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Enhancing high-temperature suitability of Ni-electroplated AISI 441 steel by soft-chromising

Louis Sadowski Cavichiolo a,b,*, Tobias Holt Nørby a, John Hald b, Karen Pantleon b

a Topsoe A/S, Power-to-X – Technology Development, Nymøllevæj 66, 2800 Kongens Lyngby, Denmark
b Technical University of Denmark, Dept. of Civil and Mechanical Engineering, Produktionstorvet, 2800 Kongens Lyngby, Denmark

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ABSTRACT

Commodity ferritic steel AISI 441, electroplated with nickel, can improve large-scale interconnect manufacturing for solid oxide cell stacks, but nickel-diffusion-induced chromium depletion in the steel surface adversely affects the oxidation behaviour. The present study explores soft-chromising to limit oxidation in Ni-coated AISI 441 during a simulated stack sealing exposure. Complementary in-situ X-ray diffraction and ex-situ electron microscopy revealed that soft-chromising favours the formation of protective external Cr(Mn)-rich oxide and lowers detrimental internal oxidation. Soft-chromising seems promising for the development of new low-cost commodity steels that allow nickel in protective coatings, thereby facilitating an interconnect design appropriate for large-scale production.

1. Introduction

Interconnects (ICs) used in solid oxide cell (SOC) stacks are typically based on ferritic stainless steels and protective coatings [1]. Due to an increasing demand to deploy the SOC technology at an industrial scale [2], it is desired to use low-cost, readily available materials for the IC application. Nickel depicts one promising material for protective coatings that can be applied to complicate geometries in mass production by cost-efficient electroplating [1,3]. During subsequent air annealing, the electroplated Ni-layer results in a uniform protective oxide scale [1,3].

One major benefit of nickel for protective oxide scales is that it serves as a chemical bonding aid towards adjacent SOC electrodes, contributing to improved electrical contact at IC/elec trode interfaces. This concept is frequently utilised to achieve excellent bonding between ICs and Ni contact layers or the Ni/YSZ fuel support on the fuel side [4,5] and can similarly improve (electrical) contacting towards oxygen electrodes on the airside of ICs [6–8].

Due to their low cost and widespread availability, commodity ferritic stainless steels are frequently investigated as ICs for SOC stacks, and promising results have been reported when protective coatings are applied [9–12]. The specific composition of stabilised steel, such as AISI 441, is attractive, partly attributed to the partitioning of silicon towards Laves phase formation in this type of alloy. Associated lower Si contents in solid solution reduce the tendency of continuous silica (SiO2) formation [13] that is electrically insulating [14] and can promote oxide spallation [15,16]. However, challenges of introducing commodity steels for ICs remain and include limited oxidation resistance due to lower chromium contents in these alloys compared to tailor-made steels for IC applications (e.g., Crofer 22 APU and Crofer 22 H). The use of electroplated nickel in protective coatings amplifies this problem, as interdiffusion between nickel and the steel causes a surface-near transformation of ferrite to austenite associated with chromium depletion [17,18]. As a result, failure of the protective chromia (Cr2O3) scale is frequently reported in commodity steels electroplated with nickel or Ni-based coatings [19–21]. Additionally, surface-near chromium depletion induced by nickel diffusion causes partial dissolution of Laves phase [22], such as formed in AISI 441 alloy, which is ascribed to detrimental niobium segregation at the scale/alloy interface [23], increasing the risk for oxide spallation during cyclic oxidation [24,25]. Consequently, when using AISI 441 alloy electroplated with nickel for the IC application, associated problems of nickel-diffusion-induced chromium depletion must be addressed. One apparent way is the addition of chromium, which previously in combination with Ni as a thin Cr—Ni overlay has been shown effective in reducing oxidation rates of engine valve steels [26]. Furthermore, chromium can be added in solid solution to a steel, which, in principle, can be done by different processes, such as direct diffusion into the steel’s surface (i.e., soft-chromising) or by deposition of Cr-rich coatings by, for example, hard
chrome electroplating or thermal spraying, followed by inward diffusion during a subsequent annealing treatment. Soft-chromising seems particularly promising, as it requires no separate annealing treatment and deploys no apparent limitations, such as health and environmental hazards, typically associated with, for example, hard chrome electroplating [27,28]. The nature of soft-chromising is a thermo-reactive deposition and diffusion (TRD) process by which the chromium content of the steel can be directly increased via the surface, increasing the available chromium “reservoir” in the steel for improved oxidation resistance. The ability to add chromium in solid solution to a steel can be envisioned to tailor chromium contents to specific needs, i.e., creating steels resembling chromium-adjusted commodity steels, and thereby supporting the development of new types of interconnect steels that facilitate the use of Ni-based type protective coatings. This is considered a more time-efficient approach than fabricating multiple test melts with varying chromium contents and should enable faster steel development.

