MICROSTRUCTURE AND CORROSION RESISTANCE OF Hf-MODIFIED NiAl LAYERS ON NICKEL BASED SUPERALLOY Ni-Cr-Co-Mo-2Ti-1.5Al

MIKROSTRUKTURA I ODPORNOŚĆ KOROZYJNA WARSTW NiAl MODYFIKOWANYCH Hf NANIESIONYCH NA NADSTOPACH Ni-Cr-Co-Mo-2Ti-1,5Al

Małgorzata ZAGÓRSKA¹, Ryszard SITEK¹, Janusz KAMIŃSKI¹, Hubert MATYSIAK², Krzysztof Jan KURZYDŁOWSKI¹

Abstract: Article discusses examination of aluminizing and Hf modification impact on the microstructure and corrosion resistance of manufactured layers with use of CVD method on a substrate of nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al. The effect of modification process on microstructure, phase and chemical composition and corrosion resistance of manufactured layers was examined. Corrosion resistance of base material and material with protective layers was also compared. The effect of Hf modifications on surface morphology and thickness of layers and corrosion resistance of substrate was demonstrated.

Keywords: superalloy, NiAl layer, intermetallic layer, oxidation, layer modification, microstructure, corrosion resistance, phase composition

Streszczenie: Warstwy ochronne na bazie międzymetalicznej fazy NiAl stosowane są powszechnie do poprawy odporności na utlenianie wysokotemperaturowe odpowiedzialnych elementów turbin silników lotniczych. W pracy omówiono wyniki badań właściwości warstw NiAl oraz warstw NiAl modyfikowanych Hf oraz ich wpływ na mikrostrukturę podłoża - nadstopu niklu Ni-Cr-Co-Mo-2Ti-1,5Al. Procesy aluminiowania realizowano metodą CVD w atmosferze wodoru jako gazu nośnego. Przeprowadzono obserwacje mikrostruktury warstw oraz podłoża, badania składu chemicznego i fazowego warstw. Stwierdzono, że wytworzone warstwy wykazują ciągłość na całej powierzchni próbek, stabilność składu chemicznego i fazowego oraz nie wpływają na mikrostrukturę stopu.

Słowa kluczowe: nadstop, warstwa NiAl, warstwa na bazie fazy międzymetalicznej, utlenianie, modyfikacja warstwy, mikrostruktura, odporność korozjna, skład fazowy

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1. INTRODUCTION

The use of protective coatings is common for the properties improvement of aircrafts responsible parts, for example turbine blades in engine hot sections. These parts are exposed to high temperatures and high rotational speeds and are mainly attacked by high-temperature oxidation and risk of corrosion damage. Moreover, frequently sea flights cause possibility of corrosion, which occurs from surface reactions with salts deposited from the atmosphere. Layers based on NiAl intermetallic phase are commonly used to increase high temperature oxidation resistance of alloys. There are four equilibrium phases in NiAl system: NiAl₃ (ε phase), NiAl (β phase), Ni₃Al (γ’ phase), Ni₂Al₃ (δ phase) and one nonequilibrium phase Ni₅Al₃ [1,2]. NiAl phase exhibits the most advantageous properties due to the requirements for aircraft engine turbine components [3,4]. This phase is characterized by good properties such as: high melting point, low density, high elastic modulus and high oxidation resistance in elevated temperatures [5,6]. However, layers based on NiAl phase does not fulfill such requirements as: good adhesion, ductility and high tensile strength at low temperatures [7]. Properties of protective layers depends on its microstructure, phase and chemical composition. Therefore, in order to improve their adhesion and strength, the modification with additional elements like Pt, Hf, Zr is used [8,9]. Such reactive elements (RE) had also a significant effect on oxidation behavior of NiAl coatings [10,1].

Hafnium has been used in nickel based superalloys as addition of 0.1÷1.0 wt.% to improve high temperature mechanical properties of equiaxed alloys [12]. Later it was discovered that Hf added in small amount to coatings on nickel and cobalt superalloys improve the adherence and durability of protective oxide scale on layers surface [13]. Moreover, it was proven that Hf addition not only reduced oxide scale growth rate but also increased oxide scale adherence [14–16].

