HIGH TEMPERATURE THERMOCYCLIC BEHAVIOUR OF A PREOXIDIZED Ni-BASE SUPERALOY 601 AND HVOF SPRAYED Ni-Cr-B-Si- AND CoNiCrAlY COATINGS

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Abstract

The high temperature thermocyclic behaviour of a preoxidized (900°C, 24 h) Ni-base superalloy 601 as well as of HVOF sprayed CoNiCrAlY and Ni-Cr-B-Si coatings was investigated in order to determine the feasibility of such materials for different applications. The samples were cyclically oxidized in air at 700°C for 288 cycles in an automatic test station. The surface morphology and the phase composition of the grown oxide scales were characterized by means of scanning electron microscopy combined with energy dispersive X-ray (SEM/EDX) and by X-ray diffraction (XRD) analysis. It was noticed that chromium and aluminum play an important role for the formation of a dense protective layer on the substrate surface, protecting it against further degradation induced by the atmosphere in different high temperature applications. The established oxide layer on the preoxidized alloy 601 exhibited a lot of micro cracks in comparison with the oxide scales grown on the Ni-Cr-B-Si- and on the CoNiCrAlY coating respectively. A certain degree of internal oxidation was observed for all investigated samples. The best behaviour under these testing conditions was noticed for the Ni-Cr-B-Si coating which revealed a continuous and dense oxide layer on the surface.

Keywords: Self Fluxing, Ni-Cr-B-Si, CoNiCrAlY, Superalloy 601, thermocyclic testing

1. INTRODUCTION

Oxidation properties of several materials are very important for some high temperature applications. Alloys with sufficient amounts of aluminum or chromium can form an Al2O3 or Cr2O3 layer on their surface by reacting with oxygen, in order to protect the base material against unwanted carburization, nitration or sulphidation. Although chromium and aluminum provide alloys corrosion resistance at high temperature, the concentration of oxygen in some industrial atmospheres is not sufficient. For this reason, it is appropriate to preoxidize the components. Regarding the literature [1-4] the preoxidation of some alloys has proved to be beneficial for high temperature applications. However, most widely used materials in aggressive high temperature environments are Nickel-based alloys, when wear resistance combined with oxidation or hot corrosion is required [5]. In most cases the base materials are coated with a protective layer. MCrAlY (M = Co, Ni or Co/Ni) alloys are typical for many applications. Self Fluxing alloys like Ni-Cr-B-Si are also used to protect steels or Ni-base materials for applications at room- or high temperature. However, the literature does not give enough informations about the thermocyclic oxidation behaviour of Ni-Cr-B-Si alloys. The only found reference is about the thermocyclic oxidation behaviour of NiCrFeSiB, investigated by M.R. Ramesh and co-workers [5]. They tested uncoated and HVOF-coated boiler tube steels in air for 50 cycles at an elevated temperature of 900°C. The holding time in the furnace was 1 h and the cooling time amounted 20 min. The oxide scale formed on the surfaces of all the NiCrFeSiB-coated steels was found to be compact and adherent. The XRD results of the coated samples subjected to oxidation reveal the presence of Cr2O3, Ni, Ni3B, Ni3Si, Ni2SiO4 and Fe2SiO4 phases. No peaks for SiO2 were present. The uncoated steels showed Fe2O3 as the major peaks. Above all, no spallation of scale was observed. This is a prerequisite for the protection against above described external influences. The aim of the present work was therefore to investigate the thermocyclic oxidation behaviour of Ni-Cr-B-Si HVOF-coated carbon steel in comparison with the well proven MCrAlY-alloys on Inconel™ 738 and an uncoated Inconel® alloy 601.
The morphology and the structure of the formed oxide scale were investigated on top as well as in cross-section by means of scanning electron microscopy combined with energy dispersive X-ray (SEM/EDX type Philips XL 30 ESEM) and by X-ray diffraction (XRD type Philips X’Pert).