In principle, a large variety of existing commodity steels can be soft-chromised and, hence, become potential candidates for the IC application. The only compositional requirement for the steel is a low amount of interstitial carbon, such that chromium can be added in solid solution (soft-chromised) [29,30], which is essential for its availability for protective chromia scale formation [31], and the formation of Cr-rich carbides is avoided (hard-chromising). Additionally, due to faster diffusion kinetics, more chromium can be added to ferritic than austenitic steels [32]. Considering the low amounts of interstitial carbon and the ferritic phase, AISI 441 steel is a promising base material for successful soft-chromising.

The present study investigates soft-chromising of AISI 441 to counteract the lower oxidation resistance resulting from the diffusion of nickel from an electroplated coating. For this purpose, short-term oxidation tests are employed to compare the oxidation behaviour of soft-chromised and virgin AISI 441 steel, coated with nickel, during a simulated SOC stack sealing exposure. Knowledge of the early oxidation behaviour during stack sealing is crucial, largely determining the nature of oxides and thereby affecting the oxidation resistance of ICs during the operation of stacks, which is further influenced by stack sealing conditions such as heating rates, maximal temperature, and holding time. Our previous work indicated that the oxidation behaviour of AISI 441 electroplated with nickel is considerably affected by interdiffusion in the subscale alloy [33]. Therefore, the present study explores the complementary use of in-situ X-ray diffraction during annealing and ex-situ microscopy to study the early oxidation behaviour in more detail. The beneficial use of soft-chromising for the early oxidation of Ni-electroplated AISI 441 is evaluated with particular emphasis on the effects of the microstructure, chemical and phase constitution of the modified steel surface on oxidation.

2. Materials and methods

2.1. Samples

The chemical composition of ferritic stainless steel AISI 441 is stated in Table 1. The steel was treated with an industrial standard 2R finish, i.e., successively cold-rolled and bright annealed (in protective atmosphere) to achieve a smooth surface, free of airborne or moisture contaminants. Steel samples were chemically etched into specimens with dimensions of (30x20x0.3) mm³. Subsequently, chromising by pack cementation was applied to one set of samples to increase chromium contents near the surface. This was done during high-temperature annealing to 900 °C and isothermal holding for 4 h in an alumina tube furnace, using argon as a protective gas. Chromium diffusion was achieved from a powder pack consisting of a halide-based activator, chromium, and an inactive filler material. Before the treatment, the tube furnace was evacuated and flushed three times with argon. The heating rate was 8 °C/min. After the chromising treatment, samples were furnace cooled.

The as-received and chromised samples were subsequently electroplated with nickel, resulting in samples termed “441-Ni” and “441-Cr-Ni”, respectively. A strike layer was deposited from a Nickel Woods bath (80 g/L NiCl₂•6H₂O - 100 g/L 37 % HCl) operated at room temperature with a current density of 5 A/dm² for 2 min, followed by a nickel layer from a Nickel Watts bath (300 g/L NiSO₄•6H₂O – 50 g/L NiCl₂•6H₂O – 40 g/L H₂BO₃) operated at 60 °C for 6 min with a current density of 2 A/dm² to achieve a total thickness of about 2 μm for the nickel coating. For 441-Ni samples, the pre-treatment consisted of alkaline degreasing in commercial solution “SlotocleanEL DCG” and a subsequent pickling step in commercial “Decasel 5” solution. The same Ni-electroplating was applied for 441-Cr-Ni samples, but additional de-smutting in 10 vol% HCl solution was performed prior to pickling to remove reaction products formed during alkaline degreasing. For more details on the chemistry and process parameters of the applied electroplating and pre-treatments, it is referred to [33].

