{3/2} peaks. These scans were performed with a 0.05 eV step size, 0.2 s dwell time, and 100 eV pass energy. Between each set of measurements, the CSAF was uniformly excavated across an $\sim 16 \text{ mm}^2$ region containing the XPS analysis site(s) by rastering a focused Ar⁺ beam operated at 3 kV and 1 μA with a backfilled Ar pressure of ${\sim}4\times10^{-3}\,\text{Pa.}$ Thermo AdvantageTM processing software was used to subtract XPS backgrounds (using the Thermo "Smart" background), fit peaks (using a fixed 30% Lorentzian/Gaussian shape), and calculate peak areas. Wagner sensitivity factors were used to adjust peak areas to determine relative atomic composition. Oxidation of the metal species increased their peak binding energies by $\sim 2 \text{ eV}$. In cases where chemical shifts caused peak splitting due to the presence of both oxidized and metallic states of one of the components, the ratio of oxidized to metallic species was estimated by fitting the spectra using two peaks with the metallic peak location and FWHM held

constant for all spectra from that measurement site. Further assignment of the oxide peaks to specific oxidation states was not attempted.

3. Results

3.1. Spatial characterization of $Al_xFe_yNi_{1-x-y}$ composition gradients

A thorough quantification of the composition distribution across a CSAF is required for translation of real space analysis locations on the CSAF into composition space. EDX was used to map $Al_x Fe_y Ni_{1-x-y}$ composition across a 12 \times 12 mm² region in the centre of each of the two CSAFs. Fig. 2 shows atomic composition contours of Al, Fe, and Ni in real space on one of the CSAFs. The contours are fit to spatially resolved EDX measurements of composition taken on a 13×13 grid of points. The corresponding set of 169 measured $Al_xFe_yNi_{1-x-y}$ compositions is plotted in the ternary composition diagram of Fig. 2. Because CSAFs are comprised of continuous composition gradients, any point in composition space located between any three of the sampled points must be present at some location on the CSAF. All of $Al_xFe_yNi_{1-x-y}$ composition space with Al content, x < 0.95 was present within the 12×12 mm² region analysed. Compositions with x > 0.95 did not fall within this region of the CSAF, but were present closer to the edge of the 14×14 mm² substrate. Despite slightly different gradient geometries, full coverage of composition-space was also obtained with the second CSAF.

EDX is most quantitatively accurate when the spectral-processing routine is calibrated using a known standard that is as close as possible in composition to the unknown. Because we measured $Al_xFe_yNi_{1-x-y}$ compositions spanning the entire ternary composition space, selection of a single-composition standard was impossible. Therefore, EDX spectra were processed without any samplespecific calibration, and indirect comparisons have been used to assess the quantification accuracy. EDX-measured binary compositions were found to agree to within 2 at.% with bulk samples of $Al_{0.05}Ni_{0.95}$, $Al_{0.10}Ni_{0.90}$, $Fe_{0.15}Ni_{0.85}$, and $Fe_{0.30}Ni_{0.70}$ alloys. Based on three independent sets of EDX composition measurements taken at 301 locations on one of the CSAFs, the average measurement-to-measurement variability for each component was found to have a standard deviation of σ = 1 at.%. Rough estimates of bulk composition obtained from XPS depth profiles performed on unoxidized CSAFs (annealed for 2 h after deposition at 427 °C and cooled to room temperature in UHV) agree with EDX-measured composition to ±5 at.% for each component. These depth profiles also confirmed that the layering assumption used for quantification in INCA ThinFilmID is reasonable; i.e. that the Al_xFe_yNi_{1-x-y} composition is homogenous across the CSAF thickness and no significant interdiffusion between the CSAF and the Mo substrate occurs as a result of annealing.

3.2. Visual identification of $Al_x Fe_y Ni_{1-x-y}$ oxidation behaviour boundaries

Visually observable changes in the colouration of $Al_xFe_yNi_{1-x-y}$ CSAFs become evident during their oxidation. Fig. 3(a) and (b) shows images of one of the CSAFs taken at $t_{ox} = 0$ and $t_{ox} = 4$ h in dry air at 427 °C. The most significant colouration changes are observed on the upper region of the CSAF at low-Al compositions, while little change is observed across a large fraction of the Al-rich lower region of the CSAF. The majority of the visual transformation had occurred by $t_{ox} = 1$ h with only minor additional change observable after $t_{ox} = 2$ and 4 h. Fig. 3(c) shows an image of the second CSAF after $t_{ox} = 4$ h and reveals the high degree of reproducibility of the visual patterns. Bearing in mind the fact that the positions of the CSAF gradients on the two Mo substrates are not identical, the reproducibility of the various features on the oxidized CSAFs is remarkable.

