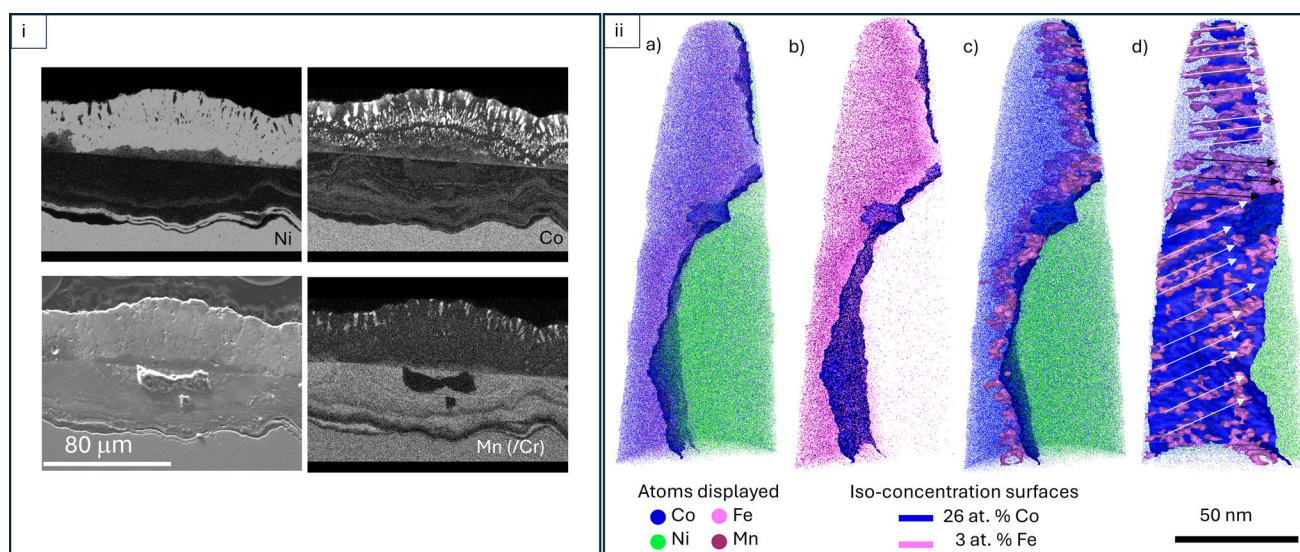


Systematic Study on the Role of Mn, Si, and Fe on the Corrosion Resistance of Ni-Based Superalloys Exposed to Air, Gaseous Sulfur Oxides and Salts



CYNTHIA RODENKIRCHEN, VICTORIA MINNS, ADRIANA ENCINAS-OROPESA, JOHN NICHOLLS, MARK HARDY, and STELLA PEDRAZZINI

This work investigates the effect of alloying elements Mn, Si, and Fe on the corrosion resistance of polycrystalline Ni-based superalloys, at 700 °C in air and 300 vpm SO₂ under 5 $\mu\text{g cm}^2 \text{ h}$ salt coating. Oxide scale morphology and composition was investigated using SEM–EDX and APT, revealing Mn–Fe-enriched Co₃O₄ particles in the upper outward growing scale as well as Si-Fe-enriched clusters in NiO. Along the NiO–Co₃O₄ phase boundary, a tight network of Fe-decorated dislocations relieving stress between the lattices was identified through APT. In the inward growing scale, Si enrichment was observed in the form of oxides and sulfides, while no Mn was detected.



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I. INTRODUCTION

TWO developmental Rolls-Royce alloys, namely Alloys 1 and 2,^{1,2} were previously reported by Hardy *et al.*³ to show improved oxidation resistance compared to the commercial turbine disc Ni-based superalloy RR1000.⁴ A key compositional consideration in the design of Alloys 1 and 2 was the addition of Si and Mn for improved resistance to environmental degradation. After oxidation heat treatment in air at 800 °C for 1000 hours, both alloys showed a reduced oxide scale

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growth rate compared to RR1000, with Alloy 2 exhibiting the lowest growth rate.³

Many studies have reported on the effect of Mn and Si on oxidation of Ni-based superalloys. For the case of Mn-containing alloys, the formation of a protective spinel MnCr_2O_4 is reported in literature.^{5–10} In some cases, it was found to reduce the oxidation rate,⁵ while in others it was found to increase the oxidation rate⁹ by promoting an increased chromia scale thickness.¹¹ One study deemed Mn detrimental to oxidation resistance due to the formation of transient oxides and increased spallation^{12,13} although another study attributed improved scale adherence under steam corrosion to the formation of Mn–Cr spinel.⁹ Wo *et al.*¹⁰ found that the combination of chromia and Mn spinel resulted in improved passivation, allowing for formation of a continuous alumina scale. Si additions lead to the formation of SiO_2 , in sufficient quantities as a protective scale,^{5,14} although more commonly as dispersed particles.¹⁴ Si has been reported to both reduce chromia growth rate^{11,13} as well as enhance chromia growth rate.¹⁴ SiO_2 has been related to increased scale spallation,^{7,13} although it is generally considered to improve oxidation kinetics.^{5,7,8,12–14}

Anzini *et al.*⁸ studied the effect of both Mn and Si on oxidation and corrosion resistance at 750 °C. For oxidised samples, they reported the formation of MnCr_2O_4 spinel in the Mn-containing alloy and of SiO_2 in the Si-containing alloy, in addition to chromia and alumina found in all alloys. The Si-containing alloy exhibited a more continuous alumina scale rather than internal alumina intrusions found in the Si-free reference alloys. After exposure of the same alloys to SO_2 , the Mn-containing alloy had formed both MnO and internal MnS, as chromia is permeable to SO_2 . Although damage depth increased due to the internal MnS, a more protective continuous surface scale was formed than in the base alloy, due to MnO formation. The Si-containing alloy did not exhibit penetrating sulfides because it formed a passivating, continuous alumina and chromia dual-layer scale. Finally, under hot corrosion conditions, *i.e.*, gaseous SO_2 and salt coating, all alloys exhibited a surface scale comprised of NiO, FeCr_2O_4 , Na_2SO_4 , low amounts of chromia/alumina and TiO_2 . The authors proposed partial dissolution of the chromia scale through acidic or basic dissolution. Internally, the base and Si-containing alloy exhibited NbS_2 sulfides whereas the Mn-containing alloy exhibited MnS. The Si-containing alloy also exhibited SiO_2 particles which were not dissolved through hot corrosion mechanisms. Overall, the addition of Si improved hot corrosion protection more than Mn and led to a significant reduction in damage depth.⁸

Although some studies reported a positive effect on mechanical strength through addition of Si, *e.g.*, improved thermal–mechanical fatigue behaviour due to greater resistance to recrystallisation and cracking¹⁵ and improved stress rupture life through promoting formation of strengthening M_{12}C carbides,¹⁶ many studies reported on the detrimental effect of Si on mechanical strength by segregation of Si to grain

boundaries and carbides, thereby reducing creep strength,^{17,18} or by promoting formation of Laves phases upon excessive additions which reduces tensile properties and stress rupture life.^{19,20} This limits the extent to which Si can be added to Ni-superalloys. Similar results were found for the previously mentioned Alloys 1 and 2 in the study by Hardy *et al.*³ Both alloys contain Si, although Alloy 1 contains a relatively high amount of 0.9 at. pct while Alloy 2 only contains 0.3 at. pct. With regards to yield and tensile strength as well as creep resistance, Alloy 2 was found to be superior to both Alloy 1 and RR1000. The relatively high content of Si of 0.9 at. pct in Alloy 1 in conjunction with the alloying elements Mo, W, Cr, and Nb led to the precipitation of undesirable Laves phases after long-term exposure to elevated temperature.³

While the previous study focused on the oxidation resistance of Alloys 1 and 2, the present work investigates the hot corrosion resistance of Alloys 1, 2, and a third alloy, Alloy 2 + Mn, which contains the same low level of Si as Alloy 2, but with an addition of Mn similar to the composition of Alloy 1. Additionally, all three alloys contain a low amount of Fe, which was added to develop an alloy that can easily be fabricated from recycled material without negatively affecting alloy stability.³

This study builds on previous work by extending the investigation from oxidation to hot corrosion resistance in three developmental Ni-based superalloys. By systematically varying Mn, Si, and Fe content, and analysing corrosion mechanisms under aggressive SO_2 / SO_3 and salt exposure, this work provides new insights into how these minor alloying elements influence scale composition, stress accommodation, and corrosion protection. The use of advanced characterisation techniques, particularly APT, reveals nanoscale phase distributions and elemental segregation not previously reported, offering a deeper understanding of corrosion behaviour in next-generation turbine disc alloys.

II. EXPERIMENTAL METHODS

Six cylindrical samples of 1 cm diameter were prepared from three alloys with systematic compositional variations of Mn and Si, fabricated by Allegheny Technologies Incorporated (ATI) Specialty Materials (Robinson) in Pittsburgh, PA, USA and ATI Forged Products in Cudahy, WI, USA through the powder metallurgy route described in Hardy *et al.*³ for their Alloys 1 and 2. The three investigated alloys are Alloys 1, 2, and 2 + Mn. Alloy 1 contains 0.6 at. pct Mn and a relatively high amount of 0.9 at. pct Si. Alloy 2 contains no Mn and a lower Si content of 0.3 at. pct Si, while Alloy 2 + Mn has the same composition as Alloy 2 but with added 0.54 at. pct Mn, similar to the content in Alloy 1.^{1,2,21} The nominal compositions of the three alloys are presented in Table I.

The samples were ground to a surface finish of 0.25 μm and corrosion heat treated at 700 °C in air and 300 vpm SO_2 , with a salt coating of 5 $\mu\text{g cm}^2\text{ h}$

consisting of 98 pct Na_2SO_4 + 2 pct NaCl , applied before treatment and after every 50 h. Samples Alloy 2-100h and Alloy 2 + Mn-100h were corrosion heat treated for a total of 100 hours whereas all other samples were corrosion heat treated for a total duration of 200 hours.

Samples were mounted and polished for microscopical investigation of the corrosion products formed on the cylindrical surface. Secondary electron SEM micrographs of all samples were taken on a Zeiss Auriga SEM operated at 5 kV. The whole cross-sectioned oxidised surface was imaged to observe oxide scale morphology and spallation. For each sample a suitable region was identified where silver paint could be applied to achieve an improved electrical connection and minimal drift for SEM-EDX scans without covering regions of interest. An Oxford Instruments EDX detector was used for SEM-EDX investigation: (i) bulk composition measurements were taken from an area of approximately $500 \times 600 \mu\text{m}$ over 40 minutes at 15 kV, (ii) EDX maps of the oxide scale were taken at 15 to 20 kV for 30 to 60 minutes, (iii) 60 seconds point ID spectra were taken from specific regions of the oxide scale at 15 to 20 kV.

