



# The influence of production method on oxidation resistance of the aluminide coatings obtained on IN 100 alloy

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Received 05.11.2011; published in revised form 01.02.2012

## ABSTRACT

**Purpose:** The comparison of three deposition of coatings method.

**Design/methodology/approach:** The diffusion aluminide coatings were deposited using the pack cementation, out of pack and CVD method.

**Findings:** The authors present in the article the results on influence of the method of manufacturing the aluminide coatings on their microstructure and oxidation resistance.

**Research limitations/implications:** The thickness analysis and the chemical composition analysis with a use of light microscopy, scanning electron microscopy and EDS analysis were performed.

**Practical implications:** This process can be used in aerospace industry to form oxidation resistant coatings.

**Originality/value:** It has been proven, that the coating obtained with CVD method, despite its small thickness, was characterized by the best cyclic oxidation resistance.

**Keywords:** Metallic alloys; Corrosion; Technological design; Thin & thick coatings; Surface treatment

**Reference to this paper should be given in the following way:**

M. Pytel, M. Góral, M. Maliniak, The influence of production method on oxidation resistance of the aluminide coatings obtained on IN 100 alloy, Archives of Materials Science and Engineering 53/2 (2012) 102-108.

## PROPERTIES

### 1. Introduction

The diffusion aluminizing process is a basic method of protection of the aircraft engine elements made of nickel alloys [6,8,11,12]. The  $\beta$ -NiAl phase is created as a result of aluminizing process of the blades made of nickel superalloys. There are three main methods of manufacturing the aluminide coatings: pack cementation, out-of-pack and the chemical vapour deposition (CVD) method. The additional variant of the powder process is the slurry method [1, 5].

The pack cementation method is used for deposition of protective coatings on the metallic surface to ensure the protection against oxidation, corrosion and damage [10]. Aluminium is the element, which is most commonly deposited to obtain the aluminide coating for the nickel based superalloys. In some cases, the introduction of Cr and Si to the coating can be beneficial with regard to the improvement of the high temperature corrosion resistance. In the conditions of high temperature aluminium in the coating is oxidized and forms a thin aluminium oxide scale, which works as the diffusion barrier and reduces the oxidizing speed of the base material.

During the pack cementation process the elements are firstly cleaned (usually shot blasting or sand blasting with aluminium oxide) in order to remove the impurities from the surface. The coated elements are placed in the closed or half-closed containers and covered with mixture of powder, which consist of metals used for deposition (and theirs alloys), the halide activating agent and inactive filler (usually aluminium oxide). The halide activating agent (e.g.  $AlF_3$ ,  $NaCl$ ,  $NH_4Cl$  i  $NH_4F$ ) are usually added in small amounts (2 to 5% wt.). The leakproof container is heated up for a certain time in protective atmosphere of argon to the temperature of 700°C to 1150°C. In those temperatures the halide activating agents are reacting with metals in the powder mixture and metal-halide vapors series such as  $AlCl$ ,  $AlCl_2$ ,  $AlCl_3$  and  $Al_2Cl_6$  with characteristic pressure distribution are created. The coating is created through the reduction of metal-halide vapors on the surface of the base material followed by diffusion in the solid state between the introduced metal and the substrate. The coatings which are obtained using this method are specified as diffusion coatings [1].

The good repeatability of manufacturing process and low costs are the main advantages of the pack cementation method [2, 3]. In the pack cementation method, the powder particles are left in the external coating of the coating [4]. If this effect is undesirable, the base material can be separated from the powder (VPA method) [4, 5].

The vapour phase aluminizing method consist in placing the coated elements while preventing their contact with the powder and granules mixture. The technological process are conducted in the retort furnaces. The neutral carrier gas is additionally introduced to the retort during the whole coating process. It enables the transfer of gases, which forms the coating and are created during the aluminizing process. The installation is designed in such a way, that the vapors created from the volatile halides have access to the external and internal surfaces of the coated element. The retort is inserted into the furnace and maintained in the selected temperature for a certain time [1].

The main advantages of the out-of-pack method are results of the contact of the coated elements with the powder. It improves the coating uniformity in the internal channels and the blade cooling holes, ensures better control over the process run, increase the coating purity without confinement of the powder particles in it (in comparison to the pack cementation method) and ability of modification of the aluminide coating by using the elements, which improves the oxidation resistance.

