High-Temperature oxidation behaviour of model Co-Re-Cr alloys at low oxygen partial pressure

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Abstract
The oxidation behaviour of four model Co-Re-Cr alloys and a commercial Co-based alloy were investigated at 1,000°C and low-oxygen partial pressure of $p(\text{O}_2) = 10^{-16}$ bar, in order to proof the feasibility of a pre-oxidation treatment. Under suitable conditions of the pre-oxidation treatment, the oxidation of the highly reactive alloying element Cr is possible. All alloys studied form a continuous and dense Cr$_2$O$_3$ scale on the metal surface. The transport of chromium to the surface occurs mainly from the Cr-rich $\sigma$-phase, which becomes completely dissolved in the surrounding matrix after long exposure times. As a result of the Cr$_2$O$_3$ scale growth depletion of Cr occurs in the near surface region, leading to internal oxidation.

Introduction
Co-Re-Cr alloys present a new class of high-temperature alloys which are promising for applications at service temperatures beyond 1,200°C. The first investigations of this class of alloys showed rather poor oxidation resistance during exposure to laboratory air [1,2]. The aim of the study at this stage of the Co-Re alloy development is to derive options for an improvement of the oxidation resistance at very high temperatures. The improvement in the oxidation resistance of numerous high-temperature alloys by a pre-oxidation treatment is well known in the literature [3,4]. In most cases, this is accomplished by the formation of a slow-growing protective oxide layer. The pre-oxidation at low oxygen partial pressure allows selective oxidation of only the highly reactive elements in the alloy. Aluminium and chromium are by far the most important reactive suitable elements for many high-temperature alloys due to the formation of protective Al$_2$O$_3$ and Cr$_2$O$_3$ oxide scales on the alloy surface. The previous study has shown that the formation of Cr$_2$O$_3$ oxide in Co-Re-Cr alloys occurs, if the oxygen partial pressure in the ambient atmosphere is lower than $10^{-15}$ bar [5]. Studying the oxidation behaviour of model Co-Re-Cr alloys at low oxygen partial pressure can contribute to an improvement in the corrosion protection in technical applications by a suitable pre-annealing of the material but should also lead to a more complete understanding of the oxidation mechanisms of this class of materials.

An atmosphere containing oxygen at a low partial pressure is intended to be used in the operating environment of the Very High Temperature Reactor (VHTR) [6-9]. Helium is applied as cooling gas and contains small amounts of impurities, typically H$_2$, H$_2$O, CO, CH$_4$, CO$_2$ and N$_2$ [10]. The detailed investigations show that water vapour is the main oxidant and that the low oxygen partial pressure is governed by the H$_2$O/H$_2$ ratio.

First approach in explaining the observed corrosion effects is usually based on the comparison of either the calculated equilibrium oxygen partial pressure or the experimentally determined oxygen partial pressure in the flowing gas with the equilibrium oxygen pressure of the oxides of all elements present in the alloy. Figure 1 shows the dependence of the equilibrium oxygen pressure on the temperature of oxide formation. In this figure, only alloying elements of the model Re-alloys studied...
are taken into account. From the thermodynamic point of view, all considered oxides are stable in the reaction of the alloy with air \((p(O_2)=0.21 \text{ bar})\) at the temperatures of interest (above 1000°C). The low \(p(O_2)\) value applied allows only selective oxidation of Cr, but not the oxidation of Co and Re.

![Diagram showing the temperature dependence of equilibrium oxygen partial pressure for the formation of various oxides (calculated by the commercial software FactSage)](image)

**Fig. 1** Temperature dependence of equilibrium oxygen partial pressure for the formation of various oxides (calculated by the commercial software FactSage)

The dependence of the equilibrium partial pressure \(p(O_2)\) of pure oxides on the metal activity of the alloying elements considered is shown in Fig. 2. The dependence for solid Re-oxides is displayed in Fig. 3. The oxygen activity increases with decreasing metal activity for all oxides. The relatively small dependence at given temperature, which is simply determined by the ratio of the stoichiometric coefficients, allows in combination with the gap of intermediate oxygen pressure the use of a partial pressure value at which the oxidation of Co and Re does not occur but the formation of \(Cr_2O_3\) is possible from the thermodynamic point of view, even if the activities of the elements concerned are very small or if depletion of the element occurs in the alloy near the surface [6]. The rather strong dependence of the equilibrium partial pressure on the metal activity shown by ReO₃ (see Fig.3) can be neglected at the oxygen partial pressure of interest.
In this paper, results are reported from an investigation of the oxidation behaviour of model Co-Re-Cr alloys at 1,000°C and low oxygen partial pressures of $p(O_2) = 10^{-16}$ bar. The study aimed at a better understanding of the oxidation mechanisms.