The compositions of the samples as measured by SEM-EDX are presented in Table I. They match well with their nominal compositions, albeit the measured Si content is larger than its respective nominal value. Most importantly, the samples can be separated into three alloy compositions: (i) Alloy 1, which contains an increased Si content as well as minor alterations in the elements Co, Mo, W, and Al compared to the other alloys, (ii) Alloy 2, which contains a low Si content, and (iii) Alloy 2 + Mn, which has the same composition as Alloy 2 albeit with addition of Mn.

Atom probe tomography (APT) specimen were prepared from the outward growing oxide scale of the Alloy 2 + Mn-100h sample and of the lower inward growing oxide scale of the Alloy 1-200h sample on a TFS Helios 5 CX DualBeam FIB-SEM and TFS Scios 2 DualBeam FIB-SEM. Atom probe tomography was run on a LEAP 5000 XR in laser mode at 50 K, with a detection rate of 0.3 pct, a pulse energy of 30 pJ, and an automatically controlled pulse rate to ensure a constant mass spectrum range.

III. RESULTS

All samples exhibited oxide scales with similar morphologies: a continuous inward and outward growing scale of similar thickness. However, spallation is also observed in all samples with some regions exhibiting a semi-detached scale, some exhibiting a fully detached scale that is still present within the surrounding resin, and other regions where the scale has been fully lost. In the case of sample Alloy 2-100h, the scale spalled notably more than in any other sample and was lost for almost the entire circumference of the sample. Such a heavy extent of spallation was not observed for sample Alloy 2-200h, which had been corroded for double the

time of Alloy 2-100h. Therefore, the lack of Mn in this alloy is unlikely to be correlated to an increased spallation.

Of each sample, SEM-EDX maps of the scale was taken to observe the distribution of elements within the scale. The SEM-EDX maps of the samples Alloy 2-100h, Alloy 2 + Mn-200h-2, and Alloy 1-200h are presented representatively in Figures 1, 2, and 3. The EDX maps of the other samples, *i.e.*, Alloy 2-200h, Alloy 2 + Mn-100h, and Alloy 2 + Mn-200h are shown in “Appendix” Figures 9, 10, and 11. The EDX maps of samples Alloy 2-100h, Alloy 2 + Mn-100h, and Alloy 2 + Mn-200h-2 (Figures 1, 10, and 2) were taken from regions exhibiting the initially grown oxide scale. The initial scale exhibits a smooth interface between outward growing and inward growing scale, indicating where the smooth uncorroded sample surface had been before corrosion treatment. The EDX maps of samples Alloy 1-200h, Alloy 2-200h, and Alloy 2 + Mn-200h (Figures 3, 9, and 11) are taken from regrown oxide scale regions where the oxide had spalled and then regrown. This is indicated by the uneven interface between inward and outward growing scale, resembling the morphology of the interface between scale and alloy before oxide scale spallation, and representing the sample surface just after spallation.

For all samples, the EDX maps show an outward growing Ni-rich scale, likely NiO with Co-rich inclusions, likely CoO or Co_3O_4 , towards the scale surface. In Mn-containing alloys, an enrichment of Mn towards the scale surface is observed which is found to overlap with the Co oxide inclusions as can be seen in Figures 2 and 3. Ta or W, which have overlapping characteristic X-ray peaks, seem to be enriched within NiO, although further studies were not able to confirm this, as will be presented below. The increased signal in the Ta and W maps likely stems from the strong signal of Ni itself. Underneath the NiO phase, there is a thin layer of an Fe-rich oxide (approx. 1 to $3 \mu\text{m}$). For EDX maps taken from initially grown oxide scale regions, the Fe-enriched line is found within the outward growing oxide scale, below the NiO phase and above an outward growing Al-rich phase, likely Al_2O_3 (alumina). This outward growing Al-rich phase is predominantly found in the initial oxide scale, and only minimally or not observable in regrown oxide scales. In these cases, the Fe-rich layer borders the interface to the inward growing scale.

The inward growing scale in all samples shows to be enriched in Cr, Al, Si, Ti, Nb, O, and S. Cr-enrichment is present throughout the whole inward growing scale, with just a thin Cr-depleted layer at the interface to the bulk metal. Al is present in various locations throughout the inward growing scale, and is always found near the interface to the bulk metal. Also Si, Nb, and S appear to be predominantly enriched in the lower parts of the inward growing scale towards the interface to the bulk metal. However, the EDX signal of Nb seems to be overlapping with S, which makes it difficult to identify which layers of the scale this element occupies. Also, it is

to note that the apparent enrichment of Mn in the inward growing scale seems to be an overlap signal from Cr.

In order to confirm elemental distribution and phase compositions within the scale of each alloy, EDX point spectra were collected from different regions of the scale on sample Alloy 2-100h, Alloy 2 + Mn-100h, and Alloy 1-200h. For each distinctive region, several points were measured and their compositions averaged. The resulting compositions are presented alongside the previously measured sample bulk compositions in Figures 4 and 12.

Figure 4(a) indicates the regions at which EDX point spectra were taken from the different regions of the initial oxide scale on the Alloy 2 + Mn-100h sample. The respective compositions are presented in Figures 4(b) and (c). Throughout, the inward growing scale is strongly depleted in Ni, Co, Fe and Mn. The composition along the interface to the bulk metal is found to vary, but generally exhibits high amounts of S, O, increased levels of Si, Ti, and in one region of Al. Cr is depleted at the interface to the bulk and the other alloying elements Ta, Mo, W, Nb are just slightly enriched. On the contrary, Cr is enriched in the bulk inward growing scale, Ti is present at around its bulk composition, while all other elements are at least slightly depleted. The O content is too large to imply the formation of chromia, although the O composition may be inflated due to residue O in the SEM-EDX chamber. The lowest layer of the outward growing scale is found rich in Al and Fe, with low levels of Ni, Ti and S. It is likely that the EDX spectra shows an overlap of NiO, alumina (Al_2O_3), and a low amount of Fe oxide. Above the Al-rich layer, EDX confirms a layer predominantly consisting of NiO, and further towards the outer surface of the scale, a mixture of Ni and Co oxide is found. For both of these layers, relatively low levels of Fe and Si (0.45 ± 0.13 and 0.25 ± 0.6 at. pct, respectively) are detected, and the surface layer also exhibits 0.57 ± 0.22 at. pct Mn.

Figure 4(d) indicates the regions at which EDX point spectra were taken from the different regions of the regrown scale on the Alloy 1-200h sample. The respective compositions are presented in Figures 4(e) and (f). For this sample, spectra from very close to the interface of the bulk were taken, where O had ingressed, but no S, and Ni is yet only slightly depleted. Si and Mo are present as well as low amounts of Fe, but all other elements are strongly depleted. Slightly above, and still considered at the interface to the bulk alloy, S has strongly ingressed and an enrichment of the elements Al, and Si, as well as of Ti, Ta and W are detected. Ni, Co, Fe, and Mn are depleted from this point on throughout the whole inward growing scale. Further within the bulk inward growing scale, Cr levels increase to levels around and slightly above bulk composition, while all other elements slightly reduce. Ti and Si are still slightly above their bulk composition, and Al, Ta, W, Nb maintain their bulk composition. The outward growing layer consists of NiO with 0.8 ± 0.4 at. pct Fe and at the surface, Co oxide with 0.9 ± 0.9 at. pct Si and 1.1 ± 0.1 at. pct Mn.

Comparing the alloys, it is found that the outward growing scale of all alloys consists of NiO with Co oxide inclusions towards the scale surface. As Co oxide is only present in small inclusions, the interaction volume may sometimes have included NiO grains which explains variations in measured compositions. For the Mn-containing alloys, Mn was found within the Co oxide particles but not in the NiO phase. In the Si-rich alloy, the measured Mn content is especially high, although this is likely an artifact of the EDX measurement, as the spectra taken of the Co oxide phase in Alloy 2 + Mn exhibit considerable amounts of Ni, which suggests that both the Co oxide and NiO phase were within the interaction volume of the EDX beam. In this case, it is expected that the Mn content is higher in pure Co oxide as no Mn is detected in NiO. Si and Fe are also found in the outward growing scale of all alloys. Fe is predominantly found in NiO, although it may be present in the Co oxide on the Alloy 2 + Mn sample. Si is found in the Ni oxide in Alloy 2 whereas it is found in both phases in Alloy 2 + Mn and found only in Co oxide in Alloy 1.

Throughout the inward growing scale, high levels of 45 to 70 at. pct O are found, and in some areas considerable amounts of up to 23 at. pct S are detected. Ni, Co, Fe, and Mn are drastically depleted throughout the whole inward growing scale, while other alloying elements are generally found to be present at similar compositions to their bulk composition or slightly depleted, with some areas in all alloys exhibiting slightly increased Cr levels, and slightly increased Ti, Si, and Al in Alloy 1. At the interface to the bulk alloy, increased levels of S, Al, Si, and Ti are found for all alloys.

Specifically regarding the elements Mn and Si, in both Mn-containing alloys, Mn is found only in the Co oxide particles of the outward growing scale and is depleted throughout the inward growing scale. This confirms that the Mn EDX maps where overlapped with characteristic X-rays emitted from Cr in the inward growing scale. For all alloys, the highest levels of Si are found at the interface of the scale to the uncorroded bulk metal, whereas in the bulk inward growing scale, Si is found in similar composition to its bulk composition. For Alloy 2, a second Si-rich layer is found at the interface between the inward and outward growing scale of the spalled and regrown scale. Also, Si is found in NiO in Alloy 2, and Alloy 2 + Mn, but found within the Co oxide particles in Alloy 1.

For more in-depth analysis of the phase compositions in the oxide scale, APT specimens were taken from the outward growing scale of the Alloy 2 + Mn-100h sample and from the inward growing scale of the Alloy 1-200h sample and their reconstructions are presented in Figures 5, 6, 7, and 8.

