On the effect of oxide scale stability on the internal nitridation process in high-temperature alloys

Dedicated to Professor Dr.-Ing. habil. Dr. h. c. Heinrich Oettel on the occasion of his 65th birthday

1. Introduction

The effect of oxide scale stability on the extent of the proceeding internal corrosion attack is an important factor determining the service life of components operating under high-temperature conditions. Once an external oxide layer has formed, its mechanical stability is primarily determined by the behaviour of the substrate/oxide system during mechanical loading [1, 2] and/or thermal cyclic exposure [3]. The knowledge about scale-degradation mechanisms and their quantification with respect to service life until failure is highly significant for life prediction of technical components. Therefore, scale-spallation-modelling programs [4–6] are useful tools, e.g., to extrapolate cyclic thermogravimetric data. Whenever a part of the external scale cracks or spalls, the following corrosion process is defined by the current thermodynamic stabilities and the diffusivities of the species involved in the corrosion process at this position.

If thermal cycling is accompanied by subsequent oxide spallation, scale-forming elements (e.g., Al and Cr) may deplete in the near-surface region rapidly. Finally, the alloy will lose its rehealing properties, i.e., its ability to form slow-growing and dense oxide scales like alumina or chromia. This leads to a transition to less-protective oxide scale formation with higher defect densities, like spinel phases, nickel or iron oxides [7]. This stage is often termed as “breakaway oxidation” and is characterized by a rapid weight gain due to the increased formation of less-protective corrosion products [8]. Microstructural degradation processes, like the dissolution of the strengthening β phase in Ni-base superalloys and nitride precipitation (e.g., TiN and AlN) [9], can occur, leading to a strong deterioration of the mechanical performance of the near-surface layer.

In the present paper, selected examples are given, referring to scale failure in combination with internal nitridation processes in nickel-base alloys. The absence of a dense, external layer can be attributed either to thermodynamic instability as shown for the chromia-forming alloy Nicrofer 7520Ti as well as to thermally induced stresses or growing stresses that are particularly present in the vicinity of edges. In order to model the interaction of scale spallation and internal corrosion processes, as it can be observed experimentally on chromia- and alumina-forming nickel-base alloys, a computer model of internal nitridation has been expanded accordingly.

2. Experimental procedure

The chemical compositions of the polycrystalline Ni-base superalloy Nicrofer 7520Ti (Alloy 80A) and the single-crystalline superalloy CMSX-4 used in this study are given in Table 1. Nicrofer 7520Ti is a chromia-forming, CMSX-4 an alumina-forming alloy. The materials were obtained as cylindrical rods of 10–12 mm diameter. In the case of CMSX-4, cylindrical rods of 10 mm diameter were machined from turbine-blade roots by spark erosion cutting (EDM).
For the thermogravimetric experiments, discs of 1 mm thickness were cut from the rods. The specimens were ground with SiC abrasive paper down to 1200 grit and polished with 1 μm diamond suspension. Prior to the corrosion tests, the specimens were cleaned ultrasonically in ethanol. The isothermal and cyclic corrosion tests were performed using a self-designed thermobalance with a sensitivity of $10^{-5}$ g, which is equipped with a computer-controlled lift that can move the specimen periodically into and out of the hot zone of the furnace within a few seconds to allow rapid heating and cooling rates. Each temperature cycle of the cyclic oxidation experiments consisted either of 5 h or 1 h dwell times at $T = 1000$ °C, and a 15 min period of cooling down to room temperature. Nitriding tests were performed in a nitrogen-based gas atmosphere, consisting of 50 vol.% N$_2$, 45 vol.% He, and 5 vol.% H$_2$. In order to suppress the formation of chromia, titanium sponge was placed close to the specimen. This lowers the oxygen partial pressure to a value below $p$(O$_2$) = $10^{-16}$ Pa.

