

Article



Corrosion of N10276 in a H_2S , HCl, and CO₂ Containing Atmosphere at 480 °C and 680 °C

Manuela Nimmervoll^{1,*}, Gregor Mori¹, Edith Bucher¹, Alexander Schmid² and Roland Haubner³

- ¹ Chair of General and Analytical Chemistry, Montanuniversität Leoben, A-8700 Leoben, Austria; gregor.mori@unileoben.ac.at (G.M.); edith.bucher@unileoben.ac.at (E.B.)
- ² OMV Downstream GmbH, A-2320 Schwechat, Austria; alexander.schmid1@omv.com
- ³ Inorganic Materials, Technische Universität Wien, A-1060 Wien, Austria; roland.haubner@tuwien.ac.at

Correspondence: manuela.nimmervoll@unileoben.ac.at

Abstract: In several industrial processes, metallic materials suffer from chlorine- and sulfur-induced high-temperature corrosion. In previous studies, several steels have been tested at laboratory scale in a simulated gas atmosphere of a pyrolysis process of anthropogenic resources. In this paper, we propose a model on the course of corrosion in a H₂S and HCl-containing atmosphere for N10276, which contains, besides iron, chromium, and nickel, also molybdenum as main alloying element. Bearing in mind the impact of the main alloying elements, as well as thermodynamic considerations and kinetic effects, the corrosion behavior of N10276 in a H₂S and HCl-containing atmosphere at 480 °C and 680 °C can be explained. In addition, the corrosion behavior of N10276 is compared with earlier tested Fe-Cr-Ni alloys and differences in the corrosion behavior are stated within this paper.

Keywords: HCl; H₂S; high-temperature corrosion; N10276

1. Introduction

High-temperature corrosion in mixed gas atmospheres is a problem of many industrial processes, e.g., ethylene dichloride production, gasification of biomass, coal, or waste. There, construction materials can suffer from chlorination and simultaneous sulfidation. If the partial pressure of oxygen is high enough and the materials can form protective oxide layers, the corrosion resistance of the materials increases. However, above 400 °C, chlorine or low molecular chlorine containing compounds, such as HCl, can migrate through the initial, protective oxide layer. There, they can form volatile metal chlorides with the base material. These metal chlorides can evaporate leading to porous and non-protective corrosion products [1-7].

Like the formation of oxide scales, also the formation of solid sulfide scales is possible if the partial pressure of sulfur is high enough. In general, metal sulfides have a much higher lattice defect concentration than the corresponding metal oxides. Therefore, diffusion coefficients in sulfides are higher resulting in faster growth rates of sulfides and less protection against corrosion compared to oxides. The only exceptions are slow growing sulfides of Mo, Nb, Mn, and Ta, which have a much lower non-stoichiometry. Research data showed that refractory-metal sulfides, such as MoS_2 , show only small stoichiometric deviations and that sulfidation rates are in the order of Cr_2O_3 [8–11].

In thermal cracking processes of anthropogenic resources, the atmosphere contains no oxygen and is reducing, but H_2S and HCl are present beside CO and CO₂. The influence of H_2S on the chlorine-induced high-temperature corrosion is not well investigated. Only a few authors, such as Bakker et al. [12,13] and Pan et al. [14] dealt with this topic and even found contrary results in some cases. Bakker et al. found an increase of the corrosion rates of iron by addition of H_2S to HCl-containing atmospheres above 400 °C. Pan et al. suggested a decrease of corrosion rate of Fe-Cr alloys due to the outward diffusion of volatile metal chlorides, which may slow down the penetration of sulfur containing species.



Citation: Nimmervoll, M.; Mori, G.; Bucher, E.; Schmid, A.; Haubner, R. Corrosion of N10276 in a H_2S , HCl, and CO₂ Containing Atmosphere at 480 °C and 680 °C. *Metals* **2021**, *11*, 1817. https://doi.org/10.3390/ met1111817

Academic Editors: Patrice Berthod and Christophe Rapin

Received: 22 October 2021 Accepted: 10 November 2021 Published: 12 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Recently, one of our industrial partners developed a new pyrolysis process of anthropogenic resources, where a mixture of post-consumer plastics and a highly aromatic residue of a refinery is cracked in a tubular reactor at high temperatures. Due to lack of knowledge about the corrosion behavior of commonly used construction materials in the atmosphere of this process, it was decided to investigate a broad range of materials with a wide variety of alloying elements. These should be specified in future works to find an appropriate reactor material. Thus, the corrosion resistance of several austenitic steels was investigated under conditions simulating the pyrolysis process of our industrial partner and some corrosion mechanisms to explain the formation of the complex corrosion layers for these materials were developed [2,3,15,16].

