CVD AND EB-PVD AS A METHODS OF THE ZIRCONIUM INTRODUCING TO THE ALUMINIDE COATINGS

PhD M. Zagula-Yavorska*, Prof. J. Sieniawski
Rzeszów University of Technology, Department of Materials Science W. Pola 2 str., 35-959 Rzeszów, Poland
E-mail: *yavorska@prz.edu.pl

Abstract: Zirconium was introduced to the aluminide coating by means of two methods: the EB-PVD method and the CVD method. Zirconium layers (1 and 3 µm thick) were deposited by the EB-PVD method on the pure nickel substrate. Than samples were aluminized by the CVD method. Aluminizing process leads to obtain triple zone coatings. The top β-NiAl zone, the middle γ'-Ni3Al zone and the inner γ - NiAl zone were observed. Intermetallic phases NiZr(NiZr2) and Ni2Zr on the border between the top and the middle zone and middle zone and the substrate were found. When zirconium was introduced to the aluminide coating during the CVD process a triple zone coating was obtained. It was found that zirconium is dissolved in the NiAl phase.

Keywords: ALUMINIDE COATINGS, CVD AND EB-PVD METHODS, ZIRCONIUM, MICROSTRUCTURE

1. Introduction

Materials used to the turbine elements production have to be resistant to high temperatures. The usage of directionally crystallized superalloys and single superalloys leads to the increase of the temperature of turbine elements work up to 1100 °C. Further increase of the temperature and times of turbine exploitation is possible by use of the protection coatings. Literature data indicates that now about 75% of the elements of aircraft engines have protective layers or coatings [1]. Coatings used in the aircraft industry are still being developed and elaborated. The widest investigations are performed for four kinds of coatings: erosion resistance coatings, thermal barrier coatings, seal coatings and oxidation resistant coatings [2-6]. Oxidation resistant coatings protect substrate materials from corrosion and oxidation.

Coatings increase stability of turbine blades and vanes. Nonmodified and modified aluminide coatings are widely used. Addition of small amount of reactive elements such as zirconium, yttrium or hafnium to aluminide coatings has beneficial effects on the oxidation behavior. This beneficial effects include improvement of adhesion of alumina scales and reduction of oxide scale growth rate [6-7]. Zirconium co-deposition with aluminum on the nickel superalloy by the CVD process was investigated by ONERA and SNECMA. Zirconium provided by the ZrOCl2·8H2O activator [8] locates far below the coating’s surface, at the interface between the β-NiAl coating and the interdiffusion zone. This interface corresponds to the initial surface of the superalloy and zirconium deposition occurs at the beginning of the process. The interdiffusion zone consists of the β-NiAl matrix and phases containing additional elements from the superalloy (Cr, Co, W, Al, Ti, Mo) [8]. During oxidation zirconium migrates towards the surface and the Zr distribution in the whole oxide layer becomes homogeneous. Zirconium may migrate via NiAl grain boundaries, where it is known to segregate [9]. Thus, Zr present in the oxide, can be expected to modify the stress relief by reducing the oxide creep rate. Aluminide coatings are produced by pack cementation, above-the-pack or chemical vapour deposition methods.

The chemical vapour deposition method has several advantages in comparison to other processes. It allows deposition of the aluminide coatings on the internal cooling canals of the turbine blades, control of the batch cooling rate and provides heat treatment of the alloys that reduces cost of the process. The chemical vapour deposition process consists of the following sub-processes [10]:

- desorption of the unnecessary reaction products. Electron beam physical vapour deposition (EB-PVD) is an advanced coating fabrication technique [11]. Guo, Sun and Gong [12] alleged the lack of evidence about the use of EB-PVD technique for aluminide coating deposition. In this study zirconium was incorporated to the aluminide coating by the CVD method. Zirconium layers (1 and 3 µm thick) were also deposited by the EB-PVD method on pure nickel substrate. Than samples were aluminized by the CVD method. The microstructure and hardness of zirconium doped aluminide coatings were examined.