The Al_xFe_yNi_{1-x-y} composition at any point on an oxidized CSAF can be estimated by transforming its real-space location into composition space using the best-fit CDM. Likewise, visually observable boundaries can be transformed into continuous composition-space boundaries. Three visually observable boundaries were identified on each of the two CSAFs after t_{ox} = 4 h delineating four composition regions that were common to both samples. Fig. 3(c) and (d) shows these real-space boundaries separate four increasingly discoloured regions of the CSAFs, labelled 1–4. EDX, Raman, and XPS analyses were used to correlate the boundaries between these regions with transitions between oxidation behaviour.



Fig. 2. Contour plots of the concentrations of Al, Fe, and Ni in one of the CSAFs as obtained from EDX measurements taken on a 13×13 grid of real-space locations over a 12×12 mm² area centred on the 14×14 mm² substrate. The ternary composition diagram shows the discrete Al_xFe_yNi_{1-x-y} compositions measured at the 169 points. Nearly complete coverage of the composition space is demonstrated. Compositions from 95 to 100 at.% Al are also present on the substrate, but fell just outside the plotted region.



Fig. 3. (a) Image of one of the $AI_xFe_yNi_{1-x-y}$ CSAFs after deposition, UHV annealing at 427 °C for 2 h, and brief (~15 min) exposure to atmosphere under ambient conditions. (b) Image of the same CSAF after oxidation in dry air for 4 h at 427 °C. (c) Cropped image (different lighting) of the second, identically oxidized $AI_xFe_yNi_{1-x-y}$ CSAF showing boundaries identified in real-space around "visually distinct" regions. The estimated location of the ternary triangle based on the best-fit CDM is also shown for reference. (d) Boundaries plotted in composition space via the best-fit CDM.

Visual analysis of CSAFs has the potential to allow extremely rapid, high-throughput, composition-space mapping of phenomena causing reproducible and distinguishable optical changes in CSAFs, but it is limited by the accuracy of the CDM used to translate from real space into composition space. The accuracy of one of the bestfit CDMs was analysed by comparing EDX-measured compositions at interpolated, real-space locations to the CDM predictions. At 220 such locations, the CDM-predicted atomic fractions of each CSAF component *i*, n_i^{CDM} , were compared to the EDX-measured fractions, n_i^{mes} , and the differences, $\varepsilon_i = n_i^{CDM} - n_i^{mes}$, were calculated. The average differences were $\bar{\epsilon}_{Al}$ = 0.5 at.%, $\bar{\epsilon}_{Fe}$ = -0.2 at.%, and $\bar{\epsilon}_{Ni}$ = -0.3 at.% with standard deviations of σ_{Al} = 1.8 at.%, σ_{Fe} = 1.7 at.%, and $\sigma_{\rm Ni}$ = 1.6 at.%. We believe that the fit of the CDM to the real-space composition distribution is the most substantial source of error in estimating the composition at any location on the surface. Error arising from determination of the real space coordinates of visual features from images is estimated to be ±0.1 mm (corresponding to <2 at.% for each component) and should be comparable to the CDM error. As illustrated in Fig. 3(b) and (c), the two Al_xFe_yNi_{1-x-y} CSAFs developed very similar visual appearances after t_{ox} = 4 h. Fig. 4(left) shows a comparison of the composition-space boundaries separating the four regions on the two CSAFs shown in Fig. 3(b) and (c). The reproducibility appears to be within the expected error of the visual analyses. Fig. 4(right) shows an average of the two sets of boundaries which will be used as the basis for subsequent discussion of the composition dependent transitions between different oxidation behaviour.

3.3. EDX-measurement of oxygen uptake during $Al_x Fe_y Ni_{1-x-y}$ oxidation

EDX was used for high-throughput analysis of the oxygen uptake that occurred across the CSAFs during each exposure to dry air at 427 °C. Determining an appropriate set of real-space measurement points required the ability to predict compositions at locations that had not been previously analysed. Therefore, the best-fit CDM for each CSAF was used to select 301 points that yielded a high-density coverage of composition space, and these were used for oxygen content measurements. EDX/ThinFilmID



Fig. 4. Left: comparison of composition-space boundaries defining similar, visually distinguishable regions on the two oxidized $Al_xFe_yNi_{1-x-y}$ CSAFs as determined by visual analysis. Right: average position of the three boundaries.

analysis at each point was used to determine its precise composition for subsequent plotting of all oxygen content data. SEM imaging of the Al-rich (x > 0.85) regions of the CSAFs revealed evidence of film dewetting upon annealing, so this region was not used for analysis of oxygen uptake.