Besides the earlier tested austenitic alloys, also the material N10276 was chosen for corrosion experiments since it was suggested by experts from an alloy manufacturer to be one of the most resistant materials in various gas atmospheres at high temperatures. After corrosion tests with N10276 under the same conditions as in the prior experiments, the material N10276 showed a different behavior. The results of N10276 are compared with the findings of the materials S31400 and N06600, which were published in previous studies [15,16]. A detailed comparison can be found in the Discussions section in Section 4.3.

2. Materials and Methods

High-temperature corrosion tests were performed at laboratory scale in an inert silica glass tube for 240 h at 480 °C and 680 °C. A scheme of the test equipment is shown in Figure 1. The test gas contained 3.8 vol.% HCl, 1.9 vol.% CO₂, 0.3 vol.% CO, 2.8 vol.% H₂, 0.02 vol.% H₂S, bal. N₂ representing the gas atmosphere of a thermal cracking process for anthropogenic resources. Partial pressures of sulfur, chlorine, and oxygen for the initial test gas atmosphere for both temperatures are given in Table 1. The gas mixture was transported via stainless steel tubes and added with a continuous gas flow of around 120 mL/min, which was verified by flow measurement. This volumetric flow rate corresponds to a linear gas flow velocity of around 0.004 m/s at 480 °C and of around 0.005 m/s at 680 °C. Before the experiments started, as well as during the heating and cooling process of the silica glass tube, the chamber was flushed with nitrogen. A more detailed experimental procedure can be found elsewhere [2,15].



Figure 1. Scheme of the testing equipment for high-temperature corrosion tests in hot gas atmospheres simulating a thermal cracking process [16,17].

Table 1. Partial pressures of sulfur, chlorine and oxygen of the given atmosphere at 480 °C and at 680 °C [bar].

Species	Partial Pressure at 480 $^\circ C$	Partial Pressure at 680 $^\circ C$
S ₂	$1.6 imes 10^{-09}$	$1.3 imes10^{-09}$
Cl ₂	$4.7 imes10^{-14}$	$7.5 imes10^{-13}$
O2	$3.6 imes 10^{-29}$	$9.1 imes 10^{-23}$

In this study, corrosion experiments were performed with the material N10276 (also known as 2.4819 or NiMo16Cr15W). The findings were compared with the results of the materials S31400 (also known as 1.4841 or X15CrNiSi25-21) and N06600 (also known as 2.4816 or NiCr15Fe), which were achieved during previous studies [3,15–17]. Table 2 shows the chemical composition of the different materials.

Table 2.	Chemical	composition	of tested	l materials	[wt.%].
----------	----------	-------------	-----------	-------------	---------

Material	Fe	Ni	Cr	С	Mn	Si	Мо	W/Co
N10276	5	59	15	0.01	1	-	16	4/2.5
S31400	52	20	25	0.07	1.5	1.5	-	-
N06600	<10	72.5	16.5	< 0.05	0.8	0.4	1	-

All samples with dimensions of 25 mm \times 10 mm \times 2 mm were ground with 1000 grit SiC paper, washed, degreased, and gauged before the tests were started. Four specimens of one material were accommodated simultaneously in the silica tube using a silica glass holder. The largest surface of each sample was aligned parallel to the gas flow as shown in Figure 2. Three corroded samples were used for the mass loss determination, one was cold mounted in epoxy resin and polished water-free with 3 µm diamond grit before they were investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). The water-free polishing was necessary to preserve water-soluble corrosion products to visualize unaltered cross sections of the corroded samples [18].



Figure 2. Appearance of corrosion products on N10276 after corrosion experiments with (a,b) magnified view.

XRD measurements were performed on a PanAlytical X'Pert Pro diffractometer (Bragg-Brentano geometry, CuK_{α 1,2} radiation (1.54060 Å, 1.54439 Å), X'Celerator multi-channel detector, zero-background silicon sample holder) with a scan length of 2.546° in the 20 range 5–70° with 10 s exposure time per scan length. The scans were then converted into 0.02° step-size bins. SEM/EDX measurements were performed after 15 s gold sputtering, using a SEM EVO MA 25[®] (Carl Zeiss AG, Oberkochen, Germany). As an electron source, a LaB6 cathode was used.

