STRATEGIES FOR OPTIMIZING THE SELF-HEALING CAPACITY OF HIGH TEMPERATURE METALLIC COATINGS

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Components that need to operate at high temperatures, for instance blades and vanes in gas turbine engines, are usually coated with a metallic layer to protect the underlying substrate against oxidation and corrosion. The protection offered by this coating relies on the formation of a continuous surface oxide layer. Oxygen from the environment reacts with an element from the coating. This is a self-healing process, as is manifested most clearly when the metal component experiences a series of thermal cycles. Then, due to thermal mismatch stresses damage, of the oxide layer occurs upon cooling. Upon subsequent high temperature exposure the damaged areas of the oxide layer on the coating will be repaired.

In this paper, strategies are explored that can be used to enhance the self-healing capacity of high temperature metallic coatings. To this end, alloys of different design (i.e. with different type, quantity and distribution of minor element additions, and/or with different size and distribution of second phase particles) were subjected to thermal cycle tests. The results from these tests were analyzed quantitatively with a thermal cycling oxidation and spallation model. From the combined experimental and modelling results two parameters were extracted: one that characterizes the amount of damage induced upon cooling and the other signifies the rate at which the oxide layer heals at high temperature. These two parameters characterize the self-healing capacity of the coating material. A map constructed with these two quantitative parameters provides a guide to optimize the coating material for its self-healing capacity.

1 Introduction

A metallic coating is often applied to components that operate at high temperatures for protection against oxidation and hot corrosion [1-3]. For example, blades and vanes in gas turbine or jet engines are protected with a MCrAlX coating, where M denotes Ni and/or Co and X a reactive element such as: Y, Zr, Hf etc. This coating offers protection by forming a continuous alumina ($\alpha$-Al$_2$O$_3$) scale at the surface. Thus, the oxide layer forms a barrier between the environment and the underlying metallic component.

The addition of Cr to the alloy promotes the exclusive formation of the $\alpha$-Al$_2$O$_3$ surface layer [4]. This has the advantage that less Al is required in the alloy, which improves the mechanical properties and increases the melting point of the alloy.

The addition of a small amount of a reactive element (up to 0.5 at. %) improves the scale adhesion enormously [5, 6, 7].
It is generally recognized that the main effect of the reactive elements is scavenging of impurities like sulphur that are inevitably present in the coating after deposition. Segregation of S to the coating/oxide interface causes a significant decrease in scale adhesion. Besides scavenging of impurities, reactive elements can significantly promote the formation of $\alpha$-Al$_2$O$_3$, reduce the oxide growth rate, suppress formation of voids at the interface and create pegs for mechanical keying [8].

At high temperatures, the protective alumina oxide layer is formed by selective oxidation of Al from the coating alloy. This is a self-healing process, as is manifested most clearly when the metal component experiences a series of thermal cycles; see Fig. 1. Then, due to thermal mismatch stresses damage by fragmentarily spallation of the oxide layer occurs upon cooling. During subsequent high temperature exposure the damaged areas of the oxide layer on the coating will be repaired. However, the continuous repairing of the oxide layer slowly consumes the reservoir of the preferred oxide-forming element in the coating. Consequently, the self-healing capacity of the coating is reduced. Once the self-healing effect ends, less-protective oxides form internally in the coating and underlying substrate, thereby deteriorating the properties of the entire component. Therefore, it is vital to find strategies that optimize the self-healing capacity of the coating and thereby prolong the life span of the metal component.

![Image: Figure 1](image-url)

Figure 1: Damage and healing of protective oxide scale on a $\beta$-NiCrAl doped with 0.2 at.% Y high temperature coating alloy in a thermal cycle test. The bright spots are damaged areas. By comparing the macrographs for different numbers of cycles it is evident that new oxide has formed at the damaged areas. The thermal cycle test was carried out with buttons of the alloy with a diameter of 10 mm in air with temperature cycles of 9 minutes heating to 1163 °C, a high temperature oxidation dwell time of 45 minutes and subsequently 10 minutes cooling in ambient air.

