

POSSIBILITIES OF USING ALUMINIDE COATING MODIFICATIONS BY NICKEL GALVANIZING WITH INTRODUCTION OF ADDITIONAL ELEMENTS: CR, SI, AND ZR

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Summary

The basic method of surface protection for aviation engine components manufactured from nickel super alloys is diffusion aluminization. There are four methods of forming aluminide coatings: pack cementation, above the pack, slurry, and chemical vapor deposition (CVD). The aluminide coatings are modified with various elements, e.g. Pt, Pd, Hf, Zr, Si, Cr, Y, etc. The paper shows results of experiments on the use of electrochemical processes in which the modifying elements are introduced in the form of powder for galvanic bath. These processes have been combined with low-activity and high-activity aluminization, as well as zircon doping in the CVD process. It has been shown that the aluminide coatings formed in the high-activity process are characterized by Al > 50% at. content. The aluminide coatings formed in the low-activity process were composed of an outer zone composed of a NiAl phase with an aluminum content < 50% at. and the diffusion zone. The aluminide coatings formed during low-activity zircon doping have similar structure. The content of elements introduced with nickel was low (up to several %), which does not provide for a desired increase in heat resistance of the modified coatings.

Keywords: aluminide coatings, protective coatings, aluminizing process, pack aluminizing, gas phase aluminizing, chemical vapour deposition, modified aluminide coatings

Modyfikowanie warstw aluminidkowych Cr, Si i Zr w procesach niklowania elektrochemicznego i chemicznego osadzania z fazy gazowej CVD

Streszczenie

Aluminiowanie dyfuzyjne jest podstawowym procesem wprowadzonym do ochrony powierzchni elementów części gorącej silników lotniczych wytwarzanych z nadstopów niklu. Warstwy aluminidkowe wytwarzane są w procesach: kontaktowo-gazowym (*ang. pack cementation*), gazowym bezkontaktowa (*ang. above the pack*), zawieszinowym (*ang. slurry*) i chemicznym osadzaniu z fazy gazowej CVD (*ang. Chemical Vapour Deposition*). Warstwy aluminidkowe dla zwiększenia ich żaroodporności modyfikowane są pierwiastkami m.in. Pt, Pd, Hf, Zr, Si, Cr, Y. W artykule przedstawiono analizę wyników badań warstw aluminidkowych, w których pierwiastki modyfikujące wprowadzono w postaci proszku do kąpeli galwanicznej w trakcie procesu niklowania. Procesy te połączono z aluminiowaniem nisko- i wysokoaktywnym, a także cyrkono-aluminiowaniem w procesie CVD. Wykazano, że warstwy

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aluminidkowe wytworzone w procesie wysokoaktywnym charakteryzują się zawartością Al >50% at. W warstwie aluminidkowej wytworzonej w procesie niskoaktywnym wyodrębniono strefę zewnętrzną - kryształów fazy NiAl o zawartości Al <50% at. oraz strefę dyfuzyjną. Zbliżoną budowę miały warstwy aluminidkowe wytworzone w trakcie cyrkono-aluminiowania niskoaktywnego. Stwierdzono małe zawartości pierwiastków wprowadzanych wraz z niklem (do kilku %).

Słowa kluczowe: warstwy aluminidkowe, procesy aluminiowania, aluminiowanie metodą kontaktowo-gazową i gazową, chemiczne osadzanie z fazy gazowej, modyfikowane warstwy aluminidkowe