2.2. In-situ XRD during annealing

In-situ X-ray diffraction (XRD) was carried out during heating to a maximum temperature of 900 °C in stagnant air, aiming at sample-specific identification of phase transformations induced by oxidation and interdiffusion between nickel and the steel, respectively. XRD measurements were done using a Panalytical Empyrean instrument and an Anton Paar XRR900 reactor chamber with an automated alignment stage. Environmental heating in the furnace-type chamber provides high-tempreature uniformity, which was controlled by placing the thermocouple directly underneath the thin samples. The temperature profile during the measurements is shown in Fig. 1a. For the recording of diffraction patterns at distinct temperatures, measurements were done during 35 holding steps intermediate to heating periods. During each holding step, three measurements of 10 min each were performed using a step size of 0.013 °2θ. After reaching 900 °C, the temperature was held for 1 h, during which XRD scans were repeated six times to investigate possible isothermal changes, which, however, were not observed. The resulting overall slow heating rate of 40 °C/h was chosen to stimulate interdiffusion, which is relevant for associated phase transformations and oxidation behaviour. In-situ XRD was performed in line focus with Bragg-Brentano geometry applying Cu-Kα1 radiation. The X-ray tube was operated using a voltage of 45 kV and a current of 40 mA. Bragg-Brentano geometry applying Cu-Kα1 radiation. The X-ray tube was operated using a voltage of 45 kV and a current of 40 mA. Fluorescence radiation was removed by a PIXcel3D 1 × 1 detector (PANalytical). Furthermore, a nickel β-filter, two soller slits, anti-scatter slits, a fixed incident beam mask, and a divergence slit were used.

2.3. Simulated SOC stack sealing exposure

Complementary to in-situ XRD measurements, which aimed at identifying phase transformations by temperature-resolved real-time measurements, the oxidation behaviour and microstructure, chemical and phase composition were ex-situ analysed after quenching from a simulated SOC stack sealing exposure at high-temperature. The exposure was performed in horizontal Carbolite CTF 12/65/550 furnaces using one-end closed mullite (3Al₂O₃•2SiO₂) tubes as a chamber.

### Table 1

<table>
<thead>
<tr>
<th>Batch</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Mn</th>
<th>Ti</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 441</td>
<td>Bal</td>
<td>17.57</td>
<td>0.19</td>
<td>0.018</td>
<td>0.018</td>
<td>0.34</td>
<td>0.14</td>
<td>0.57</td>
<td>0.002</td>
<td>0.025</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Samples were heated in stagnant air with the same heating rate as applied during in-situ XRD measurements, i.e., 40 °C/h from room temperature to a maximum temperature of 900 °C, and isothermal holding was applied for 9 h for the ex-situ analysed samples. Before reaching 900 °C, some samples were water quenched from selected temperatures, corresponding to relevant phase transformations indicated by previous in-situ XRD analysis. Accordingly, samples were investigated either after quenching from 525, 730, 800, and 900 °C or after isothermal holding at 900 °C for 9 h and subsequent quenching, as shown in Fig. 1b.

2.4. Materials characterisation

Cross-sections of quenched 441-Ni and 441-Cr-Ni samples were prepared by sectioning and subsequent cross-sectional ion milling with the broad ion milling system IM4000. During ion milling, an acceleration voltage of 6 kV, a discharge voltage of 1.5 kV, a milling time of 2 h, and an argon flow of 0.08 cm³/min were used. Microstructure, chemical, and phase analysis were done on cross-sections using scanning electron microscopy (Zeiss Gemini SEM 1 Sigma 300). A backscatter electron (BSE) detector was used during imaging, revealing compositional contrast of the multi-layered cross-sections. The microscope was operated with an acceleration voltage of 5 kV for high image resolution. Chemical analysis by energy-dispersive x-ray spectroscopy (EDS) was performed with an acceleration voltage of 15 kV using an Ultim Max Oxford EDS detector. EDS depth profiles for the various samples quenched from different temperatures were acquired to quantify the evolution of chemical composition in the surface-near region of the steel resulting from interdiffusion. Specifically, rectangular EDS maps (aspect ratio 1:16) were recorded at various distances from the surface and distinct areas on the cross-sections, taking into account local heterogeneities in chemical composition and microstructure. The in-depth distance was measured from the external scale/steel interface or from the sample’s surface if the oxide scale was absent. Individually displayed points in measured profiles correspond to the central points of respective rectangular EDS maps. Microstructure and EDS analysis were further complemented by site-specific phase identification using electron backscatter diffraction (EBSD) analysis, which was done using the same SEM at an acceleration voltage of 15 kV. A CMOS EBSD detector by Oxford and a step size of 50 nm were used during acquisition, while post-processing of as-measured data without any cleaning of non-indexed points was done with the MTEX software [34].

