The influence of iron and cobalt on the type II hot corrosion behavior of NiCr model alloys

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Abstract
The type II hot corrosion behavior of the alloys NiCr20, NiCr20Co10, and NiCr20Fe10 is investigated at 700°C in synthetic air + 0.5% SO2 for up to 300 hr. Pure Na2SO4 and a eutectic mixture of MgSO4–Na2SO4 are applied as deposits. The kinetics are investigated via dimensional metrology and correlated to the micro-structural progression of the corrosion by examining the cross-sections. All alloys exhibit two-stage corrosion kinetics, with initially low and subsequently increased metal losses. Independent of the deposit composition, the metal loss after the longest exposure time is increased by the alloying element cobalt, whereas it is decreased for the iron-containing alloy. All alloys show increased metal losses when exposed to the MgSO4–Na2SO4 deposit. The time to the propagation stage is similar for all tests. During the stage of low metal loss, all alloys develop a chromia scale and internal chromium sulfides. When the propagation stage is reached, chromium and nickel can be found along with oxygen and sulfur within the pit. Nickel is dissolved into the deposit, where it precipitates.

KEYWORDS
fireside corrosion, hot corrosion, nickel-based alloy, sodium sulfate, type II

1 | INTRODUCTION

Hot corrosion is a high-temperature corrosion mechanism accelerated by salt deposits, which has been observed in turbine engines used in aero and marine applications. Thin films of Na2SO4 were identified as the main cause of the attack. The heat exchangers and boilers in coal- and oil-fired power plants suffer from fireside corrosion, a mechanism analogous to hot corrosion. Nowadays, these parts are manufactured from Fe-based alloys, but the application of Ni-based alloys is discussed for higher steam temperatures in the 700°C technology to increase turbine efficiencies as well as biomass co-combustion to reduce the use of fossil fuel.

The mechanism of hot corrosion changes with temperature in the range of 500–1,000°C and depends on gas and deposit compositions as well as on the oxides formed. Besides these factors, the formation of a molten deposit is most detrimental to the corrosion resistance and is therefore of special interest. Below the melting temperature of Na2SO4 at 884°C, the mechanism is called type II hot corrosion and molten deposits occur as eutectic mixtures between this salt and corrosion products.

One of the major features of hot corrosion is the acid–base chemistry of the molten salt. The Na2SO4 partially decomposes according to the equilibrium

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\[ \text{Na}_2\text{SO}_4 \leftrightarrow \text{Na}_2\text{O} + \text{SO}_3. \quad (1) \]

According to the Lewis description, \( \text{Na}_2\text{O} \) is the base and \( \text{SO}_3 \) the acid. Accelerated corrosion occurs as oxides react with the salt and the reaction products are dissolved in the deposit. The occurrence of reaction and the dissolution of compound, as well as its amount, depend on the acidity of the salt, which is measured as \( p(\text{SO}_3) \) or \( a(\text{Na}_2\text{O}) \). The acidic dissolution of nickel occurs according to the equilibrium in Equation (2), the main reaction for type II hot corrosion of Ni-based alloys. The more acidic the salt, the more will the oxide dissolve:

\[ \text{NiO} + \text{SO}_3 \leftrightarrow \text{NiSO}_4. \quad (2) \]

The acidity of molten \( \text{Na}_2\text{SO}_4 \) depends on the gas composition, impurities in the salt, and temperature. Gaseous \( \text{SO}_3 \) is present in combustion atmospheres and its concentration depends on the fuel as well as on the temperature. The influence of the fuel is especially vital for coal-fired power plants, where different coals, biomass, and different firing conditions can alter the \( \text{SO}_3 \) concentration.\(^6,16,17\) Calculations show that \( \text{SO}_3 \) dominates at temperatures below 700°C, whereas it decreases toward higher temperatures in favor of \( \text{SO}_2 \).\(^18\) As a result, type II hot corrosion generally occurs by acidic dissolution. \( \text{NiSO}_4 \) dissolves in \( \text{Na}_2\text{SO}_4 \) and both form a eutectic mixture with a melting temperature of 671°C.\(^19\) A certain \( \text{SO}_3 \) partial pressure needs to be present (depending on temperature; \( -3 \times 10^{-4} \text{ bar at 700°C} \)) to form enough \( \text{NiSO}_4 \), resulting in the formation of the molten eutectic. At higher \( \text{SO}_3 \) partial pressure (\( >-2 \times 10^{-5} \text{ bar at 700°C} \)), even solid \( \text{NiSO}_4 \) is thermodynamically stable in contact with the gas phase instead of \( \text{NiO} \), and the dissolved \( \text{NiO} \) is expected to precipitate as \( \text{NiSO}_4 \). Other alloying elements can dissolve as well and form low melting sulfate eutectics (\( \text{CoSO}_4 \)). Also, additional sulfates (\( \text{MgSO}_4 \) and \( \text{K}_2\text{SO}_4 \)) and oxides (\( \text{V}_2\text{O}_5 \)) can occur in deposits and can form eutectics with \( \text{Na}_2\text{SO}_4 \), which melt at lower temperatures than pure \( \text{Na}_2\text{SO}_4 \).\(^19\) Impurities or oxides, which are very acidic or basic, influence the acidity of the deposit and therefore alter the dissolution mechanism and the solubility of the oxides. The dissolution reaction itself also changes the acidity of the salt due to the reaction with the acidic or basic part of \( \text{Na}_2\text{SO}_4 \). If sulfidation and oxidation occur, a decrease in acidity is expected as \( \text{SO}_3 \) is consumed by these reactions.\(^20\)

