PVD DEPOSITION OF HAFNIUM IN ALUMINIDE COATINGS

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Abstract: The paper presents comparison of microstructures of hafnium modified aluminide coatings deposited in two different ways on pure nickel. In the first way a hafnium layer was deposited by the EB-PVD method, subjected to the diffusion treatment for 6 hours and than aluminum was deposited by the CVD method. In the second method, double layers of hafnium (3 μm thick) and aluminum (3 μm thick) were deposited by the EB-PVD method on the nickel substrate. The double layers were subjected to diffusion treatment at 1050 °C for 6 h. The obtained coatings were examined by the use of an optical microscope (microstructure and coating thickness) and a scanning electron microscope (chemical composition on the cross-section of the modified aluminide coating). In aluminide coatings deposited by the CVD process, an outward nickel diffusion via the hafnium layer and inward aluminum diffusion to the surface of nickel lead to the formation of a diffusion zone. Hafnium forms a layer of intermetallic phases with nickel in the diffusion zone. Diffusion treatment for 6 h of nickel with hafnium and aluminum layers lead to formation of the Ni5Hf phase.

Keywords: PVD METHOD, CVD METHOD, ALUMINIDE COATINGS, HAFNIUM

1. Introduction

Protective aluminide coatings deposited on superalloys are degraded by the loss of Al due to oxidation of the coating surface to form aluminum oxide and by interdiffusion with the underlying substrate [1]. It accelerates the rate of the oxide growth and results in the loss of the coating strength and deformation of the coating. Therefore, as to improve the oxidation resistance of the coating it is necessary to slow oxide scale growth and improve its adherence [2-5]. Aluminum concentration gradient between the superalloy and the coating is the driving force of the Al loss. Candidate diffusion barrier materials should retard Al diffusion at high temperatures, possess good thermo-mechanical compatibility with the substrate and the coating and remain relatively stable for extended periods of time at high temperature. The addition of small amount of reactive elements such as: hafnium, zirconium, yttrium and cerium has a beneficial effect on oxidation behavior since [6-7]. This beneficial effect includes an improvement of adhesion of alumina scales and reduction of oxide scale growth rate. Pint et al. [8,7] allege that hafnium doped cast alloys proved that hafnium doping of β-NiAl and Ni-Pt aluminides reduces the parabolic rate constant by a factor of ten and even possibly to be more efficient than platinum addition. Hafnium addition to the nickel superalloy decreases the propensity for rumping oxides when it diffuses into coating and to the growing aluminum oxide [9,7].

Hafnium is a reactive metal with melting temperature of 2225 °C. Hafnium has extremely high chemical reactivity with various materials: oxygen, nitrogen, hydrogen and carbon [7, 10]. Cochrard et al [11, 7] showed, that small content of hafnium (0.1 - 1.0 % wt) improves high temperature mechanical properties. Due to the significant beneficial effects of hafnium addition on the oxidation resistance of nickel based superalloys, processes of diffusion coating were intensively investigated. Howment research corporation [12-13] incorporates hafnium into platinum aluminide coatings by CVD method. Addition of small amount of hafnium (<1 wt %) to the coating and controlling its level and distribution in aluminide coatings remains an open issue [14]. Nesbitt et al. and Warnes et al. suggest that NiAl – based alloys containing small amount of reactive elements (hafnium or zirconium) added with or in place of platinum exhibit further improvements of the lifetime [15-16]. The reactive elements addition to these alloys causes an improvement of the alumina scale adhesion and a reduction of the growth rate of the scale by the segregation of reactive elements' ions on the scale grain boundaries and alloy-scale interface [17]. Research at the General Electric Company resulted in the development of several new overlay coating and alloys containing 2 % at. hafnium and/or zirconium and up to 5 % at. chromium [18, 7]. Oxidation resistance of these coatings was comparable to modern (Ni,Pt) diffusion coatings.

Chemical vapour deposition process consists of the following sub-processes [10]:

- transport of the gas reagent to the substrate surface,
- adsorption of the gas reagent on the substrate surface,
- chemical reaction between the gas reagent and the substrate elements,
- nucleation and growth of the coating,
- desorption of the unnecessary reaction product.

Electron beam physical vapour deposition (EB-PVD) is an advanced coating fabrication technique reported by [11]. Guo, Sun, Gong [12] alleged the lack of evidence about the use of EB-PVD coating technique for aluminide coating deposition. In this study hafnium was incorporated to the aluminide coating by the EB-PVD method. Coatings deposited in two different ways. In the first way a hafnium layer was deposited by the EB-PVD method, subjected to the diffusion treatment for 6 hours and than aluminum was deposited by the CVD method. In the second method, double layers of hafnium (3 μm thick) and aluminum (3 μm thick) were deposited by the EB-PVD method on the nickel substrate. The double layers were subjected to diffusion treatment at 1050 °C for 6 h. The microstructure of hafnium doped aluminide coatings deposited in two different ways was investigated.