3. Results and discussion

3.1. Effects of soft-chromising before oxidation

After the performed soft-chromising treatment of AISI 441 steel, XRD and EDS analyses confirmed the addition of Cr without the formation of new phases, such as Cr-rich carbides. This agrees with the low carbon content of AISI 441 and hence indicates that samples were indeed soft-chromised (not hard-chromised), leading to the desired solute chromium enrichment from the surface of the steel into its bulk as revealed by EDS depth profiling shown in Fig. 2. The figure displays the chromium profile of virgin 441-Ni and soft-chromised 441-Cr-Ni after samples have the additional Ni-electroplating, providing a virtually pure Ni coating of approximately 2 μm thickness on top of the steels. Note that electroplating pre-treatments further remove potential surface contaminants if any such should remain leftover after soft-chromising, which otherwise could affect the subsequent oxidation behaviour. Hence, the surface of the soft-chromised and virgin AISI 441 steel are identical after
electroplating and both samples are considered plain steels, albeit of two different chromium concentrations. Specifically, Fig. 2 shows that 441-Cr-Ni exhibits highest chromium contents of 45 wt.-% at the steel surface, which after Ni-electroplating, becomes the coating/steel interface. A noticeable chromium enrichment of at least 18.4 wt.-% compared with the constant chromium in the virgin steel (17.6 wt.-% Cr) is detected throughout the bulk. This is attributed to fast interdiffusion kinetics in the ferritic steel. Soft-chromising did not interfere with the subsequent application of the Ni-electroplated coating, which appears well-adherent and uniform for the 441-Cr-Ni (Fig. 3d) and 441-Ni sample (Fig. 3c).

The microscopic investigation in Fig. 3 shows that high-temperature annealing during soft-chromising causes grain growth away from the steel surface, i.e., in the non-chromium-enriched bulk. The high-temperature annealing during soft-chromising also affects the distribution of NbSi-rich Laves phase. Laves phase forms as precipitates at grain boundaries and within grains, as is typical for AISI 441 alloy [13], which is here identified based on the niobium signal in the EDS map (Fig. 4). In Fig. 3, Laves phase is visible by either light or black spots, representing either the Nb-rich particles (light) or craters (black) that likely were induced during ion milling preparation, knocking out some of the hard particles. For 441-Ni, Fig. 3c shows a local depletion of Laves phase in the surface-near steel. For 441-Cr-Ni, on the other hand, Laves phase also forms in the surface region of the steel (Fig. 3d). Enhanced Laves phase formation near the surface is considered relevant for the oxidation behaviour of minor elements (Nb, Si), which will be elaborated under the influence of nickel diffusion in Section 3.4.

3.2. Phase evolution during in-situ annealing

In-situ XRD was used to determine distinct temperatures of relevant phase transformations during heating to 900 °C in air, as shown in Fig. 5 and Table 2. In the first view, the two samples with and without chromium seem to behave very similar during heating (cf. Fig. 5a and b). For both sample 441-Ni and sample 441-Cr-Ni, only peaks associated with Ni (PDF-card: 04-0850) from the coating and with ferrite (α-Fe, PDF-card: 06-0696) of the steel are detected at room temperature (the expected small fraction of Laves phase according to Fig. 3 does not result in peaks of sufficient intensity). During heating, Fig. 5 reveals the formation of austenite (γ-Fe(Ni,Cr), PDF-card: 33-0397), which originates from the diffusion of nickel into the initial ferrite (α-Fe) of the steel and counter-diffusion of steel components (mainly Fe and Cr) into the nickel coating. For an identical 441-Ni sample, we previously reported austenite formation and attributed it to interdiffusion in the surface region of the steel [33]. Here, austenite also formed for the sample 441-Cr-Ni with increased Cr content at a slightly higher temperature of 550 °C compared with 525 °C for 441-Ni (cf. Table 2). In general, the determination of transformation temperatures from XRD must be taken with care because it requires peaks of sufficient intensity; thus, a sufficient volume fraction of the phase must be present, and the possible effect of crystallographic texture cannot be considered in the present study. Nevertheless, the slightly higher temperature of austenite formation might be attributed to the chromium enrichment, which imposes a ferrite stabilising effect.

Fig. 5 further indicates sample oxidation after or simultaneously with interdiffusion, resulting in a multi-phase oxide scale for both samples consisting of nickel from the coating and constituents from the steel due to
to their upward diffusion during heating. The different oxide phases correspond to different layers in the oxide scale. Here reported PDF cards were chosen corresponding to the main chemical constituents in the detected oxide phases, which are supported by EDS measurements in Section 3.3, without the possibility of assigning a distinct chemical stoichiometry to oxide phases with varying chemical concentrations. For both samples, it is suggested that a type NiO phase (PDF-card: 44-1159) forms at a lower temperature than the subsequently formed spinel type (CrMn$_2$O$_4$, PDF-card: 71-0982) and chromia phase (Cr$_2$O$_3$, PDF-card: 74-0326). The more complex solid solutions of the oxides formed in reality, considering additional dissolved metal constituents, will be indicated in Section 3.3.