On the basis of the change of acidity throughout the salt film, Rapp and Goto\(^21\) proposed that a negative solubility gradient from the oxide–salt interface must be present if a continuous attack is observed. Without this gradient, the deposit would become saturated with the dissolved species and the attack would slow down as long as no new salt is deposited. The gradient results in the precipitation of the dissolved oxides in the salt and a continuous dissolution and precipitation mechanism can be established.

To fulfill this criterion, multiple simultaneous reactions are necessary. Combinations of sulfidation along with basic dissolution\(^20\) as well as basic dissolution of highly acidic oxides, such as molybdenum or tungsten, along with the acidic dissolution of other oxides (enhanced by the molybdate or tungstate ions)\(^22\) were proposed for hot corrosion at temperatures above the melting point of \( \text{Na}_2\text{SO}_4 \). For lower temperatures, Luthra\(^23,24\) first proposed a \( 3\text{Co}^{2+}/2\text{Co}^{3+} \) exchange mechanism, which is, however, not applicable to Ni-based alloys. It is argued that chromium cannot be dissolved, but it can be oxidized. However, it does not form a protective scale due to the rapid dissolution of cobalt. More recent studies incorporate or propose a synergistic effect for different Co-, Fe-, and Ni-based alloys.\(^4,25,26\) If two oxides are present and the acidity of the salt allows for the acidic dissolution of one oxide and basic dissolution of the other, the negative solubility criterion will be fulfilled for both and the overall corrosion will be enhanced.\(^27\)

The kinetics of type II hot corrosion is often observed to have two distinct stages.\(^28–30\) During the first incubation stage, the corrosion is slow and, similar to oxidation, a parabolic rate law is proposed to be applicable with similar rate constants. The absence of a molten deposit can hinder increased corrosion. The transition to the subsequent propagation stage is accompanied by the formation of a molten phase and the loss of the protective oxide scale. During this stage, rapid metal loss occurs, which is proposed to follow linear kinetics. The transition does not occur on the whole surface at once. The type II hot corrosion forms pits, on which corrosion products precipitate and form porous unprotective scales.

In the present study, alloys \( \text{NiCr}_{20}, \text{NiCr}_{20}\text{Fe}_{10}, \) and \( \text{NiCr}_{20}\text{Co}_{10} \) are investigated with two different deposits. One deposit is pure \( \text{Na}_2\text{SO}_4 \), which is solid at the beginning of the exposure, whereas the other, a \( \text{MgSO}_4–\text{Na}_2\text{SO}_4 \) eutectic mixture, is molten.\(^31\) The influence of \( \text{MgSO}_4 \) on salt chemistry is not clear. On the basis of the electrochemical experiments at higher temperatures, some authors predict that \( \text{MgSO}_4 \) has little-to-no influence in acidic conditions, as present in this study,\(^25,32,33\) whereas others observed reduced attack due to \( \text{MgSO}_4 \) additions to \( \text{Na}_2\text{SO}_4 \).\(^31,34\) The chromium content of 20 wt% was chosen, as higher amounts are known to reduce the attack significantly. Investigations of commercial alloys with 20 wt% chromium show a high scatter.\(^35–39\) This high scatter indicates the strong influence of the alloying elements, which is the focus of this investigation, thus making this composition most suitable.
2 | EXPERIMENTAL SECTION

2.1 | Melting and sample preparation

For the melting of alloys NiCr20, NiCr20Fe10, and NiCr20Co10, 30 g per ingot was weighed with a maximal deviation from the nominal composition of ±0.01 g per component (XS2002S; Mettler Toledo). The starting materials were nickel (99.99%; Alfa Aesar), chromium (99.995%; Alfa Aesar), iron (99.99%; Alfa Aesar), and cobalt (99.95%; Alfa Aesar). The alloys were melted in an induction furnace (Titan 3,3; Linn High Therm GmbH), followed by centrifugal casting. For each alloy, three cylindrical ingots with a diameter of 13 mm and a length of approximately 20 mm were cast and cut into 2.2-mm thick coupons. These coupons were ground to a P800 SiC finish while being glued to a sample holder to ensure parallel surfaces (see Section 2.3). The coupons were rinsed with acetone and ultrasonically cleaned in ethanol. The thickness was measured at three positions with a micrometer screw gauge. The alloy compositions were measured using energy-dispersive X-ray spectroscopy (EDS) on one sample per alloy at three different positions. Mean values are shown in Table 1. The chromium content is reduced for alloys due to its evaporation during the melting process.