2. Experiment

The commercial nickel of 99.95 % wt purity was used in this study. The cylindrical samples of the 20 mm diameter and 5 mm high were cut and grounded up to SiC No 1000, degreased in ethanol and ultrasonically cleaned. Zirconium thin layers (1μm and 3 μm thick) were deposited by the EB-PVD method. In this method, material to evaporate (placed in a water-cooled Cu crucible) is melted by focused high energy electron beam. Power density in electron beam spot (on the surface of the material) can reach over 40 kW/cm² and any material around the spot can be easily evaporated. Well-cooled walls of crucible, protect the material against contamination by Cu. After the evaporation process, material can be easily evacuated (it does not stick to the crucible). Additional advantage of this method is that material can have any form (wire, sheet pieces, pellets, etc) and can be easily supplemented in the crucible. For this work Balzers ESQ 110 (four hearts crucible) electron beam evaporator was used. Electrons emitted from a hot tungsten cathode (Fig. 1), are initially focused by the Wehnelt electrode than, are accelerated by the electric field to the anode and achieve energies up to 10 keV. Under the influence of the magnetic field, electron beam is focused and deflected (by an angle of 270°), forming on the surface of the material in the crucible a high energy electron spot. Due to four hearts crucible of ESQ 110, it is possible to obtain up to 4 different material layers on the substrate in one vacuum process.

All layers were deposited on motionless Ni substrates. The distance between the evaporating source (crucible) and substrates was 150 mm.

In this conditions, the rate of the material deposition (v) depends on the electron beam power:
\[ P_E = U_E \times I_E \]  \hspace{1cm} (1)

where \( U_E \) – anode voltage and \( I_E \) – electron beam current (cathode emission current).

Deposition rates for Hf were established as follows:
\[ v_{Zr} = 1.0 \, \mu m/min \] for \( I_E = 310 \, mA \), \( U_E = 9.5 \, kV \)

Technological stages for Hf layers deposition were as follows:
- substrates cleaning in a detergent and placing in a substrates holder
- pumping the chamber to \( p = 2 \times 10^{-6} \, hPa \)
- substrate heating to \( 300 \, ^\circ C \) (\( t_H = 20 \, min \))
- evaporation of the Hf layer with the deposition rate (v) mentioned in order to obtain the proper coating thickness (evaporation time \( t_E = 50 \, s \))
- crucible rotation (changing the position to another material)
- cooling substrates to \( 50 \, ^\circ C \) (about 1 hour)
- venting the chamber.

The aluminide coatings were made using the CVD equipment BPXPR0325S manufactured by IonBond company (Fig. 2). Aluminizing process was conducted for 8h at the temperature 1000 \( ^\circ C \). Aluminium chloride vapour (AlCl\(_3\)) was produced in an external generator I (Fig. 1), at 330 \( ^\circ C \) according to the reaction:
\[ 2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2. \]

Then the saturating atmosphere was transported in a stream of hydrogen gas into the CVD reactor, where nickel samples were placed. The AlCl\(_3\) vapour reacted with the nickel at the temperature 1000 \( ^\circ C \) and grains of intermetallic phase NiAl were formed according to the reaction:
\[ 2AlCl_3 + 2Ni + 3H_2 \rightarrow 2AlNi + 6HCl. \]

The microstructure of the surface and cross-sections of the coatings were investigated by an optical microscope Nikon Epiphot 300, a scanning electron microscope (SEM) Hitachi S-3400N and an energy dispersive spectroscope (EDS). The coatings thicknesses were determined by means of the NIS-Elements software.

3. Results and discussion

The microstructure of coatings in which both hafnium and aluminum were deposited by the EB-PVD method and then subjected to diffusion treatment for 6 hours is presented in Figure 3. The diffusion treatment leads to formation of the \( \gamma - (NiAl) \) phase in which inclusions of the phase enriched with hafnium are observed. According to the Ni-Hf phase diagram [19], chemical composition of these phases corresponds to the Ni\(_5\)Hf phase. The EDS linear analysis on the cross-section indicates that intermetallic phases are distributed up to about 20 \( \mu m \) below the samples surfaces (Fig. 4).

After the diffusion treatment process, hafnium formed the Ni\(_5\)Hf intermetallic phase, whereas aluminum did not form any phases with nickel nor hafnium. Its concentration is almost the same along the investigated cross-section. Therefore, it may be assumed that aluminum dissolves in nickel and \( \gamma - (NiAl) \) solid solution is being formed.