Attributed to higher chromium contents, Fig. 5 additionally reveals sigma phase (σ) formation for 441-Cr-Ni at temperatures above 675 °C (Fig. 5b). The sigma phase remains present up to 900 °C, which is not expected based on thermodynamic stability and will further be addressed in Section 3.4. Furthermore, even at 900 °C, both ferrite (α) and austenite (γ) are detected (Fig. 5). Since ferrite is located in the ferritic bulk of the steel, thus, below the formed austenitic interdiffusion zone, detecting both phases indicates that the X-ray penetration depth completely covers the surface region of interest. From the overview in Table 2, it becomes apparent that the revealed temperatures of relevant phase formation vary only slightly for each phase from one sample to the other. Due to the abovementioned limitations of precise temperature determination from XRD, it was decided to quench both samples from the same temperatures, i.e., 525, 730, 800 and 900 °C, before they were investigated ex-situ by microscopy (see Sections 3.3 and 3.4). Specifically, 525 °C was selected to represent the initial stages of simultaneous interdiffusion and nickel oxidation. At 730 °C, spinel and chromia oxides have formed in both samples, and additionally, sigma phase is expected to be visible in 441-Cr-Ni.

3.3. Effects of soft-chromising on external oxide formation

The microstructure of 441-Ni and 441-Cr-Ni after quenching from different temperatures during the simulated SOC stack sealing exposure is presented in Figs. 6 and 7, respectively. The designation of oxides and layers in the micrographs is based on in-situ XRD (cf. Fig. 5 and Table 2) and chemical analysis (EDS, not shown here). For both samples, micrographs indicate simultaneous oxidation and interdiffusion of nickel at 525 °C. This corresponds with the formation of an austenitic interdiffusion zone (termed “IDZ” in Figs. 6 and 7) and NiO phase, as earlier indicated by in-situ XRD. The dissolution of Fe and Cr in NiO becomes additionally apparent from EDS analysis, suggesting a Ni(Fe,Cr)O$_3$ rock-salt oxide (cf. Figs. 6 and 7). At 730 °C, micrographs in Figs. 6b and 7b further reveal a Cr(Mn)-rich oxide scale below Ni(Fe,Cr)O. This oxide scale corresponds with chromia (Cr$_2$O$_3$) and spinel (CrMn$_2$O$_4$) as determined by in-situ XRD (Fig. 5), which, according to EDS analysis, additionally contain varying concentrations of dissolved Fe and Ni.

EDS depth profiles were further measured for the surface-near steel perpendicular to the interface, with the outermost measuring point located just below the scale/stainless interface. The resulting data (Fig. 5) support interdiffusion between nickel from the coating and the ferritic steel, which appears to start at 525 °C and accelerates further at higher temperatures. As a result of interdiffusion, a chromium depth profile establishes. The profile indicates chromium depletion as a result of the lower chromium solubility and diffusion kinetics in the formed austenite and due to additional oxide-near chromium consumption by the formed dual phase Cr(Mn)-rich oxide (cf. Fig. 8). Fig. 6 shows that austenite formed in this way impairs Cr(Mn)-rich oxide formation on sample 441-Ni. Specifically, the oxide appears non-continuous, undulated, and porous (Fig. 6b-d), and partly forms branches (Fig. 6b) or islands (Fig. 6d). As a result of lacking chromium below the oxide, Fe-rich corrosion products form at temperatures above 730 °C, as indicated in Figs. 6b-d. The Fe-rich oxide partly dissolves but remains present after isothermal holding for 9 h at 900 °C (Fig. 6e). Fe-rich oxide formation was not observed explicitly by in-situ XRD, but this may be due to peak overlap with other oxide phases. The Fe-rich oxide being either spinel-type or hematite (Fe$_2$O$_3$) phase can hardly be distinguished from earlier suggested Cr-rich spinel (CrMn$_2$O$_4$) and chromia (Cr$_2$O$_3$) phases by XRD. In either case, the Fe-rich oxide forms as the outermost oxide layer (Fig. 6), where it might deteriorate contact points between interconnects and other stack components, lowering stack robustness. Further, it likely accelerates oxidation rates during initial oxidation stages, which, combined with deteriorated contact, might lead to premature stack failure.