2. EXPERIMENTAL

The chemical composition of the Inconel® alloy 601, CoNiCrAlY and the self fluxing alloy Ni-Cr-B-Si are given in Table 1. The samples were machined to specimens with a size of ~10 x 10 x 5 mm and their surfaces were ground down with 1000-grit SiC abrasive paper. The specimens were degreased in acetone and dried in hot air before testing. Prior to the test the Ni-base superalloy 601 was additional isothermal outsourced in air at 900°C for 24 hours. After the cooling down process of the superalloy 601 all samples were exposed in a thermocycling test station (type BWM – individual concept) in air at 700°C for 288 cycles, about 1 week. The exposure time in the furnace was 30 min, the cooling time amounted 5 min.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Si</th>
<th>B</th>
<th>Ni</th>
<th>Co</th>
<th>Al</th>
<th>Y</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 601:</td>
<td>23</td>
<td>≤0,5</td>
<td>/</td>
<td>60,5</td>
<td>≤1</td>
<td>1,3</td>
<td>/</td>
<td>≤18</td>
</tr>
<tr>
<td>CoNiCrAlY:</td>
<td>28</td>
<td>0,7</td>
<td>/</td>
<td>bal.</td>
<td>32,7</td>
<td>8</td>
<td>0,6</td>
<td>/</td>
</tr>
<tr>
<td>Ni-Cr-B-Si:</td>
<td>10</td>
<td>3,1</td>
<td>2,1</td>
<td>bal.</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>2,5</td>
</tr>
</tbody>
</table>

3. RESULTS AND ANALYSIS

3.1 ALLOY 601 (NiCr23Fe)

The surface morphology of the thermocyclic oxidized alloy 601 and the corresponding EDX-spectrum is shown in Fig.1 and Fig. 2. Based on the technical quantification limit of EDX-detector, only elements with a concentration of more than 1% can be detected.

Fig. 1 Morphology of the grown oxide scale on the surface of alloy 601 after thermocycling

Fig. 2 EDX- spectrum alloy 601

Fig. 3 depicts the formation of oxide bumps at higher magnitude which are localized along the grain boundaries (Fig. 1 as well), on places with the highest oxidation scale. The research results have confirmed the known theory, that the diffusion rate in grain boundaries is much higher in comparison with the volume diffusion. The presence of cracks in this area confirms the high oxidation growth rate which induces a high degree of residual stresses followed inevitably by crack evolution. Cross-section SEM investigations of the
established oxide layer on the preoxidized alloy 601 revealed the presence of further microcracks which are mostly oriented perpendicular to the sample surface (see Fig. 4). These cracks would enable considerable diffusion paths for unwanted carbon, sulphur or nitrogen ingress in industrial processes. Moreover, there is clearly to notice, that below the formed oxide scale on the sample surface, which contains a mixture of \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) (based on XRD results), a certain degree of internal oxidation occurred along the grain boundaries as well. EDX-analysis of the dark grey formed oxides identified Al and O.

![Fig. 3 SEM-micrograph of the grown oxide scale on the surface of the thermocycled alloy 601](image1)

![Fig. 4 SEM-micrograph of the oxidized alloy 601 in cross-section](image2)

### 3.2 CoNiCrAlY

The surface morphology of the oxide scale grown on the thermocyclic oxidized CoNiCrAlY coating is shown in Fig. 5 at lower (1000x) respectively at higher (5000x) magnitude. Based on the shape of the formed oxides, one may conclude that the oxide scale consists of a mixture of single metal oxides or even spinel oxides.

![Fig. 5 SEM-micrographs of the formed oxide scale on the surface of the thermocycled CoNiCrAlY coating](image3)

The function of the protection coating for MCrAlY alloys is connected with the dissolution of the aluminum-containing reservoir \( \gamma'\)-NiAl. If the precipitation within the microstructure is already consumed, the aluminum-content has already sunk so deep in the \( \gamma\)-Ni-matrix that the protection of the base material is no longer possible [6]. The most important function of a MCrAlY alloy would no longer be available because e.g. the \( \text{Al}_2\text{O}_3 \) protective layer cannot be formed. XRD investigation of the oxidized sample still revealed beside the
mixture of the formed oxides the presence of the γ'-Ni₃Al phase (9%, see Fig. 6), observation which certifies that the Al-reservoir is not yet exhausted. Cross-section SEM investigations of the oxidized CoNiCrAlY-coating demonstrate the formation of a very thin oxide scale, which is not uniform distributed on the surface concerning its thickness.