## 2 Experimental

A series of high temperature coating alloys of different design (i.e. composition and microstructure; see Table 1) were subjected to thermal cycle testing. First, three baseline compositions in the Ni-rich portion of the Ni-Cr-Al phase diagram were selected: (i) $\gamma$ Ni-27Cr-9Al (fcc), (ii) $\beta$ Ni-4.5Cr-38Al (bcc) and (iii) $\gamma+\beta$ Ni-20Co-20Cr-24Al (compositions in at.%). Each baseline composition was tested with and without addition of 0.2 at.% Y as reactive element. Next, for the $\beta$ phase alloy coating, the type and amount of minor element additions were optimized. Besides Y, also Zr and Hf as reactive element addition were tested, and their amount was varied between 0.05 and 0.2 at.%. The single phase $\gamma$ Ni-27Cr-9Al and $\beta$ Ni-4.5Cr-38Al alloys were produced using high purity (>4N) Ni, Cr, Al and reactive elements (>3N) Y, Zr or Hf using the same batches of metal powders and so contain constant levels of impurities. These alloys were cast in the form of a cylindrical rod with a diameter of 12-15 mm.
Subsequently, these alloys were homogenized and re-crystallized by annealing in a sealed quartz tube filled with argon at 1100 °C during more than 100 h. The two phase γ+β Ni-20Co-20Cr-24Al cast alloy was supplied by Axel Johnson Metals Inc. (CA, USA). This alloy was also used to produce a 1 mm thick freestanding coating using electron beam physical vapour deposition (EB-PVD) by Sulzer Metco Coatings (Lomm, The Netherlands). For refining of the microstructure by laser surface melting (LSM) the same alloy was used (see for details Refs. [9, 10]). Disc-shaped specimens with a diameter of 10 mm and a thickness of 2 mm were for all alloys using spark-erosion. Prior to thermal cycle oxidation, the surfaces of the samples were ground and polished with 1 μm diamond paste as the final polishing step. After each polishing step the samples were thoroughly cleaned ultrasonically with isopropanol and dried by pure compressed nitrogen. Finally, the chemical compositions were determined by electron probe X-ray microanalysis (EPMA).

Thermal cycling oxidation tests were executed to assess the self-healing performance of the alloys. For each alloy design, i.e. composition and microstructure, two test specimens were prepared. These thermal cycle oxidation tests were performed in a furnace containing four horizontal ceramic tubes at the National Aerospace Laboratory (Marknesse, The Netherlands). Annealed alumina crucibles containing the specimens were placed within the ceramic tubes, which were inserted into and withdrawn from the furnace at the start and end of each cycle, respectively. Each temperature cycle comprised 9 minutes heating to 1163 °C, a high temperature oxidation dwell time of 45 minutes and subsequently 10 minutes cooling all in ambient air. Prior to thermal cycling and after certain numbers of cycles the mass of each specimen was weighed at room temperature using a microbalance. These data were used to obtain an experimental net mass change curve as function of cycle number for each sample.

Table 1: Alloy compositions and microstructures used for optimizing self-healing capacity of high temperature coatings (compositions in at.%)  

<table>
<thead>
<tr>
<th>Base composition</th>
<th>Type of reactive-element addition</th>
<th>Quantity of reactive-element addition</th>
<th>Processing / microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ Ni-27Cr-9Al</td>
<td>- / Y</td>
<td>0.2 %</td>
<td>Cast</td>
</tr>
<tr>
<td>γ+β Ni-20Co-20Cr-24Al</td>
<td>- / Y</td>
<td>0.2 %</td>
<td>Cast / LSM / EB-PVD</td>
</tr>
<tr>
<td>β Ni-4.5Cr-38Al</td>
<td>- / Y / Zr / Hf</td>
<td>0.05 % / 0.1 % / 0.2 %</td>
<td>Cast</td>
</tr>
</tbody>
</table>

3 Evaluation of self-healing capacity

A useful method to quantify the self-healing behaviour of a coating alloy is by simply monitoring the weight change in a thermal cycle test; see Sect. 2. In a thermal cycle test a specimen of the coating alloy experiences a series of temperature cycles in an oxidizing environment. Each cycle comprises heating to the oxidation temperature, a period at the oxidation temperature and cooling to room temperature. The experimentally determined net mass change curves as function of cycle number are the sum of the mass gain due to healing at the high temperature dwell of a thermal cycle and the mass loss due to damage upon cooling; see Fig. 2. To extract the amount of healing and damage during each cycle from the experimental data, a thermal cycling oxidation and spallation model can be used. From the various models available, the model developed by Smialek was adopted [11]. In this model, the sample surface of the alloy is envisioned to be divided into $n_0$ segments of equal area $F_A = 1/n_0$.  