**Material and Experimental Procedure**

Four model Co-based alloys were investigated in this study: (i) two ternary Co-Re-Cr alloys and (ii) two quaternary alloys Co-Re-Cr-C. The chemical composition of these model alloys is given in Table 1. The commercial Co-based alloy X-40 was used as reference alloy (see Table 2).

**Table 1**

<p>| chemical composition (in at.%) of the model Co-Re alloys studied |</p>
<table>
<thead>
<tr>
<th>Model alloy</th>
<th>Cr</th>
<th>Re</th>
<th>C</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-17Re-23Cr</td>
<td>23</td>
<td>17</td>
<td>---</td>
<td>bal.</td>
</tr>
<tr>
<td>Co-17Re-30Cr</td>
<td>30</td>
<td>17</td>
<td>---</td>
<td>bal.</td>
</tr>
<tr>
<td>Co-17Re-23Cr-2.6C</td>
<td>23</td>
<td>17</td>
<td>2.6</td>
<td>bal.</td>
</tr>
<tr>
<td>Co-17Re-30Cr-2.6C</td>
<td>30</td>
<td>17</td>
<td>2.6</td>
<td>bal.</td>
</tr>
</tbody>
</table>

**Table 2**  Chemical composition (in at.%) of the commercial alloy X-40 used as reference alloy

<table>
<thead>
<tr>
<th>Cr</th>
<th>C</th>
<th>Si</th>
<th>Ni</th>
<th>Mn</th>
<th>Fe</th>
<th>W</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.5</td>
<td>2.4</td>
<td>2.1</td>
<td>9.9</td>
<td>1.1</td>
<td>2.1</td>
<td>2.4</td>
<td>bal.</td>
</tr>
</tbody>
</table>

The thermogravimetric measurements were carried out in a gas-tight thermobalance which is shown schematically in Fig. 4. To obtain a low value of oxygen partial pressure a suitable mixture of He, H₂ and H₂O was used. The initial gas mixture of 90% He and 10% H₂ was saturated with water vapour by passing through a water bath. The content of water vapour could be adjusted by exactly controlling the temperature of the water bath. The oxygen partial pressure as well as the temperature were exactly controlled by means of an oxygen sensor complemented with a thermocouple and placed directly below the specimen. The gas tube to the furnace was heated up (to a temperature higher than the used dew point) in order to avoid the condensation of water vapour. The thermogravimetric experiments were carried out at 1000°C for 100 hours.

Samples with a dimension of 10x10x2 mm³ with rounded edges to avoid typical edge effects on oxidation were used for the thermogravimetric study. The samples were ground using SiC paper down to 1200 grit and were cleaned ultrasonically in ethanol prior to oxidation. A hole of 1 mm diameter was drilled for hanging the samples.
Fig. 4 Schematic representation of the thermogravimetric device with the arrangement used for the He-H₂/H₂O gas mixture adjustment.

The oxidized samples were embedded in epoxy, ground and polished using diamond paste of 1 µm as the last step of preparation. The morphology and composition of the oxide scales were analysed by means of scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy.

Results
The thermogravimetric results obtained from exposure at 1000°C and an oxygen partial pressure of $p(O_2) = 10^{-16}$ bar are presented in Fig. 5. The continuous increase of the thermogravimetric curves indicates that no spallation of the oxide layers occurs during isothermal exposure. Among the model Co-Re-Cr alloys, the highest oxidation kinetics is exhibited by the two alloys containing 30 at.% of Cr. The alloy Co-17Re-30Cr-2.6C shows a change in oxidation kinetics. A slow oxidation rate is abruptly increased after approximately 50 hours of exposure. This may be attributed to the formation of microcracks, microchannels or rupture of a dense and continuous scale after extended reaction, which, in turn, increases the oxidation rate [4].

The addition of C to the alloy Co-17Re-30Cr affects its oxidation behaviour in a detrimental manner, whereas the C in the alloy Co-17Re-23Cr improves the oxidation resistance by reducing the rate of mass gain. It is remarkable that the commercial alloy X-40 exhibits the lowest oxidation rate.
Fig. 5 Weight gain versus oxidation time - measured during oxidation at 1000°C and an oxygen partial pressure of about $10^{-16}$ bar.