During the CVD process the halide vapors, such as  $AlCl_3$ , are created inside the gas external generators by transferring the  $HCl$  or  $Cl_2$  through the aluminium granules in the temperature of approx. 300°C. The generators used for creating the halides are separated from the chamber with coated elements. The aluminized

elements are attached inside the retort and are usually annealed in the temperature range of 1000 to 1100°C. The  $AlCl_3$  halide vapours are obtained in the external generator through the chemical reaction between transferred  $HCl$  and the aluminium alloy granules. The additional Cr-Al granules are placed inside the retort in the way of the transferred gases for the high activity aluminizing process. The reactive elements, such as Y, Hf and Zr are used for modification of the aluminide coating in order to improve the properties. Additional generators are attached to the retort.  $AlCl_3$  has a high vapour pressure (it sublimates in the temperature of 178 °C). The halide vapors are transported to the external surface and the internal channels with a use of the carrier gas (argon and hydrogen) and the proper arrangement of the elements inside the reactor. The  $AlCl_3$  vapors react with aluminium in the presence of  $H_2$  and create  $AlCl$ .  $AlCl$  interacts with nickel on the element surface and forms the  $\beta$ -NiAl coating [7,9].

The aluminizing process using CVD method has a few advantages in comparison to the other techniques: pack cementation method and out-of-pack method. The chemical composition of the coating can be modified through the introduction of many elements from independent generators. The deposition rate of the coating can be independently controlled. After the coating deposition, the thermal treatment can be conducted without taking out the elements, what result in reduction of manufacturing costs. The coatings are formed during the CVD process as a result of outward growth according to the low activity mechanism [1].

The application of aluminizing process using the slurry method through the diffusion annealing is widely used for obtaining aluminide coatings on the surface of the turbine blades. The slurry consists of the powders such as Al, Al-Si, Al-Si (Y, Ce, B) etc. characterized by the grain size below 40  $\mu m$  (as its active component) and the dissolvent.

The slurry is spread on the surface of the blades located in special equipment preventing from coating other elements, which can not be saturated. The slurry coating on the blade surface is air-dried and visually analysed afterwards. The elements are placed into the container, with a use of special holders, in order to prevent the damage of the dried slurry. The parts are submitted to annealing in vacuum or in the argon atmosphere or in air atmosphere (in case of finishing). The annealing parameters are selected according to the conditions of the thermal treatment of saturated alloy. The facility of saturation with several elements such as aluminium and chromium, silicon and aluminium, aluminium and boron etc.

The main disadvantage of this method is the necessity of manual spreading of the slurry. It causes the thickness unevenness on the blade surface. The acceptable differences of the coating thickness between the blades from the same batch are of 20 to 50  $\mu m$ , but the real fluctuation can be larger [1-5].

Table 1.  
The chemical composition of Inconel 100 alloy

Alloy	The elements content, % wt.								
	Ni	Cr	Co	Mo	Al	Ti	C	B	Zr
Inconel 100	60	10	15.0	3.0	5.5	4.7	0.18	0.014	0.06