A relative measure of oxygen content was obtained using the ratio of the O-to-Mo EDX signals at the selected locations on each CSAF after t_{ox} = 0, 1, 2, and 4 h total oxidation time in dry air at 427 °C. The oxygen content (C_0) and change in oxygen content (ΔC_0) after $t_{ox} = 0$, 1, and 4 h total oxidation time are shown in Fig. 5 for the CSAF imaged in Fig. 3(c). The data for 2 h are not shown because the oxygen uptake from 1 to 4 h was very slow. Since the specific value of the ratio of the O-to-Mo EDX signals is simply proportional to the absolute oxygen content, C_0 and ΔC_0 are plotted using arbitrary units on a scale from 0 to the maximum C_0 value measured on either CSAF. The three composition maps on the left present the total C_0 in the CSAF after oxidation for $t_{ox} = 0, 1, 1$ and 4 h. The two maps on the right represent ΔC_0 in the intervals from 0 to 1 h and from 1 to 4 h. Cursory inspection of Fig. 5 reveals oxygen uptake trends that appear to correlate with the visually identified regions 1-4 in composition space. The CSAF exposed to air for 15 min at 25 °C (t_{ox} = 0 h) exhibits only a small, measurable C_0 with a maximum at $x \cong 0.60$. However, from $t_{ox} = 0$ to 1 h, there is a significant ΔC_0 across all of composition space except region 1, and especially in the Fe-rich side of region 4. Further oxidation to t_{ox} = 4 h resulted in a negligible ΔC_0 across regions 1, 2, and 3. The total C_0 after $t_{ox} = 4$ h is clearly higher in regions 2 and 3 than in region 1; however, the maps of ΔC_0 clearly show that this oxygen uptake primarily occurred in the first hour of exposure and the CSAF appears to be effectively passivated for $t_{ox} > 1$ h.

EDX allows reproducible measurement of C_0 across composition space using a single CSAF. Three independent measurements of C_0 were made for $t_{ox} = 0, 1, 2, \text{ and } 4$ h at each of the 301 analysis points on the CSAF and used to calculate an average, \overline{C}_0 . For the C_0 ($t_{ox} = 4$ h) data shown in Fig. 5, the average measurement-to-measurement variability of C_0 (normalized by \overline{C}_0) was found to have a standard deviation of $\sigma = 7\%$. The values displayed at each point on the composition-space plots are \overline{C}_0 . Because the reported values of C_0 are normalized by the Mo EDX signal, they can be compared between the two CSAFs. Fig. 6 shows the comparison of the final C_0 ($t_{ox} = 4$ h) measured in the CSAFs shown in Fig. 3(b) and (c). The oxygen content maps from the two CSAFs are very similar, indicating good reproducibility and validating the methodology.

3.4. Raman and XPS characterization of $Al_x Fe_y Ni_{1-x-y}$ oxidation behaviour

Raman spectroscopy was used to identify oxide phases that formed in different regions of the CSAF imaged in Fig. 3(c) after t_{ox} = 4 h. At each location, we observed one of only five characteristic Raman spectra, indicating the presence of NiO, NiFe₂O₄ spinel,



Fig. 5. EDX-measured oxygen content (C_0 , left) and the change in oxygen content from the previous exposure (ΔC_0 , right) plotted in composition space for one of the Al_xFe_yNi_{1-x-y} CSAFs after t_{ox} = 0, 1, and 4 h. The regions identified by visual analysis are overlaid for reference. No significant uptake of additional oxygen is detectable at any composition above ~25 at.% Al after the first hour at 427 °C in dry air.



Fig. 6. Comparison of EDX-measured oxygen content, C_0 , across composition space for the two Al_xFe_yNi_{1-x-y} CSAFs after oxidation in dry air for 4 h at 427 °C. The results appear to be very reproducible despite slight differences between the gradient geometry, thickness, and sampling compositions of the two CSAFs.