2. Experiment

The commercial nickel of 99.95 % wt purity was used in this study. The cylindrical samples of 20 mm diameter and 5 mm high were cut and ground 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 be of any form (wire, sheet pieces, pellets, etc) and can be easily introduced to 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 270º), 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:

\[ P_E = U_E \times I_E \]

where \( U_E \) – anode voltage and \( I_E \) – electron beam current (cathode emission current). Deposition rates for Zr were established as follows:

- transport of the gas reactant to the substrate surface,
- adsorption of the gas reactant on the substrate surface,
- chemical reaction between the gas reactant and the substrate elements,
- nucleation and growth of the coating,
\( v_{Zr} = 1.0 \, \mu m/min \) for \( I_e = 310 \, mA, \ U_e = 9.5 \, kV \)

Technological stages for Zr 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 Zr 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.

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

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 (\( \text{AlCl}_3 \)) was produced in an external generator I (Fig. 1), at \( 330^\circ C \) according to the reaction: \( 2\text{Al}+6\text{HCl} \rightarrow 2\text{AlCl}_3+3\text{H}_2 \). Then the saturating atmosphere was transported in a stream of hydrogen gas into the CVD reactor, where nickel samples were placed. The \( \text{AlCl}_3 \) vapour reacted with the nickel at the temperature \( 1000^\circ C \) and grains of intermetallic phase \( \text{NiAl} \) were formed according to the reaction: \( 2\text{AlCl}_3+2\text{Ni}+3\text{H}_2 \rightarrow 2\text{NiAl}+6\text{HCl} \). Zirconium was also incorporated during the CVD process. Zirconium chloride vapour was produced in an external generator at \( 440^\circ C \) according to the reaction: \( 2\text{Zr}+6\text{HCl} \rightarrow 2\text{ZrCl}_3+3\text{H}_2 \). The saturated atmosphere was transported in a stream of hydrogen gas into the CVD reactor, where nickel samples were placed. The \( \text{AlCl}_3 \) and \( \text{ZrCl}_3 \) vapour reacted with nickel and intermetallic phase \( \text{NiAl(Zr)} \) was formed.

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

Phase composition of investigated coatings was executed using ARL XTRA X-ray diffractometer, equipped with a filtered copper lamp with the voltage of 45kV and heater current of 40mA.

Adhesion evaluation of the layers was made using the scratch test on the CSM REVETEST device, by moving the diamond indenter along the examined specimen’s surface with the gradually increasing load.

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

2. Results and discussion

The zirconizing - aluminizing CVD process of the nickel substrate at \( 1050^\circ C \) during 8h leads to the triple zone aluminide coating formation (50 \( \mu m \) thick). In the first zone, on the top of the coating, the proportion of Ni to Al corresponds to the \( \beta\text{-NiAl} \) phase (Fig. 3, table 1). The chemical composition of the second zone, which is adjacent to the \( \beta\text{-NiAl} \) phase, corresponds to the \( \gamma'\text{-Ni}_3\text{Al} \) phase (Fig. 4). The chemical composition of the third, inner zone, corresponds to the \( \gamma\text{-Ni(Al)} \) phase. Chemical composition of the zone below \( \gamma\text{-Ni(Al)} \) phase is same as the matrix composition, that is pure nickel. Zirconium does not form any inclusions, but dissolves in the coatings phases.

Fig. 3. Microstructure of the zirconium aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature \( 1050^\circ C \), time 8h.

Wang et al. [13] proved that enthalpy of the NiAl phase formation is about -67 kJ/mol at \( 1000^\circ C \). Enthalpy of the \( \text{Ni}_3\text{Al} \) phase formation is about -42 kJ/mol at \( 1000^\circ C \). Small values of the enthalpy of formation indicate on the favorable conditions of the intermetallic phase formation.

XRD phase analysis confirmed the existence of the NiAl phase in the coating (Fig. 5).
Table 1: Phase and chemical composition of the zirconium aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h (Fig. 3).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical composition, % at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>β-NiAl</td>
<td>41.14</td>
</tr>
<tr>
<td>γ'-Ni₃Al</td>
<td>26.17</td>
</tr>
<tr>
<td>γ-Ni(Al)</td>
<td>6.58</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 4. Chemical composition on the cross-section of the zirconium aluminide coating deposited by CVD method on the nickel substrate.