The composition, phases, and morphology of the corrosion products formed within the external scale and the subsurface region of the alloys were investigated by scanning electron microscopy (SEM) of the corroded surfaces and of cross-sections of the exposed specimens.

### Table 1. Chemical composition (in wt.%) of the Ni-base superalloys studied.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Co</th>
<th>Ta</th>
<th>Mo</th>
<th>Re</th>
<th>Hf</th>
<th>W</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicrofer 7520Ti</td>
<td>bal.</td>
<td>20.2</td>
<td>1.6</td>
<td>2.7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.2Fe</td>
<td></td>
</tr>
<tr>
<td>Ni–20Cr–6Ti</td>
<td>bal.</td>
<td>20</td>
<td>–</td>
<td>6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>CMSX-4</td>
<td>bal.</td>
<td>6.0</td>
<td>5.6</td>
<td>1.0</td>
<td>10.0</td>
<td>6.0</td>
<td>0.6</td>
<td>3.0</td>
<td>0.1</td>
<td>6.0</td>
<td>–</td>
</tr>
</tbody>
</table>

### 3. Results

#### 3.1. Corrosion of chromia-forming alloys

**a) Exposure to oxidizing atmosphere**

During isothermal exposure of the commercial alloy Nicrofer 7520Ti, an NiO scale is formed on the surface of the specimens (Fig. 1a). Underneath this scale, a mixture of different oxide phases is present followed by an internal-oxidation zone consisting of aluminium oxide (Al$_2$O$_3$) and titanium oxide (TiO$_2$) precipitated preferentially along alloy grain boundaries.

The formation of a thick external oxide scale mainly consisting of Cr$_2$O$_3$ results in a decrease of the nitrogen diffusion to sub-surface regions. Although near to the surface, the formation of oxides is more probable than the formation of nitrides (due to the higher stability of most oxides); the formation of nitrides becomes more likely deeper in the alloy, where the oxygen activity has dropped to very low levels.

#### 3.2. Nitriding experiments

During nitriding, the formation of a thin AlN layer is observed on the specimen surface. The nitriding process leads to a significant mass gain, as shown in Fig. 2b.

Fig. 1. Oxidation of Nicrofer 7520Ti exposed to laboratory air at 1000°C for 100 h. (a) external and internal corrosion products, and (b) thermogravimetrically measured mass gain vs. time.

Fig. 2. Exposure of the alloy Nicrofer 7520Ti to nitriding atmosphere at 1000°C for a duration of 100 h. (a) internal precipitation zone consisting of a thin AlN and a thick TiN zone, and (b) thermogravimetrically measured mass gain vs. time.
values. As a result, only a small amount of internal TiN was found below the oxide scale. The mass gain during isothermal exposure of Nicrofer 7520Ti at 1000 °C follows a parabolic rate law (Fig. 1b). This characteristic behaviour supports the assumption that the corrosion processes are controlled by solid-state diffusion.

b) Exposure to nitriding atmosphere

Exposure of the alloy Nicrofer 7520Ti to a nitrogen-based atmosphere with low oxygen fugacity (\( p(O_2) < 10^{-16} \) Pa) and high nitrogen fugacity (\( p(N_2) = 5 \times 10^4 \) Pa) does not result in the formation of an external oxide scale as it was observed for the case of exposure to laboratory air. Figure 2a shows an SEM micrograph of a cross section of a Nicrofer 7520Ti specimen exposed for 100 h at 1000 °C to N\(_2\) atmosphere. A much thicker (>100 μm) internal nitride precipitation zone can be observed as compared to internal oxidation, because the diffusion of nitrogen is faster than that of oxygen in the Ni-base matrix [11]. No preferential precipitation along grain boundaries was observed as it happens during exposure to laboratory air (see Fig. 1a). The isothermal thermogravimetric measurement in N\(_2\) atmosphere revealed a parabolic rate law for the internal nitridation process (Fig. 2b).