Introduction

The basic method of surface protection of aircraft engine components manufactured from nickel superalloys is diffusion aluminizing. As a result of aluminizing elements made of nickel superalloys, a β -NiAl phase is formed. Four methods of producing aluminide coatings are currently used: pack cementation, above the pack, slurry, and chemical vapour deposition (CVD) [1]. In the pack cementation method, the coated elements are placed in closed or semi-closed containers and covered with a powder mixture. The mixture consists of metal elements intended for deposition (or their alloys), halide activators (e.g. AlF_3 , NaCl , NH_4Cl , and NH_4F), and neutral filler (usually aluminum oxide). The coating is formed by the reduction of metal halide vapours on the surface of the substrate, followed by the diffusion of the introduced Al and the nickel superalloy material. [2]. Gas methods (VPA, vapour phase aluminizing and out of pack) are known from some publications [3,4] The coated parts are placed in such way that they do not come into contact with the powder or granules constituting the source of aluminum. The advantages of gas-phase methods are: higher coating purity, process repeatability, and low manufacturing costs. It is possible to modify the aluminide coating by elements which increase resistance to oxidation. The Howmet company [5] is developing Chemical Vapour Deposition (CVD). In this method, halide vapours, e.g. aluminum chlorides, are formed by passing HCl gas through Al granules at a temperature of about 300°C. The process takes place in external generators. AlCl_x vapours react with Ni and form a β -NiAl coating on the substrate (nickel superalloy). For the high-activity aluminizing, additional Cr-Al granules are placed in the gas flow path inside the retort. Elements modifying aluminide coatings (e.g. Y, Hf, and Zr) are introduced from additional generators. In the CVD method it is possible to cover internal cooling channels of turbine blades however the disadvantage of the method is high equipment costs.

The aluminide coatings are modified with various elements, e.g. Pt, Pd, Hf, Zr, Si, Cr, Y, etc. The elements are introduced by diffusion (mainly CVD) or galvanic methods (e.g. Pt, Pd etc.). [6,7] Galvanic nickel plating with the introduction of powder materials is used, among others, in forming abrasion resistant coatings [8].

With a view to reducing costs of aluminizing processes, the article presents experiments on the application of electrochemical processes in which the modifying elements are introduced in the form of powder into galvanic bath.

Experimental

In order to reduce the cost of aluminizing, there was proposed a new solution (Fig. 1). The MAR M200 nickel superalloy with composition (wt. %): Al-4, Hf-2.4, W-12.6, Nb-1.2, Ti-2.5, Cr-7, Co-9, Ni-bal. was used as a base material. The sample with diameter 14 mm and 4 mm thickness were used in research. The doping elements- Zr, Cr, and Si in the form of powder with grain size below 20 μm were added to the electroplating solution based on the Watt's solution. After electroplating process, the three types of CVD-aluminizing processes were conducted:

- low activity aluminizing,
- high activity aluminizing, and
- low activity aluminizing with Zr doping.

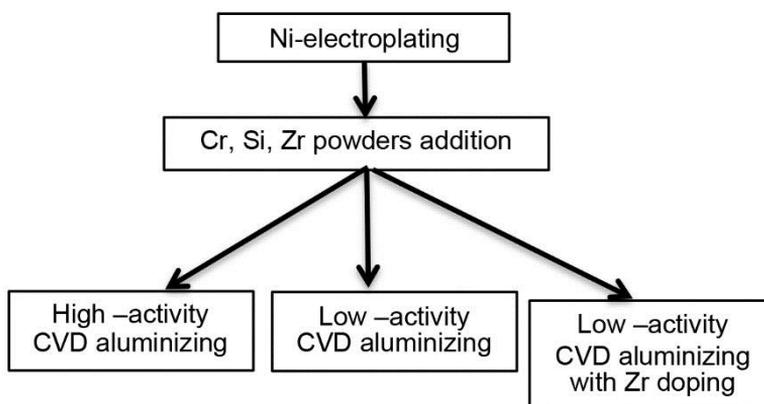


Fig. 1. Scheme of proposed modified aluminide coatings manufacturing process

Aluminizing was carried out with the use of the Bernex BPX Pro 325s. The aluminizing time was 12 hours, the temperature of the low-activity aluminizing process – 1040°C and that of the high-activity aluminizing – 959°C. In the high-activity aluminizing process, Al-Cr granules were additionally introduced. In the Zr doping process, zirconium was introduced in the form of ZrCl_4 produced in an external generator.

The microstructure was examined using Hitachi SEM S-3400 scanning electron microscope. The analysis of the chemical composition was carried out using the Thermo EDS adapter. Coating thickness measurements were taken with the use of the Zeiss AxioVision rel. 4.8.