Aircrafts engine elements are usually constructed of heat and high-temperature creep resistant materials, which include nickel and cobalt based superalloys. Alloy Ni-Cr-Co-Mo-2Ti-1.5Al is one of γ’-strengthened Ni-based superalloys. This alloy is characterized by very good mechanical properties in temperature range 650÷925°C, due to its chemical composition and appropriate heat treatment parameters [17,18]. In addition, this material exhibit low content of Ti and Al, which results in a low volume fraction of strengthening phase γ’ Ni₃(Al, Ti) [19,20]. That makes this alloy suitable in joining (for example by welding), what is important in manufacturing heat resistant turbine components. Furthermore, its working temperature range enables increase of operating temperature of aircraft engines, what simultaneously enlarges the risk of corrosion damages.

In this work Ni-Al based layers (modified by Hf) on nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al were characterized. The effect of modification process on microstructure, phase and chemical composition and corrosion resistance of manufactured layers was examined. Corrosion resistance of base material and material with protective layers were also compared.

2. EXPERIMENTAL METHODS

Cast nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al (composition shown in Table 1) in precision vacuum casting process was prepared as a substrate material. Castings were cut into samples, which were sandblasted and ultrasonic cleaned. The hafnium-doped aluminide coatings were made using the Chemical Vapor Deposition method (CVD) in equipment
manufactured by IonBond company. The aluminizing process was performed in two ways. In the first one the aluminizing process was conducted for 12 h, at the temperature 1040°C, under a pressure of 150 hPa, in the presence of AlCl₃ and in atmosphere of hydrogen as a carrier gas. Intermetallic phase NiAl was formed according to the reaction:

\[ 2\text{AlCl}_3 + 2\text{Ni} + 3\text{H}_2 \rightarrow 2\text{AlNi} + 6\text{HCl} \]  

The second way of aluminizing process consist of two stages: first for 1 h, at the temperature 1040°C, under a pressure of 150 hPa, in the presence of AlCl₃ and in atmosphere of hydrogen as a carrier gas. In second stage Hf modification from external generator were carried out for 6.5 h.

<table>
<thead>
<tr>
<th>wt.%</th>
<th>C</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>Co</th>
<th>Al</th>
<th>B</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0598</td>
<td>0.066</td>
<td>0.0036</td>
<td>0.006</td>
<td>20.27</td>
<td>8.21</td>
<td>2.320</td>
<td>10.02</td>
<td>1.74</td>
<td>0.003</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 1. The chemical composition of cast nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al

Microstructure analysis were carried out by an scanning electron microscope (SEM) HITACHI SU 70, equipped with energy dispersive spectroscopic (EDS) Thermo Noran. Manufactured layers were observed on the surface and in cross-section, in backscattered electrons (BSE) contrast, which is used to detect contrast between areas with different chemical compositions. Chemical composition and maps of element distribution were carried out by energy dispersive spectrometry. The coatings thickness were determined by means of ImageJ graphic software, ten measurement for each sample were performed. Phase composition of layers was investigated using Bruker D8 X-ray diffractometer, by CuKα radiation.

Corrosion resistance of based material (BM), material with pure NiAl layer and material with Hf modified NiAl layer was examined by impedance and potentiodynamic methods in AutoLab PGSTAT 100 potentiostat. Investigations were carried out in acidified (pH 5) solution of 0.1 M NaCl at room temperature. To stabilize corrosion potential samples were kept in a corrosive solution for about 1 h before testing. Impedance measurements were realized in the frequency range \(10^5\text{÷}10^3\) Hz, with an sinusoidal signal amplitude 20 mV, in three-electrode system:
- tested electrode,
- reference electrode (saturated calomel electrode SCE),
- auxiliary electrode (platinum).

Impedance spectra were analyzed using the EQUIVCRT Baukampa program. According to obtained spectra various replacement systems were used: with two \(R(RQ)(RQ)\), \(R(Q[R(RQ)])\) or three \(R(RQ)(Q[R(RQ)])\) time constants. Replacement system, which is commonly applied in localized corrosion tests, was used for samples with coatings. Whereas spectra for base material was analyzed using replacement system \(R(RQ)(RQ)\), which is dedicated for multiphase materials. Obtained spectra are shown in the form of Bode plots. Potentiodynamic examinations were carried out in an identical three-electrode system, polarizing material with the rate of potential changes 0.2 mV/s.
3. RESULTS AND DISCUSSION

The results of SEM observation of manufactured layers are shown in Figure 1. A polyhedral shape grains was observed on the surface of NiAl layers (Fig. 1a), which is typical surface morphology of diffusion aluminide coatings. An overall surface composition of NiAl phase was tested by EDS analysis. Samples coated with Hf-modified aluminide layers exhibit a different surface morphology – homogeneous distributed fine-grained crystallites (Fig. 1b). EDS analysis showed a composition of NiAl phase with bright areas containing about 1.5 at.% of Hf.