Figure 6a shows a cross section of the alloy Co-17Re-23Cr after exposure to He-H$_2$/H$_2$O mixture for 100h at 1000°C. A continuous, about 20µm thick Cr-oxide layer ($\text{Cr}_2\text{O}_3$) has formed on the surface of the alloy. A zone of internal oxidation of Cr-oxide exists underneath the $\text{Cr}_2\text{O}_3$ outer layer. The bright metallic phase shown in Fig. 6a was identified as the intermetallic $\sigma$-phase, which is rich in Cr. It is remarkable that the $\sigma$-phase has almost completely dissolved in the near surface region (within the internal oxidation zone). The oxide surface is homogenous and no evidence of pores and/or cracks was observed (see Fig. 6b).
Fig. 6 Oxidation behaviour of the alloy Co-17Re-23Cr exposed to \( p(\text{O}_2) = 10^{-16} \) bar at 1,000 °C for 100h; (a) cross section observation and (b) surface morphology; (*) Detachment of the oxide scale as a result of metallographic preparation

Figure 7 shows the cross section and the corresponding EDX analyse of the near-surface region of the alloy Co-17Re-30Cr after exposure to the He-H\(_2\)/H\(_2\)O mixture at 1,000°C for 100h. The closed, continuous and about 50µm thick Cr\(_2\)O\(_3\) oxide layer appears to adhere well to the base metal. Similar to Co-17Re-23Cr, a zone of internal oxidation of Cr-oxide was found. It should be noted that preferentially the bright \( \sigma \)-phase is attacked, i.e., the formation of internal Cr\(_2\)O\(_3\) oxide occurs at the interface matrix/\( \sigma \)-phase). The dissolution of the \( \sigma \)-phase in the near-surface region is not detected as observed for the other alloys containing a smaller concentration of Cr (see Fig. 6a).
Fig. 7 Metallographic cross-section and EDX analysis of the Co-17Re-30Cr specimen oxidized at \( p(O_2) = 10^{-16} \) bar at 1,000 °C for 100h.

Figure 8 shows a cross section of the alloy X-40 after exposure to He-H₂/H₂O mixture at 1,000°C for 100h. The alloy forms a continuous, dense oxide layer which was identified as Cr₂O₃. An expanded zone of internal oxidation is also clearly visible.

Fig. 8 Oxidation behaviour of the commercial alloy X-40 exposed to \( p(O_2) = 10^{-16} \) bar at 1,000°C for 100h.
Discussion
In general, the type of oxide formed depends on the chemical composition of the alloy, the oxidation temperature and oxygen partial pressure [4]. For the alloy system Co-Re-Cr, only the oxide Cr$_2$O$_3$ is thermodynamically stable at the oxygen partial pressure of $p(O_2) = 10^{-16}$ bar at 1,000$^\circ$C. Much of the early data on Cr$_2$O$_3$ scale growth rates and mechanisms have been reviewed by Kofstad, who concluded that transport processes through growing Cr$_2$O$_3$ scales may, depending on the microstructure of the scale, involve lattice and grain boundary diffusion and vapor transport of the reactants along microcracks. Microchemical analysis of all alloys near the oxide/alloy interface reveals a considerable depletion of Cr as a result of the establishment of the protective Cr$_2$O$_3$-layer. For example, Fig. 9 illustrates the Cr-depletion in the alloy Co-17Re-30Cr. It is observed that the Cr depletion leads to a Cr concentration being nearly 50% of the initial Cr content in the alloy. This phenomenon was found in numerous investigations of different alloy systems [7, 8, 11, 12]. Hence, after longer exposure times, the Cr activity at the scale/alloy interface, which determines the corrosion reactions, differs from the initial values due to the depletion effect. That leads, in turn, to the internal oxidation, if the oxygen concentration gradient in the alloy is small, since the solubility product of Cr$_2$O$_3$ is exceeded remote from the alloy/oxide interface.

![Cr-depletion in the near-surface zone of the alloy Co-17Re-30Cr](image)

**Fig. 9** Depletion of Cr in the near-surface zone of the alloy Co-17Re-30Cr after exposure to $p(O_2) = 10^{-16}$ bar at 1,000$^\circ$C for 100h.

The oxidation kinetics of all alloys can be described by a parabolic rate equation:

$$\left(\frac{\Delta m}{A}\right)^2 = 2k_p t,$$

where $\Delta m$ represents the mass change, $A$ is the total surface area of the sample, $k_p$ is the parabolic rate constant and $t$ is the oxidation time.