The APT reconstruction presented in Figure 5(a) shows the (Ni, Co)O phase with around 40 at. pct Ni and 15 at. pct Co. Two Fe-Si-rich clusters are found in the reconstruction, as highlighted by an iso-concentration surface of 1 at. pct (Fe + Si). A proxigram through these surfaces is presented in Figure 5(b), revealing a low presence of Mn within the clusters. Peak decomposition delivers more accurate compositions of the different regions, shown in Figure 5(c). It shows that the clusters

Table I. Nominal Compositions of all Six Samples as well as Experimentally Verified Compositions as Determined Through 40 minute EDX Scans over Areas of Approximately $500 \times 600 \mu\text{m}^2$

	Sample	Ni	Co	Cr	Mo	W	Fe	Mn	Al	Ti	Ta	Nb	Si
Nominal	Alloy 1	bal.	15.0	14.0	1.3	1.0	1.0	0.6	7.0	3.5	1.6	0.9	0.9
EDX	Alloy 1-200h	52.6	14.7	14.0	1.45	1.29	1.02	0.57	6.90	3.57	1.72	0.95	1.3
Nominal	Alloy 2	bal.	15.6	14.0	1.4	1.1	1.0	0	6.8	3.5	1.6	0.9	0.3
EDX	Alloy 2-100h	52.7	15.5	13.9	1.65	1.45	1.02	0.08	6.75	3.47	1.68	1.0	0.75
EDX	Alloy 2-200h	52.6	15.5	14.0	1.62	1.44	1.00	0.11	6.78	3.48	1.69	0.97	0.79
Nominal	Alloy 2 + Mn	bal.	15.6	14.0	1.4	1.1	1.0	0.6	6.8	3.5	1.6	0.9	0.3
EDX	Alloy 2 + Mn-100h	52.4	15.5	14.1	1.58	1.38	0.93	0.57	6.72	3.48	1.74	0.93	0.70
EDX	Alloy 2 + Mn-200h	52.1	15.5	14.0	1.66	1.41	0.95	0.65	6.82	3.48	1.64	0.99	0.82
EDX	Alloy 2 + Mn-200h-2	52.3	15.3	14.0	1.65	1.46	0.93	0.66	6.70	3.57	1.71	0.97	0.76

The main compositional difference between the alloys^{1,2,21} is a systematic variation of the Mn and Si content.

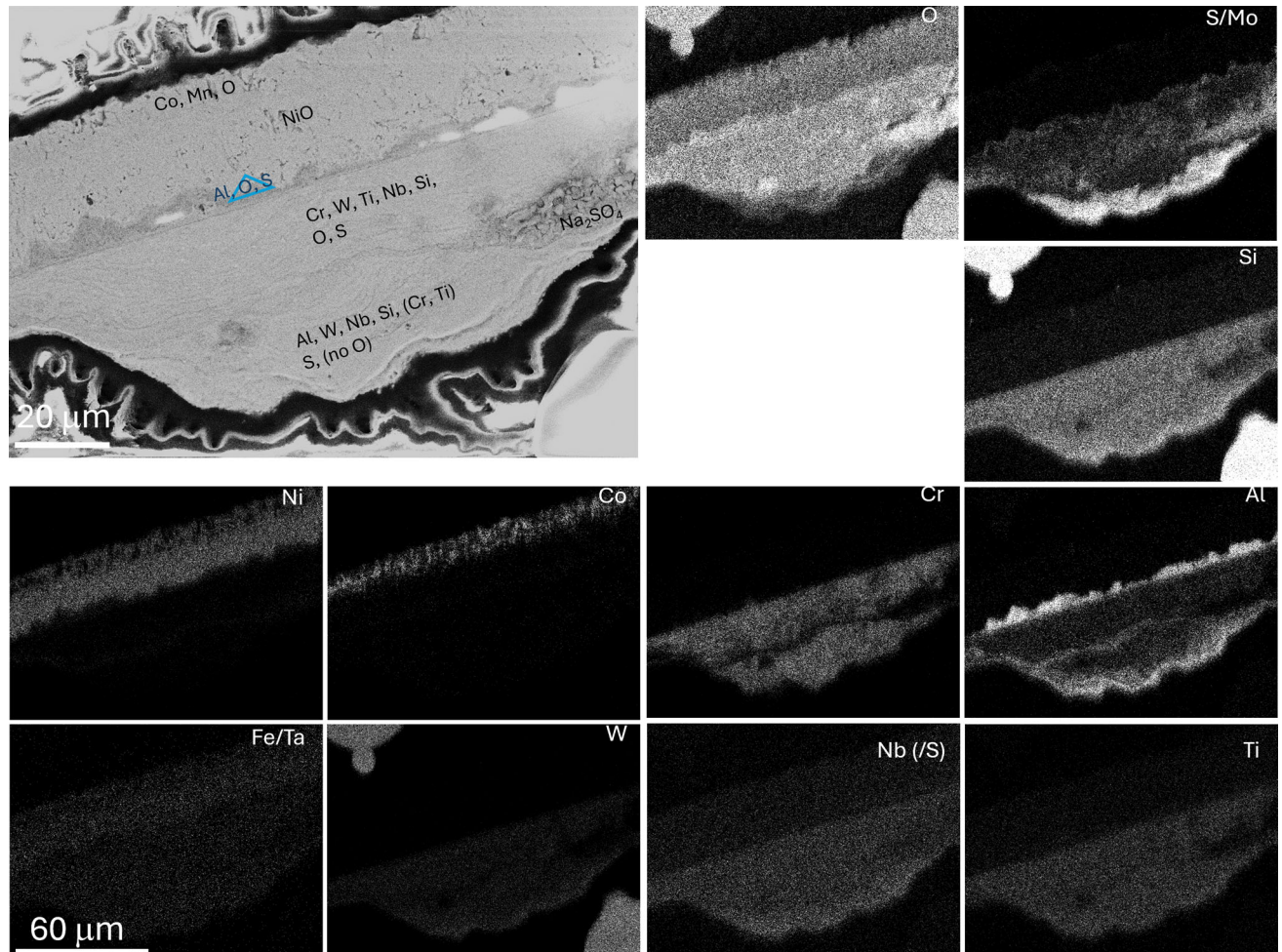


Fig. 1—EDX maps of the corroded sample Alloy 2-100h.

reach a composition of around 3.2 at. pct Fe, 1.4 at. pct Si and 0.2 at. pct Mn, with a slight increase in O content from 45.4 at. pct O in the NiO phase to 47 at. pct O in the clusters and a reduction of Ni from 38.8 to 32.4 at. pct and of Co from 15.4 to 14 at. pct. While the 1D composition profile does not show any interfacial segregation, peak decomposition on the interface region shows a slight increase in Ni content to 39.8 at. pct, and a reduction of O to 44.9 at. pct and

of Co to 13 at. pct. The increase in Ni at the interface implies that Ni was pushed out of the cluster and the reduction in O implies that O was drawn into the cluster, likely to form SiO_2 ionic compounds. Interestingly, Co is slightly reduced in the cluster and even more strongly reduced at the interface region.

Figure 6 shows the reconstruction of another APT specimen taken from the outward growing scale of Alloy 2 + Mn-100h. In this specimen, both the NiO

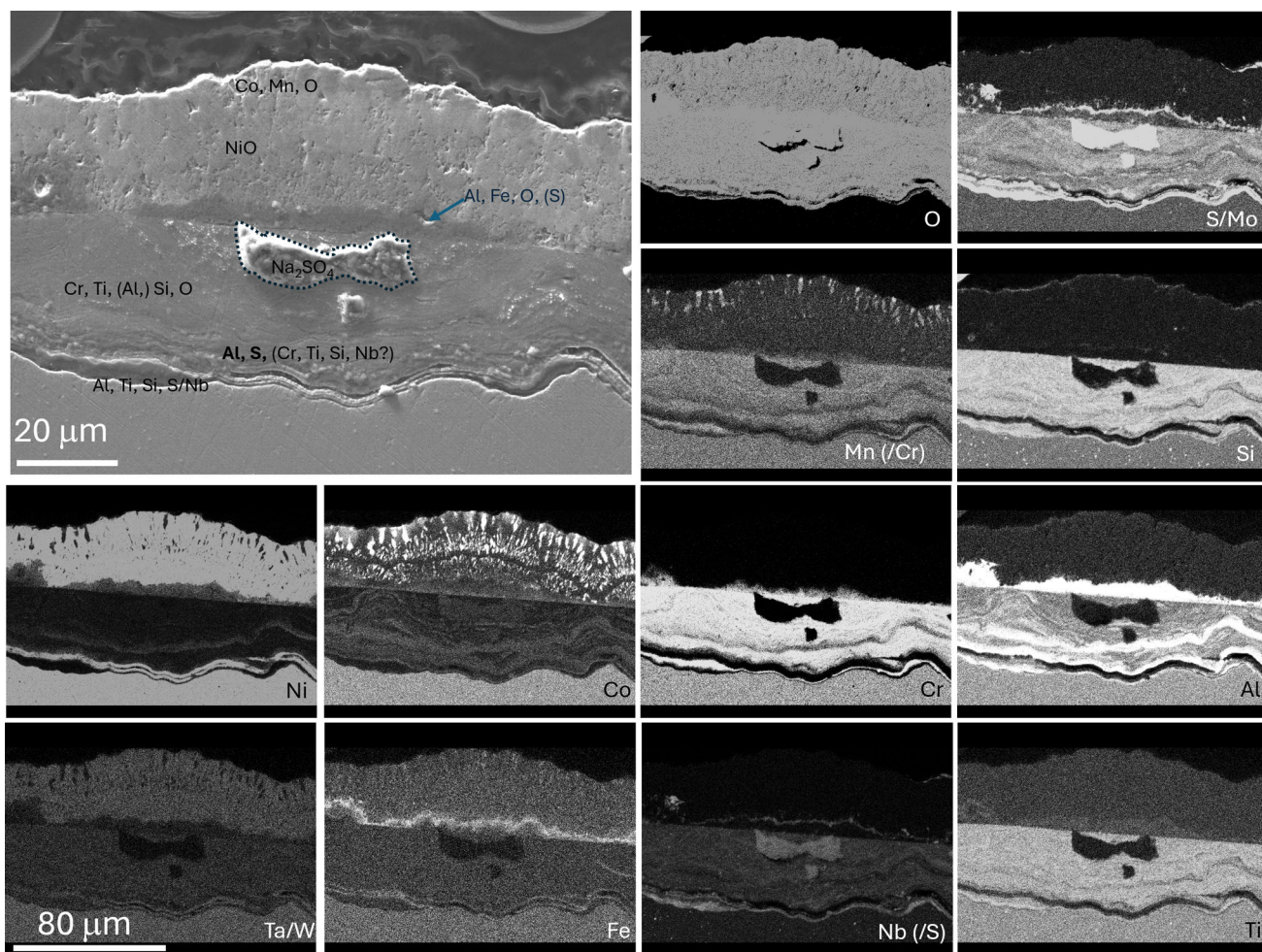


Fig. 2—EDX maps of sample Alloy 2 + Mn-200h-2, corroded for 200 h.

as well as the Co oxide phase are detected as presented in Figure 6(a), showing atoms of Co, Ni, Fe, and Mn, and an iso-concentration surface of 26 at. pct Co highlighting the phase boundary. Only the Fe and Mn atoms are shown alongside the Co-iso-surface in Figure 6(b), revealing that both elements are present only within the Co oxide phase. Additionally, near the interface to the NiO phase, only Fe is present. A 3 at. pct Fe iso-concentration surface highlights the Fe-rich layer within the Co oxide along the phase boundary in Figure 6(c). When rotating the reconstruction, as presented in Figure 6(d), it becomes apparent that Fe is enriched in linear features that are parallel to each other in three separate sections along the phase boundary. It is unlikely that the features are caused by spinodal decomposition, as the features are merely slightly enriched in Fe, from 1.3 to 4.4 at. pct and spinodal decomposition usually occurs at the same time throughout the whole volume where the composition is metastable, and will hence result in a lattice-like morphology, rather than in parallel features confined to the phase boundary, as the ones observed in our

results.^{22,23} Instead, these features are believed to be Fe-decorated dislocations, due to their parallel nature and the fact that they follow the phase boundary, likely releasing stress between the lattices.