2.2 | Hot corrosion tests

For the hot corrosion test, salt was applied on all surfaces of the samples. Pure Na₂SO₄ and a 48 mol% MgSO₄-52 mol% Na₂SO₄ mixture were dissolved in water and dropped on the samples using a pipette. During this process, the samples were heated via a heating plate. The amount of salt was controlled to 15 mg/cm² by weighing after evaporation of the water. In the case of the 300-hr exposure, a new salt was applied every 100 hr. The specimens were cut 2 mm above the middle part and the remaining 2 mm were ground, water-free, to a P1200 grit finish using petroleum as a lubricant. The polishing was performed with 3- and 1-μm diamond suspension, again water-free, using petroleum. The examination of the cross-sections was performed with a light microscope (Leica DM RME), a scanning electron microscope (Philips XL 40) equipped with an EDS sensor (EDAX) and an electron microprobe analysis (Jeol JXA-8100). To ensure conductivity for electron microscopy, the cross-sections were coated with carbon.

As type II hot corrosion is known to manifest via local pits, the mass change is not a valid representation of the corrosion attack. Following the work of References\[28,29,42-44\], a dimensional metrology technique was employed as a quantitative measurement of the corrosion attack, which is shown schematically in Figure 2. The initial thickness of the specimen was measured before the exposure (see Section 2.1). From a reference plane, which is in the middle between both surfaces, the residual metal is measured from light microscope images. At least 270 measurements per sample were conducted, evenly distributed over the cross-section. By subtracting the residual metal from the initial thickness, the metal loss is obtained and can be plotted sorted as a cumulative probability plot. The cumulative probability plot represents the percentage of the surface showing the corresponding or a higher metal loss, which can be interpreted as the probability that the corresponding or a higher metal loss occurs after the exposure time.

| Alloy     | Ni (wt%) | Cr (wt%) | Fe (wt%) | Co (wt%) |
|-----------|----------|----------|----------|----------|
| NiCr20    | 80.4     | 19.6     |          |          |
| NiCr20Fe10| 70.8     | 19.1     | 10.1     |          |
| NiCr20Co10| 70.1     | 19.6     |          | 10.3     |
3 | RESULTS AND DISCUSSION

3.1 | Kinetics

The kinetics of the hot corrosion of the NiCr alloys is shown in the cumulative probability plots in Figure 3. All alloys exhibit a two-stage kinetics, with an initial stage of low metal loss rates, the incubation stage, and a subsequent stage of increased metal loss, the propagation stage. The time to propagation as well as the metal loss rates during propagation can be estimated using the graphs shown in Figure 3.

FIGURE 1  Schematic drawing of the horizontal tube furnace used for the hot corrosion testing

FIGURE 2  Schematic presentation of the determination of the cumulative probability plots. (a) Measurement of the initial sample thickness. (b) Cross-section. (c) Microscopic examination of the cross-section. (d) Measured residual metal. (e) Sorted residual metal plotted as a function of the cumulative probability. (f) Metal loss (residual metal subtracted from the initial thickness) plotted as a function of the cumulative probability.
3.1.1 | Time to propagation

The transition to propagation is defined by a steep increase in metal loss, and it is observed for all alloys between 100 and 300 hr, except NiCr20Fe10 with a MgSO₄–Na₂SO₄ deposit and NiCr20Co10 with a Na₂SO₄ deposit, which transition between 24 and 100 hr. The increased metal losses of the NiCr20 alloys with both deposits and the NiCr20Co10 with Na₂SO₄ after 300 hr are only observed on 60–70% of the surface, whereas increased metal losses of the other samples after 300 hr are observed on the whole surface. For the two cases, when samples are in the propagation already after 100 hr, the metal loss is increased only on 15–20% of the surface. For these two cases, the time to propagation can be calculated by assuming a linear rate law during the propagation stage and neglecting metal loss from the incubation stage. As the transition occurs locally, the percentage of the surface must be considered. The time to propagation for 10% of the surface is calculated to be...