Microstructure characteristics of cross-section reveal that in both cases coatings are continuous and composed of two zones: an external additive layer and an internal interdiffusion layer separated with a thin porous interface (Fig. 1c,d).

Measurements of layers thickness are shown in Table 2. Thickness of pure aluminide layers is about 35 μm, whereas for Hf-modified NiAl layers it is approximately 47 μm. The thickness of each zone is respectively, in order from the surface, about 20 μm and 15 μm for pure NiAl layer, while 31 μm and 17 μm for Hf-modified NiAl layer.

For each sample bright columnar precipitates and grey similar to equiaxed were observed in interdiffusion layer. Some differences occur in additive layers and in porous interface. In modified layers some bright fine equiaxed particles are present in thin interface. Furthermore in this samples also bright particles along the grain boundaries in matrix of additive layer were observed.

Figure 1. Surfaces (a, b) and cross-sections (c, d) of NiAl and NiAl+Hf modified layers on nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al
Table 2. The thickness of manufactured NiAl and NiAl+Hf layers

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Full layer</th>
<th>External layer</th>
<th>Internal layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl</td>
<td>35</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>NiAl+Hf</td>
<td>47</td>
<td>31</td>
<td>17</td>
</tr>
</tbody>
</table>

Multicomponent structure of manufactured layers was confirmed by images of elements distribution over the cross section and corresponding surface X-ray phase analysis (Fig. 2). Additive layers, in both pure NiAl layers and Hf-modified layers, composed mainly of NiAl phase. XRD analysis indicate that for pure layers it is Al\textsubscript{1.1}Ni\textsubscript{0.9} phase and for modified layers it is Al\textsubscript{0.42}Ni\textsubscript{0.58}. Whereas in internal layer occur two types of precipitates, both rich in Mo and Cr. During EDS mapping no Hf was detected, suggesting that Hf content is below EDS detection limit. However, small bright precipitates, visible in thin porous interface between external and internal layers (Fig. 3a) and at the grain boundaries in external layer (Fig. 3b), proved to be rich in Hf. EDS analysis confirm that particles at the interface contains about 19.39 at.% of Hf and particles at grain boundaries comprise about 4.28 at.% of Hf.

The impedance spectra of investigated materials are presented in Figure 4. They indicates that aluminizing process increases the electrochemical heterogeneity of the substrate, because additional maxima of phase angle appears on Bode plots. Location of peaks in high frequency range (approximately 10\textsuperscript{3} Hz) shows that substrate material is sensitive to pitting corrosion. Peaks occurring in lower frequencies range (10\textsuperscript{-1} Hz) describes electrochemical parameters of passive layer. Data compiled in Table 3 points a positive effect of CVD coating on corrosion resistance changes.
It is demonstrated by increased values of resistance $R_t$: $2.5 \times 10^5 \ \Omega \text{cm}^2$ for BM, $5.9 \times 10^5 \ \Omega \text{cm}^2$ for NiAl layer and $19.6 \times 10^5 \ \Omega \text{cm}^2$ for NiAl+Hf layer with relatively high-capacitive nature of coating. However, due to significant electrochemical heterogeneity of substrate, areas with increased electrochemical activity ($n \approx 0.75$), where electrochemical corrosion could initiate. It can be presumed that these locations during potentiodynamic test will become places of pits incubation.

