MIKROSTRUCTURAL CHANGES OF AIR PLASMA SPRAYED CoNiCrAlY COATING AFTER REMELTING

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Abstract
The samples in present study were prepared by air plasma spraying (APS) of CoNiCrAlY coatings onto the nickel-based superalloy INCONEL 713LC substrate surface. Immediately, after the spraying was onto the CoNiCrAlY coatings outer surface pressed an high purity aluminium sheet by means of uniaxial cold pressing technique. After that the samples were annealed at the temperature of 650°C for different dwell-time in argon-flow atmosphere. The modified CoNiCrAlY coatings enriched by aluminium were produced. Moreover the voids, imperfectly melted powder particles, and oxide scale present in original plasma sprayed coating microstructure were eliminated. The scanning electron microscope (SEM) was used to record the modified coatings microstructure. Changes in chemical composition were studied by means of energy dispersive microanalysis (EDX).

Keywords:
M-CrAlY coatings, air plasma spraying, heat treatment, remelting, microstructure

1. INTRODUCTION
Superalloys are the most reliable and cost effective structural material widely used in aircraft and industrial gas turbine applications. The components like internal combustion chambers, impellers and shafts of turbojet engines are subjected to varying temperature and stress load cycles during their operation conditions. Within these cycles the component material undergoes a number of degradation processes, especially oxidation and high-temperature corrosion [1, 2].

The superalloys surface does not have adequate level of such critical elements as Al and Cr to impact oxidation and corrosion resistance for complete service live of produced components. Increasing Al and Cr concentration, therefore, would apparently be a logical solution to increase oxidation capability and high-temperature corrosion resistance. However, a high concentration of Al leads to produce brittle intermetallic (NiAl3 and Ni3Al) phases with lower melting points and unsufficient creep resistance. The idea to modify the superalloy and increase their surface properties by Al using CVD, slurry or out of pack deposition processes was firstly applied in the 1960s and found a wide application area. Since the 1980s, some types of overlay coatings found an application in turbine blades. Recent overlay coating production technologies enables to control required chemical composition, thickness, and appropriate combination of physico-chemical and mechanical properties. In recent practice well established M-CrAlY coatings (M = Ni or/and Co) are widely applied as a standalone “overlay coatings” or as a “bond coatings” in thermal barrier coating systems [3, 4].

The paper deal with the study of microstructural changes and phase transformations after the remelting of M-CrAlY plasma sprayed coatings, where these coatings are at the same time enriched by aluminium and relieve of voids, imperfectly melted particles, and oxides scale present.
2. EXPERIMENTAL

Commercially available polycrystalline nickel-base superalloy Inconel 713LC, supplied by PBS Velká Bítěš, a.s., Czech Republic, was used as a substrate material. Their nominal composition is listed in Table 1. Surface of specimens (10 x 10 x 5 mm) was ground with abrasive paper up to #800 and washed with acetone in ultrasonic cleaning bath for 15 min before the coating deposition. The CoNiCrAlY powder with average particle 45 - 65 μm (GTVM GmbH, Germany) and nominal composition, see Table 1, were sprayed onto the substrate surface by means of air plasma spray technique. The average thickness of the CoNiCrAlY coating was about 125 μm.

<table>
<thead>
<tr>
<th>Tab. 1 Chemical composition of substrate alloy and powder [at. %]</th>
<th>C</th>
<th>Al</th>
<th>Nb</th>
<th>Ti</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Co</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Inconel 713LC</td>
<td>0.23</td>
<td>12.07</td>
<td>1.19</td>
<td>0.92</td>
<td>12.74</td>
<td>2.65</td>
<td>bal.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powder CoNiCrAlY</td>
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<td>21.21</td>
<td>27.73</td>
<td>bal.</td>
<td>0.30</td>
<td></td>
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</table>

An aluminium sheet of 99.999 % high purity was pressed (10.5 t) by uniaxial cold pressing technique (CBJ 500-6 hydraulic press). Specimens were heated to 650°C for 0, 2 and 5 hrs in Heraeus tubular furnace with argon-flow atmosphere. Scanning electron microscope (SEM) Philips XL30 was used for microstructural evaluation. Chemical composition was measured by means of energy dispersive X-Ray spectrometr (EDX) EDAX.