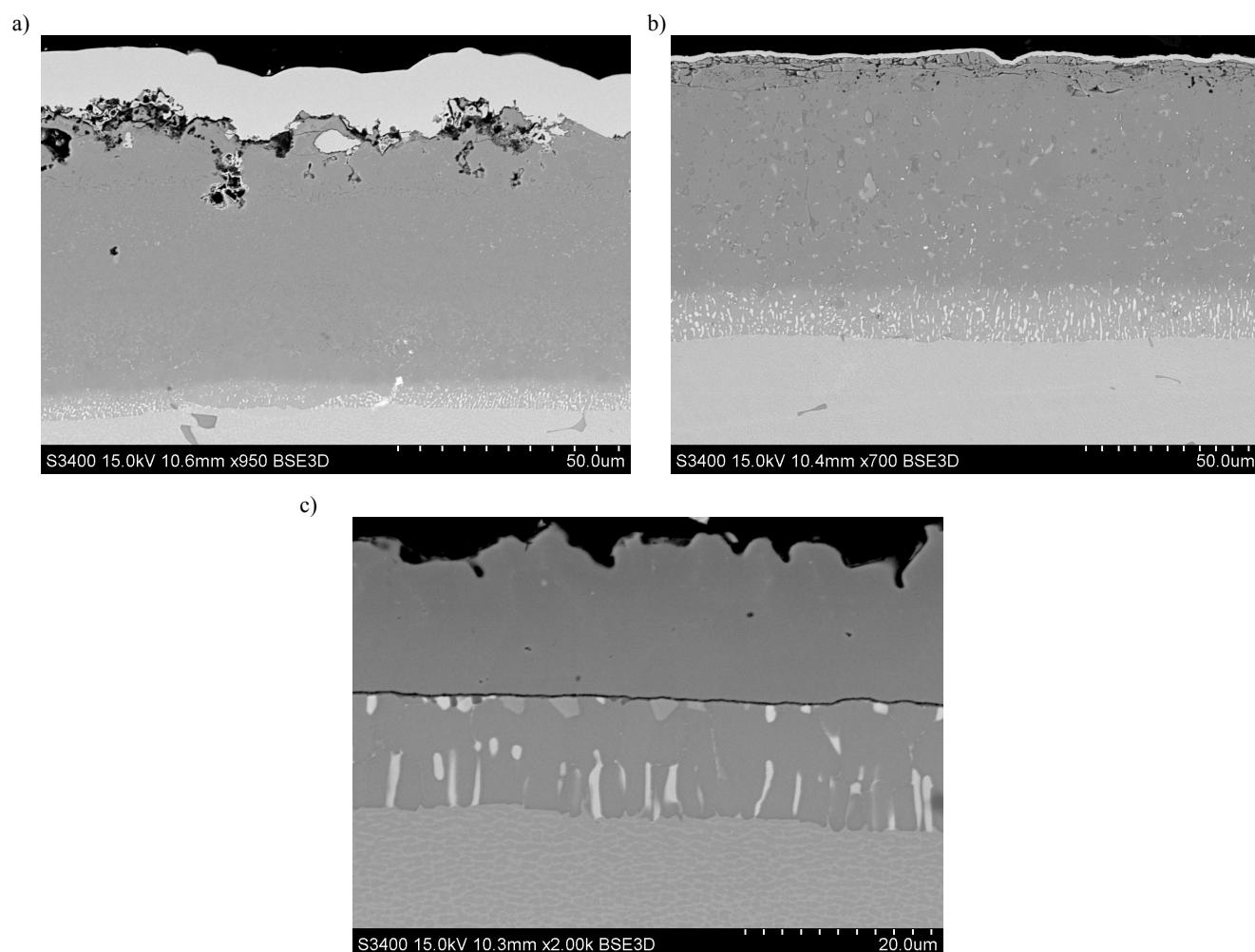


Fig. 1. Microstructure of aluminide coatings deposited by a) pack cementation, b) VPA, c) CVD methods on IN 100 superalloy

## 2. Experimental

The nickel-based high-temperature IN-100 type alloy was used as a base material. Its chemical composition is presented in the Table 1. The samples were coated with aluminide coatings with a use of three different technologies. The aluminizing process using the slurry method involved twofold immersion, drying and two-hour diffusion annealing in the temperature of 950°C and hydrogen atmosphere. The annealing process of the aluminide coating by applying the out-of-pack method was performed in the temperature of 1000°C and with a use of Cr-Al granules and  $\text{AlF}_3$  activating agent. The chemical vapour deposition process was executed using the BPX Pro 325S device (Ion Bond company). The aluminide coating were obtained during the four-hours process in the temperature of 1000°C with hydrogen chloride flow of 1.4 NLPM and hydrogen flow of 10.5 NLPM.

The oxidation resistance test was performed in the chamber furnace in static laboratory air and the temperature of 1100°C.

The twenty-three hour cycles of exposure in the high temperature and the one-hour cooling were utilized.

The microstructure analysis was performed with a use of the S-3400 scanning electron microscope (Hitachi company) equipped with the EDS attachment (Thermo company).