Peak decomposition was used to extract phase compositions of the NiO phase, the Co oxide phase and of a Fe-rich dislocation. For this, isolated volumes of the phases were taken. For the Co oxide, a volume away from the Fe-enrichment was chosen as indicated in Figure 7(a). For the Fe-rich volume, one dislocation was chosen by isolating the volume using the Fe iso-concentration surface, also indicated in Figure 7(a). The decomposed compositions are presented in Figure 7(b), confirming that the Ni oxide is indeed (Ni, Co)O with approximately 10.8 at. pct Co in solid solution within the NiO phase. The Co oxide composition is ambiguous and could indicate both CoO or Co₃O₄ with approximately 3.7 at. pct Ni, 0.8 at. pct Mn, and 1.2 at. pct Fe in solid solution. The Fe-rich dislocation is found to have a composition very similar to the Co oxide, albeit with a slightly increased Ni and Mn content (5.3 and 0.9 at. pct, respectively) and a considerable increase in Fe content to 4.4 at. pct. It is

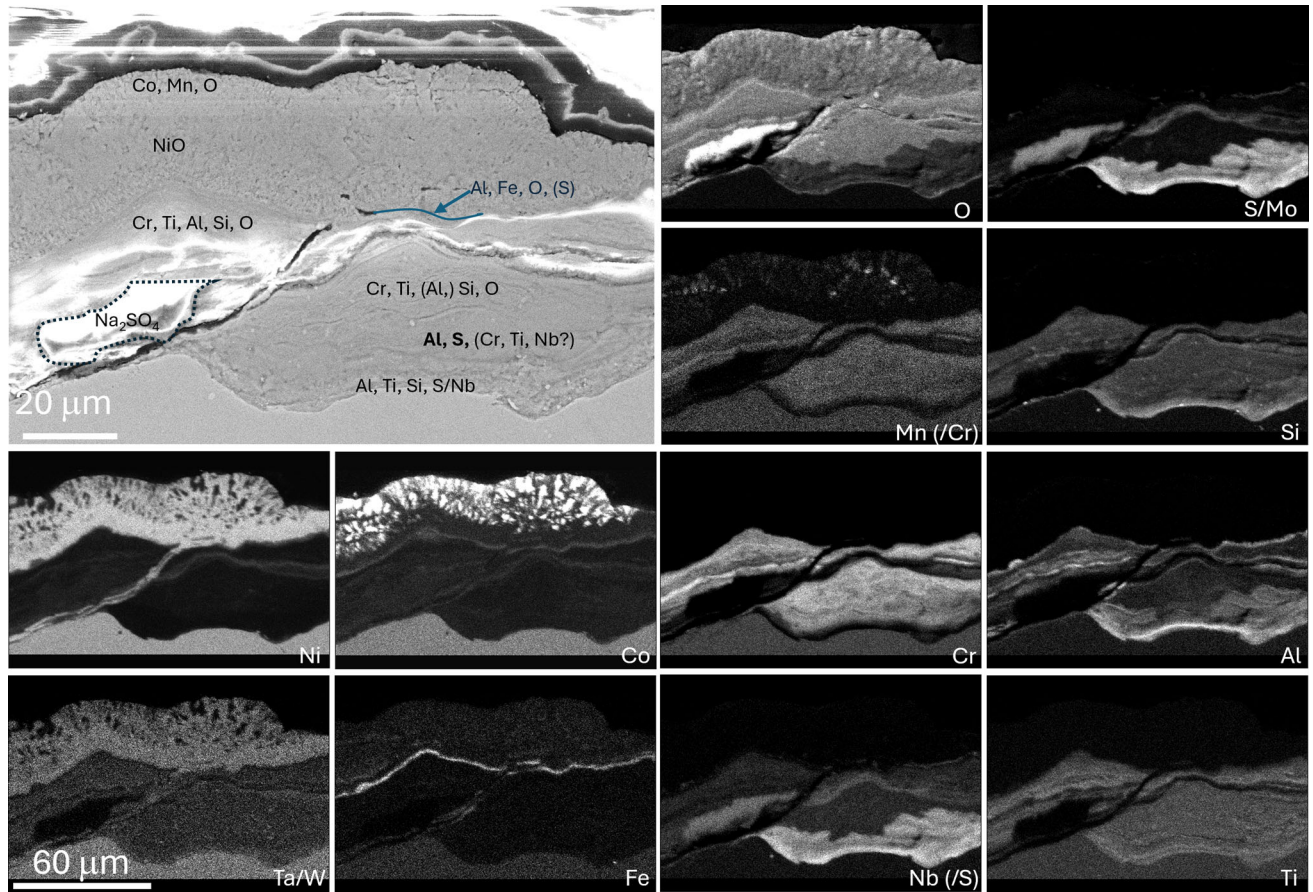


Fig. 3—EDX maps of sample Alloy 1-200h, corroded for 200 h.

unlikely to present the formation of a new phase. Instead, it is well-known that defects facilitate elemental segregation, and therefore it is suspected that the dislocations enable increased dissolution of Fe in the Co oxide phase, and potentially act as diffusion channels through the scale. Also, the presence of the dislocations leads to the assumption that the Co oxide is Co_3O_4 , as this phase has a different lattice structure than NiO and would explain the need for dislocations to relieve stress between the lattices.

A 1D composition profile across the phase boundary, its origin depicted by arrow c in Figure 7(a), is presented in Figure 7(c). The interface between Co_3O_4 and NiO is approximately 7 nm thick and does not show any segregation. The Mn composition peaks approximately 6 nm from the start of the interfacial region, and is rapidly depleted before the transition from Co_3O_4 to NiO begins, while the Fe composition peaks around 3 nm from the start of the interfacial region and gradually depletes over the full width of the interface. Figure 7(d) shows a 1D composition profile across the Fe-decorated dislocations, taken from the region indicated by arrow d in Figure 7(a). The fluctuation of Fe composition between approximately 1 and 4 at. pct can be seen, while Mn shows only slight compositional fluctuations and the elements O, Co, and Ni stay constant throughout.

Figure 8 shows an APT reconstruction from the lower inward growing scale of the Alloy 1-200h sample. A large number of ion species were detected in this specimen, and the reconstruction reveals strong compositional variations on a nm scale. The most dominant ion species, namely Al, TiO, Cr, and CrO are depicted in the reconstruction. Individual phases could not be identified due to strong mixing of the ion species over small volumes. However, the mixed oxide can be observed to contain predominantly oxides or sulfides of Ti, Al, and Cr. The Ti rich regions also contain low levels of Ta and Nb (below 5 at. pct). Mn and Si are only present in trace quantities and were not found to precipitate separate phases in this mixed region.

IV. DISCUSSION

This work studied the effect of hot corrosion on Alloys 1, 2, and 2 + Mn, exhibiting variations in Mn and Si content. Previous work by Hardy *et al.* on these alloys studied the effect of oxidation in air at 800 °C and found that the scale consisted predominantly of outer rutile (TiO_2), followed by chromia and internal alumina intrusions. For the Mn containing alloy, a MnCr_2O_4 spinel was identified from XRD. In the present case, XRD was not possible as samples were received mounted. However, from SEM-EDX and APT analysis,