The calculated parabolic oxidation rates of all alloys studied as well as some literature data of the parabolic rate constant for Cr$_2$O$_3$-forming alloys at 1,000$^\circ$C are shown in Table 3. The calculated parabolic constants are in a good agreement with the literature data. The comparison of rate constants for chromium oxidation reported by Young shows however a remarkable degree of scatter, namely, three orders of magnitude at 1,000$^\circ$C [17]. Caplan and Sproule explained that the difference in observed weight change kinetics is related to the different scale morphologies [14].
seems reasonable that the polycrystalline oxide grows rapidly due to the fast chromium grain boundary diffusion, leading to developing compressive stresses in the scale, while the single oxide scale grows slowly due to the extremely slow lattice diffusion of chromium. In this case, new oxide would form at the free outer surface, generating no stress. Data obtained in this study are in the same order of magnitude as other measured parabolic rate constants involving grain boundary diffusion.

Table 3  Comparison of the measured values of the parabolic rate constant $k_p$ with literature data.

<table>
<thead>
<tr>
<th>$k_p$, [g$^2$ cm$^{-4}$ s$^{-1}$]</th>
<th>Alloy studied/alloy system/reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 · 10$^{-12}$</td>
<td>Co-17Re-23Cr</td>
</tr>
<tr>
<td>1.6 · 10$^{-12}$</td>
<td>Co-17Re-23Cr-2.6C</td>
</tr>
<tr>
<td>4.7 · 10$^{-12}$</td>
<td>Co-17Re-30Cr</td>
</tr>
<tr>
<td>9.3 · 10$^{-12}$</td>
<td>Co-17Re-30Cr-2.6C</td>
</tr>
<tr>
<td>1.5 · 10$^{-12}$</td>
<td>X-40</td>
</tr>
<tr>
<td>4.5 · 10$^{-12}$</td>
<td>Co-base alloy DZ40M [13]</td>
</tr>
<tr>
<td>8 · 10$^{-12}$</td>
<td>Ni-20Cr+Si [6]</td>
</tr>
<tr>
<td>8 · 10$^{-12}$</td>
<td>pure Cr [14]</td>
</tr>
<tr>
<td>4 · 10$^{-12}$</td>
<td>Ni-base alloy IN 718 [12]</td>
</tr>
<tr>
<td>6 · 10$^{-12}$</td>
<td>Fe-20Cr [15]</td>
</tr>
<tr>
<td>5 · 10$^{-12}$</td>
<td>Ni-30Cr-0.2C [16]</td>
</tr>
</tbody>
</table>

The detrimental effect of the $\sigma$-phase on the mechanical properties of alloys as a consequence of high brittleness is well-known and reported by numerous authors [18,19]. According to the thermodynamic calculation (see. Fig. 10), the amount of $\sigma$-phase increases by a factor of three when the content of Cr in the alloy increases from 23 at.% up to 30 at.%. Because of the high amount of Cr and the resulting high volume fraction of the $\sigma$-phase in the alloy Co-17Re-30Cr, some cracks along the $\sigma$-phase were detected in a sample of this alloy (see Fig.11) prior to oxidation testing. Cracks appear to be a simple path for oxygen to penetrate into the alloy accelerating the oxidation rate (see Fig. 5). The addition of C to the alloy Co-17Re-30Cr was found to exhibit a negative influence on the oxidation behaviour in that manner that the amount of cracks in samples of the alloy Co-17Re-30Cr-2.6C obviously increases leading to a higher oxidation rate (see Fig. 5).
Fig. 10 Phase distribution in the Co-17Re-xCr system depending on Cr-concentration (calculated by the commercial software FactSage)

Fig. 11 Oxidized crack along the σ- phase in the alloy Co-17Re-30Cr after exposure to $p(O_2) = 10^{-16}$ bar at 1000°C for 100h.

Apart from detrimental mechanical properties of the σ-phase, its oxidation resistance is rather poor. It was shown in the previous study [1] that the σ-phase is preferentially attacked during high-temperature oxidation in air as compared to the metallic matrix. This is not surprising because the σ-phase is rich in the highly reactive element Cr (see Fig. 12). The high content of Cr and consequently the high volume fracture of the σ-phase in the alloy Co-17Re-30Cr decelerate the dissolution of the σ-phase as compared to the alloy with lower Cr concentration, namely 23% Cr. After the same exposure time, the alloy Co-17Re-23Cr shows a zone free of σ-phase (see Fig. 6a), while alloy Co-17Re-30Cr exhibits merely a zone with attacked or rather partially dissolved σ-phase (see Fig. 7).