## 3. Results and discussion

### 3.1. Microstructure of coatings

The microstructure analysis proved, that there are significant differences in the structure of the aluminide coating depending on the manufacturing method. The coating formed using the slurry method was characterized by the largest thickness as in Figure 1a). The average coating thickness for this method was of 85.07  $\mu\text{m}$ . The measured values of coating thickness ranged from 74.59  $\mu\text{m}$  to 100.91  $\mu\text{m}$ . It resulted in the large diversity on the section of

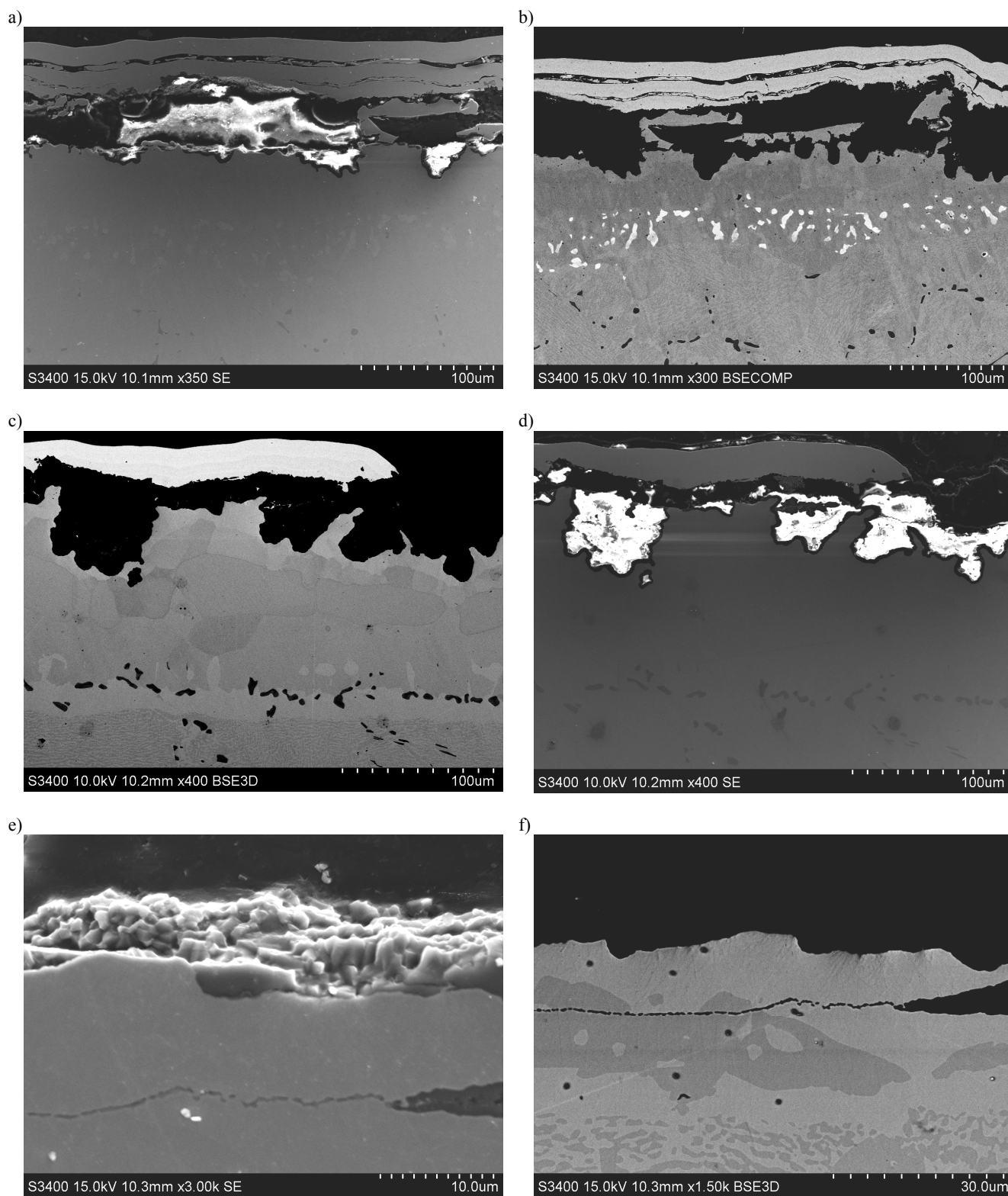


Fig. 2. The microstructure of the aluminide coatings obtained with a), b) a slurry method, c), d) VPA method, e), f) CVD method after the cyclic oxidation tests (23h/1100°C)

