An Oxidation Study of NiCoCrAl Coatings Produced by Electrolytic co-Deposition Method

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NiCoCrAl metallic compounds are used as bond coats for thermal barrier coatings. These composite coatings were obtained by electrodeposition under DC conditions from a Watts bath containing suspended Cr and Al particles. Electrodeposition of a composite coating is a low-cost method to produce bond coats for thermal barrier coatings. The co-deposition studies were performed by using an Inconel 718 substrate. Oxidation resistance and microstructural study are discussed in this study.

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1. Introduction

Hot section parts of gas turbines, such as blades and vanes, are exposed to high temperature in service. Thermal barrier coatings (TBC) are used to shield the metallic substrate, such as nickel based super alloy, providing thermal and oxidation protection. TBCs usually consist of two coatings: a thermally insulating ceramic topcoat, and a bond coat (BC). A slow growth barrier layer, generally of Al\textsubscript{2}O\textsubscript{3}, is needed to be formed since this layer is the most important part of the TBC system during oxidation providing adhesion between the TBC and the substrate [1].

MCrAl coatings (where M represents Ni or Co) are commonly used as BC to protect super alloys at elevated temperatures above 900°C. BC are generally deposited by APS, high velocity oxyfuel, low pressure plasma spray, cathodic arc/ion plasma deposition or by EB-PVD [2].

The electrolytic co-deposition process is an alternative method which offers low cost of bond coat deposition. Besides, with this technique, all surfaces exposed to liquid electrolyte are coated, including blind holes, where the liquid can penetrate [3]. However, the commercial potential of this method for TBC system has not been fully realized due to the lack of information about the oxidation resistance.

Several researchers have evaluated bond coatings for thermal barrier coating (TBC) by electrodeposition techniques [4–6]. The growth rate and spallation resistance of alumina scales can vary widely depending on the composition [7]. Different coating compositions provide different protective properties due to the nature of the different oxides growing on them. Many studies are reported about oxidation behavior of NiCoCrAl coating produced with other techniques (plasma spray, EB-PVD). However, there are no sufficient reports concerning the effect of composition of the electrodeposited coating on the oxidation behavior.

Hence, the aim of this study was to investigate the oxidation behavior of NiCoCrAl composite coatings deposited by electrolytic co-deposition technique.

2. Materials and equipment

Nickel composite coating was prepared by using a Watts-type bath containing 240 g/l of nickel sulphate (NiSO\textsubscript{4}·6H\textsubscript{2}O), 50 g/l of nickel chloride (NiCl\textsubscript{2}·6H\textsubscript{2}O), 40 g/l of boric acid (H\textsubscript{3}BO\textsubscript{3}), 5–15 g/l of cobalt sulphate (CoSO\textsubscript{4}·7H\textsubscript{2}O). 0.2 g/l of surfactant were added. Analytical reagents and distilled water were used to prepare the plating solution.

A nickel sheet of 99.99% purity with dimensions of 250 × 300 × 100 mm\textsuperscript{3} was used as anode and the Inconel 718 with radius of 200 mm was used as cathode. For deposition of composite coatings, Cr (40 µm) and Al (1 µm) particles were used. Samples were cleaned and activated according to ASTM B343 procedure. All coatings were fabricated using DC electrodeposition method at the current density of 8 A/dm\textsuperscript{2} with deposition time of 45 min at 50°C. The pH of the plating solution was maintained at 4, which was adjusted by adding sulphuric acid or sodium hydroxide when necessary.

The composite plating was carried out in a beaker. The heated bath was stirred by a magnetic stirrer. The anode and cathode were vertically positioned in the bath. The samples were heat treated at 1000°C for two hours in argon atmosphere. The specimens were ultrasonically cleaned for SEM and XRD analysis. The phase composition of the deposits was characterized using X-ray diffraction (RIGAKU Miniflex 600) with Cu K\textsubscript{α} radiation. The scan rate was 1 °/min and 2θ ranged from 20° to 80°. The isothermal oxidation tests were carried out in a muffle furnace at 950°C.

3. Results and discussion

According to SEM images, both Cr and Al particles are well incorporated into the Ni matrix. As shown in

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Fig. 1 the spherical particles are uniformly distributed on the coarse particles. Firstly, chromium particles were absorbed by nickel atoms, then the nickel particles started to form slowly around the chromium particles through encapsulation and incorporation of other metal particles. The EDX analysis shows that the fine spherical particles are Al and the coarse particles are the Ni coated Cr particles. Table I shows the results of EDX analysis of the composite coatings. The EDX analysis was carried out at five different locations and the average value was taken.

### TABLE I

Results of the EDX analysis of the as-deposited coatings

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Ni [wt.%]</th>
<th>Co [wt.%]</th>
<th>Cr [wt.%]</th>
<th>Al [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>46</td>
<td>24</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>a2</td>
<td>56</td>
<td>27</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>a3</td>
<td>73</td>
<td>15</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>a4</td>
<td>76</td>
<td>11</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

Fig. 2. Weight gain kinetics during isothermal oxidation at 950 °C.

Figure 3 shows XRD spectra of the samples oxidized at 950 °C. The XRD result for a4 sample shows that the oxide structure includes NiO and CoCr$_2$O$_4$ spinel oxides formed on the coating. The lowest weight gains were seen in a1 sample. When the amount of Al was 14 wt.%, Al was needed to form Al$_2$O$_3$. Figure 4c supports the XRD result, where the whisker-like Al$_2$O$_3$ is seen on the surface of the coating.

Fig. 3. XRD spectra of the oxidized samples.

The specimens with formed Al$_2$O$_3$ (a1) exhibits better oxidation resistance than the other specimens. This situation can be explained as follows. The mass gain of the coating is dependent on the composition of TGO. Nickel and cobalt based spinel type oxides (such as NiCr$_2$O$_4$, CoCr$_2$O$_4$) have substantially higher growth rates than Al$_2$O$_3$ and also a relatively large Pilling-Bedworth ratios (PBR, which is the volume ratio of the formed oxide to the metal consumed) [10].

The cross-section morphology of the sample oxidized in air is shown in Fig. 4a. The oxide scale consists of three layers. The outer layer mainly consists of (Ni,Co)O, the intermediate layer consists of Ni, Co, Cr mixed spinel type oxides and the inner layer consists of Cr rich oxide crystals.

The SEM images support the XRD results with the exception of Fig. 4d. Figure 4d shows Cr rich oxide crystals in the cross section of the a4 sample. The chromium oxide structure could not be seen in the XRD results. The reason of this is that the Cr oxide crystals were grown in the inner layer of the coating. Figure 4b shows the sharp edged NiO crystals formed on the surface of the coating.
Conclusions

Using the electroplating method Cr and Al particles were assembled into Ni, Co coating. It is an easy and cost effective method to produce bond coats for thermal barrier coatings. The results imply that the Al particles promote formation of $\text{Al}_2\text{O}_3$. SEM analysis shows that the chromium oxide scales are present inside the coating.

Acknowledgments

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References