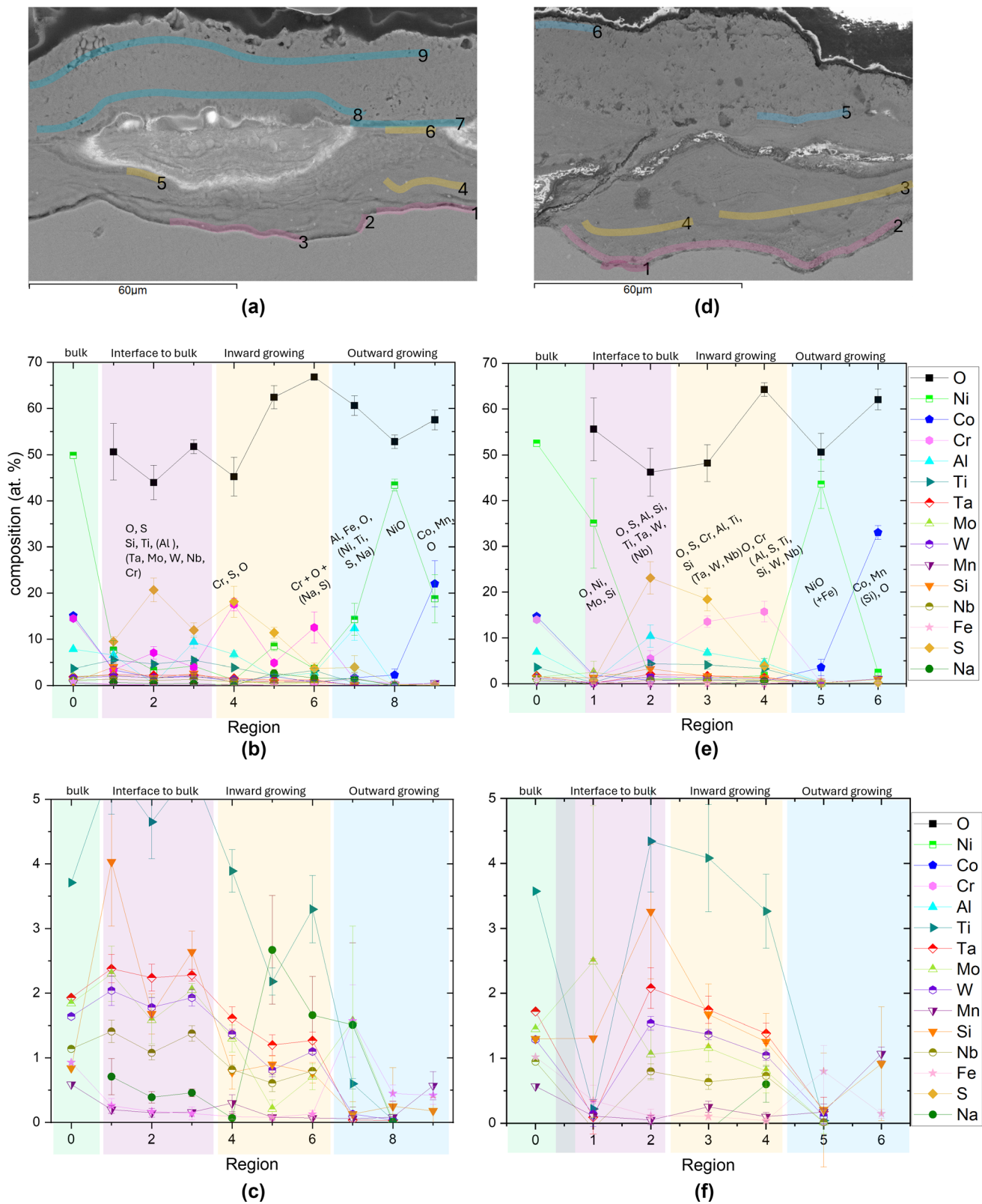


Fig. 4—(a) SEM micrograph of Alloy 2 + Mn-100h, indicating locations of point spectra presented in (b, c); (d) SEM micrograph of Alloy 1-200h, indicating locations of point spectra presented in (e, f).

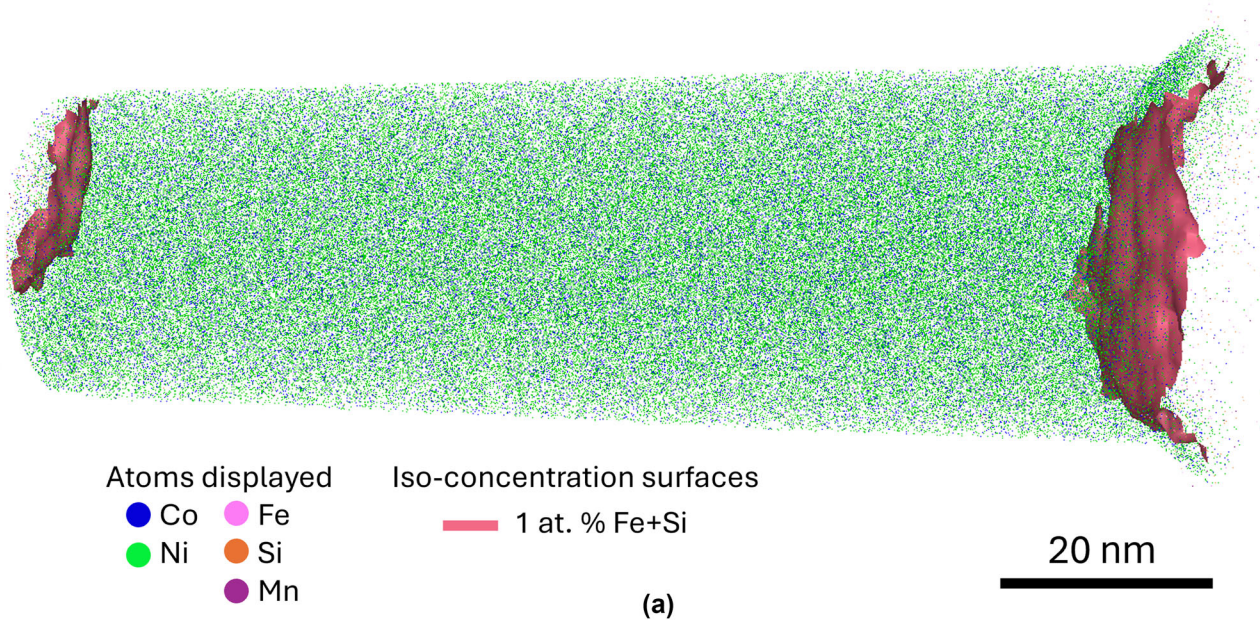
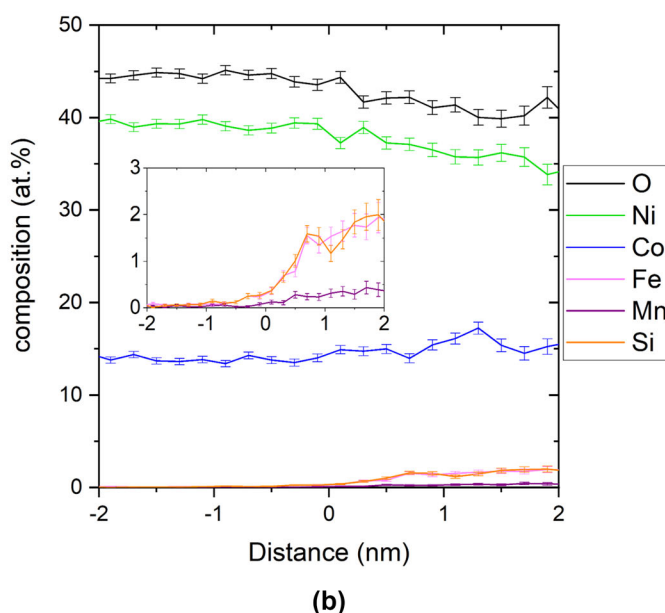
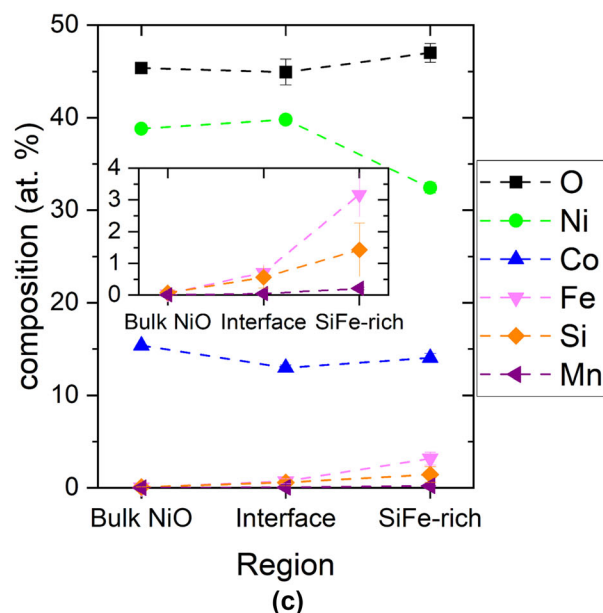


Fig. 5—(a) Reconstructed APT tip taken from the outward growing oxide scale of Alloy 2 + Mn-100h, showing NiO with two Fe-Si-rich clusters highlighted by an iso-concentration surface of 0.8 at. pct Fe, (b) proxigram through the iso-concentration surfaces, and (c) decomposed compositions taken from the bulk, the interface region, and the clusters.

it was found that the oxide scale after hot corrosion treatment at 700 °C differed significantly from a scale grown under oxidation in air at 800 °C. Specifically, Mn-Cr spinel could not be identified in the scale. Also, internal intrusions, specifically, alumina, were not found. Instead, a uniform and continuous inward and outward growing scale was observed for all alloys.

SEM-EDX and APT showed the outward growing scale of all samples consisted of predominantly NiO with Mn-containing Co oxide inclusions towards the surface of the scale. From the APT composition this oxide could be either CoO or Co₃O₄, although it is

suspected to be Co₃O₄, as the Ellingham diagram for the given temperature of 700 °C, indicates that Co₃O₄ forms at a higher oxygen partial pressure than NiO, which explains why the Co oxide particles are found at the surface of the scale. The Gibbs free energy of formation of CoO on the other hand is slightly below that of NiO at this temperature and would therefore be expected to form underneath the NiO scale.

Mn was not detected in NiO by EDX, and APT generally confirmed this. Ta/W EDX maps were influenced by an overlap to Ni, and APT confirmed that these elements were not present in the outer scale, contrary to