Due to austenite formation, surface-near chromium contents of oxidised 441-Cr-Ni are lowered compared to the ferritic bulk, as was the case for 441-Ni. However, soft-chromising essentially limits the depletion of Cr as indicated by EDS depth profiles (cf. Figs. 5b vs a), revealing that chromium contents in the surface-near austenite are considerably higher for 441-Cr-Ni than for 441-Ni throughout the simulated SOC stack sealing exposure. As a result, a more protective dual phase Cr(Mn)-rich layer is present for 441-Cr-Ni, as visible in Figs. 7c-e. The formed oxide scale appears less undulated and porous than on 441-Ni. Contrary to 441-Ni, micrographs in Fig. 7 further reveal the absence of Fe-rich oxides for 441-Cr-Ni throughout the simulated SOC stack sealing exposure. This corresponds with surface-near chromium contents in the range of typical reported threshold values to prevent Fe-breakaway corrosion (16–20 wt.%Cr for ferritic stainless steels [35,36]), as opposed to chromium values below such critical values for 441-Ni sample (cf. Fig. 5b vs 8a). The higher initial Cr/Fe ratio in the surface region of 441-Cr-Ni (cf. Fig. 2) might additionally play a role in limiting the upward diffusion of Fe before protective Cr(Mn)-rich oxide formation. Finally, a higher Ni/Fe ratio, as observed in the surface-near austenite for 441-Cr-Ni compared to 441-Ni (Fig. 8b vs a), is well-

Fig. 4. Surface-near EDS elemental maps of 441-Cr-Ni before oxidation.
known to reduce iron dissolution in chromia scale and, hence, can help to protect against the formation of Fe-rich oxides of fast oxidation rates [37]. Consequently, the present observations indicate that surface-near austenite formation is detrimental to protective oxide scale formation, but soft-chromising alleviates this problem considerably. The role of the here applied stack sealing parameters should be further considered. A slow heating rate of 40 °C/h was chosen to enhance interdiffusion between the coating and steel. From the EDS depth profiles in Fig. 8, it becomes apparent that nickel enriches in both samples, mainly between 525 and 730 °C. At higher temperatures, already dissolved nickel diffuses inward, but no additional nickel seems to enter the steel, which is attributed to oxidation of the nickel coating and additional formation of the Cr(Mn)-rich oxide scale, acting as a barrier layer to nickel diffusion. This suggests that mainly faster heating in the relevant temperature range (525–730 °C) can reduce nickel enrichment in the steel. Although likely diffusion of nickel into the steel cannot be prevented entirely, the combination of soft-chromising and a faster heating rate during stack sealing at 525–730 °C might limit the detrimental effects of nickel-diffusion-induced chromium depletion.

Fig. 5. Phase identification as determined by in-situ XRD analysis during heating and isothermal holding at 900 °C of (a) 441-Ni and (b) 441-Cr-Ni.

Table 2
Phase formation temperatures in [°C] for 441-Ni and 441-Cr-Ni as determined from the evolution of peak positions during in-situ XRD phase analysis.

<table>
<thead>
<tr>
<th></th>
<th>Austenite</th>
<th>NiO</th>
<th>Spinel</th>
<th>Chromia (Cr₂O₃)</th>
<th>Sigma phase (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>441-Ni</td>
<td>525</td>
<td>525</td>
<td>575</td>
<td>700</td>
<td>/</td>
</tr>
<tr>
<td>441-Cr-Ni</td>
<td>550</td>
<td>525</td>
<td>600</td>
<td>675</td>
<td>675</td>
</tr>
</tbody>
</table>

known to reduce iron dissolution in chromia scale and, hence, can help to protect against the formation of Fe-rich oxides of fast oxidation rates [37]. Consequently, the present observations indicate that surface-near austenite formation is detrimental to protective oxide scale formation, but soft-chromising alleviates this problem considerably. The role of the here applied stack sealing parameters should be further considered. A slow heating rate of 40 °C/h was chosen to enhance interdiffusion between the coating and steel. From the EDS depth profiles in Fig. 8, it becomes apparent that nickel enriches in both samples, mainly between 525 and 730 °C. At higher temperatures, already dissolved nickel diffuses inward, but no additional nickel seems to enter the steel, which is attributed to oxidation of the nickel coating and additional formation of the Cr(Mn)-rich oxide scale, acting as a barrier layer to nickel diffusion. This suggests that mainly faster heating in the relevant temperature range (525–730 °C) can reduce nickel enrichment in the steel. Although likely diffusion of nickel into the steel cannot be prevented entirely, the combination of soft-chromising and a faster heating rate during stack sealing at 525–730 °C might limit the detrimental effects of nickel-diffusion-induced chromium depletion.
3.4. Effects of soft-chromising on internal oxidation