Internal nitridation can also take place as a consequence of the occurrence of cracking or spalling of the oxide scale. In order to demonstrate this phenomenon on the Ni-base model alloy, Ni–20Cr–6Ti was first exposed to laboratory air at 1000 °C for a duration of 100 h, leading to the formation of a dense and adherent Cr\(_2\)O\(_3\) scale. Afterwards, a crack in the Cr\(_2\)O\(_3\) scale was generated by means of a diamond-wire saw, and the specimen was then exposed to nitriding atmosphere at 1000 °C for 100 h [12]. Figure 3 shows the damaged Cr\(_2\)O\(_3\) scale with a deep internal TiN precipitation zone just below the cracked oxide scale.

3.2. Corrosion of the alumina-forming alloy CMSX-4

Due to the higher thermodynamic stability of Al\(_2\)O\(_3\) as compared to Cr\(_2\)O\(_3\) and its very low defect concentration, a superficial alumina film is the most favourable oxide scale to be formed on high-temperature alloys, in order to establish a high protection to further corrosive attack of the substrate, especially at very high temperatures (>1000 °C), when chromia starts to form volatile oxidation products (e.g., CrO\(_3\)).

![Cr\(_2\)O\(_3\)](image)

Fig. 3. Internal nitridation of the model alloy Ni–20Cr–6Ti as a consequence of an artificial crack in the Cr\(_2\)O\(_3\) scale, Ref. [12].

With the formation of a very thin Al\(_2\)O\(_3\) scale, no internal nitridation is expected. However, a primary cause for material degradation is due to repeated cooling and heating, which causes the generation of thermal stresses in the oxide/substrate system. If the oxide scale is not able to withstand the arising stresses, the oxide scale will fail due to cracking if the scale—substrate adherence is not sufficient, spallation will occur. Then, the metal surface is exposed directly to the corrosive atmosphere, leading to further consumption of the oxide scale-forming element Al, resulting in a depletion below the critical concentration, which is necessary for the formation of a superficial, protective Al\(_2\)O\(_3\) scale. Eventually, this gives rise to fast corrosion attack, causing the so-called “breakaway oxidation” accompanied by internal corrosion [4, 5]. Cyclic oxidation testing in the laboratory is one of the fundamental ways to rate the high-temperature corrosion resistance of materials in a realistic way. The cycling frequency is an important variable to evaluate oxide scale integrity of Ni-base alloys [13].

In order to evaluate the influence of the dwell time on the corrosion behaviour of an alumina-forming Ni-base alloy, the alloy CMSX-4 was exposed to laboratory air at 1100 °C for a total duration of 100 h with two different hot/cold dwell times (1 h/0.25 h and 5 h/0.25 h). Figure 4 shows the measured mass changes vs. time representations. Obviously, the dwell time has a strong influence on the corrosion mechanism. During the initial oxidation stage (<5 h), there is a mass gain for both dwell times, and the oxidation follows a parabolic rate law with comparable rate constants. This finding allows for the assumption that up to 5 h exposure there is no influence of the cycling frequency on oxidation kinetics. However, after 5 h exposure, the sample subjected to short dwell times (1 h heating/0.25 h cooling) experienced a progressive, much faster mass loss than the specimen subjected to long dwell times (5 h heating/0.25 h cooling).

Figure 5 shows a cross-section of the alloy CMSX-4 exposed to air under thermal-cycling conditions with a dwell time of 1 h at 1100 °C and a 0.25 h cooling period for a total duration of 100 h. It can be seen that on some local sites the alumina scale had failed, leading to the oxidation of the elements Ni, Cr, and Co as well as to internal corrosion attack (TiN, Al\(_2\)O\(_3\)).