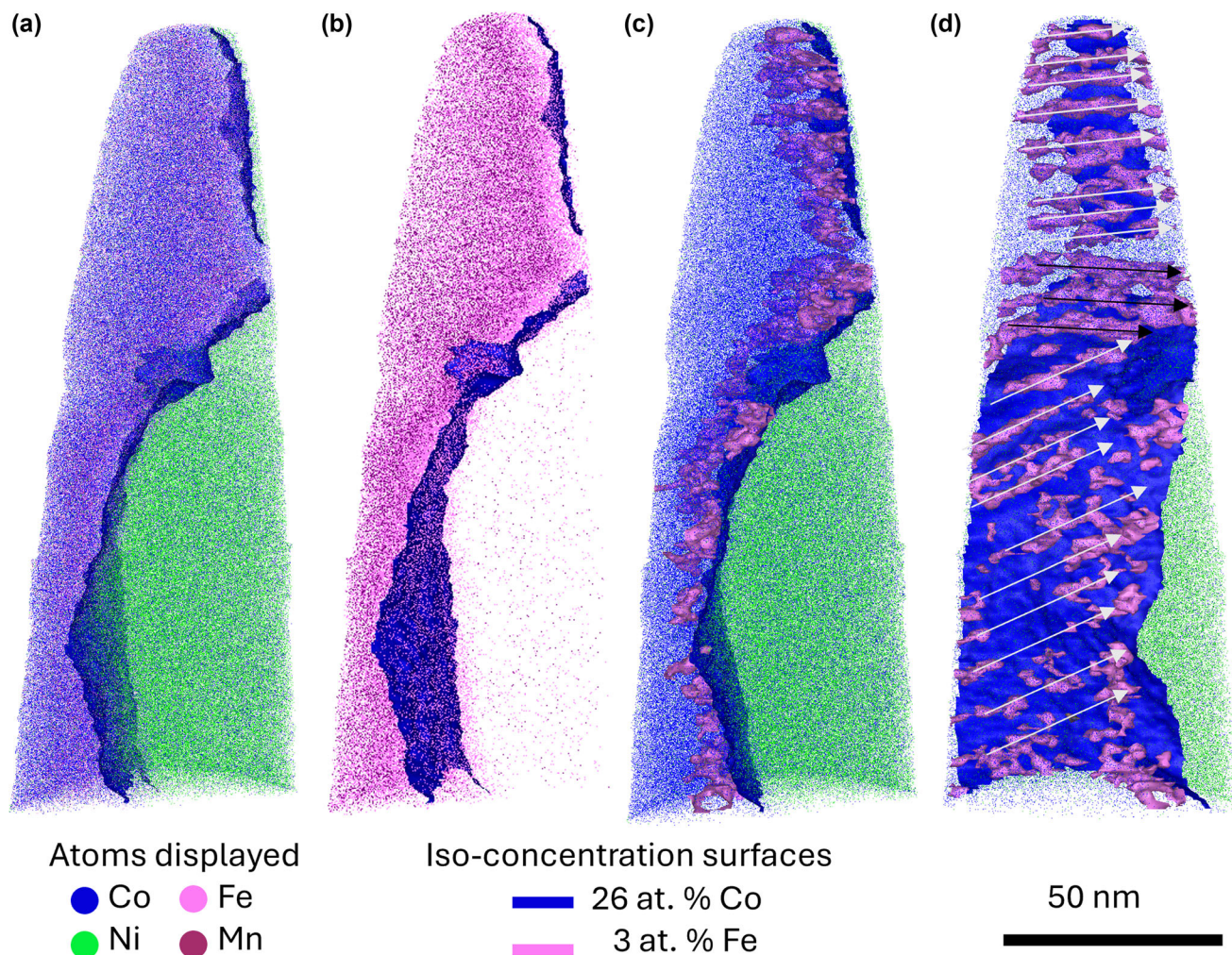


Fig. 6—Reconstruction of APT tip taken from the outward growing scale of Alloy 2 + Mn-100h, containing both a Co_3O_4 as well as a NiO phase. (a) Both phases shown by Co, Ni, Fe, Mn atoms and a Co-rich iso-concentration surface, (b) Fe and Mn are only found within Co_3O_4 , (c) 3 at. pct Fe iso-concentration surface highlights Fe-enrichment along phase boundary, and (d) rotated view on the tip reveals parallel 1-dimensional Fe-rich features, believed to be Fe-decorated dislocations along the phase boundary.

the EDX maps. A thin Fe-enriched layer was detected in all EDX maps below NiO and above any Al-rich oxide present. The composition of this layer was not detected, therefore it can only be speculated that this layer may be an Fe oxide. Ellingham diagrams indicate that this could be FeO or Fe_3O_4 , as these are more stable and can form at lower oxygen partial pressures than Fe_2O_3 , NiO, CoO, and Co_3O_4 at the corrosion treatment temperature of 700 °C. At this temperature, the Gibbs free energy of formation of FeO and Fe_3O_4 overlap.²⁴

The Gibbs free energy of the inward growing oxides Cr_2O_3 and Al_2O_3 is even lower than that of FeO. Therefore, if the Fe-rich layer is indeed a Fe oxide phase, it is likely to be FeO or Fe_3O_4 . However, this would need to be confirmed by further characterisation. SEM-EDX reveals that the inward growing scale contains O and S, as well as roughly bulk levels of Cr, Al, Ti, Si, and Nb, while Ni, Co, Fe, and Mn are strongly depleted throughout. At the interface to the bulk uncorroded metal, Cr is also strongly depleted while S, Al, Si, and Ti are enriched. Overall, Mn was

found only in the outward growing Co_3O_4 particles, and Si was found predominantly in the low inward attack and at the interface to the bulk metal, although EDX also detected Si in low amounts in the outward growing scale.

APT results from the outward growing scale confirm Mn throughout the Co_3O_4 phase and also confirm the lack of Mn in the bulk NiO phase, with the only exception being 0.2 at. pct Mn in Fe–Si-rich clusters within NiO, a composition below the detection limit of the EDX. Si and Fe are also detected in the outward growing scale by EDX point-scans, and APT revealed that Fe is found both in the Mn-rich Co_3O_4 inclusions, as well as in Fe–Si-rich clusters in NiO.

The Fe–Si-rich clusters contain 3.2 at. pct Fe which substituted for Ni, as has been seen in previous works.²⁵ Si also substitutes for Ni/Co, and additionally draws in further O, as Si is usually found as SiO_2 . O increases by 1.6 at. pct, matching the 1.4 at. pct Si content of the clusters. The Mn content of 0.2 at. pct is negligible. The composition retrieved from the proxigram does not

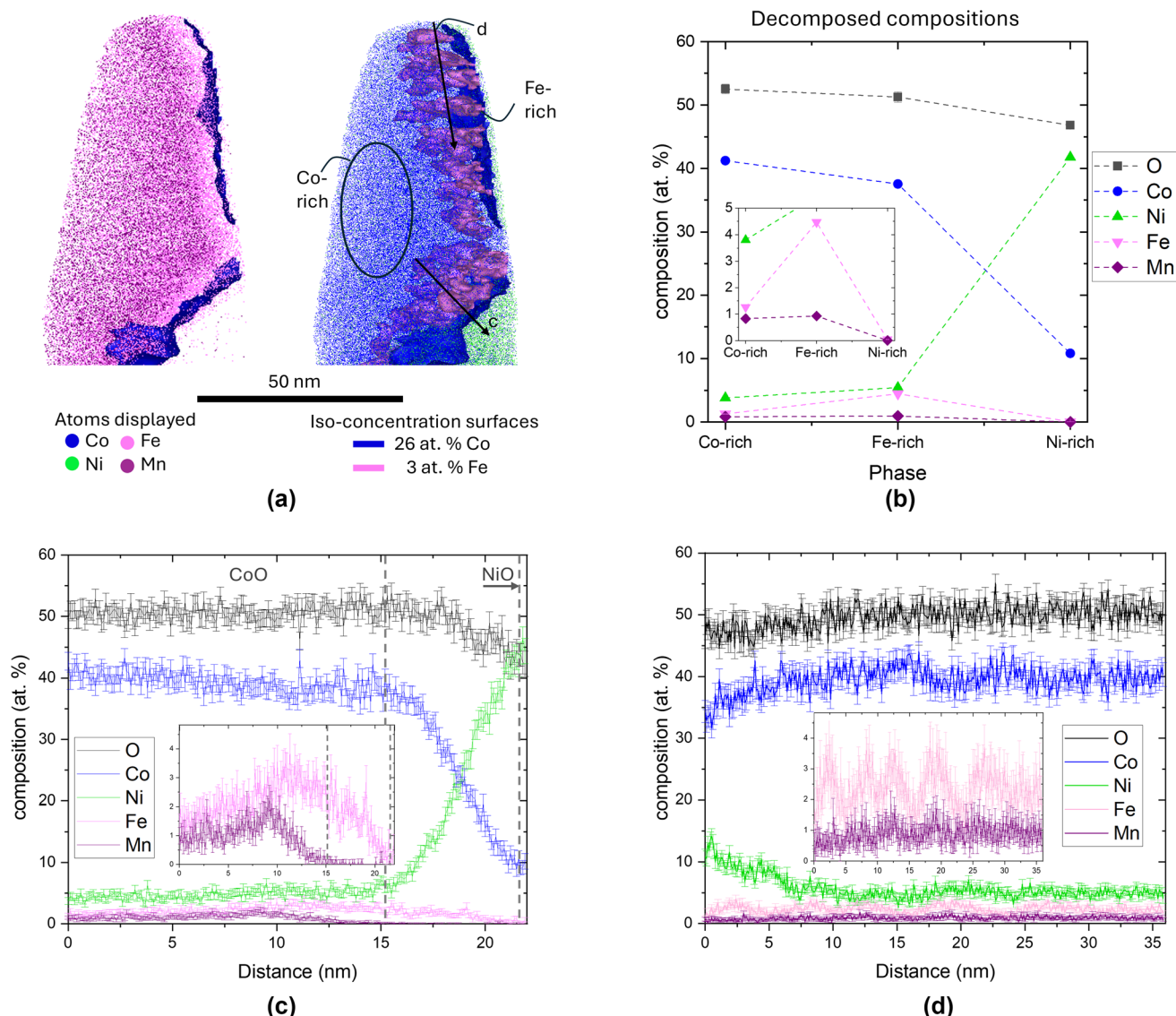


Fig. 7—Compositional analysis of the different phases found. (a) APT reconstruction with indicators for compositional analysis, (b) decomposed compositions of the Co₃O₄ phase, NiO phase, and Fe-decorated dislocation, (c) 1D composition profile through phase boundary (see arrow c in a), and (d) 1D composition profile through dislocations (see arrow d in a).

seem to accurately describe the changes in composition when comparing with the results from the peak decomposition. The proxigram shows a decrease in O content within the clusters, while the peak decomposition reveals an increase in O composition. This demonstrates the importance of peak decomposition in APT analysis when the mass spectrum contains multiple, overlapping ion species. Also, segregation at the interface to the clusters is not observed in the proxigram but can be detected through peak decomposition of the mass spectrum taken from the interfacial region through the use of a shell region of interest. This reveals an excess of Ni at the interface, which implies that Ni is pushed out of the cluster. O content is slightly reduced at the interface which implies inward diffusion of O. However, the error on the O composition for the interface is stronger than for other determined compositions.

Therefore the observed reduction of O may not be accurate. Co is reduced in the clusters, but it is reduced even more strongly at the interface.

There is approximately 1.3 at. pct Fe and 0.8 at. pct Mn in solid solution throughout the Co₃O₄ phase. For pure elements, solubility of Fe in Co at room temperature is relatively low (2 pct) but high for Ni.²⁶ However, while pure Fe, Mn, and Co have different crystal structures likely causing the low solubility of Fe in Co, they can all form spinels of the form M²⁺M₂³⁺O₄, as the oxidation states + 2 and + 3 are available for all three transition metals. Therefore, the Fe and Mn can occupy both the M²⁺ as well as the M³⁺ lattice sites.