3. RESULTS AND DISCUSSION

3.1 As-sprayed coating microstructure

Initial state of the samples of plasma sprayed CoNiCrAlY coatings with the pressed aluminium sheet is shown in Figure 1. The resulting CoNiCrAlY coating microstructure is typical for the technology used. It consist of remelted splats “flattened powder particles”, small amount of porosity, oxide scale and unmelted particles. The aluminium sheet consist of homogenous Al solid solution (FCC crystal lattice structure). The plasma sprayed CoNiCrAlY coatings could be created by three phases: CoNi-solid solution, β-CoAl intermetallic phase, and α-Al2O3 oxide. No apparent diffusion layers were observed at the interface in between the CoNiCrAlY coating and the substrate or at interface in between the CoNiCrAlY coating and the aluminium sheet.

![Fig. 1 SEM backscattered electron micrograph of CoNiCrAlY coating deposited on the Inconel 713 LC surface after the aluminum sheet pressing.](image-url)
3.2 Coatings microstructure changes after the thermal exposure

The CoNiCrAlY coating microstructure after the annealing at the temperature 650°C for 0 hrs with pressed aluminium sheet onto the CoNiCrAlY coating surface is shown in Figure 2(a). There is minor change in comparison with the as-sprayed coating microstructure only. The upper part of CoNiCrAlY coating was enriched by aluminium, the voids, imperfectly melted powder particles, and oxides presented in original plasma sprayed coating microstructure were eliminated. New light grey phase formation at the interface between the CoNiCrAlY coating and the aluminium sheet was observed, see Figure 2(c).

![SEM backscattered electron micrographs of modified coating system on Inconel 713 LC after annealing - 650°C/ 0 hrs (Ar). (a) overview of substrate/coating/aluminium interfaces, (b) detail of remelted aluminium region, (c) detail of remelted CoNiCrAlY coating region and (d) detail of interface in between the remelted and unmelted CoNiCrAlY coating.](image)

Based on EDX measurement (Table 2) corresponding to cross marks locations in Fig. 2 and known phases stoichiometry were estimated the expected phases. These are intermetallics Al$_3$(Co,Ni) (point 3), Al$_7$Cr (point 4) and Al solid solution (points 5, 6, 7) in the remelted part region of CoNiCrAlY coating and pure aluminium (point 1) and Al$_3$(Co,Ni) intermetallic phase (point 2) in the remelted aluminium sheet region.

![Chemical composition estimated by EDX analysis, corresponding with Fig. 2](image)

**Table 2** Chemical composition estimated by EDX analysis, corresponding with Fig. 2 [at. %]

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<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tbody>
<tr>
<td>Al</td>
<td>99,3</td>
<td>81,0</td>
<td>82,3</td>
<td>79,1</td>
<td>85,0</td>
<td>82,8</td>
<td>78,2</td>
<td>18,0</td>
</tr>
<tr>
<td>Cr</td>
<td>0,7</td>
<td>12,7</td>
<td>4,4</td>
<td>4,2</td>
<td>6,0</td>
<td>20,7</td>
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<tr>
<td>Co</td>
<td>10,1</td>
<td>12,7</td>
<td>3,8</td>
<td>6,7</td>
<td>6,6</td>
<td>9,2</td>
<td>33,9</td>
<td></td>
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<tr>
<td>Ni</td>
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<td>5,0</td>
<td>2,1</td>
<td>3,9</td>
<td>6,4</td>
<td>6,6</td>
<td>27,4</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>2,3</td>
<td></td>
<td></td>
<td></td>
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</table>
More significant changes in coating system microstructure can be observed after the annealing at the temperature 650°C for 2 hrs (Fig. 3(a)). In comparison with as-sprayed coating microstructure the remelted aluminium region (Fig. 3(b)) consist of three different phases.

**Fig. 3** SEM backscattered electron micrographs of modified coating system on Inconel 713 LC after annealing - 650°C/ 2 hrs (Ar), (a) overview of substrate/coating/aluminium interfaces, (b) detail of remelted aluminium region, (c) detail of remelted CoNiCrAlY coating region and (d) detail of interface in between the remelted and unmelted CoNiCrAlY coating.

Based on EDX analysis listed in Table 3 the intermetallic phase Al₂Cr (point 1), Al solid solution dispersed by fine Al₃(Ni,Co) intermetallic phase (points 2) and Al₂O₃ oxide scale (point 3) can be expected. Within the remelted coating region (Fig. 3(c)) was apparent the formation of an Al solid solution with fine dispersed Al₃(Ni,Co) (points 5, 7), Al₂Cr (point 4), Al₃Ni (point 6) and Al₃(Co, Ni) (point 8) intermetallic phases. Slight increase of the remelted coating region thickness was recorded. Due to the porosity coarsening after the remelting of CoNiCrAlY coating a large amount of small voids were eliminated. The coarse pores were observed within the intermetallic strengthened aluminium region.