Results

Modified aluminide coatings obtained in the high-activity CVD process

In the first process, on a galvanic nickel coating in which the chromium powder was introduced, there was carried out a high-activity CVD process. The measurements taken subsequently showed an average thickness of 39.89 μm (Fig. 1a, table 1). An analysis of the chemical composition in the micro-areas presented in Fig. 2a was conducted. The areas 1-4 located in the outer zone were thoroughly analyzed. It was shown that in the outer zone there occurred two areas. The external area (marked 1-3 in Fig. 2a) was characterized by an aluminum content of 51.8-52.6 at. %, while the internal area (marked as 4 in Fig. 2a) - about 40% at. In this area the niobium, titanium and tungsten were presented. In the external area, the chromium content was smaller (1.4-1.7 at. %), while in the internal area it was higher (>5 at.%) In the diffusion zone (area 5, Fig. 2a), the chromium content exceeded 15 at. %. Also observed in this zone were tungsten, titanium, and niobium.

As a result of galvanic nickel plating, during which introduced was silicon powder and high-activity aluminizing, there was formed a coating with an average thickness of 58.65 μm (Fig. 2b). Analysis of the chemical composition carried out in the micro-areas of the outer zone showed an average aluminum content of 47.8 at. % (area 8 in Fig. 2b). The aluminum content was changing from 53.4 at.% in the subsurface area (area 6 in Fig. 2b) to 37 at.% near the diffusion zone (area 7, Fig. 2b, table 1). The silicon content in the outer zone was 0.2% at. In the diffusion zone (area 9), the aluminum content was 22.9 at. % and the silicon content - up to 4.5 at.%.

The aluminide coating formed by galvanic plating of the Ni coating with the introduction of zirconium and high-activity CVD aluminizing was characterized by a thickness of 47.91 μm (Fig. 2c). Analysis of the chemical composition showed that the largest content of zirconium (8.9 at.%) was observed in area 10 (Fig. 2c). The aluminum content in this spot was approx. 47 at. %. The average aluminum content in the outer zone was 47.2 at. % (area 13, Fig. 2c). The average content of zirconium in the outer zone did not exceed 1 at. % In the area marked 12 (in Fig. 2c) located just above the diffusion zone, the aluminum content was smaller and amounted to approx. 36.3% at. In this area, the content of chromium and titanium was also increased. In the diffusion zone (area 14, Fig. 2c), besides aluminum and nickel, also observed were chromium, titanium, and tungsten.