Micrographs in Figs. 6 and 7 combined with EDS chemical analysis (not shown here) indicate the additional formation of internal Si-rich oxides during the simulated SOC stack sealing exposure below the external oxide scale, described above. The morphology of the internal Si-rich oxide appears discontinuous. NbSi-rich Laves phase dissolution for both samples is observed in the surface-near interdiffusion zone (termed “IDZ” in Figs. 6 and 7). Consequently, higher amounts of silicon are anticipated in solid solution with the steel, which promotes the formation of Si-rich oxide. Similarly, Laves phase dissolution should increase niobium contents in solid solution. For 441-Ni, preferred niobium segregation occurs at the scale/steel interface, as visible in Fig. 9, after isothermal holding at 900 °C. Preferred niobium segregation originates from a niobium activity gradient induced by surface-near chromium depletion [23]. It should be noted that, in contrast to 441-Ni, no such segregation was observed for the soft-chromised 441-Cr-Ni sample. This is likely attributed to higher chromium contents in the interdiffusion zone of 441-Cr-Ni (cf. Fig. 8b), lowering the niobium activity gradient enough to prevent segregation. Furthermore, Fig. 6e indicates that 441-Ni, compared to 441-Cr-Ni, experiences Laves phase dissolution deeper in the steel, i.e., in the steel bulk adjacent to the interdiffusion zone. In the case of 441-Cr-Ni, the shallower depth of Laves phase dissolution should lower the amount of niobium in solid solution, which contributes to the absence of interfacial niobium segregation.

Comparing the appearance of Si-rich oxides in Figs. 6 and 7, it becomes further apparent that soft-chromising affects Si-rich oxide formation. Like in the case of niobium, less Laves phase dissolution is associated with less silicon in solid solution with the steel, resulting in reduced oxidation and a more discontinuous Si-rich oxide morphology for 441-Cr-Ni. Reduced Si-rich oxidation might also be due to the formation of a Cr-enriched layer below the interdiffusion zone of 441-Cr-Ni, which is revealed in micrographs after quenching from 730 and 800 °C (cf. Fig. 7b and c). This layer appears to bind considerable amounts of silicon (Fig. 10) otherwise available for upward diffusion and oxidation. According to the EBSD phase analysis in Fig. 11a, the layer locally constitutes sigma phase, which has previously been reported to form under the influence of nickel diffusion in steels of higher chromium contents than virgin AISI 441 [38] and agrees with its formation for 441-Cr-Ni sample. Apart from higher chromium contents in
the surface-near 441-Cr-Ni, silicon additions to sigma phase are further known to extend its thermodynamic stability compared to binary Fe–Cr to temperatures above 830 °C \cite{32,39}, which agrees with results from in-situ XRD that detected sigma phase at such high temperatures (cf. Fig. 5b). Even though EBSD phase analysis indicates (slow) decomposition of sigma phase at higher temperatures of 900 °C and prolonged isothermal holding (cf. Fig. 11b and c), an overall beneficial impact might remain, lowering Si-rich oxidation. Additional effects of sigma should be clarified in future studies, considering the role of increased phase stability at lower temperatures, i.e., during stack service, typically operated in the range of 600–850 °C \cite{2}. As indicated from the present results, shorter isothermal holding times during stack sealing would likely increase the retained sigma phase fraction at the onset of stack operation and could affect the overall stack performance.

Furthermore, both internal Si-rich oxide formation and niobium segregation at the scale/steel interface are expected to affect the spallation resistance of the oxide scale during cyclic oxidation exposure, which is expected in intermediate shutdowns during stack operation. The adhesion of oxide scales plays a significant role for stack robustness, considering that a single spallation event leads to immediate and permanent loss of contact between the interconnect steel and other components of the stack. Thicker interfacial Si-rich oxide \cite{15} or Nb-rich precipitates \cite{24,25} of continuous morphologies seem more detrimental to scale adhesion than minor, discontinuous segregates. Since soft-chromising enhances the discontinuous morphology of Si-rich oxide and entirely avoids niobium segregation at the scale/steel interface, scale preservation should be higher for 441-Cr-Ni than 441-Ni. Increased oxide adherence for 441-Cr-Ni is further suggested from micrographs in Fig. 7, revealing less oxide-near pore formation than in the virgin 441-Ni sample (Fig. 6). Additionally, growth stresses from oxide scales in general and the Fe-rich oxide in 441-Ni likely play a role, increasing the risk for oxide spallation. In soft-chromised 441-Cr-Ni selective chromia oxidation seems favoured, and the formation of Fe-rich oxide is prevented (cf. Fig. 7), which likely leads to a less detrimental oxide-near stress state than in the case of virgin 441-Ni. Apart from the surface-near chromium contents, Fe-rich oxidation relates to internal Si-rich oxidation, which can promote selective chromia formation and reduce respective oxidation rates of the scale \cite{40,41}. Hence, some internal Si-