The mass loss was evaluated after all corrosion products were removed. For this purpose, the samples were cleaned with 5% hydrochloric acid for 30 s in an ultrasonic bath and with a wired brush. The additional mass loss of the materials due to the attack of

the hydrochloric acid and the wired brush was determined in prior experiments and was considered to be negligible [17].

Thermodynamic calculations were performed with the software FactSageTM (FactSage 8.1, GTT Technologies, Herzogenrath, Germany), whereby partial pressures and equilibrium concentrations of all species at 480 °C and 680 °C were calculated, based on the composition of the gas mixture mentioned above.

3. Results

After all corrosion experiments, N10276 showed a layer of golden and adherent corrosion products, whereby no scale spallation took place, as shown in Figure 2. In addition, elongated aggregates, which were a mixture of metal sulfides (MoS_2 , Ni_3S_2 , ($Ni_{0.713}Cr_{0.287}$)($Ni_{0.019}Cr_{0.981}$)₂S₄, Mo_3NiS_4), grow on the surface (Figure 2b).

In contrast, the corrosion products formed on S31400 and N06600, during experiments at 680 °C, were black and consisted mainly of pure chromium sulfides (Cr_2S_3 and Cr_3S_4) [15]. After tests at 480 °C, S31400 still showed a black corrosion layer, but the corrosion products of N06600 consisted also of nickel sulfides and were reminiscent of the corrosion products that formed on N10276.

Additionally, colorless crystals were detected at the colder parts of the silica glass tube after every corrosion experiment. XRD identified these crystals as FeCl₂, which evaporated from the samples, was carried away with the gas flow and crystallized outside of the furnace. The amount of detected FeCl₂ increased with rising temperature, which was an indication for the high vapor pressure of metal chlorides at high temperatures.

3.1. Evaluation of Corrosion Rate

The corrosion rates of the different materials are shown in Figure 3. At 480 °C, N10276 showed the highest corrosion resistance with a corrosion rate of around 0.17 mm y⁻¹ compared to S31400 and N06600, both with a corrosion rate of around 0.40 mm y⁻¹. At 680 °C, the behavior changed and N10276 had the worst performance with a corrosion rate of around 2.14 mm y⁻¹ compared to S31400 with a corrosion rate of around 1.63 mm y⁻¹ and N06600 with a corrosion rate of around 0.12 mm y⁻¹.



Figure 3. Corrosion rates vs. temperature of the tested alloys after corrosion experiments at 480 $^{\circ}$ C and 680 $^{\circ}$ C.

3.2. Phases Identified in the Corrosion Layer

SEM images and corresponding EDX mappings of metallographic cross sections of N10276 after corrosion tests at 480 $^{\circ}$ C and 680 $^{\circ}$ C are shown in Figures 4 and 5.



Figure 4. N10276 after 240 h at 480 $^\circ C.$ SEM and EDX element mapping of the cross section.



Figure 5. N10276 after 240 h at 680 °C. SEM and EDX element mapping of the cross section.

At 480 °C, the grown corrosion layer reaches a thickness of around 20 μm and the EDX mapping reveals a layer of nickel sulfide containing some iron, which formed above

a layer enriched in chromium (Figure 4). This looked similar to the corrosion layer that formed on N06600 and S31400, where also a layer of nickel sulfide containing some iron had formed above a chromium and oxygen containing layer. In addition, N10276 showed an accumulation of molybdenum in the corrosion zone. Chlorine and oxygen could be detected inside the whole layer of corrosion products.

At 680 $^{\circ}$ C, a thicker corrosion layer of up to 130 μ m has grown on the sample surface compared to lower temperatures. This is in correlation with the increasing corrosion rate of N10276 (Figure 3). A depletion of main alloying elements can be seen at the border area of the base metal. The layer of corrosion products consists mainly of clearly separated chromium and nickel sulfides, whereby also small amounts of molybdenum could be detected in the outer sulfide layer (Figure 5). Although no oxygen was found in the nickel sulfides, some oxygen could be detected in the chromium sulfide layer and inside the porous border area. Almost no iron could be identified inside the corrosion products, but as FeCl₂ crystals at the colder parts of the testing equipment. Porosity has occurred below the original substrate surface due to the evaporation of the volatile metal chlorides. An accumulation of chromium oxides and molybdenum is noticeable in this area. Sulfur and chlorine were able to penetrate through the corrosion products to the porous structure of the base metal. The behavior of N10276 at 680 °C is different to all other tested materials. Previous tested materials showed a continuous chromium sulfide layer on the surface above a chromium oxide layer instead of the clearly separated nickel sulfides and chromium sulfides.