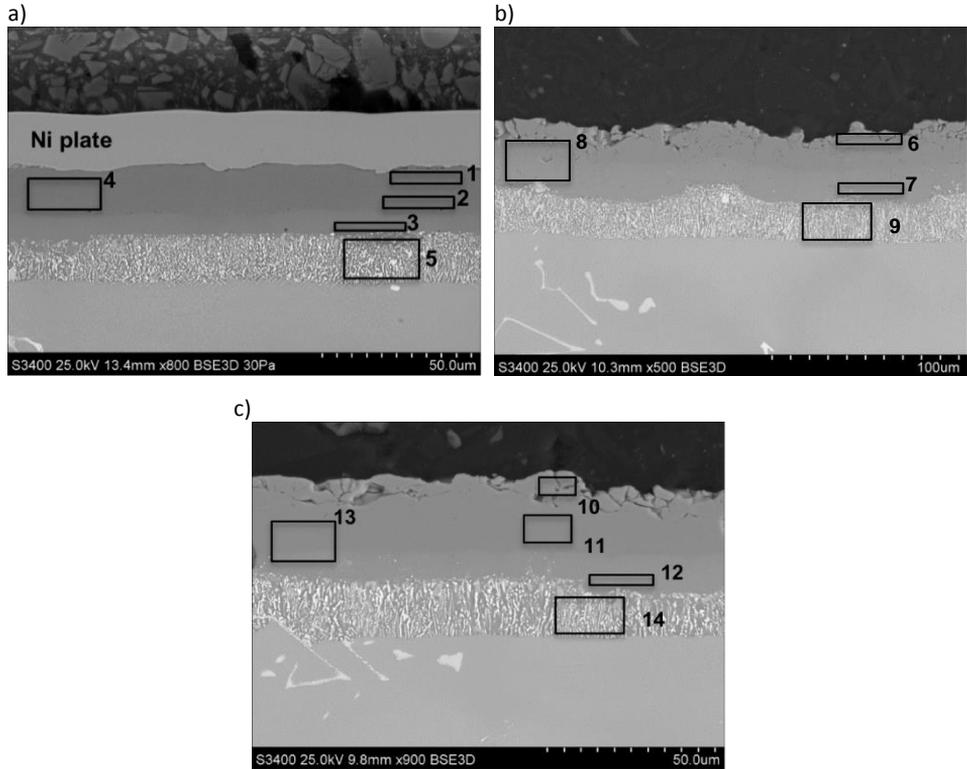


Fig. 2. Microstructure of aluminide coatings obtained by a) Cr+Ni, b) Si+Ni, c) Zr+Ni electroplating and high activity CVD aluminizing

Table 1. Results of chemical analysis in areas presented on Fig. 2a-c

| Area | Elements content, at. % | | | | | | | |
|------|-------------------------|-----|------|------|-----|-----|-----|-----|
| | Al | Ti | Cr | Ni | Zr | Nb | W | Si |
| 1 | 52.6 | | 1.4 | 45.6 | 0.1 | | 0.2 | |
| 2 | 52.0 | 0.2 | 1.4 | 46.0 | 0.5 | | | |
| 3 | 51.8 | | 1.7 | 46.1 | 0.4 | | | |
| 4 | 39.8 | 1.6 | 5.6 | 52.7 | 0.3 | | | |
| 5 | 26.4 | 3.0 | 15.6 | 47.0 | 0.2 | 0.9 | 6.8 | |
| 6 | 53.4 | | 1.2 | 45.5 | | | | |
| 7 | 37.0 | 1.4 | 5.6 | 55.0 | | | | 1.0 |
| 8 | 47.8 | 0.4 | 2.6 | 49.0 | | | | 0.2 |
| 9 | 22.9 | 2.1 | 14.2 | 47.5 | | | 8.8 | 4.5 |
| 10 | 47.0 | 0.3 | 1.4 | 42.4 | 8.9 | | | |
| 11 | 51.9 | | 0.9 | 46.7 | 0.5 | | | |
| 12 | 36.3 | 1.7 | 6.3 | 55.5 | 0.2 | | | |
| 13 | 47.2 | 0.3 | 2.1 | 50.0 | 0.3 | | | |
| 14 | 26.1 | 3.1 | 14.9 | 49.4 | | | 6.4 | |

Modified aluminide coatings obtained in the low-activity CVD process

Modification of the aluminide coating was carried out in two stages consisting of nickel galvanizing with the introduction of chromium powder, followed by low-activity aluminization by the CVD method. The resulting coating had an average thickness of 43.75 μm (Fig. 3a). The average aluminum content in the zone of the outer aluminide coating (area 3 in Fig. 3a) was 40 at. %, and chromium at 3.8 at. %. The aluminum content decreased towards the substrate from 44.6 at. % in the near-surface area (area 1, Fig. 3a) to 35 at.% near the diffusion zone (area 2 in Fig. 3a). Found in the outer zone were titanium and hafnium. In the diffusion zone (area 4 in Fig. 3a) the aluminum content dropped below 26 at.%. Also the presence of tungsten was detected.

The aluminide coating formed as a result of galvanizing a nickel coating with silicon powder, followed by low-activity aluminizing by the CVD method, had an average thickness of 43.66 μm (Fig. 3b). The average aluminum content in the outer zone was 41% at. (area 3 in Fig. 3b) and changed from 46.8 at.% (area 5 in Fig. 3b) in the near-surface area to 36.9 at. % around the diffusion zone (area 6 in Fig. 3b). The silicon content in the outer zone was small and amounted to 0.1-0.3 at. %. Also present in the outer zone were chromium and titanium. In the diffusion zone (area 8 in Fig. 3b), the aluminum content decreased to 23.6-26.4 at.%, while the silicon content was higher – 1.5-1.8 at.%. The content of chromium, titanium, and tungsten was also higher in this zone. The presence of niobium was also observed.

The aluminide coating produced during nickel galvanizing with the introduction of zirconium powder followed by low-activity aluminizing had an average thickness of 43.99 μm (Fig. 3c). Analysis of the chemical composition in the outer region showed that the zirconium content near the diffusion zone (Fig. 3c, area 10) was 1.4 at.% The aluminum content in this area was 35.2 at.% The average aluminum content was approx. 41.1% at. (area 11 in Fig. 3c). In the near-surface area, the presence of chromium and titanium was also found. In the diffusion zone (area 12 in Fig. 3c), the aluminum content was low and amounted to about 26 at.%.