![Mass change of CMSX-4 alloy](image)

Fig. 4. Mass change of CMSX-4 alloy during exposure to laboratory air at 1100 °C for two different hot/cold dwell intervals: 1 h/0.25 h and 5 h/0.25 h.
3.3. Modelling and computer simulation

Generally, internal corrosion phenomena can be described by Wagner’s theory of internal oxidation [14], where (i) only one internally precipitating compound BO\textsubscript{v} of high thermodynamic stability in an alloy AB, and (ii) a substantially higher diffusion coefficient \(D\) of the corrosive species as compared to the one of the reacting alloying element \(D_B\) is assumed. In a simplified form, the precipitation depth \(n\) is a function of the exposure time \(t\) and can be expressed as:

\[
\frac{n^2}{\mathcal{v}} = \frac{D_0 c_0^B}{v v_B} t
\]

where \(c_0^B\) is the concentration of the corrosive species at the surface, \(c_0^B\) is the initial concentration of the reacting alloying element, and \(v\) is the stoichiometric coefficient of the precipitating compound BO\textsubscript{v}.

However, a treatment of internal corrosion problems that involve more than one precipitating species, compounds of moderate stability, high diffusivities of the metallic elements, or time-dependent changes in the test conditions (e.g., temperature or interface concentrations) is not possible by applying Eq. (1). The simulation of such a system requires a numerical approach which combines the processes of diffusion and chemical reactions.

The observations presented in this paper serve as the experimental basis to expand such a computer model that has been developed recently to simulate internal corrosion phenomena [15] for high-temperature corrosion processes under isothermal conditions. The central part of this program is a two-dimensional finite-difference diffusion calculation for all species involved in the corrosion process. The formation of corrosion products, e.g., internal oxides and nitrides, is taken into account by the commercial library of thermodynamic subroutines ChemApp, which determines the concentrations of precipitates and dissolved species according to local thermodynamic equilibrium.

As mentioned above, internal nitridation of technical Ni-base alloys is a process which occurs due to the loss of the ability of the bulk material to form a protective oxide scale or due to cracks within the oxide scale. Generally, the computer model is capable to consider such phenomena. The key factor is the correct definition of a criterion for the occurrence of damage in the oxide scales, since the formation of cracks and spallation can be attributed to different mechanisms. In this context, the model considers thermal stresses caused by temperature changes, stresses due to oxide scale growth, and mechanical stresses from external loading [16].

As an example, Fig. 6 represents the calculated concentration profiles of TiN as well as of nitrogen and titanium dissolved in the model alloy Ni–20Cr–6Ti underneath the cracked Cr\textsubscript{2}O\textsubscript{3} scale, as it is shown in the experimental part in Fig. 3.
Spallation of the oxide scale can be calculated using the cyclic oxidation spalling program (COSP) developed by Lowell et al. [17, 18]. An important assumption of this model is that the oxide scale growth rate depends only on the oxide scale thickness, and that oxide growth kinetics does not change during thermal cycling exposure. Figure 7 shows the comparison between the calculated (using COSP) and the measured mass change during cyclic oxidation of the model alloy Ni–20Cr–6Ti exposed to laboratory air at 1000 °C [19, 20].

4. Discussion

A parabolic corrosion rate is always expected when the chemical reactions are controlled by solid-state diffusion. After the formation of a dense superficial oxide scale, the corrosion process can only proceed if at least one of the reactants from the atmosphere or the substrate material can diffuse through the oxide scale.

The oxidation of the chromia-forming alloy Nicrofer 7520Ti results in a thick oxide scale during exposure at 1000 °C to air. A careful investigation of the growth mechanism of this oxide scale reveals the formation of pores within the oxide scale, indicating the original position of the substrate surface. That means, the oxide scale grows due to both, outward diffusion of cations and inward diffusion of oxygen anions.

Under thermal cycling oxidation conditions, the oxidation kinetics of Nicrofer 7520Ti is almost not influenced by the cycling condition (see Fig. 8). No spallation was observed as it usually occurs for alumina-forming alloys. The formation of the inner oxide scale and the preferential oxidation along alloy grain boundaries (see Fig. 1) probably promotes interlocking, leading to an increase of the oxide scale adherence.