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For each cycle $j$, it is assumed that during the high temperature dwell time $\Delta t$, each segment in the oxide scale with thickness $d_{ox}$ grows according to parabolic growth kinetics: $d_{ox}^2 = k_p t$, where $k_p$ is the parabolic growth rate constant and $t$ the oxidation time. This is a valid assumption for most of the oxide scales formed upon high temperature oxidation [12]. Furthermore, it is assumed that during each cycle, spalling of one of the thickest segments of the scale occurs at the oxide/metal interface upon cooling. The model is schematically represented in Fig. 3 and displays both oxide growth at high temperature and spallation upon cooling for $n_0 = 5$ and $j = 1, 2, 3$ and 6. Following these model assumptions, the total amount of healing $H$ as function of the cycle number can be described as:

$$H = \begin{cases} \frac{F_A \sqrt{k_p t}}{2} \left( \frac{1}{3} n_0^{3/2} + \frac{1}{3} j^{3/2} \right), & j \leq n_0 \\ \frac{F_A \sqrt{k_p t}}{2} \left( j n_0^{1/2} + \frac{1}{3} n_0^{3/2} \right), & j > n_0 \end{cases}$$  \hspace{1cm} (1)$$

The corresponding total amount of damage $D$ occurring upon cooling as function of cycle number can be expressed as:

$$D = \begin{cases} -S_c \frac{F_A \sqrt{k_p t}}{2} \left( j^{1/2} + \frac{2}{3} j^{3/2} \right), & j \leq n_0 \\ -S_c \frac{F_A \sqrt{k_p t}}{2} \left( \left( j + \frac{1}{2} \right) n_0^{1/2} - \frac{1}{3} n_0^{3/2} \right), & j > n_0 \end{cases}$$ \hspace{1cm} (2)$$

where $S_c$ is the molecular weight ratio of oxide to oxygen in a given oxide ($S_c = 2.12$ for $\alpha$-Al$_2$O$_3$). Finally, the net mass change per unit area ($\Delta W/A$) as function of cycle number, given as the sum of $H$ and $D$, can be written as:

$$\frac{\Delta W}{A} = \begin{cases} \frac{F_A \sqrt{k_p t}}{2} \left[ \frac{1}{2} (2n_0 - S_c) j^{1/2} + \frac{3}{2} \left( 1 - 2S_c \right) j^{3/2} \right], & j \leq n_0 \\ \frac{F_A \sqrt{k_p t}}{2} \left[ \left( 1 - S_c \right) j - \frac{1}{2} S_c \right] n_0^{1/2} + \frac{3}{2} \left( 1 + S_c \right) n_0^{3/2} \right], & j > n_0 \end{cases}$$ \hspace{1cm} (3)$$

In Eqs. (1) - (3) a different expression is used for cycle numbers $j$ larger than $n_0$, since there is an additional weight loss due to spallation that occurred previously up to $n_0$ cycles; see also Fig. 3.

Examination of Eq. (3) reveals that the data in a thermal cycle experiment, i.e. net mass change versus the number of cycles, can be described with only two parameters: the parabolic growth rate constant $k_p$ (a measure for the capacity to repair the oxide layer) and the area fraction of spallation $F_A$ (a measure for the damage susceptibility of the oxide layer).
Together, $k_p$ and $F_A$ are a measure for the self-healing capacity of the coating alloy. Optimum self-healing capacity is achieved when $k_p$ and $F_A$ have small values.

Figure 2: Illustration of the course of the net mass change (blue line) as function of number of cycles upon thermal cycle oxidation testing calculated using a thermal cycle oxidation interface spalling model [11]. The net mass change is the sum of the mass gain due to oxide healing (red line) and the mass loss due to oxide spallation (magenta line).