Curves shown in Figure 5 indicate that tested materials are in passive state with varied persistence of passive layer. CVD coatings manufactured on nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al enhance its corrosion resistance. It is confirmed by reducing corrosion current density: $0.09 \ \mu A/cm^2$ for BM, $0.023 \ \mu A/cm^2$ for NiAl layer and $0.007 \ \mu A/cm^2$ for NiAl+Hf layer (Fig. 4), as well as increasing corrosion potential of substrate (respectively -230 mV., -120 mV, -130 mV). However, due to cathode nature of coatings and aggressive corrosive environment (presence of chloride ions and increase in hydrogen ion concentration close to the value, in which active dissolution of aluminum compounds is observed, pH = 5) the stability of aluminum layer is insignificant. It is shown by significant changes in current density in passive areas, as well as the low values of breakthrough potential, above which initiation of pitting corrosion occurs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Replacement system</th>
<th>Parameter</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base material</td>
<td>R(RQ)(RQ)</td>
<td>$R (\Omega \text{cm}^2)$</td>
<td>81</td>
<td>2.16*10^5</td>
<td>1.46*10^4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y_{\text{ocp}}(F/cm^2 s^{n-1})$</td>
<td></td>
<td>3.00*10^5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td></td>
<td>0.86</td>
<td>1.00</td>
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</tr>
<tr>
<td>NiAl layer</td>
<td>R(Q[R(RQ)])</td>
<td>$R (\Omega \text{cm}^2)$</td>
<td>76</td>
<td>1.00*10^5</td>
<td>5.95*10^5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y_{\text{ocp}}(F/cm^2 s^{n-1})$</td>
<td></td>
<td>5.60*10^6</td>
<td>2.80*10^6</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>$n$</td>
<td></td>
<td>0.85</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>NiAl+Hf modified layer</td>
<td>R(Q)[R(RQ)]</td>
<td>$R (\Omega \text{cm}^2)$</td>
<td>73.5</td>
<td>6.04*10^4</td>
<td>1.96*10^6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$Y_{\text{ocp}}(F/cm^2 s^{n-1})$</td>
<td></td>
<td>1.78*10^5</td>
<td>8.20*10^6</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td></td>
<td>0.71</td>
<td>0.83</td>
<td>0.85</td>
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</table>
Figure 4. Impedance spectra for nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al: a) base material, b) with NiAl layer and c) with NiAl+Hf modified layer

Figure 5. Potentiodynamic curves of nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al for: base material, with NiAl layer and with NiAl+Hf modified layer
Table 4. Electrochemical parameters from potentiodynamic analysis of nickel based superalloy Ni-Cr-Co-Mo-2Ti-1.5Al: base material, with NiAl layer and with NiAl+Hf modified layer

<table>
<thead>
<tr>
<th>Material</th>
<th>(i_{\text{kor}}(\mu\text{A/cm}^2))</th>
<th>(E_{\text{kor}}(mV))</th>
<th>(E_{\text{np}}(mV))</th>
<th>(i_{\text{pas}}(\mu\text{A/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base material</td>
<td>0.09</td>
<td>-230</td>
<td>640</td>
<td>1.74</td>
</tr>
<tr>
<td>NiAl layer</td>
<td>0.023</td>
<td>-120</td>
<td>25</td>
<td>0.97</td>
</tr>
<tr>
<td>NiAl+Hf modified layer</td>
<td>0.007</td>
<td>-130</td>
<td>10</td>
<td>0.12</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Above study showed the effect of Hf modification process on microstructure, phase and chemical composition and corrosion resistance of manufactured NiAl layers. Corrosion resistance of base material and material with protective layers was also compared. The effect of Hf modifications on surface morphology and thickness was proved. At NiAl layers (35 \(\mu\)m) surface a polyhedral shape grains was observed, while NiAl+Hf modified layers (47 \(\mu\)m) revealed homogeneous distributed fine-grained crystallites. In both cases coatings are continuous and composed of two zones: an external additive layer and an internal interdiffusion layer separated with a thin porous interface. For each sample bright columnar precipitates and grey similar to equiaxed were observed in interdiffusion layer. In addition in NiAl+Hf modified layers bright particles rich in Hf in thin interface and along the grain boundaries in matrix of additive layer were observed. It was indicated that alumining process increases the electrochemical heterogeneity of the substrate and that CVD coatings showed positive effect on corrosion resistance. Manufactured layers reduce corrosion current density and increase corrosion potential of substrate. However, due to cathode nature of coatings and aggressive corrosive environment the stability of aluminum layer is insignificant.

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LITERATURE