 α -Fe₂O₃, a mixture of NiFe₂O₄ spinel and α -Fe₂O₃, or no Ramanactive oxides; representative spectra are shown in Fig. 7(left). Fig. 7(right) shows the distribution of oxide phases in ternary composition space for the 61 Al_xFe_yNi_{1-x-y} compositions at which Raman spectra were obtained. Phases were identified by qualitative comparison of the measured Raman spectra with those for known Al, Fe, and Ni oxide phases [38–48]. FeO does not form below ~570 °C, so it was not considered [37,49]. Ranges of reported peak locations for possible phases are summarized in Table 1 [38–48]. Raman spectra characteristic of Fe₃O₄, FeAl₂O₄, or NiAl₂O₄ were not observed on the CSAF. The known Raman spectra of NiO, NiFe₂O₄ spinel, and α -Fe₂O₃ were sufficient to allow assignment of all 61 spectra obtained from the oxidized Al_xFe_yNi_{1-x-y} CSAF. It is important to note that the results in Fig. 7 correspond only to the Raman-active oxide phases present in detectable quantities at a given location. This is not necessarily a complete listing of all the oxides phases that could have formed. For instance, while α-Al₂O₃ exhibits characteristic Raman scattering, amorphous Al_2O_3 and γ - Al_2O_3 do not [42,50]. Given the oxidation temperature of 427 °C, it is expected that any pure Al oxide formed would be amorphous Al_2O_3 and/or γ - Al_2O_3 [4,9,18,51]. Because Al oxidizes more readily than Fe and Ni, Al₂O₃ is likely to be present; however, as the transition to α -Al₂O₃ at temperatures <900 °C is negligibly slow, it is likely to remain in the amorphous Al_2O_3 or γ - Al_2O_3 forms and, therefore, be undetectable by Raman [4,14,50]. The results of the Raman analysis show that the four regions identified on the basis of visual inspection contain different oxide phases. Regions 1 and 2 do not contain detectable quantities of any Raman-active oxides, but have probably formed Al₂O₃. Region 3 contains α -Fe₂O₃ as the only Raman-detectable oxide phase. Region 4 contains NiO, NiFe₂O₄ spinel, and α -Fe₂O₃.

XPS depth profiling was performed on the CSAF imaged in Fig. 3(c) in order to determine both the composition and chemical state of the alloy as a function of depth into the CSAF. Fifteen locations were chosen near the boundaries identified by visual inspection. Comparison of cross-sectional composition and chemical state of the CSAF at points on opposite sides of a boundary reveals whether the boundary demarcates a transition in oxidation behaviour. It is important to note that XPS depth profiles obtained from CSAFs that had been annealed in vacuum but only exposed to air during transfer to the XPS instrument (i.e. for conditions corresponding to $t_{ox} = 0$ h) confirm that the initial distribution of components across the film thickness was homogeneous. After $t_{ox} = 4$ h, the distribution becomes extremely inhomogeneous at many



Fig. 7. Left: characteristic examples of the five types of Raman spectra observed at 61 locations across one of the $Al_xFe_yNi_{1-x-y}$ CSAFs after $t_{ox} = 4$ h in dry air at 427 °C. The spectra have been offset and magnified by the indicated factors for ease of viewing and are labelled with the oxide phases to which they are assigned. Characteristic peak locations are marked for NiO at 518 cm⁻¹; for NiFe₂O₄ at 202, 338, 491, 570, and 701 cm⁻¹; and for α -Fe₂O₃ at 221, 243, 289, 297, 407, 496, 610, 658, and 1313 cm⁻¹. Right: a ternary composition diagram showing the composition regions in which each type of spectrum was observed. The NiFe₂O₄ + α -Fe₂O₃ spectrum is indicated by the combination of NiFe₂O₄ and α -Fe₂O₃ markers. The boundaries identified by visual analysis are overlaid for reference.

 Table 1

 Ranges of major peak locations observed for Raman shifts (cm⁻¹) [38–48].