Figure 3: Illustration of the thermal cycle oxidation interface spalling model [11]. The mass gain due to oxide healing (blue and magenta), the mass loss due to oxide damage (magenta) and the net mass gain on the alloy surface (blue) for cycle numbers $j = 1, 2, 3$ and $6$ are displayed. For simplicity, only five oxide segments ($n_0 = 5$) are presented, with $k_p$ the parabolic oxide growth rate constant and $F_A$ the area fraction of spallation.

4 Results

A series of high temperature coating alloys of different design (i.e. composition and microstructure; see Sect. 2) were subjected to thermal cycle testing to find guidelines for the design of MCrAlX coatings to optimize their self-healing capacity from a combination of experiments and modelling. The experimental net weight change per unit of area as a function of the cycle number for all alloys tested, is presented in Figs 4, 5 and 6.
The two parameters \((k_p, F_A)\) expressing the self-healing capacity of the coating alloys were determined from the experimental data, by fitting the weight change data recorded in the thermal cycle tests to Eq. (3) using a linear least-square method. The results are displayed as a map in Fig. 7. From the mass change curves and the self-healing capacity map (i.e. \(F_A\) versus \(k_p\)) the following observations can be made. 

First, the three different types of alloys: (i) \(\gamma\) Ni-27Cr-9Al (fcc), (ii) \(\beta\) Ni-4.5Cr-38Al (bcc) and (iii) \(\gamma+\beta\) Ni-20Co-20Cr-24Al doped with 0.2 at.% Y are considered. All three alloys have different Cr/Al ratio, but have sufficient Cr and Al to produce a protective \(\alpha\)-\(Al_2O_3\) layer on the coating surface at high temperatures [4]. However, the \(\beta\) phase alloy shows a much better self-healing performance than both the \(\gamma\) phase and \(\gamma+\beta\) phase alloy; see Fig. 7. This is due to both a smaller amount of spallation \((F_A)\) and a lower oxidation rate \((k_p)\) for the \(\beta\) phase alloy. 

One explanation for the smaller the amount of spallation of the oxide layer developed on the \(\beta\) phase alloy than that of the oxide layer developed on the \(\gamma\) phase as well as the \(\gamma+\beta\) alloy, may be the lower value of the coefficient of thermal expansion for the \(\beta\) phase alloy [13]. Then, smaller thermal mismatch stresses develop in the oxide layer on the \(\beta\) phase alloy than in the oxide layer on the \(\gamma\) phase and the \(\gamma+\beta\) alloy upon cooling. The \(\gamma\) phase and \(\gamma+\beta\) phase alloy display similar amount of spallation \((F_A)\), but the oxidation rate of the \(\gamma\) phase alloy \((k_p)\) is higher than that of the \(\gamma+\beta\) phase alloy. Thus, the self-healing capacity increases with the Al content of the alloy. 

Next, an addition of a small amount of a reactive element to the alloys has a drastic effect on the scale adhesion. The alloys without reactive element addition showed excessive damage upon thermal cycle oxidation. From the start of the thermal cycle test the specimens of the alloys without reactive element lost weight (see Fig. 4), because no adherent protective scale was formed at the surface of these alloys. A minimal amount of the reactive element is necessary to scavenge in particular the indigenous impurity sulphur in the alloy [7]. The self-healing capacity is clearly improved if the amount of reactive element is increased; see for example the effect of Y in Figs 5a and 7. However, above a certain level no improvement is achieved. For example, the \(\beta\) phase alloy with 0.1 at.% Zr and with 0.2 at.% Zr show the same self-healing capacity; see Figs. 5b and 7. A high level of doping with a reactive element can be inefficient (over doping). For example, the \(\beta\) phase alloy with 0.1 at.% Hf shows a much higher oxide scale growth rate \((k_p)\) than the same alloy but with 0.2 at.% Hf (see Figs 5c and 7). This is due to the formation of a significant amount of \(\text{HfO}_2\), besides \(\text{Al}_2\text{O}_3\), during high temperature oxidation. Although all three reactive elements considered in this work have a high affinity to sulphur, Zr shows the best self-healing performance (cf. Fig. 7). This may be due to the higher solid solubility of Zr in the \(\beta\) phase alloy compared with that of Y and Hf, resulting in a more efficient impurity scavenging by Zr. 