![Fig. 6 XRD-analysis of the oxidized NiCoCrAlY](image)

![Fig. 7 SEM-micrograph of the oxidized CoNiCrAlY-coating in cross-section](image)

3.3 Ni-Cr-B-Si

SEM investigations of the oxide scale grown on the surface of the Ni-Cr-B-Si coating revealed a plate like morphology (Fig. 8a and b). Previous investigations of other researches [2] have shown that chromium exhibits a plate like structure. This remark was confirmed by the EDX analysis (see Fig. 9).

![Fig. 8 SEM-micrographs of the formed oxide scale on the surface of the thermocycled Ni-Cr-B-Si coating](image)

![Fig. 9 EDX- spectrum of the plate like products from the surface of the oxidized Ni-Cr-B-Si coating](image)
The existance of NiO beside the cromium oxide which has formed on the surface of the sample has also been confirmed by X-ray diffraction (XRD) analysis (Fig. 10) and element mapping techniques (Fig. 11) as well. Ni-oxides can lead to enhanced catalytic cracking of methane and soot deposition under reducing conditions [7]. Therefore it would also make sense to preoxidize the specimens in controlled atmospheres at very low O₂ activities, e.g. at pO₂ = 10⁻²³, in N₂-H₂ so that no Fe or Ni oxides are formed which would be reduced later in some process gases [1, 4].

Contrary to the manufacturers description, the Ni-Cr-B-Si has been found to contain a minor percentage of aluminum (0,08 mass% demonstrated by UV-spectral analysis) and identified in form of internal oxidation in the element mapping from Fig. 11. This fact simplifies the evaluation of the SEM micrographs in cross-section. The chromium oxide layer grown on the top of the Ni-Cr-B-Si coating is very dense (see Fig. 12), but with a bad adhesion to the substrate, due to the presence of the brittle SiO₂ layer formed below the Cr₃O₈ scale. Some of the microcracks present in this region were partially induced by the metallographic preparation. An internal oxidation, characterized by the formation of aluminum oxides along the grain boundaries occurred in the area below the Cr₃O₈- repectively SiO₂-layer formed on the sample surface. Furthermore a depletion of the fine dispersed NiCr (β) and Ni₃Cr (γ') phases was noticed as well.

4. CONCLUSION

To evaluate the cyclic oxidation resistance of a preoxidized (900°C, 24 h) Ni-base superalloy 601 as well as of HVOF sprayed CoNiCrAlY- and Ni-Cr-B-Si coatings, oxidation tests were performed at 700 °C for 288 cycles. The holding time in the furnace was 30 min. and the cooling time amounted 5 min. The evaluation of the oxide layer was performed using SEM-EDX and XRD techniques.
The results obtained from this work are summarized below:

- The resistance of aluminum- or chromium-containing alloys can be improved significantly by a thin Al₂O₃ or Cr₂O₃ oxide layer on the sample surface produced by a controlled preoxidation treatment.
- The established oxide layer on the preoxidized alloy 601 exhibited a lot of micro cracks in comparison with the oxide scales grown on the Ni-Cr-B-Si and on the CoNiCrAlY coating respectively.
- A certain degree of internal oxidation was observed for all investigated samples.
- The best behavior under these testing conditions was noticed for the Ni-Cr-B-Si coating which revealed a continuous and dense oxide layer on the surface.
- The obtained results revealed the feasibility of the Ni-Cr-B-Si alloys when subjected to thermocyclic oxidation in comparison with conventional alloys (alloy 601 or MCrAlY coatings).

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LITERATURE