α -Fe ₂ O ₃	Fe ₃ O ₄	NiO ^a	NiFe ₂ O ₄	$FeAl_2O_4$	$NiAl_2O_4$
α-Fe ₂ O ₃ 220-227 236-247 282-293 295-299 396-412 492-498 596-613	298–306 533–550 662–696	510–518	NIFe ₂ O ₄ 200–207 325–340 483–491 555–574 695–704	~200 ~800	~320 ~370 ~560 ~600 ~690 ~720 ~770
651–659 1304–1322					~810 ~830

^a The single NiO peak was reported by authors studying nanocrystalline samples.

compositions. The image in Fig. 8(upper left) shows the depth profile locations on the CSAF. Fig. 8(a)–(g) shows the depth profiles at seven of these locations. The total Ar⁺ sputter time is explicitly measured during the depth profiles and shown across the top of each plot. Approximate depths are shown at the bottom of each plot assuming an etch rate of 2 nm/min, which was estimated based on CSAF thicknesses determined from QCM measurements of deposition fluxes. The XPS spectra were used to estimate the oxidized CSAF composition vs. depth at each point in terms of Al, Fe, and Ni in both their metallic and oxidized states and Mo. At no point was any Mo oxide detected. Given the relative sensitivities of the XPS peaks, the detection limits are estimated to be \sim 4. 1. 0.5. and 1 at.% for Al. Fe. Ni. and Mo. respectively. The depth profiles from various points on the CSAF indicate that there are four phenomenologically distinct types of alloy oxidation behaviour whose $Al_xFe_yNi_{1-x-y}$ composition dependence is delineated by the three boundaries that were identified visually. Region 1 XPS depth profiles, Fig. 8(a) and (b), appear to show a continuous layer of oxidized Al at the CSAF surfaces with no detectable oxidized Fe or oxidized Ni at any depth. Depth profiles from region 2, Fig. 8(c) and (d), reveal a thin surface layer containing oxidized Fe and/or Ni with a subsurface enrichment of oxidized Al, below which oxidized Fe and Ni are no longer detected. Region 3 depth profiles, Fig. 8(e) and (f), are similar to those in region 2, but with less pronounced subsurface enrichment of oxidized Al, below which some oxidized Fe is observed. Finally, region 4 depth profiles, Fig. 8(g), reveal extensive oxidation of all alloy components across the CSAF thickness.

4. Discussion

The sub-micron CSAF thickness that can be deposited using the RSM-CSAF deposition tool has limited our $Al_xFe_vNi_{1-x-v}$ oxidation

studies to a temperature of 427 °C; experimental issues begin to arise at higher temperatures due to film instability and the increased rate of oxidation. AlFeNi-based alloy operating conditions of practical interest typically fall in the range 600-1200 °C, where the passivation mechanisms in alumina-forming alloys can result in oxide layering structures with thicknesses >10 µm developing over hundreds or thousands of hours [6,12,17,18,22]. The investigation of early oxidation behaviour in CSAFs at 427 °C can, however, provide crucial insights into the behaviour of bulk materials at higher temperatures. Of particular interest is the N_{AI}^* required for establishment of a continuous Al₂O₃ scale during the initial stages of oxidation. Based on Pettit's study of AlNi, we expect that $N_{Al}^* > N_{Al}^{**}$ in $Al_x Fe_y Ni_{1-x-y}$ at 427 °C, i.e. the Al concentration required for initial establishment of an Al₂O₃ scale is higher than the Al concentration required to maintain its steady-state growth [34]. Thus, the compositions along the boundary between passivated and non-passivated regions of our Al_xFe_vNi_{1-x-v} CSAFs define N_{AI}^* (x, y). Identification of passivated regions in the Al_xFe_yNi_{1-x-y} CSAFs was aided by the oxygen content data collected with EDX; alloy compositions with a passivating Al₂O₃ scale did not exhibit measurable oxygen uptake after the continuous Al₂O₃ layer was established. Based on the oxygen uptake data presented in Fig. 5, it appears that passivation occurs within the first hour of oxidation in dry air at 427 °C (by t_{ox} = 1 h), after which large portions of the composition space experience no further measurable oxygen uptake through 4 h total exposure time (see ΔC_0 from $t_{ox} = 1$ to 4 h, Fig. 5(lower right)).

Oxidation behaviour was assessed continuously across $Al_xFe_yNi_{1-x-y}$ composition space by correlating the visually identified regions 1-4 with the data obtained from EDX, Raman, and XPS depth profiling. Region 1 corresponds to passivation by exclusive formation of a continuous, surface Al₂O₃ scale, as shown schematically in Fig. 9. The depth profiles obtained from this region (Fig. 8(a) and (b)) show that the surface is covered by a continuous layer of oxidized Al that is \sim 2–4 nm in thickness with some additional oxidized Al in the subsurface; no other oxidized species are detected. As noted earlier, given the oxidation conditions used in this work, the Al oxide is likely to be amorphous Al₂O₃ and/or γ -Al₂O₃ [4,9,18,51]. Oxygen uptake measurements (Fig. 5) show $\Delta C_0 \simeq 0$ across region 1 from t_{ox} = 0 to 1 h in dry air at 427 °C, suggesting that the Al₂O₃ formation primarily occurred during the brief exposure to air at room temperature that occurred on removal from the RSM-CSAF deposition chamber. Passivation of region 1 is indicated by the continued lack of detectable oxygen uptake during heating at 427 °C for up to 4 h (i.e. $\Delta C_0 \simeq 0$ from t_{ox} = 1 to 4 h). C_0 (t_{ox} = 4 h) is the lowest of the four regions because