Fig. 5. XRD results of aluminide coating deposited by CVD method on the nickel substrate.

The results of the scratch test revealed that layers obtained by the EB-PVD method have good adhesion to the nickel substrate. The load from 0 to 10 N does not lead to destruction of layers. Aluminizing process of the zirconium layer (1 µm thick) deposited on the nickel substrate leads to the Ni₅Zr intermetallic phase formation at the boundary of the Ni₃Al and Ni(Al) phases (Fig. 6).

Large zirconium content (about 56 % at) was found at the boundary of the top zone (β-NiAl phase) and the second zone (γ'-Ni₃Al phase) (Table 2, Fig. 7).

Chemical composition at the phase boundary between the NiAl and Ni₃Al zones corresponds to the NiZr and NiZr₂ phases according to the Ni-Zr phase diagram.

The increase of the zirconium layer thickness from 1 to 3 µm before aluminizing process does not change both phase and chemical composition of the aluminide coating. Aluminide coating consists of three zones (Fig. 8). The Ni₅Zr phase was found at the Ni₃Al/Ni(Al) zone boundary (Table 3).

Table 2: Phase and chemical composition of the zirconium modified (1 µm zirconium thick deposited by EB-PVD method) aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h (Fig. 6).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical composition, % at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>β-NiAl</td>
<td>41.0</td>
</tr>
<tr>
<td>NiZr/Ni₂Zr</td>
<td>7.25</td>
</tr>
<tr>
<td>γ'-Ni₃Al</td>
<td>23.75</td>
</tr>
<tr>
<td>Ni₅Zr</td>
<td>-</td>
</tr>
<tr>
<td>γ-Ni(Al)</td>
<td>6.58</td>
</tr>
</tbody>
</table>

Fig. 6. Microstructure of the zirconium modified (1 µm zirconium thick deposited by EB-PVD method) aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h.

Fig. 7. Chemical composition on the cross-section of the zirconium modified (1 µm zirconium thick deposited by EB-PVD method) aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h (Fig. 6).
Fig. 8. Microstructure of the zirconium modified (3 µm zirconium thick deposited by EB-PVD method) aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h.

### Table 3: Phase and chemical composition of the zirconium modified (3 µm zirconium thick deposited by EB-PVD method) aluminide coating deposited by CVD method on the nickel substrate. Deposition temperature 1050 °C, time 8h (Fig. 8).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical composition, % at</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-NiAl</td>
<td>40.98 58.95 -</td>
</tr>
<tr>
<td>NiZr/NiZr2</td>
<td>- 43.07 56.94</td>
</tr>
<tr>
<td>γ'-Ni3Al</td>
<td>22.82 73.97 3.21</td>
</tr>
<tr>
<td>NiZr</td>
<td>- 83.86 16.14</td>
</tr>
<tr>
<td>γ'-Ni(Al)</td>
<td>6.6 93.40 -</td>
</tr>
</tbody>
</table>

### 3. Conclusion

The zirconizing - aluminizing CVD process of the nickel substrate at 1050 °C during 8 h leads to the triple zone aluminide coating formation. Zirconium does not form any inclusions, but dissolves in the coatings phases. Hardness of aluminide coating is about 500 HV. Zirconium layers 1 and 3 µm thick were also deposited onto the Ni substrate by the EB-PVD method. The layers have a good adhesion to the Ni substrate.

The structure of zirconium modified (1 and 3 µm thick deposited by EV-PVD method) aluminide coating is the same as aluminide coating deposited by the CVD method. The zirconium serves as marker and forms intermetallic phases NiZr and NiZr2 or NiZr2. The intermetallic phases are located at the boundary between the top and inner zones and the inner zone and the substrate. The increase of zirconium layer thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does not change phase and chemical composition of the aluminide coating. The volume fraction of the NiZr phase thickness from 1 to 3 µm does

### Acknowledgment

The presented research was supported by the National Science Centre, Poland, project number 2011/01/B/ST8/05036.

### 4. Literature