Some of the Fe in the Co₃O₄ phase is found to segregate in 1D periodic and linear features along the phase boundary to NiO. These features are unlikely to

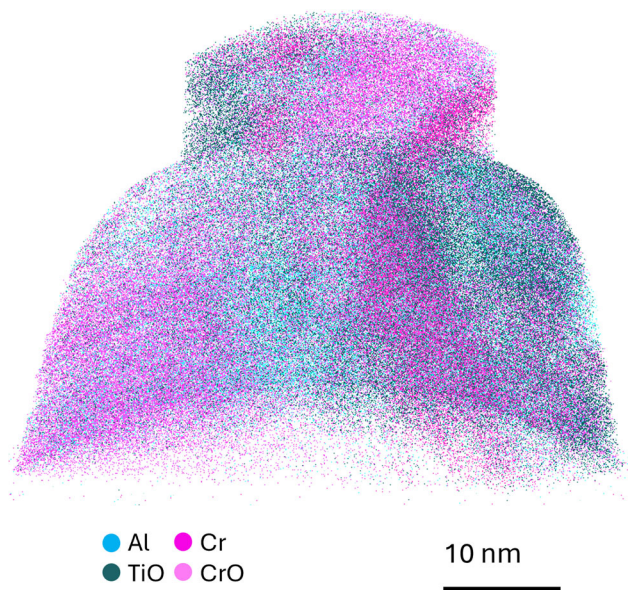


Fig. 8—APT reconstruction of tip taken from lower inward growing scale of Alloy 1-200h, showing the distribution of the dominant ions Al, TiO, Cr, and CrO.

be caused by spinodal decomposition because of their parallel nature. Spinodal decomposition would occur simultaneously throughout the whole volume and result in a network of more random shape. Also, these Fe-rich features are only found at the phase boundary (PB), although Fe is present throughout Co_3O_4 , even though not as strongly as near the PB. Instead of spinodal decomposition, it is likely that the observed features are dislocations along the phase boundary releasing interfacial stress between the rocksalt structured NiO and the spinel structured Co_3O_4 lattice. The Fe composition at the dislocations only reaches a value of around 4.4 at. pct, which is insufficient for the formation of a separate phase such as an Fe oxide. Instead, it seems that the larger Fe atoms²⁷ are attracted to preferentially fill the space at the dislocations. The presence of Fe at the dislocations is not believed to be a sign that the dislocations act as a diffusion pathway outwards as the Co_3O_4 phase is fully enclosed by NiO and there is no evidence of an Fe-rich oxide at the surface of the scale. As the Co_3O_4 phase grows alongside NiO, and Fe-decorated dislocations alleviate stress between the lattices, elemental diffusion and phase growth by displacement of the phase boundary becomes energetically unfavourable. The tight dislocation network freezes the phase boundary in place, which likely causes the Co_3O_4 phase to grow outwardly into columnar phases. These columnar phases within the NiO scale may strengthen the scale as crystal growth perpendicular to loading direction means that the scale is less likely to spall.

APT on the inward growing scale was less successful than the outward growing scale because of stronger inhomogeneity, the presence of voids, and strongly insulating phases. However, one APT experiment resulted in sufficient data to observe the strong compositional variations on a nanoscale. Around 1 ± 0.5 at.pct

Si and around 10 ± 5 at. pct S were detected in the bulk, although peak decomposition would be needed for more precise compositional results.

V. SUMMARY AND CONCLUSIONS

Overall, the study highlights how minor alloying elements Si and Mn influence corrosion scale composition and structure, offering insights into stress accommodation, phase formation, and the interplay between thermodynamics and microstructural evolution.

Three alloys with varying Si and Mn content were exposed to corrosive salts and sulfur oxides to investigate corrosion mechanisms using SEM and APT. All alloys developed a layered surface scale with both outward and inward growth. The outward scale consisted mainly of NiO, with Co_3O_4 near the surface, a thin Fe-rich layer, and an underlying Al-rich layer. The inward scale was a mixed Al–Cr–Ti oxide.

Mn was incorporated into the Co_3O_4 phase and found in trace amounts within Si–Fe-enriched NiO clusters, but no Mn–Cr spinel or internal alumina/sulfide intrusions were observed—differing from previous reports on oxidation-only cases. Fe was distributed across the scale, notably enriched at dislocations within Co_3O_4 , suggesting stress accommodation due to lattice mismatch. Si enrichment was detected at the inward scale/bulk interface, with nanoscale oxide and sulfide phases identified by APT.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

APPENDIX: OXIDE SCALE SEM-EDX

SEM–EDX maps of the oxide scale of the samples Alloy 2-200h, Alloy 2 + Mn-100h, and Alloy 2 + Mn-200h are shown in Figures 9, 10, and 11. The elemental distribution shows the same features as observed for the samples Alloy 2-100h, Alloy 2 + Mn-200h-2, and Alloy 1-200h presented in Figures 1, 2, and 3.

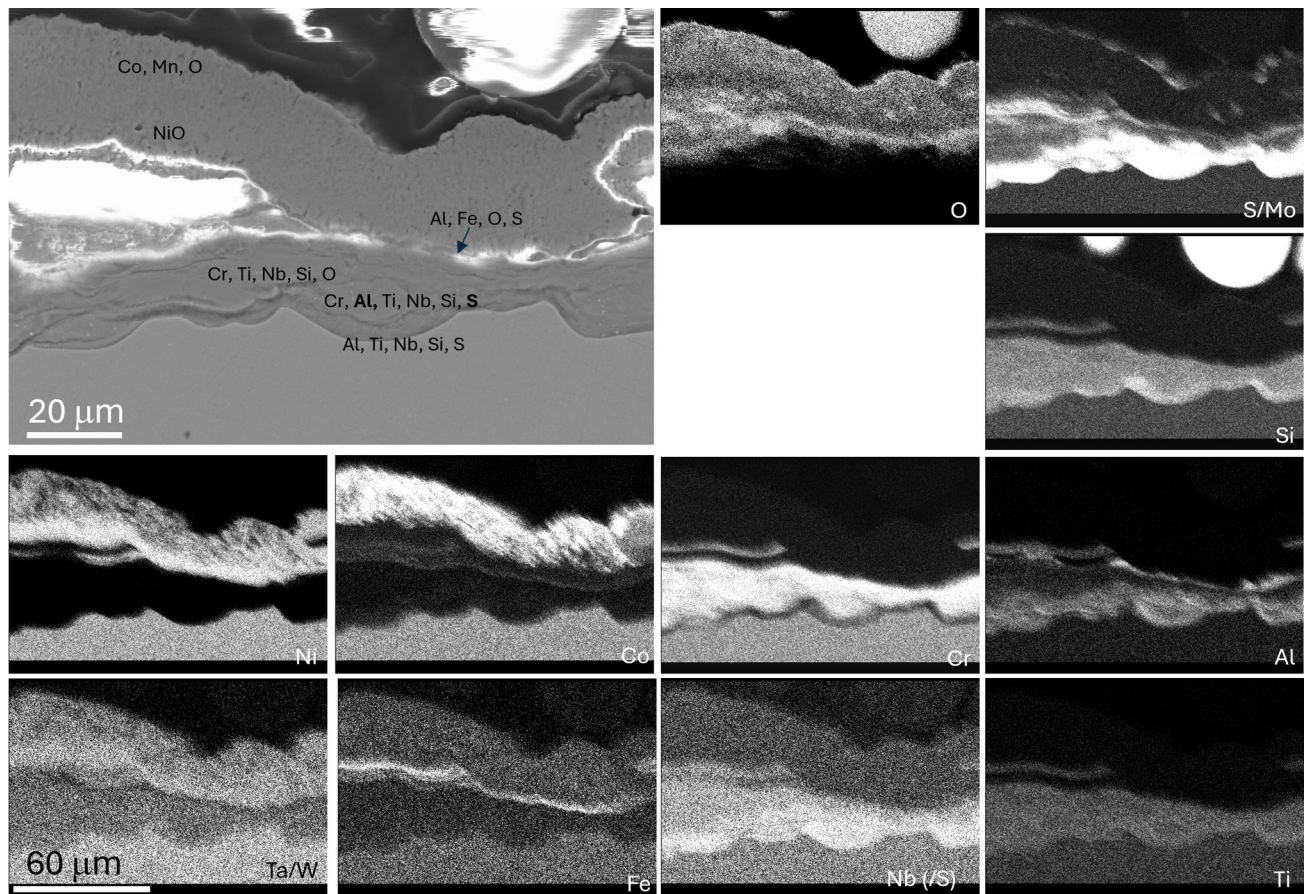


Fig. 9—EDX maps of the corroded sample Alloy 2-200h.

Point ID spectra were taken from a thin, regrown scale of the Alloy 2-100h sample as presented in Figure 12. At the lowest corrosion layer, *i.e.*, the interface to the bulk alloy, Co, Ni, Cr, and Fe are strongly depleted while Si and Ti are enriched (2.75 ± 1 at. pct Si and 4 ± 2 at. pct Ti, compared to 0.75 and 3.5 at. pct in the bulk, respectively). Al is also slightly enriched and the elements Ta, Mo, W, Nb are present at bulk alloy composition. A high amount of approx. 11.5 ± 4.3 at. pct S is found, as well as 55 ± 9 at. pct O. In the bulk inward growing scale,

Co, Ni, and Fe are still strongly depleted and little S is detected, while Cr is enriched and all other alloying elements are present at compositions slightly below their bulk values. At the interface between inward and outward growing scale, a region with increased Si and S is detected. The outward growing scale consists of NiO and Co oxide with Si, and Fe found within the NiO regions, and Mo found in low levels throughout the outward growing scale. Similar observations were made for the other alloys, presented in Figure 4.