Fig. 8. Upper left: the 15 locations (white circles) on an $A_x Fe_y Ni_{1-x-y}$ CSAF (on a Mo substrate) at which XPS depth profiles were obtained after t_{ox} = 4 h in dry air at 427 °C. (a)–(g) The depth profiles obtained at the correspondingly labelled locations show the relative atomic concentrations of AI, Fe, Ni, and Mo in metallic or oxidized states as measured by XPS after Ar⁺ etch times marked by the hashes above each plot. Similar oxidation profiles are observed within each of the visually identified regions 1–4. Increasing oxidation of Fe and/or Ni has occurred on moving from region 1 to region 4.

oxygen is only present in the thin Al_2O_3 scale at the surface and any trace Al_2O_3 precipitates beneath it. As expected, the Raman spectra (Fig. 7) do not show peaks in this region since neither amorphous Al_2O_3 nor γ - Al_2O_3 are Raman active and no other oxides are present.

Oxidation of the CSAF in region 2 appears to have resulted in the formation of a continuous, subsurface Al_2O_3 scale underneath a thin layer of Fe and/or Ni oxides (Fig. 9). The depth profiles



Fig. 9. Schematic representations of the types of oxidation behaviour proposed for regions 1–4 on the $Al_xFe_yNi_{1-x-y}$ CSAFs exposed to dry air for 4 h at 427 °C. The composition-space boundary of region 4 appears to define N_{Al}^* (*x*, *y*), the critical threshold for establishment of a passivating Al_2O_3 scale. The boundary between regions 1 and 2 demarcates a transition in the continuous Al_2O_3 scale from the surface.

(Fig. 8(c) and (d)) show formation of \sim 5–10 nm of Fe and/or Ni oxides under which there is extensive enrichment of oxidized Al. If the subsurface enrichment of oxidized Al corresponds to a continuous Al_2O_3 scale of comparable thickness (~3 nm) to the surface Al_2O_3 scale observed in region 1, it is quite likely that the depth profiles missed the point of continuous, 100% oxidized Al because of the coarse spacing (\sim 10 nm) of the sampling at this depth. The lack of Fe or Ni oxides below the subsurface layer of oxidized Al suggests that it is, in fact, a continuous Al₂O₃ scale. This is further supported by the oxygen uptake data (Fig. 5) which shows $\Delta C_0 \simeq 0$ from t_{ox} = 1 to 4 h, indicating passivation. The small, detectable ΔC_{0} from $t_{ox} = 0$ to 1 h and the slight visual discolouration that occurred during this exposure indicate that, unlike region 1, the passivation of region 2 was not completely developed during the room temperature exposure to air. $C_0 (t_{ox} = 4 \text{ h})$ is higher than that in region 1 due to the oxygen present in the Fe and/or Ni oxides at the surface. Raman spectra (Fig. 7) do not show peaks across most of region 2 despite the presence of Fe and/or Ni oxides, most likely because the layers are too thin to be detected.

The oxidation behaviour of region 3 is more difficult to interpret than those of regions 1 and 2. The $C_0(t_{ox} = 4 \text{ h})$ in region 3 is similar to region 2 (Fig. 5) and from t_{ox} = 1 to 4 h, $\Delta C_0 \simeq 0$, both suggesting that region 3 is passivated, but the depth profiles (Fig. 8(e) and (f)) seem to suggest that there is only partial subsurface enrichment of oxidized Al. Below this layer there appears to be some penetration of Fe oxide into the CSAF. One model that is consistent with the data is the growth of Fe oxide nodules during initial oxidation interrupting an otherwise laterally continuous Al2O3 scale (Fig. 9), a well-known phenomenon in binary AlFe alloys [6,9,37]. The growth of nodules with Fe₂O₃ shells and Fe₃O₄ cores at an AlFe alloy surface can retard establishment of a continuous Al₂O₃ layer, but Al₂O₃ can ultimately form beneath the nodules, preventing their further growth and passivating the alloy bulk against further oxidation. Such behaviour could lead to a continuous but "wrinkled" subsurface scale, consistent with the observed depth profiles; no plane parallel to the surface contains 100% oxidized Al, and the bottoms of nodules yield some Fe oxide signal below the depth of greatest oxidized Al enrichment, but not extending deep into the alloy. Raman analysis (Fig. 7) revealed the presence of α -Fe₂O₃ across region 3, consistent with this description of the alloy