Modified aluminide coatings obtained in the low-activity Zr-doping CVD process

The modification process of the diffusion aluminide coating consisted in combining of nickel galvanizing with the introduction of metal powders, followed by the implementation of the CVD aluminizing process with the simultaneous introduction of zirconium (Zr-doping). The first of the analyzed was an aluminide coating formed as a result of the nickel galvanizing process with the introduction of chromium, followed by low-activity aluminizing by the CVD method with the additional introduction of zirconium. The formed coating had an average thickness of 37.93 μm (Fig. 4a).

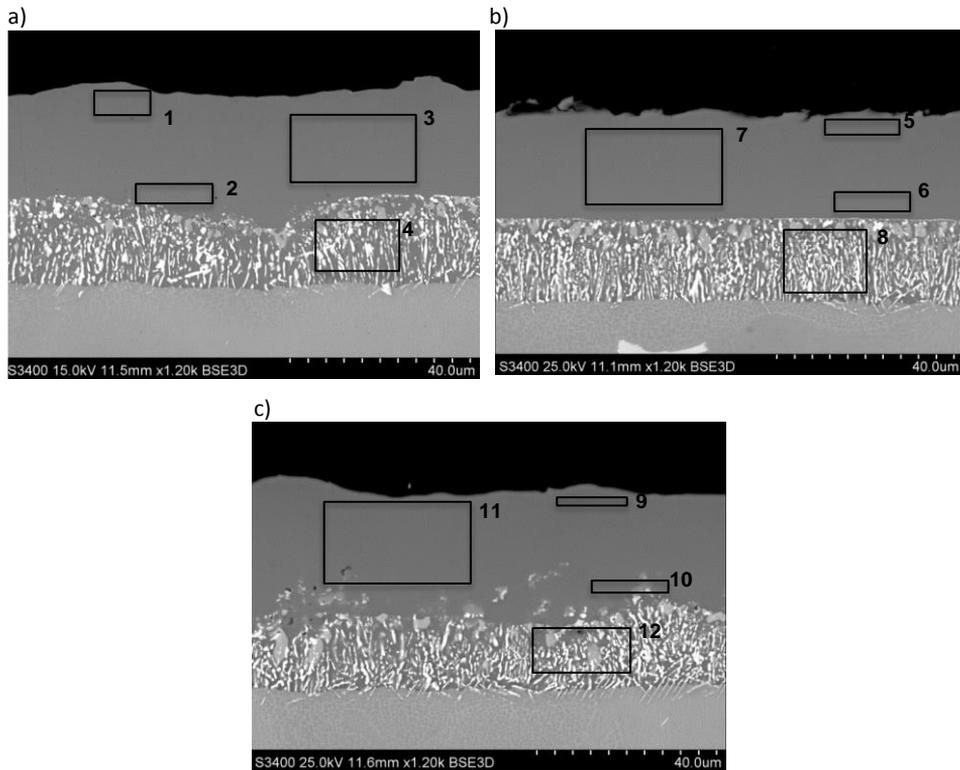


Fig. 3. Microstructure of aluminide coatings obtained by a) Cr+Ni, b) Si+Ni, c) Zr+Ni electroplating and low activity CVD aluminizing