Main difference of the corrosion behavior of N10276 at both temperatures, was that the material formed a layered and continuous structure of corrosion products at 480 °C, whereby separated crystals of different compositions formed at 680 °C. In addition, the deepness of corrosive attack of the base material increased at higher temperatures. XRD analysis of the corrosion products of N10276 revealed the phases MoS₂, Ni₃S₂, and Cr₂O₃, besides mixed sulfides of molybdenum, nickel and chromium (Figure 6). Pure chromium sulfides, such as Cr₂S₃ and Cr₃S₄ (Figure 7), which were found as corrosion products in previous studies, were not found for N10276.



Figure 6. XRD diffraction pattern of corrosion products formed on N10276.



Figure 7. XRD diffraction pattern of corrosion products formed on S31400 and N06600 at 680 °C. [19].

4. Discussion

4.1. Derivation of the Corrosion Mechanism

Due to the presence of several corrosive gas components and the resulting complexity of various simultaneous corrosion reactions, it is not possible to calculate the actual gas composition inside the corrosion layer. Thus, thermodynamic calculations of the base metal and the initial test gas atmosphere are only valid, if at all, for the initiation of the corrosion process. Due to constantly changing conditions and unpredictable concentration gradients inside the corrosion layer, thermodynamic data could only give a rough indication for the underlying corrosion mechanism and are not sufficient. For example, thermodynamic equilibrium calculations of iron with the given gas atmosphere at 680 °C revealed the formation of solid iron sulfide. However, after corrosion experiments at 680 °C no iron sulfide was detected in the corrosion layer by EDX or XRD analysis. Iron was only found in form of FeCl₂ crystals at the colder parts of the testing equipment. Kinetic effects and the high vapor pressure of FeCl₂ at 680 °C (around 4.4×10^{-03} bar) seem to be the reason for the suppression of the conversion of $FeCl_2$ to iron sulfide. A second example of constantly changing concentrations can be given for the formation of the detected FeCl₂ according to Equation (1). It must be taken into account that the reaction of the base metals with HCl produces hydrogen, which, however, is a reducing agent and thus reduces the reaction to metal chlorides. Thus, with increasing H₂ content the metal becomes more stable again.

$$Fe + 2 HCl \rightarrow FeCl_2 + H_2$$
 (1)

Therefore, thermodynamic data are not sufficient to describe the observed corrosion processes and the suggested corrosion reactions and mechanisms in the following chapters are derived by combining experimental findings (EDX mappings, XRD analysis) and kinetic considerations.

Corrosion Reactions

The entire corrosion process and the underlying chemical reactions can be divided into different areas. On the one hand, it is about the attack of HCl on the metallic material and on the other hand about the diffusion of the formed chlorides and subsequent reactions to oxides and sulfides.

As shown in several studies, HCl can penetrate the initial passive oxide layer of the materials, which naturally forms as soon as metals are exposed to a surrounding environment [20–23]. Most passive films are polyatomic combinations of metals and oxygen, whereby one of the most common passive layers is Cr_2O_3 . Cracks and pores in the passive layers are potential paths for chlorine through the oxide. However, it was shown that chlorine could also infiltrate a continuous oxide scale. In the case of chromium, it was suggested that the chlorine ions replace the oxygen ions in the Cr_2O_3 lattice and diffuse through the passive layer to the scale-alloy-interface [20–23]. It is assumed that the substitution of oxygen is easier for chlorine than for HCl, which agrees with the findings of Abels et al. [23], who revealed that chlorine is the more corrosive specimen than HCl. However, HCl of the test gas atmosphere is still able to move through the initial oxide layer of the materials. This could also be seen in the Cl-EDX mappings, where chlorine was detected in the border area of N10276. There it can react with the base metal (Me) to form metal chlorides according to Equation (2).

$$n HCl + Me \rightarrow MeCl_n + \frac{n}{2} H_2$$
 (2)