Fig. 10. Summary of $Al_xFe_yNi_{1-x-y}$ oxidation behaviour observed in this study after 4 h at 427 °C in dry air and a comparison with similar results reported by other authors. Sakiyama describes behaviour transitions at compositions >40 at.% Fe that are very phenomenologically similar to those observed in this study, but finds different locations for the boundaries demarcating these transitions. The results reported by Pettit and Prescott show Al content must be increased with decreasing temperature to maintain oxidation resistance, possibly explaining the differences in boundary locations between studies at different temperatures.

oxidation behaviour and its morphology. Fe_3O_4 was not observed with Raman and may not have formed during the early oxidation, though it could be present in undetectable quantities.

The CSAF oxidation behaviour in region 4 is consistent with internal oxidation of the alloy (Fig. 9). The depth profiles (Fig. 8(g)) show extensive penetration of oxides deep into the CSAF. Raman (Fig. 7) reveals the presence of NiO, NiFe₂O₄, and/or α -Fe₂O₃ depending on the atomic ratio of Ni and Fe. The highest values of $C_O(t_{ox} = 4 \text{ h})$ are observed across much of region 4 (Fig. 5) and, with the exception of compositions from \sim 70–95 at.% Ni, measureable oxygen uptake continues up to 4 h (i.e. $\Delta C_O > 0$ from $t_{ox} = 1$ to 4 h). Based on the depth profiles and Raman spectra, the compositions in region 4 with \sim 70–95 at.% Ni appear to be "pseudo-passivated" by a layer of NiFe₂O₄ (most likely due to its slow growth rate at 427 °C), but do not exhibit Al₂O₃-based passivation.

By combining all the results from the CSAF studies, early oxidation of Al_xFe_yNi_{1-x-y} alloys in 427 °C dry air can be described in terms of four types of behaviour (Fig. 9) that subdivide composition space into regions. Regions 1, 2, and 3 are passivated by a surface Al₂O₃ scale, a subsurface Al₂O₃ scale, and a subsurface Al₂O₃ scale with interspersed Fe oxide nodules, respectively. The boundary of region 4 defines the trajectory of $N_{AI}^{*}(x, y)$ across the ternary composition space. This boundary follows a complex path from Al_{0.26}Ni_{0.74} to $Al_{0.17}Fe_{0.83}$, with a maximum N_{Al}^* at $Al_{0.29}Fe_{0.26}Ni_{0.45}$ and a minimum N_{Al}^* at Al_{0.15}Fe_{0.74}Ni_{0.11}. It is difficult to compare these results with work done by others, partly because of the relatively low temperature of our study, and partly because the full Al_xFe_vNi_{1-x-v} composition space has never before been investigated comprehensively. A few relevant comparisons have been found, however [9,18,34]. Fig. 10 summarizes our results and related data from the literature. The previously published boundaries were reported from studies using bulk alloy samples, dry oxygen, and oxidation temperatures at least 173 °C higher than the 427 °C used in our study. Based on a study of 19 single-composition $Al_xFe_yNi_{1-x-y}$ alloys, Sakiyama describes three regions of oxidation behaviour at 600 °C for Fe content, y > 0.40 that are qualitatively similar to our observations for regions 2-4, but reports significantly different boundary locations in composition space [18]. This discrepancy might be explained by the difference in oxidation temperature between studies. Prescott reports in a review of AlFe oxidation that the minimum Al atomic fraction needed for "complete protection" against Fe oxide nodule formation is 0.10 at 1000 °C, but 0.21 at 600 °C, and Pettit found that *N*^{*}_{Al} in AlNi is 0.10 at 1100 °C, but 0.17 at 900 °C [9,34]. These findings indicate that Al content must be increased as oxidation temperature is decreased in order to maintain a given level of oxidation resistance in both binary AlFe and AlNi alloys, which is consistent with the differences between the boundary locations determined from our $Al_xFe_yNi_{1-x-y}$ CSAF results and those from the higher-temperature studies.