![Fig. 7. Backscatter electron SEM images of 441-Cr-Ni after quenching from (a) 525 °C, (b) 730 °C, (c) 800 °C, (d) 900 °C and (e) isothermal holding for 9 h at 900 °C. The interdiffusion is designated as IDZ and sigma phase as σ.](image-url)
rich oxidation might benefit the oxidation behaviour of interconnects, while the morphology of Si-rich oxide should be discontinuous to avoid the electrical insulating effects of silica impairing stack performance. In our previous study, we suggested that nickel diffusion induces such discontinuous Si-rich oxide morphology \[33\], which seems further promoted by the additional application of soft-chromising, as shown in this study. Hence, soft-chromising appears to overall improve the early resistance to fast oxidation and oxide spallation of Ni-electroplated AISI 441, which we intend to further validate in future studies by long-term cyclic oxidation tests.

4. Conclusion

Combining commodity steels with electroplated Ni-based protective coatings is considered promising for upscaling the production of interconnects (ICs) used in SOC stacks. However, associated risks of nickel-diffusion-induced chromium depletion limit the lifetime of commodity steels, impairing their suitability as ICs. On the example of the commodity steel AISI 441 electroplated with nickel, this study revealed the beneficial use of soft-chromising to limit oxidation during a simulated stack sealing exposure. Results demonstrate that due to substantial chromium depletion in the surface-near steel, virgin AISI 441 becomes unfit for the IC application unless upgraded in chromium. Soft-chromising, on the other hand, significantly improves protective Cr (Mn)-rich oxide formation and also lowers the extent of detrimental internal oxidation, thereby facilitating the use of Ni-based protective coatings for AISI 441 steel. Although long-term tests are pending, the present results of early stages are promising for the use of soft-chromising to pave the way for a new generation of high-volume interconnect steels that can help to enable large-scale manufacturing.

Fig. 8. Temperature-dependent EDS depth profiles acquired from site-specific locations of quenched samples. The distance from the scale/steel interface is indicated. Cr (blue) and Ni (red) contents are displayed for (a) 441-Ni and (b) 441-Cr-Ni at the specific temperatures during the simulated SOC stack sealing exposure.
of ICs. Specifically, soft-chromising could function as a fast-track development tool for an unprecedented variety of new tailor-made “commodity” steels by optimising the chromium concentration of existing steels in a straightforward manner.

The present study further emphasises the benefit of complementary in-situ X-ray diffraction and ex-situ microscopy studies to elaborate the oxidation behaviour under complex interdiffusion between an electroplated nickel coating and a steel with and without soft-chromising. Based on this approach, specific (advantageous) effects of soft-chromising on oxidation can be postulated:

1. Soft-chromising increases chromium contents in the sub-scale austenitic interdiffusion zone, enhancing the protective scale formation of chromia-type ($\text{Cr}_2\text{O}_3$ with fractions of Fe and Ni) and spinel ($\text{CrMn}_{1.5}\text{O}_4$, with fractions of Fe and Ni) phase. As a result, soft-chromising prevents detrimental iron corrosion at potential contact points towards other SOC stack components, likely lowering IC oxidation and improving stack robustness during its lifetime.

2. Soft-chromising reduces internal silicon oxidation and averts niobium segregation at the scale/alloy interface, which, combined with reduced external oxidation, should lower the risk of scale spallation. Validation of the resistance towards oxide scale spallation remains to be done, including the evaluation of the stress state in the oxide and adjacent steel.

3. Soft-chromising stabilises temperature- and time-dependent sigma phase that forms locally below the formed austenitic interdiffusion zone due to piled-up chromium contents. Sigma phase has previously not been observed under air-side exposure of ICs but appears to dissolve almost entirely after air annealing for 9 h at 900 $^\circ$C. The effects of (temporary) sigma phase formation on stack performance need to be clarified in future studies.

**CRediT authorship contribution statement**

Louis Sadowski Cavichiolo: Writing-Original draft, Investigation, Formal analysis, Methodology.

Tobias Holt Nørby: Funding acquisition, Writing - Review & Editing, Conceptualization, Resources, Supervision.

John Hald: Funding acquisition, Writing - Review & Editing, Project administration, Resources, Supervision.

Karen Panteleon: Writing - Review & Editing, Resources, Formal analysis, Verification, Methodology, Supervision.
Declarations of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability
The raw/processed data cannot be shared at this time as the data is also part of an ongoing study.

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[6] L.S. Cavichiolo et al. Fig. 11. EBSD phase map of 441-Cr-Ni after quenching from (a) 730 °C, (b) 900 °C and (c) isothermal holding for 9 h at 900 °C. The interdiffusion zone is designated as IDZ and sigma phase as σ.
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