Therefore, the main alloying elements nickel, chromium, iron, and molybdenum, show different reactivity with HCl depending on the temperature and its local availability in the corrosion zone [17]. Referring to [24], the reactions of Mo with HCl and the corresponding chlorides are complex, because $MoCl_n$ with n = 2 to 6 are known. The Mo-Cl phase diagram shows that at 680 °C only $MoCl_2(s)$ is present in addition to a gas phase. At 480 °C there is $MoCl_3(s)$ in addition to the gas phase. $MoCl_4$ could be the main compound in the gas phase. However, except FeCl₂ that was found on the colder parts of the silica tube, no other metal chlorides could be identified by XRD. This could be due to their volatile behavior and a too small amount to be detected or due to a too fast conversion to other corrosion products since the metal chlorides can react with oxygen and sulfur compounds of the gas phase. Which reactions ultimately take place in the corroded zone depends on the chemical reactivity of the components and their local concentrations, as already mentioned.

Since reactions of CO_2 with metal chlorides are very unlikely, the formation of H_2O according to the water gas equilibrium is assumed (Equation (3)).

$$CO_2 + H_2 \leftrightarrow H_2O + CO$$
 (3)

This H_2O can react with the metal chlorides to the detected oxides, whereby the reaction with chromium chlorides to Cr_2O_3 , which was also found by XRD, is favored (Equation (4)).

$$3 \operatorname{H}_2O + 2 \operatorname{CrCl}_2 \to \operatorname{Cr}_2O_3 + 4 \operatorname{HCl} + \operatorname{H}_2 \tag{4}$$

Additionally, reactions of the metal with H_2S to the corresponding sulfides can take place. Reaction equations for the formation of Fe, Ni, Cr and Mo sulfides are shown in Equations (5) to (8).

$$H_2S + FeCl_2 \rightarrow FeS + 2 HCl$$
(5)

$$H_2S + NiCl_2 \rightarrow NiS + 2 HCl$$
 (6)

$$3 \operatorname{H}_2 S + 2 \operatorname{CrCl}_2 \to \operatorname{Cr}_2 S_3 + 4 \operatorname{HCl} + \operatorname{H}_2 \tag{7}$$

$$2 H_2 S + MoCl_4 \rightarrow MoS_2 + 4 HCl$$
(8)

After corrosion experiments at 680 °C, no iron sulfide could be detected in the corrosion layer, although thermodynamic calculations indicated its thermodynamic stability. Only FeCl₂ crystals were present in the colder parts of the testing equipment. Kinetic effects and the high vapor pressure of FeCl₂ at 680 °C seem to be the reason for the suppression of the conversion to iron sulfide.

With progressive corrosion, the corrosion layer becomes more porous due to the continuous evaporation of the metal chlorides, especially at higher temperatures. Thus, H_2S is also able to diffuse through the corroded zone to the base material, where it can react with the metallic phases still present there. These would be predominantly Mo and

Ni (Equations (9) and (10)) since Cr and Fe are mainly consumed by the formation to metal chlorides and oxides as discussed before.

$$H_2S + Ni \rightarrow NiS + H_2$$
 (9)

$$2 \operatorname{H}_2 S + \operatorname{Mo} \to \operatorname{MoS}_2 + 2 \operatorname{H}_2 \tag{10}$$

The interactions of the different reactions, at 480 $^{\circ}$ C and 680 $^{\circ}$ C are discussed in a corrosion model in the following chapter.

4.2. Suggested Corrosion Mechanisms

Considering the achieved results, EDX mappings, chemical reactions, vapor pressures of halides and diffusion gradients, a corrosion mechanism for N10276 at 480 $^{\circ}$ C as well as at 680 $^{\circ}$ C is suggested.

4.2.1. Corrosion Mechanism of N10276 at 480 °C

Figure 8 shows a schematic illustration of the proposed corrosion mechanism for N10276 at 480 $^{\circ}$ C (derived from Figure 4). The course of corrosion can be described as follows:

- HCl penetrates the initial oxide layer of the metal and metal chlorides are formed. The formation of metal chlorides is primarily based on the enthalpy of formation. The concentration of the elements is also important, because if a base metal has been removed by corrosion, a more noble metal can subsequently be attacked. In the present case, the last metal to react would be Mo.
- If the vapor pressures of the formed chlorides are high enough, the MeCl_n will diffuse outward of the corrosion layer. With decreasing vapor pressure, a bigger amount of MeCl_n will remain inside the layer. Thus, iron and nickel chlorides will diffuse faster since vapor pressures of those species are higher than for molybdenum and chromium chlorides (FeCl₂ > NiCl₂ > MoCl₄ > CrCl₂).
- As soon as the MeCl_n reach the surface of the corrosion layer, they can react with H₂S of the gas phase and form the corresponding sulfides.
- CO₂ reacts with H₂ to form H₂O, which further reacts with the remaining MeCl_n in the corrosion layer to form oxides. In the present case the H₂O will mainly react with CrCl₂ to form Cr₂O₃ since it has the lowest vapor pressure and therefore most of the chromium chloride will remain in the corrosion layer.
- With progressive corrosion, the porosity increases due to evaporation of metal chlorides. Consequently, H₂S has direct access to the base metal, where it can react with the main alloying elements to the corresponding sulfides.