The thermodynamic stability diagram (see Fig. 9) suggests the formation of a variety of corrosion products that are thermodynamically stable during exposure to oxygen/nitrogen mixtures at 1000 °C. Following this, the outermost part of the scale should be composed of a mixture of different oxides containing nickel, titanium, and aluminium.

Although the nitrides TiN and AlN are stable for low oxygen partial pressures, only a very small amount of TiN was formed during oxidation in laboratory air because of the very low nitrogen diffusivity through the oxide scale. However, when the oxide scale is damaged, e.g., by the formation of cracks (see Fig. 3), the substrate surface is exposed to an atmosphere strongly enriched in nitrogen and, as a consequence, internal nitridation can occur. During exposure of Nicrofer 7520Ti to nitriding atmosphere with an oxygen partial pressure less than $p(O_2) = 10^{-16}$ Pa, the formation of a Cr$_2$O$_3$ scale was suppressed, permitting the penetration of nitrogen into the substrate, and resulting in internal precipitation of AlN and TiN. Since TiN is the most stable compound, AlN is formed only close to the substrate surface.

The formation of a continuous superficial Al$_2$O$_3$ scale on the surface is possible when the initial aluminium concentration in the alloy is sufficiently high ($c_{Al} > 5$ wt.%). Al$_2$O$_3$ has a very low defect concentration [7], leading to the formation of a slow-growing and protective oxide scale.

It was shown in this study that an enhanced mass loss during the cooling cycle occurs, when alumina-forming alloys are exposed to air under thermal cycling conditions. The main reason for this behaviour is the difference in the coefficient of thermal expansion between alumina and the underlying metal substrate. The cycle frequencies seem to play an important role during thermal cycling exposure. During exposure at a higher cycle frequency, an increased mass loss compared to that with low cycle frequency was observed. As a consequence of this, the strong aluminium
depletion during thermal cycling exposure leads to a transition in the corrosion behaviour: oxidation is governed by “breakaway oxidation”. It has been shown that internal nitridation occurs as a consequence of cracks in the oxide scale or spallation of the protective oxide. Modelling of this phenomenon requires a numerical approach rather than the analytical solution of Wagner [14], since time-dependent boundary and initial conditions as well as the local thermodynamic equilibrium have to be taken into account. The combination of the finite-difference technique and the thermodynamic program ChemApp, as introduced in the previous chapter, is a promising and expandable way to model internal corrosion processes as a consequence of oxide scale failure.

5. Conclusions

- The internal precipitation rates of Ti and Al nitrides in chromia- and alumina-forming alloys obey a parabolic rate law. This indicates that the corrosion mechanisms are controlled by solid-state diffusion of all the reacting species.
- Inward oxide growth in chromia-forming alloys inhibits oxide scale spallation during thermal cycling exposure, due to an interlocking effect caused by intergranular oxidation. However, when the oxide scale is cracked, nitrogen can penetrate into the alloy, leading to internal nitride precipitation (especially TiN and AlN) due to their high thermodynamic stability.
- An enhanced mass loss due to spallation of a non-adherent Al$_2$O$_3$ scale is observed during cyclic oxidation of alumina-forming alloys, leading to internal corrosion.
- A numerical simulation model was developed to quantitatively describe the internal nitridation process as a result of a cracked oxide scale. The combination of the finite-difference technique with the thermodynamic program library ChemApp provides a powerful tool to predict complex high-temperature corrosion processes.
- Cyclic oxidation can be treated using the cyclic oxidation spalling program (COSP), by which oxide spalling can be predicted in good agreement with experimental results.

The financial support of Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. The authors thank Alstom Power, Baden, Switzerland, and Krupp VDM, Altena, Germany, for providing the materials used in this study.

References


(Received October 14, 2004; accepted February 8, 2005)

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