**FIGURE 3** Cumulative probability plots of alloys NiCr20, NiCr20Fe10, and NiCr20Co10 exposed to Na₂SO₄ (a,c,e) and MgSO₄–Na₂SO₄ (b,d,f) after 24, 100, and 300 hr. In graph (a), the 24-hr exposure is missing due to a local defect, which results in an increased metal loss. In graph (f), the 300-hr exposure is missing because the specimen is completely corroded in some areas and no residual metal is measured (the initial thickness of this specimen is 1.56 mm).
31 and 23 hr for NiCr20Fe10 and NiCr20Co10 alloy, respectively. Furthermore, the alloys differ regarding the uniformity of the attack. The most uniform attack is observed for NiCr20Fe10 alloy (standard deviation of the area in propagation: $\sigma$: 25 and 53 $\mu$m for Na$_2$SO$_4$ and MgSO$_4$–Na$_2$SO$_4$ tests, respectively). The highest standard deviation is shown for the NiCr20Co10 sample tested with Na$_2$SO$_4$ ($\sigma$: 162 $\mu$m), whereas metal loss after testing with the eutectic mixture is not measured, as no residual metal is found locally. The standard deviation of NiCr$_{20}$ with the eutectic mixture is not measured, as no residual deposit, whereas the NiCr$_{20}$Co$_{10}$ alloy transitions earlier with a MgSO$_4$ deposit, which is considered as the incubation stage.

The time to propagation is similar for all alloys with Na$_2$SO$_4$ and MgSO$_4$–Na$_2$SO$_4$ deposits, and the two earlier transitions occurred only on 15–20% of the surface. As the microstructure of the incubation stage is independent of the alloy composition to a high degree, a similar time to the propagation and a similar percentage of the corroded surface after 300 hr are expected for all alloys. The minor, but observed, differences are subsequently discussed by considering alloy and salt composition.

When comparing the time to propagation, the NiCr$_{20}$Fe$_{10}$ alloy transitions earlier with a MgSO$_4$–Na$_2$SO$_4$ deposit, whereas the NiCr$_{20}$Co$_{10}$ alloy transitions earlier with pure Na$_2$SO$_4$. This can be explained by considering two counteractive effects of the different deposits. First, diffusion in a liquid salt is faster than in a solid deposit. A molten deposit is, therefore, often stated as being necessary for the transition to propagation stage. The MgSO$_4$–Na$_2$SO$_4$ mixture is liquid at the test temperature and can, therefore, result in an earlier transition to the propagation stage, as is shown schematically in Figure 4. A contrary trend can be expected due to a more rapid early sulfation reaction. Jones et al. have shown that in pure Na$_2$SO$_4$, more cobalt oxide can be dissolved than in the eutectic mixture of MgSO$_4$–Na$_2$SO$_4$ and that the sulfation reaction is especially sluggish for the eutectic mixture. Their hot corrosion investigation of CoCrAlY coupons showed a more rapid reaction with a Na$_2$SO$_4$ deposit. Luthra et al. compared the hot corrosion kinetics of NiCr$_{30}$ and CoCr$_{30}$ alloys with pure Na$_2$SO$_4$ and with saturated MeSO$_4$–Na$_2$SO$_4$ mixtures (Me = Ni/Co), and they showed that the initial sulfation reaction is faster for the tests with pure Na$_2$SO$_4$ during early stages, whereas the rate is the same after longer exposure times. This was interpreted as a reduced driving force for the sulfation reaction. The reduced solubility in the MgSO$_4$–Na$_2$SO$_4$ deposit results in faster (local) saturation of the salt and therefore in a reduced driving force during the initial dissolution reaction. The result is a later transition to the propagation stage, which is shown schematically in Figure 4. Our previous investigation of iron-based chromia forming model alloys showed an analogous tendency. The later sulfation effect is especially relevant for the cobalt-containing alloy because cobalt is a strong sulfate former and also forms a low melting eutectic with Na$_2$SO$_4$. A similar Fe$_2$(SO$_4$)$_3$–Na$_2$SO$_4$ eutectic exists, but the SO$_3$ partial pressure needed for its establishment is just above the partial pressure in the present tests. The different times to propagation of the iron-containing alloy can be the result of the salt being liquid from the beginning. The reason for the more uniform corrosion of the NiCr$_{20}$Fe$_{10}$ alloy with both deposits could not be elucidated within this study. For the NiCr$_{20}$ alloy, the effect of the faster sulfation with Na$_2$SO$_4$ tests is less pronounced in comparison with the NiCr$_{20}$Co$_{10}$ alloy because nickel is a less favorable sulfate former. In the case of the MgSO$_4$–Na$_2$SO$_4$ salt with the NiCr$_{20}$ alloy, the reduced sulfation as well as the initial liquid salt are counteractive effects and result in a similar time to propagation in comparison with the Na$_2$SO$_4$ exposure. The slight increase in metal loss for the NiCr$_{20}$Co$_{10}$ samples, which are stated to be in the incubation stage, is associated with the formation of small pits discussed in Section 3.2.2.

### 3.1.2 Metal loss

To compare the rate of metal loss, the time to propagation and the maximum metal loss must be considered. As only one data point in the propagation stage is available for most of the tests, it is not possible to make a conclusive statement regarding the rate of metal loss. The discussion will, therefore, focus on the maximum metal loss after 300 hr. The highest metal losses after 300 hr are observed for the NiCr$_{20}$Co$_{10}$ alloy, followed by the NiCr$_{20}$ alloy and at last the NiCr$_{20}$Fe$_{10}$ alloy. The metal loss is always higher for the tests with the eutectic salt mixture. The rate of metal loss is lower when there is an
earlier transition to the propagation stage. This is the case for the test of NiCr20Fe10 with MgSO4–Na2SO4 and of NiCr20Co10 with Na2SO4.