4.2.2. Corrosion Mechanism of N10276 at 680 °C

Figure 9 shows a schematic illustration of the proposed corrosion mechanism for N10276 at 680 $^{\circ}$ C (derived from Figure 5). The course of corrosion at can be described as follows:

- HCl penetrates the initial oxide layer and metal chlorides are formed. The formation of FeCl₂ and CrCl₂ is favored, but the formation of small amounts of nickel and molybdenum chlorides is also likely.
- Depending on the vapor pressure the formed metal chlorides can diffuse outward (FeCl₂ > CrCl₂ > NiCl₂ > MoCl₄).
- On the surface, the metal chlorides react with the H₂S, whereby Cr₂S₃ and nickel sulfides are preferentially formed. As shown in Figure 5, it is noticeable that nickel sulfide and Cr₂S₃ crystallites are clearly separated from each other. After an initial nucleation, the two phases grow separately. Small amounts of Mo were measured evenly in the two sulfides formed. Due to the very high vapor pressure of FeCl₂ and the fast evaporation of this compounds no further reaction with the gas phase takes place. Thus, no iron sulfides were detected.

- CO₂ reacts with H₂ to H₂O, which reacts with the remaining metal chlorides inside the corrosion layer to form oxides.
- With progressive corrosion, the porosity increases due to evaporation of metal chlorides. Consequently, H₂S has direct access to the corroded zone of the base metal and can react with metallic Ni and Mo to the corresponding sulfides.
- Main driving force for the mass loss at 680 °C is the faster evaporation of the metal chlorides due to higher vapor pressures compared to 480 °C. This could also be verified by the increasing amount of detected FeCl₂ at the colder parts of the test equipment at higher temperatures.



Figure 8. Schematic illustration of the proposed corrosion mechanism for N10276 at 480 °C.



Figure 9. Schematic illustration of the proposed corrosion mechanism for N10276 at 680 °C.

4.3. Comparison of N10276 with Previously Investigated Steels

Compared to S31400 and N06600, N10276 showed the lowest corrosion rate at 480 °C (Figure 3). This could be due to the lower vapor pressures of formed metal chlorides. Since N10267 contains less iron than previously tested materials, the porosity formed by the evaporation of FeCl₂, which has the highest vapor pressure of all metal chlorides, is lower. Additionally, less FeCl₂ could be detected at 480 °C. Thus, the sulfidic corrosion layers formed on N10276 are not rapidly destroyed by evaporation of metal chlorides. Therefore, they represent a good diffusion barrier, and the corrosive components cannot easily penetrate the corrosion layer. Finally, yet importantly, the high molybdenum content and the formation of MoS₂ could also improve the protective effect of the corroded zone as found in other research studies [8–11].

At 680 °C the situation is reversed and N10276 shows the highest corrosion rates compared to the other materials (Figure 3). The high corrosion rates are likely due to the coincidence of various causes. Compared to N06600, N10276 contains less Ni but a high amount of Mo (Table 2). Since Ni is a major contributor to corrosion resistance at high temperatures, this could be one of the factors. In the case of N06600, the nickel remains almost metallic under these conditions, but for N10276 the nickel formed a sulfide on the surface. N10276 contains less Fe and Cr. Thus, the two elements are faster consumed by corrosion processes and nickel could be earlier attacked by HCl to form NiCl₂. The NiCl₂ diffuses outwards of the corrosion layer and forms nickel sulfide as soon as it contacts H₂S.

Additionally, the strong increase in corrosion rate of N10276 at 680 °C can be explained by the rising vapor pressures of formed metal chlorides with temperature. As already shown in previous studies, the formation of metal chlorides and their vapor pressures at elevated temperatures play an important role in the corrosion behavior of the materials [2,3,15–17]. Even if the materials can form protective scales, the materials are not able to preserve the protectiveness due to continuous evaporation of metal chlorides.