Finally, for the two phase \(\gamma+\beta\) alloy, the size of the \(\beta\) precipitates was varied by using three different alloy processing routes [10]: (i) casting, resulting in to a coarse microstructure (\(\beta\) size \(\sim 20\ \mu\text{m}\)), (ii) laser surface melting (LSM), producing a fine microstructure (\(\beta\) size \(\sim 3\ \mu\text{m}\)) and (iii) EB-PVD, resulting in a very fine microstructure (\(\beta\) size \(\sim 1\ \mu\text{m}\)). The results of the thermal cycle tests (Fig. 6) clearly prove that the self-healing capacity (Fig. 7) is improved when refining the microstructure of the alloy (i.e. with decreasing size of the \(\beta\)-precipitates). Then, the supply of Al from the alloy to the oxide/alloy interface to form \(\alpha\)-\(Al_2O_3\) is faster due to the diffusion along the \(\gamma/\beta\) grain boundaries.
Figure 4: Weight change per unit of area as a function of the cycle number in a thermal cycle test of different alloys for high temperature coatings (cf. Table 1); one undoped β phase NiCrAl alloy, the other alloys were doped with 0.2 at.% Y. The thermal cycle test was carried out with buttons of the alloys with a diameter of 10 mm in air with temperature cycles of 9 minutes heating to 1163 °C, a high temperature oxidation dwell time of 45 minutes and subsequently 10 minutes cooling in ambient air. The solid lines represent the fitting of the oxidation and spallation model (Eq. (3)) to the data points.

Figure 5: Weight change per unit of area as a function of the cycle number in a thermal cycle test of different β phase NiCrAl alloys for high temperature coatings (cf. Table 1); (a), (b) and (c) doped with resp. Y, Zr and Hf. The thermal cycle test was carried out with buttons of the alloys with a diameter of 10 mm in air with temperature cycles of 9 minutes heating to 1163 °C, a high temperature oxidation dwell time of 45 minutes and subsequently 10 minutes cooling in ambient air. The solid lines represent the fitting of the oxidation and spallation model (Eq. (3)) to the data points.
Figure 6: Weight change per unit of area as a function of the cycle number in a thermal cycle test of as cast, laser surface melting (LSM) and electron beam physical vapour deposited (EB-PVD) $\gamma+\beta$ phase NiCoCrAlY alloy for high temperature coatings (cf. Table 1). The thermal cycle test was carried out with buttons of the alloys with a diameter of 10 mm in air with temperature cycles of 9 minutes heating to 1163 °C, a high temperature oxidation dwell time of 45 minutes and subsequently 10 minutes cooling in ambient air. The solid lines represent the fitting of the oxidation and spallation model (Eq. (3)) to the data points.

Figure 7: Self-healing capacity map of alloys for high temperature coatings (cf. Table 1). The parabolic oxide growth rate constant $k_p$ expresses the capacity to repair the oxide layer and the area fraction of spallation $F_A$ expresses the damage susceptibility of the oxide layer for adhesive failure. The poor self-healing undoped alloys are outside the range of this graph.
5 Conclusions

A thermal cycle oxidation test is a valuable tool to determine the self-repair of the protective oxide scale formed at the surface of high temperature alloys. The amount of damage $D$ induced upon cooling and the rate at which the oxide layer heals $H$ at high temperature can be extracted quantitatively with a combined oxidation and spallation model from the net weight change observed as a function of the number of thermal cycles. From this analysis, the self-healing capacity of a high temperature alloy can be characterized with only two parameters: the parabolic growth rate constant $k_p$ and the area fraction of spallation $F_s$ of the oxide layer.

A series of thermal cycle tests with differently designed alloys and the determination of their self-healing capacity provided guidelines to improve high temperature metallic coatings. The best self-healing capacity is obtained with a $\beta$ phase NiCrAl alloy doped with a small amount of Zr. Up to a certain level, the self-healing capacity increases with the amount of reactive element added. The self-healing capacity of the $\gamma$ phase NiCrAl alloy is significantly lower than that of the more brittle $\beta$ phase NiCrAl alloys. A finer alloy microstructure (i.e. a small grain size) enhances the self-healing capacity during cyclic high temperature oxidation.

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