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Temperature and oxidation resistance of the ODS materials MA 956 and PM 2000

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ABSTRACT. The objective of the present paper was to show the various macro-/microstructural appearances of the ODS materials MA 956 and PM 2000 at the surface and in the bulk after exposure to high temperatures in combustion chambers (gaseous environment). At the surface a chromium oxide layer forms above the alumina layer originally formed after preoxidation. At locations where the surface has been melted these two oxide layers disappear and an iron oxide showing cracks forms at the surface. Several cracks run into the material. In the bulk material due to high thermal gradients a porosity of up to 18% in MA 956 and 2% in PM 2000 develops during operation (Kirkendall effect). With longer operation times, at higher temperatures and probably in other environments (chemical cracking of the fuel) internal oxidation or niobriding of aluminium and/or formation of chromium carbides take place.

1 Introduction

The two ODS materials MA 956 and PM 2000 are oxide-strengthened iron-chromium-aluminium alloys produced by mechanical alloying and with similar chemical compositions. The alloys are strengthened by an yttrium oxide dispersoid that remains effective at temperatures up to the melting point (1482°C) of the material [1]. A high temperature annealing treatment (1300°C for 0.5 h) is required to develop the desired grain structure (pancake shaped) and a preoxidation to protect the alloy against oxidation and hot corrosion. These attributes make the alloy especially suitable for gas turbine combustor chambers components. The present paper shows the investigation of such components which had already been in operation, in respect to their temperature and oxidation resistance.

2 Investigations

2.1 Chemical analysis

The chemical compositions of the two materials examined by electron microprobe are given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>MA 956</th>
<th>PM 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.08 ± 0.01</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>0.05 ± 0.01</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>Al</td>
<td>0.04 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
</tbody>
</table>

The material PM 2000 contains about 1% more aluminium and 0.1% more titanium than MA 956. About 0.1% Silicon was found in MA 956 whereas PM 2000 contains no silicon.

2.2 Preoxidation

Before putting the components into the combustion chamber a preoxidation at 1305°C for 0.5 h is performed. The formation of a dark layer of non uniform thickness has been observed for PM 2000 in the SEM and is shown in Figure 1. The average layer thickness consisting of alumina is about 1 to 2 μm.

2.3 Changes during operation

The components which had been in operation show various changes in surface, oxide structure and in the bulk. In the following these changes of combustion components operated in a gaseous environment are reported.

2.3.1 Surface

At the surface individual bright areas consisting of iron oxide have been formed (Fig 2). In these areas cracks at the surface are visible. Other components show an increase of the surface roughness (Fig. 3). At these zones a high level of iron has been detected by the EDX-analysis of the SEM. A crack running from the transition zone...
flat-rough surface into the rough surface has been observed.

2.3.2 Oxide structure
Microsections have been taken from the components to reveal the structure of the oxide layers. The components show an increase of the alumina thickness in the material during operation. A thickness of up to 5 μm has been measured for MA 956 and up to 10 μm for PM 2000. On various components a bright chromia layer shown in Fig. 5 and detected by the EDX-analysis has been formed above the original alumina layer. Aluminium and chromium concentration depth profiles have been determined by the electron microprobe. This is shown in the following diagrams.

2.3.3 Bulk
The two materials show porosity after operation (Fig 5). The porosity has been measured by an image analysis system. In Table 2 the measured values are reported for the two alloys.

Table 2: Porosity and Pore Sizes

<table>
<thead>
<tr>
<th>Material</th>
<th>Max. Porosity (%)</th>
<th>Max. Size of the pores [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA 956</td>
<td>18</td>
<td>200</td>
</tr>
<tr>
<td>PM 2000</td>
<td>2</td>
<td>100</td>
</tr>
</tbody>
</table>

A precipitation of dark cube-like particles has taken place in the bulk during operation (Fig. 6). The particles consist mainly of alumina. In the lower part of Fig. 6 the visible pores show a narrow border consisting of alumina.

Cracks running from the surface towards the interior of the material have been observed in components where the surface roughness has increased during operation and the surface consists mainly of iron oxide (Fig. 7). Such a surface region is shown in Fig. 3. The crack is transgranular.