Compared to S31400, the difference in the corrosion rate to N10276 is much smaller at 680 °C. S31400 has a higher iron content and thus, significantly more FeCl₂ evaporates. However, due to a higher chromium content, the material S31400 can form a more consistent Cr_2O_3 layer (reaction of CrCl₂ with formed H₂O (Equation (4)). In total, the resulting corrosion layer of S31400 forms a slightly better diffusion barrier than that of N10276.

5. Conclusions

The material N10276 was tested under conditions simulating a thermal cracking process of anthropogenic resources. Contrary to previous tested Fe-Cr-Ni alloys [2,3,15–19], N10276 additionally contains the alloying element molybdenum (16 wt.%) and only very little iron (5 wt.%). Thus, the material showed a different corrosion behavior in the HCl and H_2S containing atmosphere, which was critically discussed in a corrosion model. The following are major conclusions obtained from this research:

- In general, the corrosion rates of all materials increased with rising temperature.
 - At 480 °C, N10276 showed a better corrosion resistance compared to previous tested materials without molybdenum.
 - At 680 °C, N10276 showed the worst performance compared to the materials without molybdenum.
- During corrosion of N10276 in a H₂S, HCl, and CO₂ containing environment, HCl attacks besides the main elements Fe, Cr, and Ni also Mo to form the corresponding metal chlorides.
- Corrosion products that formed on N10276, where different to those formed on previously tested Fe-Cr-Ni alloys.
 - At 480 °C, all materials formed a layer of nickel sulfide containing some iron, which formed above a layer enriched in chromium. Contrary to the other materials, N10276 also showed an accumulation of molybdenum in the corrosion zone.

- At 680 °C, N10276 formed separated nickel sulfides containing molybdenum and chromium sulfides compared to previous tested Fe-Cr-Ni alloys, which formed a chromium sulfide layer below a chromium oxide layer but no nickel sulfides. The nickel sulfide and chromium sulfide crystals that form on N10276 do not form a tight diffusion barrier and further corrosion can take place. These circumstances lead to the high rate of corrosion of N10276.
- At high operation temperatures alloys with high molybdenum content are not necessarily beneficial for the corrosion resistance of materials in complex gases.

As soon as a mixture of more than one corrosive gas component is available in the atmosphere, corrosion mechanisms are more complex and reaction products are sometimes hard to predict. Thermodynamic data are not sufficient to describe the present corrosion mechanisms since the gas pressures and concentration gradients inside the corrosion layer change due to a variety of simultaneous chemical reactions. Thus, it is only possible to describe the underlying corrosion mechanisms by combining practical findings and kinetic considerations.

Author Contributions: Conceptualization, M.N., G.M. and R.H.; methodology, M.N. and A.S.; formal analysis, M.N. and A.S.; investigation, M.N. and A.S.; resources, M.N., A.S. and E.B.; data curation, M.N., A.S. and E.B.; writing—original draft preparation, M.N.; writing—review and editing, M.N., G.M. and R.H.; visualization, G.M., A.S., E.B. and R.H.; supervision, G.M., A.S. and R.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: The materials were provided by Sandvik, which is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Doublet, S.; Schütz, M.; Latreche, H. Development of corrosion assessment diagrams for high temperature chlorine corrosion— Part I. Oxid. Met. 2009, 72, 1–30.
- Schmid, A.; Mori, G.; Haubner, R.; Weil, M.; Hönig, S. Behaviour of S31400 and S32205 steels in HCl- and H₂S-containing gas atmospheres under a low oxygen partial pressure between 480 and 680 °C. *Mater. Corros.* 2018, 69, 1–10. [CrossRef]
- Schmid, A.; Mori, G.; Strobl, S.; Haubner, R.; Hönig, S. Corrosion of various Fe and Ni based alloys in HCl, H₂S containing environments, with low oxygen partial pressure, at 680 °C. In Proceedings of the EUROCORR 2017, Prague, Czech Republic, 3–7 September 2017.
- 4. Bramhoff, D.; Grabke, H.J.; Schmidt, H.P. Influence of HCl and N₂ on high temperature corrosion in atmospheres with low oxygen pressures. *Werkst. Korros.* **1989**, *40*, 642–650. [CrossRef]
- 5. Asteman, H.; Spiegel, M. Investigation of the HCl (g) attack on pre-oxidized pure Fe, Cr, Ni and commercial 304 steel at 400 °C. *Corr. Sci.* 2007, *49*, 3626–3637. [CrossRef]
- 6. Bramhoff, D.; Grabke, H.J.; Schmidt, H.P. *The Role of Active Elements in the Oxidation Behaviour of High Temperature Metals and Alloys*; Elsevier: Brussels, Belgium; Luxembourgh, 1989; pp. 335–349.
- 7. Bakker, W.T. The effect of chlorine on mixed oxidant corrosion of stainless steel. Mater. High Temp. 1997, 14, 197–206. [CrossRef]
- 8. Przybylski, K.; Grzesik, Z. Sulfidation of metallic materials. In *Developments in High-Temperature Corrosion and Protection of Materials*; Woodhead Publishing Limited: Camebridge, UK, 2008; pp. 599–638.
- 9. Schütze, M. Fundamentals of High Temperature Corrosion. Mater. Sci. Technol. 2013, 67–130. [CrossRef]
- Mrowec, S. Similarities and Differences in Defect Dependent Properties of Transition Metal Sulphides and Oxides. *Inorg. Chem.* 1989, 9, 55–99.
- 11. Rau, H. Estimation of the Homogeneity Range of MoS₂. J. Phys. Chem. Solids 1980, 41, 765–767. [CrossRef]
- 12. Bakker, W.T.; Perkins, R.A. Beyond mixed oxidant corrosion-corrosion phenomena in gasifiers. Presented at Ninth Annual EPRI Conference on Gasification Power Plants 1990, Palo Alto, CA, USA, 16–19 October 1990.
- 13. Bakker, W.T.; Perkins, R.A. Materials for Coal Gasification; ASM International: Cincinnati, OH, USA, 1988; pp. 85–96.