The sequence NiCr20Co10, NiCr20, and NiCr20Fe10 ranked by metal loss can be explained by considering the influence of the additional alloying elements on the reaction mechanism. The acidic solubility of cobalt oxide in Na2SO4 is higher than nickel oxide at the same SO3 partial pressure at 927°C. The solubility of iron oxide is lower than both previously mentioned oxides at 927°C, whereas the solubility of chromium oxide is even lower. This ranking is believed to be the same at 700°C. As this ranking of solubilities (Co3O4 > NiO > Fe2O3) correlates with the metal loss of the alloys (NiCr20Co10 > NiCr20 > NiCr20Fe10), it can be argued to be responsible for the effect of the alloying elements. Furthermore, the negative effect of cobalt as an alloying element is in agreement with observations in the literature that cobalt-based alloys are generally more susceptible to type II hot corrosion. In addition to the solubility, this is attributed to the lower melting temperature of the eutectic, the lower SO3 partial pressure needed for its formation, and a 3Co2+/2Co3+ diffusion mechanism. In contrast, the SO3 partial pressure is too low for the formation of the liquid eutectic Fe2(SO4)3–Na2SO4, and the positive influence of iron can be explained by the reduced activity of nickel in the NiCr20Fe10 alloy in comparison with the NiCr20 alloy. This leads to the assumption that dissolution and precipitation are the rate-determining processes. The presence of nickel, the main dissolved species, in the most advanced pits is in agreement with this assumption. In the pit, diffusion occurs mainly along with the sulfides (see Section 3.2.3) if they form an interconnected network because both the chemical and self-diffusion are several orders of magnitude higher in the sulfide than in the oxide. However, for nickel, cobalt, and iron, no correlation between faster diffusion in the sulfide and metal loss is observed. The influence of the alloying elements is described schematically in Figure 4.

Independently from the alloy composition, the MgSO4–Na2SO4 deposit results in a higher metal loss after 300 hr than pure Na2SO4. This is expected, because molten salts are generally associated with higher diffusion and dissolution rates, but deposits from the propagation stage are generally molten and even high amounts of NiSO4(s) are observed. This effect requires further investigations on the chemistry and viscosity of different salt compositions.

### 3.2 | Microstructure

#### 3.2.1 | Incubation stage

During the incubation stage, all alloys develop a pure chromia scale, which is shown for the NiCr20 alloy after exposure for 100 hr with a Na2SO4 deposit in Figure 5. Pores are found at the oxide–substrate interface. In the substrate, the internal formation of chromium sulfide precipitates and a chromium depletion zone are observed. The depletion zone is larger when chromium sulfides are present. Locally, chromium oxides are observed in the deposit, as shown in Figure 6. In some areas, the salt close to the oxide scale has a green color and small amounts of

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FIGURE 5  Electron microprobe analysis image and element maps of a cross-section of a NiCr20 alloy after hot corrosion testing for 100 hr with a Na2SO4 deposit in synthetic air + 0.5% SO2 atmosphere
Chromium can be measured (depending on position up to 1.5 at% via EDS).

The formation of a predominantly chromium oxide scale is expected, as it is the most stable oxide in contact with the gas phase. The observation of the green color and the chromium oxide in the deposit near the oxide scale is the result of transient oxidation as well as a dissolution and precipitation mechanism. These observations were made independently from the state of the deposit (liquid or solid). The formation of the internal chromium sulfides is explained in the literature by the diffusion of SO$_2$ or SO$_3$ through the oxide scale via microcracks.\footnote{50–52} Below the oxide scale, the oxygen partial pressure is reduced (i.e., to the equilibrium partial pressure of Cr–Cr$_2$O$_3$), which results in an increased sulfur partial pressure due to the equilibrium described in the following equations:

\begin{align}
S_2 + 2O_2 & \rightleftharpoons 2SO_2, \quad (3) \\
SO_2 + \frac{1}{2}O_2 & \rightleftharpoons SO_3. \quad (4)
\end{align}

The chromium concentration in the depleted subsurface zone is too low to form chromium sulfides; instead, the sulfur diffuses inward (faster than the chromium outward), where the formation of internal chromium sulfides takes place with the increase in the chromium concentration. As the sulfides trap the chromium, an increased chromium depletion is observed when the sulfides are present. Chromium depletion decreases the capability of the alloy to maintain a protective oxide scale. The observed dissolution reaction of the oxide scale will further decrease this capability, as the oxide thickness is reduced.