Where there are carbon deposits on the surface and the surface of the components is strongly degraded by temperature, then needle-like phases (dark) and cube-like phases (less dark) have been observed in the SEM (Fig. 8). X-ray determination of element distributions from such regions have been taken in the electron microprobe (Fig. 9 to 12). The needle-like phase consists mainly of aluminium nitride and the cube-like phase mainly of chromium carbide. The two phases have been analysed quantitatively in the microprobe. The results are listed in the following Table 3.

Table 3: Chemical composition of a.) Needle-like phase and b.) Cube-like phase

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentr. in a.) (wt-%)</th>
<th>Elements</th>
<th>Concentr. in b.) (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.5</td>
<td>Cr</td>
<td>68.8</td>
</tr>
<tr>
<td>Ti</td>
<td>4.6</td>
<td>Ti</td>
<td>0.02</td>
</tr>
<tr>
<td>Al</td>
<td>52.9</td>
<td>AI</td>
<td>0.1</td>
</tr>
<tr>
<td>Y</td>
<td>5.4</td>
<td>Y</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe</td>
<td>6.1</td>
<td>Fe</td>
<td>24.4</td>
</tr>
</tbody>
</table>

3 Discussion
The two ODS alloys MA 956 and PM 2000 have approximately the same chemical composition. Microprobe measurements show that PM 2000 contains 1 % more aluminium and 0.1 % more titanium than MA 956. Consequently PM 2000 exhibits thicker oxide layers than MA 956 (a layer thickness of 10 micrometer was measured). MA 956 shows layers of up to 5 micrometer. The layers on both alloys consist mainly of alumina, that means that the two alloys are mainly alumina (α-Al2O3) forming materials. After preoxidation the components have an alumina layer thickness of about 1 to 2 μm, i.e. the alumina layer grows in thickness during operation.

High temperature gradients cause, in the bulk material of MA 956, a porosity of up to 18 %. The maximum size of the pores is about 100 μm. In PM 2000 a porosity of a maximum of 2 % is observed. Probably MA 956 already contains a certain porosity originating from mechanical alloying under argon before operation. The formation of the porosity can be explained by the Kirkendall effect. A supersaturation of the material with
vacancies produces a condensation of these defects on dislocations [2]. The vacancies move probably from the surface into the bulk. In the opposite direction, as concentration depth profiles show, there is a diffusion of chromium atoms. Consequently there is a depletion of chromium in the bulk and chromium oxide forms on the surface. The directions of diffusion, thermal gradient and grain boundaries were aligned in the investigations. As both alumina and chromia scales were able to form, this is probably an oxidising/nitriding system.

There are areas on the surface where bright zones containing mainly iron have been observed. The original alumina layer is no longer present. These areas probably mark locations where the surface has been melted. Iron oxide cannot provide protection against further oxidation.

Several components show internal oxidation of aluminium, precipitation of aluminium nitride or the formation of chromium carbide. These features are found if there is a strong damage of the oxide structure due to very high temperature influence or if there are deposits of carbon on the components due to cracking of the gaseous fuel. At these locations the protective alumina scale has probably been permeable or has been no longer present. Formation of such precipitates has two important consequences [3]:

(i) aluminium is removed from the alloy substrate, thereby reducing its ability to maintain an alumina layer
(ii) large precipitates could influence the mechanical properties considerably

Transgranular cracks running from the surface into the bulk have been observed. The location of crack initiation is the surface where cracking has already been observed in the iron oxide. Thermal stresses probably causes the nucleation and growth of the crack. It was estimated that between 1144 and 1396°C the threshold stress for crack initiation should be about 70 MPa and at 1477°C about 55 MPa [4].

4 Acknowledgements
The author is grateful to the department KWRB4 in particular, to Mr. Stalder and Mr. Brunner for providing specimens and Dr. Balbach for helpful discussions.

5 References
[1] F. Perry, Oxide-Dispersion-Strengthened P/M Alloys..., Industrial Heating, 1982

Fig. 1: Oxide structure after preoxidation
Fig. 2: Bright areas (iron oxide) on the surface
Fig. 3: Roughness increase of the surface
Fig. 4: Chromia layer above the alumina layer