Fig. 12 Element distribution in the σ-phase of the alloy Co-17Re-30Cr (calculated by the commercial software FactSage)
During oxidation, Cr is continuously transported from the \( \sigma \)-phase to the surface leading to the formation of a \( \text{Cr}_2\text{O}_3 \) scale on the surface. With increasing time, the \( \sigma \)-phase appearance in the near-surface region becomes brighter due to the partial loss of chromium. Part of Cr in the \( \sigma \)-phase becomes simultaneously oxidized (see Fig. 13). If the concentration of chromium in the \( \sigma \)-phase has fallen below the critical value, the \( \sigma \)-particles are complete dissolved in the surrounded hcp-matrix. The process leads, in turn, to the depletion of Cr in the near surface region and hence to the internal oxidation discussed above. A schematic illustration of these changes is presented in Fig. 13.

![Fig. 13](image)

**Fig. 13** Oxidation behaviour of the alloy Co-17Re-30Cr-2.6C exposed to \( p(\text{O}_2) = 10^{-16} \) bar at 1000°C for 100 hr; (a) morphology of the near-surface region and (b) details of the \( \sigma \)-phase attacked.

Prior to oxidation, Co-Re-Cr alloys exhibit a two phase microstructure, which consists of the \( \sigma \)-phase (depicted as a bright phase in Fig. 14a) and the hcp matrix. In the initial stage of the oxidation a thin film of \( \text{Cr}_2\text{O}_3 \)-oxide is formed on the metal surface as a result of the reaction of Cr with gaseous oxygen absorbed on the metal surface (see Fig. 14b). Once the film becomes continuous and dense, the reaction may only proceed through a solid-state diffusion of the reactants, namely, chromium and oxygen. As shown in Fig. 14c, the transport of Cr occurs mainly from the Cr-rich \( \sigma \)-phase of the near surface region, which becomes enriched in Re and Co. This feature is portrayed as a brighter \( \sigma \)-phase (see Fig. 14c,d). The chemical composition of the \( \sigma \)-phase continuously changes at this stage of oxidation because of the chromium outwards diffusion. When the reaction proceeds, the \( \sigma \)-phase becomes thermodynamically instable and hence dissolves in the surrounding hcp matrix. As a result of the \( \text{Cr}_2\text{O}_3 \) scale growth, depletion of Cr occurs in the near-surface region, which consequently leads to the internal oxidation as shown in Fig. 14d.
The best oxidation resistance of all Co-Re-Cr alloys investigated was shown by the alloy Co-17Re-23Cr-2.6C. Apart from the lowest parabolic rate constant listed in Table 3, the thinnest zone of internal oxidation was detected. The beneficial effect of carbon addition can be attributed to the effect of C-gathering through the formation of Cr-carbides suppressing the formation of σ-phase, which exhibits poor oxidation resistance as discussed above.

The question, whether a pre-oxidation treatment at low oxygen partial pressure promotes the formation of a Cr$_2$O$_3$ scale in such a way that this oxide layer can reliably prevent severe oxidation of the metallic substrate also at high oxygen partial pressure (e.g., in laboratory air), is still open. The oxidation behaviour in air at high-temperatures of Co-Re-Cr specimens pre-oxidized at low oxygen partial pressure is currently under investigation and the results will be published in a separate paper.

**Conclusion**

In this study, the sole formation of Cr$_2$O$_3$ oxide on four model Co-Re-Cr alloys at 1,000 °C as a consequence of exposure to an oxygen partial pressure of about 10$^{-16}$ bar adjusted by means of He-H$_2$/H$_2$O gas mixture was verified experimentally. All alloys form a continuous and dense Cr$_2$O$_3$ scale on the metal surface. The transport of chromium to the surface occurs mainly from the Cr-rich σ-phase, which dissolves in the surrounding matrix after long exposure times. While the alloy Co-17Re-23Cr shows a near-surface zone free of σ-phase, the higher Cr concentration of alloy Co-17Re-30Cr prevents the σ-phase from dissolution. As a result of the Cr$_2$O$_3$ scale growth depletion of Cr occurs in the near-surface region leading to the internal oxidation of Cr at the same distance from the surface.

**Acknowledgements**

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**References**