On many specimens (NiCr$_20$ MgSO$_4$–Na$_2$SO$_4$: 100 hr, NiCr$_{20}$Fe$_{10}$ Na$_2$SO$_4$: 24 and 100 hr, NiCr$_{20}$Fe$_{10}$ MgSO$_4$–Na$_2$SO$_4$: 100 hr, NiCr$_{20}$Co$_{10}$ Na$_2$SO$_4$: 24 hr, NiCr$_{20}$Co$_{10}$ MgSO$_4$–Na$_2$SO$_4$: 24 hr), small local pits are observed, as shown in Figure 7. In the area of these pits, severe internal sulfidation is observed, which is accompanied by chromium depletion. Close to the substrate, the pits contain a chromium-rich oxide scale, and in between this scale and the initial chromium oxide scale, chromium, nickel, sodium, sulfur, and oxygen (and cobalt) are found. The chromium here is also present as oxide, whereas other elements can be present as a part of a liquid sulfate mixture. This mixture is locally green in color.

For the formation of these pits, the oxide scale must have lost its protective properties; severe internal
sulfidation around these pits is in agreement with the previously described reduced oxide stability due to sulfidation. The increased sulfidation, however, can also be the result of the breakdown of the protective oxide scale. When chromium is depleted, the loss of the protective properties results in the contact of the nickel-rich subsurface zone and the deposit. Due to the high SO$_3$ partial pressure in the atmosphere, this results in the acidic dissolution of nickel into the deposit, according to Equation (2). In the case of the experiments with Na$_2$SO$_4$ deposits, this acidic dissolution results in the melting of the deposit. The eutectic mixture is observed in Figure 7 below the initial oxide scale, and it has infiltrated the pit. The thick chromium scale below this infiltrated area can be established when the corrosion front reaches less depleted areas and the oxygen partial pressure is sufficient for its formation.

Besides the previously described reaction sequence based on the observed microstructure, the following reactions are proposed to have an influence on the resistance of the alloys to type II hot corrosion and are worth mentioning, but they, however, require further investigations. Taking into account the severe sulfidation of chromium and its influence on the stability of the oxide scale, one might also consider the sulfidation of nickel when the oxide scale is still protective. In the Ni–S system, the sequence of phases is nickel, Ni–S liquid eutectic, Ni$_3$S$_2$, Ni$_1$–$_x$S, NiS$_2$, and S$_2$.[33] Thermodynamic calculations show that the S$_2$ partial pressure for the formation of the Ni–S liquid eutectic is four orders of magnitude higher than for chromium sulfide at 700°C. However, at the oxide–substrate interface, the S$_2$ partial pressure exceeds this equilibrium partial pressure between chromium and its sulfide. Here the formation of the Ni–S liquid eutectic only becomes possible when the chromium depletion is severe enough. This could be another factor in the breakdown of the oxide scale, because it is unlikely that the oxide scale remains protective over a liquid phase. The type II hot corrosion of nickel was extensively studied in the literature.[43,53–57] In addition to the previously described dissolution reaction, nickel oxides as well as sulfides are generally observed and can form as intermediate compounds. For pure nickel, self-sustained fluxing is not observed because a negative solubility gradient cannot be established. Following the work of References[4,25,26], the additional basic dissolution of chromium can provide this gradient and enhance the corrosion rate via a synergistic effect. The solubility of chromium oxide in Na$_2$SO$_4$ is estimated to be near its solubility minimum and the dissolution mechanism depends on other reactions (see Section 1).[25] As the observed sulfidation, oxidation, and acidic dissolution decrease the acidity, the basic dissolution of chromium oxides is possible. If the synergistic effect is not established, the corrosion will slow down as the salt becomes saturated. This might influence the re-establishment of the observed chromium oxide scale.

3.2.2 Transition to the propagation stage

For NiCr$_{20}$Co$_{10}$ alloys after 24 hr and for the test with a MgSO$_4$–Na$_2$SO$_4$ deposit after 100 hr, slightly larger pits with a different microstructure are sporadically observed (1–4 pits per cross-section). A slight increase in metal loss is observed and associated with these pits. In comparison with the previously described pits, instead of a dense chromium oxide scale, all pits show a porous scale at the interface with the substrate. One of the typical pits is shown in Figure 8. The porous scale is rich in chromium and sulfur; however, only smaller amounts of nickel and oxygen are present. Above this scale, chromium oxide is found in the pit, and in contrast to the previously described pit, no nickel is found here. In contrast to the previously described pits, the substrate below the pit shows no depletion. In the salt, nickel is presently dissolved and precipitated as an oxide.