Fig. 1. Scheme of the apparatus of the EB-PVD method.

Fig. 2. A scheme of equipment for deposition of aluminide coatings by the CVD method.

Fig. 3. Microstructure on the cross-section of the Hf 3 \( \mu m \) thick and Al 3 \( \mu m \) thick coatings deposited by the EB-PVD method after the 6h diffusion treatment.

Fig. 4. A scheme of equipment for aluminizing.
Table 1. Chemical composition on the cross-section of the Hf 3 µm thick and Al 3 µm thick coatings deposited by the EB-PVD method after the 6h diffusion treatment

<table>
<thead>
<tr>
<th>Point</th>
<th>Phase</th>
<th>Chemical composition, % at Al</th>
<th>Ni</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>γ-Ni(Al)</td>
<td>9.86</td>
<td>88.38</td>
<td>1.76</td>
</tr>
<tr>
<td>2</td>
<td>Ni, Hf</td>
<td>-</td>
<td>88.5</td>
<td>14.28</td>
</tr>
<tr>
<td>3</td>
<td>Ni, Hf</td>
<td>-</td>
<td>85.76</td>
<td>14.24</td>
</tr>
<tr>
<td>4</td>
<td>γ-Ni(Al)</td>
<td>7.44</td>
<td>85.69</td>
<td>6.87</td>
</tr>
<tr>
<td>5</td>
<td>Ni, Hf</td>
<td>-</td>
<td>86.54</td>
<td>13.46</td>
</tr>
<tr>
<td>6</td>
<td>γ-Ni(Al)</td>
<td>5.25</td>
<td>94.02</td>
<td>0.73</td>
</tr>
<tr>
<td>7</td>
<td>Ni</td>
<td>-</td>
<td>100.00</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>γ'-Ni(Al)+Ni, Hf</td>
<td>8.89</td>
<td>87.36</td>
<td>3.75</td>
</tr>
</tbody>
</table>

The microstructure of the coating deposited by both EB-PVD and CVD methods is presented in Figure 6. The phase enriched with hafnium is formed 25 µm below the sample’s surface. Its chemical composition corresponds to the Ni2AlHf phase. The chemical composition of the above area corresponds to the β-NiAl, whereas the chemical composition of the area below, corresponds to the γ'-Ni3Al.

Table 2. Chemical composition on the cross-section of the Hf 3 µm thick coatings deposited by EB-PVD method after the 6h diffusion treatment and Al deposited by the CVD method

<table>
<thead>
<tr>
<th>Point</th>
<th>Phase</th>
<th>Chemical composition, % at Al</th>
<th>Ni</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>β-NiAl</td>
<td>42.92</td>
<td>56.95</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>β-NiAl</td>
<td>39.22</td>
<td>60.61</td>
<td>0.16</td>
</tr>
<tr>
<td>3</td>
<td>Ni2AlHf</td>
<td>40.46</td>
<td>48.00</td>
<td>11.54</td>
</tr>
<tr>
<td>4</td>
<td>Ni2AlHf</td>
<td>31.95</td>
<td>31.38</td>
<td>36.67</td>
</tr>
<tr>
<td>5</td>
<td>Ni2AlHf</td>
<td>30.48</td>
<td>53.01</td>
<td>16.51</td>
</tr>
<tr>
<td>6</td>
<td>γ'-Ni3Al</td>
<td>36.65</td>
<td>61.81</td>
<td>1.54</td>
</tr>
<tr>
<td>7</td>
<td>γ'-Ni3Al</td>
<td>24.84</td>
<td>73.74</td>
<td>1.41</td>
</tr>
<tr>
<td>8</td>
<td>γ'-Ni3Al</td>
<td>12.13</td>
<td>87.69</td>
<td>0.17</td>
</tr>
</tbody>
</table>

4. Conclusion

The method of aluminum deposition on the nickel substrate with hafnium layers (3 µm thick) has a tremendous effect on the microstructure of the coatings. In coatings deposited by the EB-PVD method aluminum dissolves in nickel, the γ-Ni(Al) phase is being formed and inclusions enriched with hafnium are distributed in the whole coating. The chemical composition of these inclusions correspond to the Ni2AlHf phase. On the other hand, aluminum deposited by the CVD method forms intermetallic compounds with nickel (β-NiAl and γ'-Ni3Al phases) and hafnium forms the Ni2AlHf phase. This phase lies 25 µm below the coatings surface, between the β-NiAl and γ'-Ni3Al zones. The coating was formed through aluminum inward diffusion and nickel outward diffusion. Both aluminum and nickel diffused through the hafnium layer.

Acknowledgment

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4. Literature