Table 2. Results of chemical analysis in areas presented on Fig. 3a-c

| Area | Elements content, at. % | | | | | | | |
|-----------|-------------------------|-----|------|------|-----|-----|-----|-----|
| | Al | Ti | Cr | Ni | Zr | Si | W | Nb |
| 1 | 44.6 | | 1.4 | 53.9 | | | | |
| 2 | 35.8 | 1.9 | 5.5 | 56.7 | 0.1 | | | |
| 3 | 40.0 | 0.7 | 3.8 | 55.5 | | | | |
| 4 | 26.1 | 2.4 | 11.1 | 52.1 | | | 8.3 | |
| 5 | 46.8 | 1.8 | 1.5 | 51.4 | 0.1 | 0.1 | | |
| 6 | 36.9 | 0.8 | 5.6 | 55.4 | | 0.3 | | |
| 7 | 41.0 | 2.6 | 3.8 | 54.2 | 0.1 | 0.2 | | |
| 8 | 23.6 | 2.4 | 23.6 | 42.1 | 0.2 | 1.5 | 5.3 | 1.1 |
| 9 | 48.0 | 0.1 | 1.1 | 50.8 | | | | |
| 10 | 35.2 | 2.7 | 5.4 | 55.4 | 1.4 | | | |
| 11 | 41.1 | 0.8 | 3.4 | 54.5 | | | | |
| 12 | 25.9 | 2.8 | 13.5 | 47.8 | 0.1 | | 0.7 | 5.3 |

Analysis of the chemical composition showed that the average aluminum content in the outer coating zone was 39.5 at.% (area 3 in Fig. 4a). The Al content changed from 44.7 at.% in the near-surface area (area 1 in Fig. 14) to 36.7 at. % near the diffusion zone (area 2 in Fig. 4a). The average chromium content in the outer coating zone was 3.6 at. % (area 3 in Fig. 4a) and changed from 1.9 at. % in the outer zone up to 5.3 at.% near the diffusion zone. Zr was present only in the near-surface zone and its content was very small – 0.1 at.%. In the diffusion zone (area 4 in Fig. 4a), there was found an increased content of tungsten, chromium, and titanium, along with the smaller amount of aluminum.

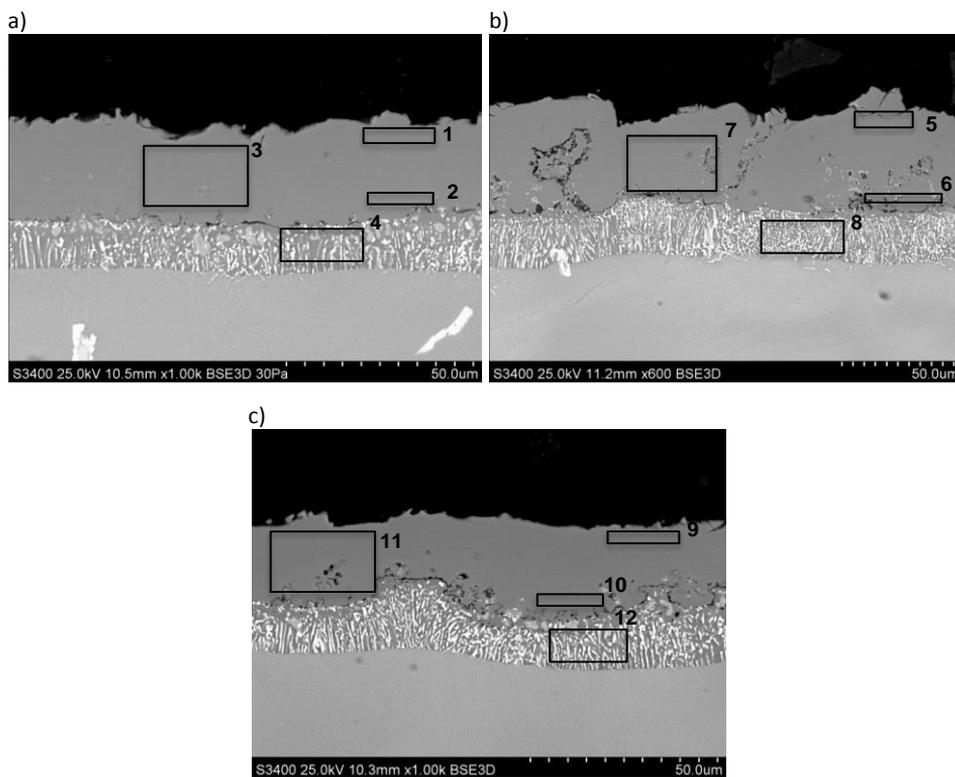


Fig. 4. Microstructure of aluminide coats obtained by a) Cr+Ni, b) Si+Ni, c) Zr+Ni electroplating and low activity CVD aluminizing with Zr doping