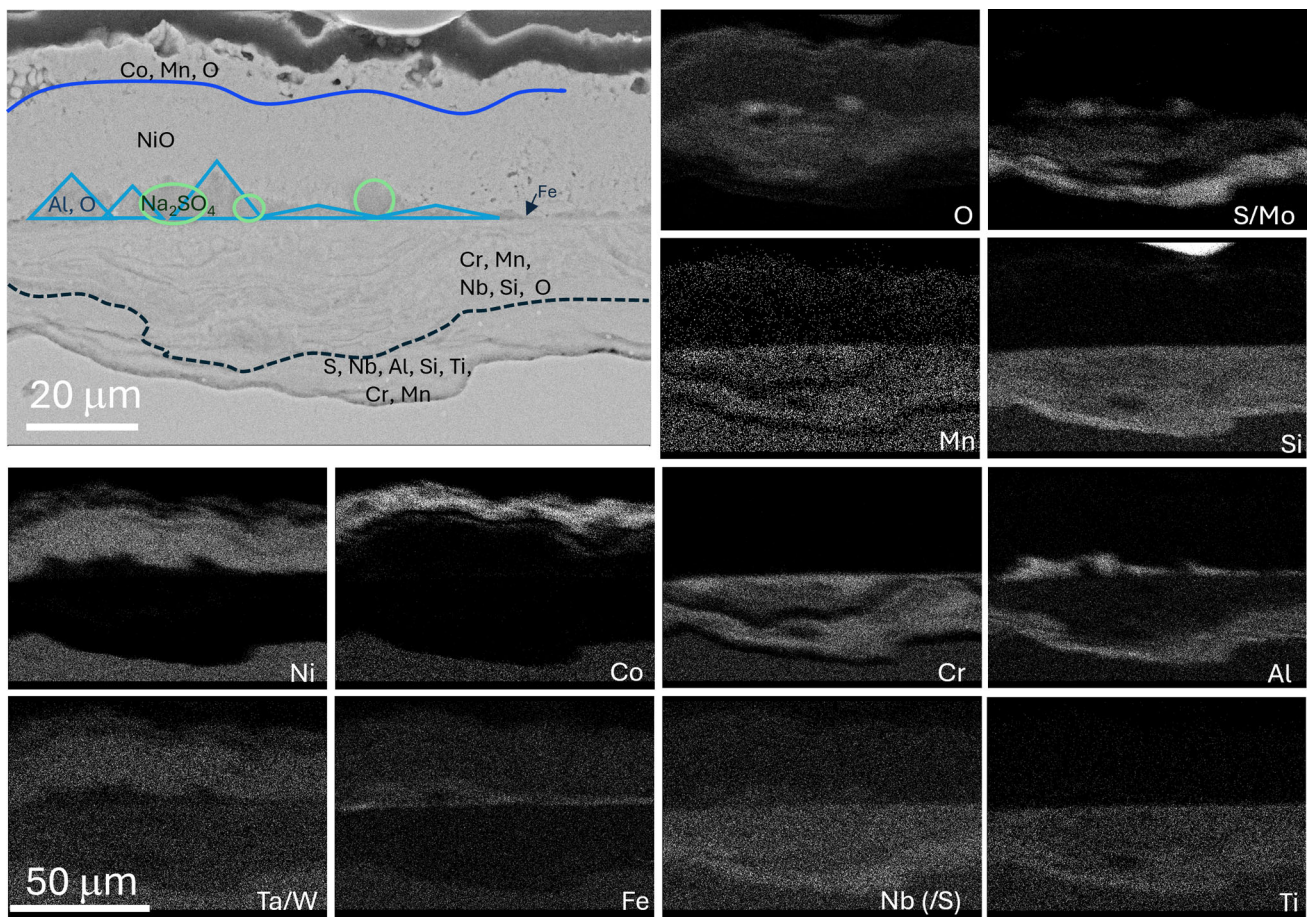


Fig. 10—EDX maps of the corroded sample Alloy 2 + Mn-100h.

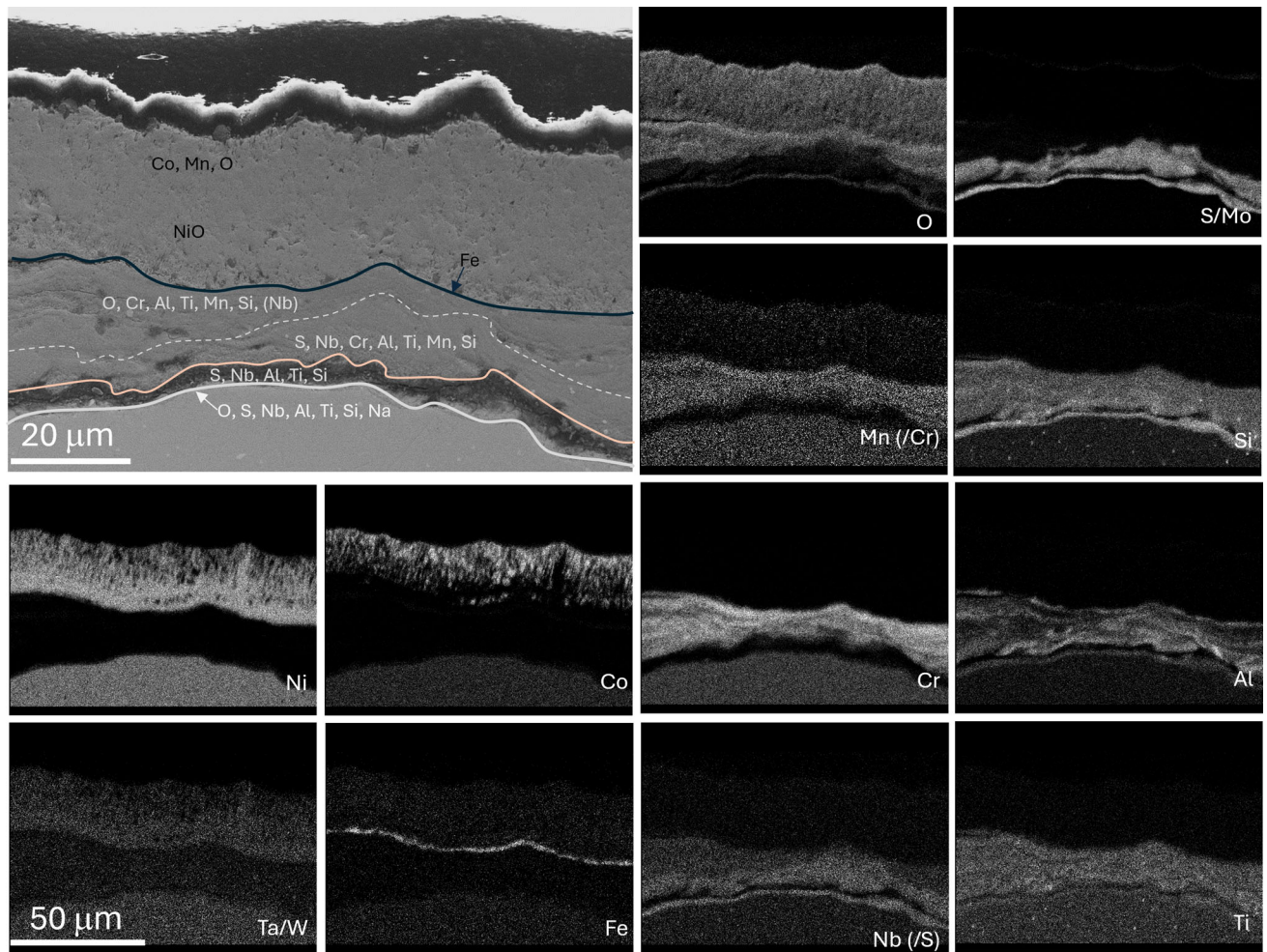


Fig. 11—EDX maps of the corroded sample Alloy 2 + Mn-200h.

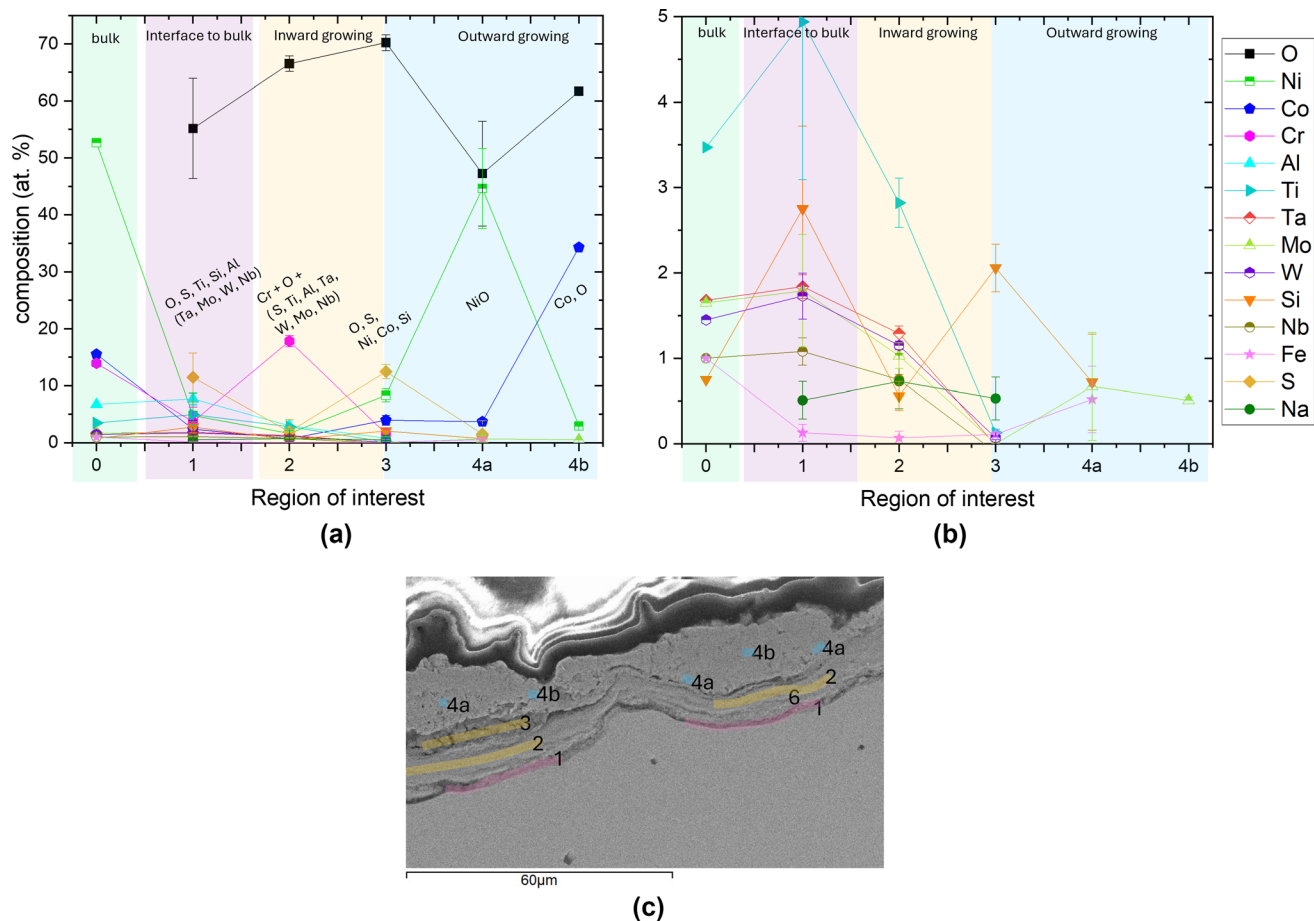


Fig. 12—(a, b) Point ID spectra taken from different layers in a thin, regrown section of the oxide scale on Alloy 2-100h as indicated in the SEM micrograph in (c).

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Systematic study on the role of Mn, Si, and Fe on the corrosion resistance of Ni-based superalloys exposed to air, gaseous sulfur oxides and salts

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