- 14. Pan, T.J. Corrosion behaviour of three iron-based alloy in reducing atmospheres containing HCl and H₂S at 600 °C. *Corr. Sci.* **2007**, *49*, 1362–1377. [CrossRef]
- 15. Nimmervoll, M.; Mori, G.; Schmid, A.; Haubner, R.; Hönig, S. Surface sulphide formation on high-temperature corrosion resistant alloys in a H₂S-HCl-CO₂ mixed atmosphere. *Corr. Sci.* **2021**, *181*, 109241. [CrossRef]
- 16. Schmid, A.; Mori, G.; Bucher, E.; Haubner, R. Model about the course of corrosion reactions of austenitic steels in H₂S-, HCl- and CO₂-containing atmospheres at 680 °C. *Oxid. Met.* **2019**, *91*, 1–10. [CrossRef]
- 17. Schmid, A.; Mori, G.; Haubner, R.; Weil, M.; Strobl, S.; Hönig, S. Comparison of the high-temperature chloride-induced corrosion between duplex steel and Ni based alloy in presence of H₂S. *Corr. Sci.* **2018**, *139*, 76–82. [CrossRef]
- 18. Schmid, A.; Mori, G.; Hönig, S.; Strobl, S.; Haubner, R. High Temperature Corrosion of Steel X15CrNiSi25-21 (1.4841) in a Mixed Gas Atmosphere. *Prakt. Metallogr. Pract. Metallogr.* 2019, *56*, 457–468. [CrossRef]
- 19. Schmid, A. Chlorine and Sulphur Induced High Temperature Corrosion in a Thermal Cracking Reactor for Anthropogenic Resources. Ph.D. Thesis, University of Leoben, Leoben, Austria, 2018.
- 20. Kunze, E. Korrosion und Korrosionsschutz; Wiley–VCH: Berlin, Gremany, 2001.
- 21. Young, D.J. High Temperature Oxidation and Corrosion of Metals; Elsevier Ltd.: Amsterdam, The Netherlands, 2016.
- 22. Stott, F.H.; Prescott, R.; Elliott, P. Corrosion resistance of high temperature alloys in gas containing hydrogen chloride. *Mater. Sci. Technol.* **1990**, *6*, 364. [CrossRef]
- 23. Abels, J.M.; Strehblow, H.H. A surface analytical approach to the high temperature chlorination behaviour of inconel 600 at 700 °C. *Corr. Sci.* **1997**, *39*, 115–132. [CrossRef]
- 24. Jehn, H.; Kurtz, W.; Schneider, D.; Trobisch, U.; Wagner, J. Mo Molybdenum, Gmelin Handbook of Inorganic and Organometallic Chemistry; Springer: Berlin/Heidelberg, Germany, 1989.