**Tab. 3** Chemical composition estimated by EDX analysis, corresponding with Fig. 3 [at.%]

<table>
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<tr>
<td>O</td>
<td>52,5</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Al</td>
<td>85,8</td>
<td>82,4</td>
<td>46,0</td>
<td>85,2</td>
<td>83,0</td>
<td>77,6</td>
<td>81,0</td>
<td>74,9</td>
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<tr>
<td>Cr</td>
<td>12,7</td>
<td></td>
<td>8,9</td>
<td>1,9</td>
<td>3,5</td>
<td>5,1</td>
<td></td>
<td>7,1</td>
</tr>
<tr>
<td>Co</td>
<td>0,5</td>
<td>9,2</td>
<td>2,7</td>
<td>7,4</td>
<td>2,3</td>
<td>7,5</td>
<td>10,7</td>
<td></td>
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<tr>
<td>Ni</td>
<td>1,0</td>
<td>8,4</td>
<td>3,2</td>
<td>7,7</td>
<td>11,7</td>
<td>6,4</td>
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<td>Y</td>
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<td>4,9</td>
<td></td>
<td>0,1</td>
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</table>

The most significant changes in a coating microstructure can be observed after the annealing at the temperature 650°C for 5 hrs, see Figure 4. The remarkable increase of remelted coating region thickness was observed and almost whole original CoNiCrAlY coating was remelted. Coarse voids were moved from
remelted coating region towards the free surface, where spallation of the rest intermetallic strengthened aluminium was obviously observed [5, 6]. Moreover, it was described in a case of NiCrAlY coatings remelting in reference [7]. Spallation of mentioned region can be probably observed after the annealing at the temperature of 650°C for dwell-time longer than 5 hrs as well.

**Fig. 4** SEM backscattered electron micrograph of modified CoNiCrAlY coating after the annealing of 650°C/5 hrs (Ar).

**Fig. 5** SEM backscattered electron micrographs of modified CoNiCrAlY coating after the annealing of 650°C/5 hrs (Ar), (a) top coating region, (b) unmelted coating/remelted coating/aluminium interface.

Based on the EDX analysis measurements listed in Table 4 the Al solid solution strengthened by fine dispersed Al$_3$(Ni,Co) (points 2, 3, 4, 5, 7) intermetallic phase and Al$_7$Cr (point 1), Al$_3$(Ni,Co,Y) (point 6), Al$_3$(CoNi) (point 8) and Al$_3$Ni$_2$ (point 9) intermetallics was formed. The cracks originate in the modified coating system microstructure due to the consequence of high aluminium concentration, which promotes the brittle NiCoAl$_3$ phase formation [8]. Based on the records of above observed phases the transparency of CoNiCrAlY coating and the aluminium sheet interface for diffusion exists. The major elements of CoNiCrAlY coating (Ni, Co and Cr) diffuse into the aluminium sheet direction and also in backward direction the diffusion of Al was confirmed. Due to the CoNiCrAlY coating enrichment by aluminium, the porosity, imperfectly melted powder particles, and oxide scale from original plasma sprayed coating microstructure were eliminated. The CoNiCrAlY coatings remelting process is apparently slower than in a case of the NiCrAlY one [7], because of the prior aluminium melt interact with cobalt and nickel within the interaction zone, where the aluminides are formed, and afterwards the CoNiCrAlY coating is going to be remelted. It should be noted, that longer dwell-time at the temperature of 650°C can be recommended to complete remelting of CoNiCrAlY coating thickness.


4. CONCLUSION

The modified CoNiCrAlY coatings enriched by aluminium were produced. Moreover the voids, imperfectly melted powder particles, and oxide scale present in original plasma sprayed coating microstructure were eliminated. Especially the voids present in the coatings microstructure cumulated itself within the top of original aluminium plated region. The cracks originate in the modified coating system microstructure due to the consequence of high aluminium concentration, which promotes the brittle NiCoAl₃ phase formation. Higher annealing temperature than 650°C and longer dwell-time could be recommended in order to remelt whole CoNiCrAlY coating thickness.

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