As these pits are larger and show a microstructure that is similar to the subsequently described pits from the propagation stage, they are proposed to be the result of the advanced corrosion stage. In contrast to the previously described pits, these larger pits were not able to re-establish a chromium oxide scale; instead, a porous chromium sulfide scale was developed, as shown in Figure 8 in comparison with Figure 7. For the formation of chromium sulfides, a lower oxygen partial pressure must be present. This can be established by the inward diffusion of the sulfur-bearing molecules and the long diffusion paths through the observed chromium oxide. The absence of nickel in the pit indicates that nickel is rapidly diffusing outward from the substrate and is dissolved into the deposit. In the stability range of chromium sulfides and the substrate, only Na$_2$SO$_4$ and nickel sulfides are stable. As here no sodium is observed, the outward diffusion of nickel is believed to occur as sulfides, in which the nickel diffusion is several orders of magnitude higher than in nickel oxide. At the corrosion front, chromium will be sulfidized first, as it is more stable. The formation of a continuous chromium sulfide scale is disrupted by the formation of nickel sulfides. The outward diffusion of nickel sulfides leaves the chromium sulfides behind with the observed high porosity. The presence of the Ni–S eutectic, which is the stable phase in contact with the substrate, will enhance this effect, as the outward migration of the liquid into the porous sulfide
and oxide could occur due to capillary effects. As no depletion is observed below the pits, the corrosion front is believed to be advancing too fast for the formation of a depletion zone.

In the deposit, the typical dissolution and precipitation mechanism is proposed to take place. The nickel (as well as cobalt) is dissolved acidically and can contribute to the melting of the deposit. Nickel is observed to precipitate in the salt. The inward diffusion of SO₃, the main oxidant, results in a positive solubility gradient, and the outward diffusion of nickel would not be expected after the salt is saturated. As discussed previously, the basic dissolution of chromium oxides can occur due to the reduced acidity and result in a synergistic effect, which establishes a negative solubility gradient. As both effects are counteractive, the precipitation in the deposit is in agreement with both the inward diffusion of SO₃ and the synergistic effect.

### 3.2.3 The Propagation stage

The most advanced pits, shown in Figures 9 and 10, develop a porous chromium sulfide scale in contact with the substrate, similar to the pits previously described. In contrast, the chromium oxide in the pit is observed along with nickel species as alternating layers or dispersed in each other. The nickel species are sulfides (closer to the substrate) and oxides (closer to the salt deposit). In between these two areas, both nickel sulfide and oxide are sometimes observed to coexist, as shown in Figure 11. The nickel sulfides in these layers were identified via EDS as NiS (ratio Ni–S 1:1) and Ni₃S₂ (ratio Ni–S 3:2). The thickness of these layers differs. The layered structure is observed for the alloys that show the highest metal loss (NiCr₂₀ MgSO₄–Na₂SO₄, 300 hr, NiCr₂₀Co₁₀ Na₂SO₄, 300 hr, NiCr₂₀Co₁₀ MgSO₄–Na₂SO₄, 300 hr).

The NiCr₂₀Fe₁₀ alloy tested for 300 hr with MgSO₄–Na₂SO₄ (Figure 12) shows a porous layered structure, consisting of chromium oxides and sulfides in the inner part of the pit and mainly chromium oxides in the outer part. Nickel was only present in small amounts in the pit. The NiCr₂₀Fe₁₀ alloy tested for 300 hr with the Na₂SO₄ deposit shows no layers and only dispersed areas of oxides and sulfides. The substrate below the pits shows no chromium depletion.

In general, large nodules accumulate over the pits, which consist of nickel oxide, sulfide and sulfate, and residual salt. As can be seen in Figure 9, nickel oxide is the main precipitate, whereas nickel sulfide is only found inside the oxide and nickel sulfate around the oxide in contact with the salt or gas. Chromium is not found...
above the initial oxide scale. The salt is rich in nickel (as well as cobalt and iron), indicating the dissolution reaction and the formation of liquid eutectics. The iron precipitated similar to the nickel as an oxide in the deposit, but generally closer to the salt–gas interface and more uniformly distributed (no nodules), which is shown in Figure 12. For this alloy, significantly more NiSO₄(s) is also found, which is also more uniformly distributed above the whole pit. The cobalt is generally found along with nickel, either as a sulfate or, to a smaller extent, as an oxide.

**Figure 9** Electron microprobe analysis image and element maps of a cross-section of a NiCr20Co10 alloy after hot corrosion testing for 100 hr with a Na₂SO₄ deposit in synthetic air + 0.5% SO₂ atmosphere, showing the microstructure of (a) precipitate in deposit and (b) the pit. Carbon is derived by embedding, thus representing porosity in the corrosion products.

**Figure 10** Optical image of a cross-section of a NiCr20 alloy after hot corrosion testing for 300 hr with a MgSO₄–Na₂SO₄ deposit in synthetic air + 0.5% SO₂ atmosphere.
After the longest exposure time, samples NiCr20 tested with Na$_2$SO$_4$ and NiCr20Co10 tested with MgSO$_4$–Na$_2$SO$_4$ showed the spallation of the corrosion products. Below the spalled corrosion products, a new salt was found, which further reacted with the substrate. The microstructure of the subsequent corrosion did not change significantly. However, the spalled corrosion product was much thicker, especially for the NiCr20Co10 sample tested with the eutectic mixture shown in Figure 13. The spalled corrosion products consisted of layers of chromium oxide and layers of a mixture of sodium, magnesium, nickel, and cobalt sulfates.