While our high-throughput, CSAF-based techniques have allowed determination of a composition-space map of early oxidation behaviour and $N_{Al}^*(x, y)$ in $Al_x Fe_y Ni_{1-x-y}$ alloys, the degree to which these results are representative of bulk alloy oxidation is uncertain. In particular, we recognize the potential for phenomenological differences in the oxidation behaviour of an $Al_xFe_yNi_{1-x-y}$ thin film and a bulk alloy of the same composition if oxide formation leads to significant depletion of one or more components from the thin-film "bulk", i.e. the reservoir of unoxidized metal. By this argument, region 4 of the $Al_xFe_yNi_{1-x-y}$ CSAFs, where oxidation is the most extensive, would be the most likely to exhibit such differences from bulk alloys. However, it is worth noting that in none of the depth profiles (Fig. 8) is there evidence of complete depletion of metallic Al from the interior of the film. In addition, preliminary comparisons using XPS depth profiling have shown clear phenomenological similarity in the oxide layering structure formed under identical conditions on CSAFs and on polished bulk alloys for both Al_{0.10}Ni_{0.90} and Fe_{0.30}Ni_{0.70} (region 4 compositions). We plan additional investigations to compare oxidation behaviour in CSAFs and bulk alloys.

5. Conclusions

Using a combination of EDX, Raman spectroscopy, and XPS analyses of $Al_xFe_yNi_{1-x-y}$ CSAFs, early oxidation behaviour in dry air at 427 °C was characterized across composition space for aluminaforming $Al_xFe_yNi_{1-x-y}$ alloys. Every possible $Al_xFe_yNi_{1-x-y}$ composition was found to undergo either internal oxidation or one of three distinguishable external oxidation events involving passivation by an Al_2O_3 scale. The value of N^*_{Al} (x, y) was observed to decrease from 0.26 in binary AlNi to 0.17 in binary AlFe, taking a complex path through ternary composition space, and reaching a maximum at $Al_{0.29}Fe_{0.26}Ni_{0.45}$ and a minimum at $Al_{0.15}Fe_{0.74}Ni_{0.11}$. The boundaries separating the composition regions exhibiting the three different external oxidation mechanisms were similarly complex.

The high-throughput methodologies developed in the course of this work increase by orders of magnitude over traditional alloy oxidation studies the speed with which composition space can be sampled. This enables comprehensive studies of the dependence of $N_{A1}^{*}(x, y)$ on composition in ternary alloys. Similar methods could be applied to 2D-CSAFs with compositions describing single planes through quaternary or higher-order alloy composition spaces. While the sub-micron thickness of the CSAFs created with the RSM-CSAF deposition tool limits investigations to early oxidation behaviour, there is no reason why other methods could not be used to prepare much thicker CSAFs for high-throughput study of alloy oxidation at higher temperatures. More importantly, the continuous nature of the results can serve as a valuable tool for developing a fundamental understanding of key factors influencing the intricate dependence of oxidation kinetics on composition in ternary or higher-order alloys.

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Appendix A

The composition distribution model (CDM) continuously describes atomic fractions, N_i , for each of j total metal components across the surface of a CSAF, in an arbitrarily defined system of orthogonal (x, y) coordinates based on 4*j* parameters:

For each component, *i*, the parameters are:

 w_i , width of the component's linear molar gradient

 h_i , maximum relative molar height of the component at its "plateau"

 α_i , *x*-coordinate at *y* = 0 of the line describing the vanishing edge of the component's gradient

 θ_i , angle of counter-clockwise rotation (in degrees) of the line describing the vanishing edge of the component's gradient from the line v = 0.

These parameters are schematically depicted in Fig. A.1. The functional form of the CDM is:

$$Y_{0,i}(\mathbf{x}) = (\tan \theta_i)\mathbf{x} - \alpha_i(\tan \theta_i)$$

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



Fig. A.1. The CDM assumes that the molar gradient of each CSAF component that has been deposited across the substrate surface is described by an infinitely long, linear "wedge". Left: two parameters (w_i and h_i) are needed to describe the dimensions of each wedge. Right: an additional two parameters (α_i and θ_i) describe the position and orientation of each wedge in an arbitrarily defined system of orthogonal (x, y) coordinates.

$$Y_{y,i}(x,y) = y - (\tan \theta_i)x$$

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

$$N_i(x,y) = \frac{A_i}{\sum_j A_j}$$

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