The aluminide coating formed by nickel galvanizing with silicon powder followed by the low-activity zircon doping had an average thickness of 53.03 μm (Fig. 4b). The obtained aluminide coating had a structure typical of the low-activity process. The average aluminum content in the outer coating zone was 39.6 at. % (Fig. 4b, area 7). The aluminum content decreased from 43.5 at.% (area 5, figure 4b) in the near-surface area down to 34.6 at.%. (area 6 in Fig. 4b) near the

diffusion zone. Zircon was observed only in the near-surface zone. In the outer zone, the highest amount of silicon (3.5 at.%) was found in area 6 – near the diffusion zone. Its average content in the aluminide coating was 0.7 at.%. (area 7 in Fig. 4b). In the diffusion zone (area 8 in Figure 4b), the silicon content was the highest and amount to 6.8 at.%. In this area, the content of nickel, chromium and titanium was increased. Also observed was tungsten.

As a result of the low-activity aluminizing process with the zirconium galvanizing of the Ni-Zr coating, there was formed a coating with a thickness of 35.11 μm . The average aluminum content in the outer zone of the formed coating was 39.3% at. (area 11 in Fig. 4c). This content was reduced from 42.1 at.% (area 9, Fig. 4c) in the near-surface zone down to 38.1 at.% near the diffusion zone (area 10 in Fig. 4c). The zirconium content was very small and amounted to an average of 0.3 at. % in the outer zone (area 11 in Fig. 4c). In the outer zone also present were chromium and titanium. In the diffusion zone, the aluminum content was lower (26.2 at.% in area 12, Fig. 4c). In this zone, the amount of chromium and titanium was increased. Also tungsten presence was detected as well in this area.

Table 3. Results of chemical analysis in areas presented on Fig. 4a-c

| Area | Elements content, at. % | | | | | | | |
|-----------|-------------------------|-----|------|------|-----|-----|-----|-----|
| | Al | Ti | Cr | Ni | Zr | W | Si | Hf |
| 1 | 44.7 | 0.1 | 1.9 | 53.2 | 0.1 | | | |
| 2 | 36.7 | 1.3 | 5.3 | 55.9 | | 0.8 | | |
| 3 | 39.5 | 0.7 | 3.6 | 56.0 | | 0.3 | | |
| 4 | 26.9 | 2.1 | 13.0 | 51.1 | | 6.9 | | |
| 5 | 43.5 | | 1.8 | 54.4 | 0.1 | | 0.3 | |
| 6 | 34.6 | 2.3 | 5.4 | 53.9 | | | 3.5 | 0.4 |
| 7 | 39.6 | 0.7 | 3.8 | 55.2 | | 7.5 | 0.7 | |
| 8 | 22.9 | 2.1 | 11.5 | 49.2 | | 2.8 | 6.8 | |
| 9 | 42.1 | 0.1 | 1.7 | 56.0 | 0.1 | | | |
| 10 | 38.1 | 1.3 | 5.1 | 55.4 | | | | |
| 11 | 39.3 | 0.6 | 3.8 | 56.0 | 0.3 | | | |
| 12 | 26.2 | 2.0 | 12.5 | 50.2 | | 9.0 | | |

Summary

The tests evidenced the possibility of combining the nickel galvanizing process with the introduction of powder grains and CVD aluminizing. It was shown that the aluminide coatings formed in the high-activity process are characterized by an aluminum content <50% at, however, still within the NiAl phase. Below this zone in the aluminide coatings there occurred a zone composed of the NiAl phase containing about 8-10% at. less aluminum, and below it – the diffusion zone. The aluminide coatings formed in the low-activity process were

composed of an external zone composed of the NiAl phase with an aluminum content > 50% at. and the diffusion zone. Similar was the structure of the aluminide coatings produced during the low-activity aluminizing with zircon doping. The content of elements introduced with nickel was low (up to several%), which does not result in an expected increase in heat resistance of the modified coatings. According to the published paper [9], the only element, which may increase heat resistance at a low content, is zirconium. The use of double zirconium doping (application of Zr powder during galvanic nickel and zircon doping) did not allow for a significant increase of its content in the aluminide coating. Neither was observed a significant increase in the thickness of aluminide coatings, which were formed on the substrate subjected to nickel plating.

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