Since the porous chromium sulfide scale is similarly already observed in 3.2.2 Transition to the propagation stage, the previously described sulfidation of both chromium and nickel and the subsequent outward diffusion of nickel sulfides remain the same. In contrast with the previously described pits, nickel is still present in the pit, either as an oxide or a sulfide. This implies that the dissolution and precipitation mechanism at the oxide–salt interface is not fast enough to dissolve all the delivered nickel.

The layered structure represents the partial pressure of oxygen and sulfur, and it can be associated with the regime in which the nickel sulfides coexist with chromium oxide, as shown in Figure 14. The formation of these layers is an effect of the diffusion kinetics, local alloying element activity, and changes in the local partial pressure. The local chromium consumption determines this behavior, as it is the strongest sulfide- and oxide-forming element present. Above a chromium sulfide scale, either outward diffusing nickel forms sulfides or chromium oxidizes with the increase in the oxygen partial pressure. The nickel oxide layers, which are observed further in the pit in the regime of higher oxygen partial pressure, are the result of the oxidation of the nickel sulfide layers. Figure 11 shows the oxidation of the sulfide layer starting from the porous oxide.
layers. Upon oxidation of sulfides, the released sulfur is advancing deeper into the substrate, where it further enhances the corrosion. The microstructure also shows that chromium does not sulfidize and subsequently oxidize, but it diffuses to form the layers, which is in contrast to the mechanism for cobalt-based alloys where the rapid dissolution of elements leaves the porous chromium oxide scale behind. For the NiCr20Fe10 alloy tested with the MgSO4–Na2SO4 deposit for 300 hr, alternating chromium oxide and sulfide layers are observed. These layers can form simultaneously with chromium when the oxidant is a sulfur- and oxygen-bearing species (SO2 or SO3). The formation of one species, oxide or sulfide, will increase the oxygen or sulfur partial pressure, respectively, and therefore allow for the formation of the other. The Cr–S2–O2 and Ni–S2–O2 stability diagrams and the profiles of the partial pressure are shown in Figure 14, based on the sulfur and oxygen partial pressures. The sulfur partial pressure was chosen instead of the SO3 partial pressure because the corrosion products suggested extremely reducing conditions. As for the NiCr20Fe10 alloy, generally smaller amounts of nickel are found in the pit and the typical layers have not formed, the corrosion is proposed to be less advanced, which is in agreement with the lower metal loss of these alloys.

The dissolution and precipitation mechanism in the deposit seems to remain the same as in the pits earlier described and only advanced. The precipitates form nodules, whose microstructure is explained by the gradient of the partial pressures. NiSO4(s) is the stable phase for the given gas composition and is found in the outer part. Throughout the nickel sulfate layer, the sulfur and oxygen partial pressure decreases and nickel oxide becomes stable below it. Inside nickel oxide, the oxygen partial pressure is reduced, which may result in the formation of nickel sulfide.

The spalled corrosion product shown in Figure 13 and especially its thickness can be explained by assuming that the sulfate layer was nickel sulfide or oxide before spallation (as observed for the other specimens). As the corrosion product spalled the nickel sulfide is oxidized and dissolved to form the observed sulfates. This dissolution is in competition with the dissolution at the corrosion front, which will, therefore, result in a slower corrosion rate afterwards. Furthermore, a decreased corrosion rate below a thick corrosion scale is expected, because the diffusion path is longer and the salt deposit is saturated. Regarding the kinetics, this means that the NiCr20Co10 alloy tested with the MgSO4–Na2SO4 deposit has encountered an even higher corrosion rate during the 100–200-hr cycle and only a reduced rate during the last cycle. This is in agreement with the previously described negative influence of cobalt.

4 | CONCLUSION

In this paper, the microstructural progression and the metal loss of alloys NiCr20, NiCr20Co10, and NiCr20Fe10 during type II hot corrosion were investigated. It was shown that during the initial stages, chromium oxide scale formation is accompanied by internal sulfidation of chromium, which increases its depletion zone. During the subsequent pit formation, nickel is dissolved into the deposit, followed by precipitation, and only small amounts of nickel remain in the pit. Chromium remains below the initial surface as an oxide and near the substrate as a porous sulfide. For the most advanced pits, nickel is also found in the pit, forming nickel sulfides and oxides along with chromium oxides. The metal loss was investigated using a dimensional metrology technique. The time to propagation is similar for all alloys, and...
the observed trends are explained by the salt chemistry. The alloys are ranked from high to low metal loss, NiCr20Co10, NiCr20, and NiCr20Fe10, which is attributed to the influence of the alloying elements on the type II hot corrosion mechanism.

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