the sample. The inner zone, with the average thickness of  $6.56 \mu\text{m}$ , was characterized by much smaller thickness range. In the near-surface area no cracks and pores were observed. The chemical composition analysis of the outer zone showed that the average aluminium content was approx 40% at., the maximal silicon content was 6 at.% and the maximal cobalt content was 6 at. %.

The aluminide coating obtained with a use of the out-of-pack method was characterized by lower thickness as in Figure 1b). In case of this method, the measured value of thickness of the coating ranged from  $60.91 \mu\text{m}$  to  $77.45 \mu\text{m}$  (the averaged coating thickness was of  $71.05 \mu\text{m}$ ). The inner coating was characterized by smaller thickness – its average value was of  $16.66 \mu\text{m}$ . The conducted chemical composition analysis of the outer zone of the coating was of 51-53 at. %. The chromium content (approx. 4 at.%) and the cobalt content (approx. 6-7 at.%) was also observed in this area. In the near-surface area cracks were present. The coatings obtained with a use of the CVD method were characterized by the smallest thickness as in Figure 1c). The average coating thickness was of  $29.36 \mu\text{m}$ . The measured coating thickness ranged from  $21.23 \mu\text{m}$  to  $34.57 \mu\text{m}$ . The chemical composition analysis showed, that the structure for the low activity process is characteristic. The average aluminium content in the outer area was approx. 40 at. %. The aluminium content in the near-surface area was approx. 47 at. %. The average chromium content in the outer zone was approx. 4 at. % and of 8 at.% for cobalt. As opposed to other coatings, no cracks were observed.

### 3.2. The results of cyclic oxidation test

The cyclic oxidation test for aluminide coatings was performed for all three methods. In case of the comparative methods, the additional cyclic oxidation test for alloy without coating was made. The mass drop below the initial value was observed already after two cycles (46 hours of exposure in the temperature of  $1100^\circ\text{C}$ ). For the samples with coating made using the slurry method, there was a mass drop below the initial value after fourteen cycles

(322 hours of exposure in the test temperature). The mass gain for the sample didn't exceed  $0.2 \text{ mg/cm}^2$ . In case of coating made using the VPA method, one could observe the weight gain followed by mass loss up to the fourteenth cycle. The samples with coating formed during CVD process were characterized by mass gain not exceeding  $0.1 \text{ mg/cm}^2$ . In this case the sample mass was practically constant up to 29th cycle (667 hours of oxidation) and then decreased its value linearly up to 41th cycle. The microstructure of aluminide coatings obtained on the IN-100 alloy after the cyclic oxidation test is presented in Figure 2. The performed investigation proved, that in all cases there was an aluminium oxide scale on the surface (the visible white separations as in Figure 2a), c) and e)). Below, one could observed the residues of aluminide coating consisting of the NiAl,  $\text{Ni}_3\text{Al}$  and nickel ( $\gamma$ ) phase.

As a results of the examinations carried out of resistance to cyclical oxidation, it was found that the best resistance to cyclical oxidation samples of IN100 superalloy coated in the CVD process are characterized. Obtained experimental data shown in Figure 4. It was also stated, that samples coated with aluminide layers obtained in the CVD process were characterized by the smallest increase in mass and the longest time and with the number of cycles for achieving by the sample initial mass, what was shown in Figure 3.

## 4. Summary

The conducted research allow to state, that the thickness of the diffusion coating and its high temperature cyclic oxidation resistance depend on the method of creating the coating. The thickest coating was obtained by applying the slurry method, and using the CVD method resulted in formation of the thinnest one as was showed in Figure 2 and also in Figure 4. The larger thickness of the outer coating in comparison to the inner (diffusion) coating is characteristic for all analysed coatings. A significant differences between the ratios of the inner coating thickness to the outer coating thickness can be observed.

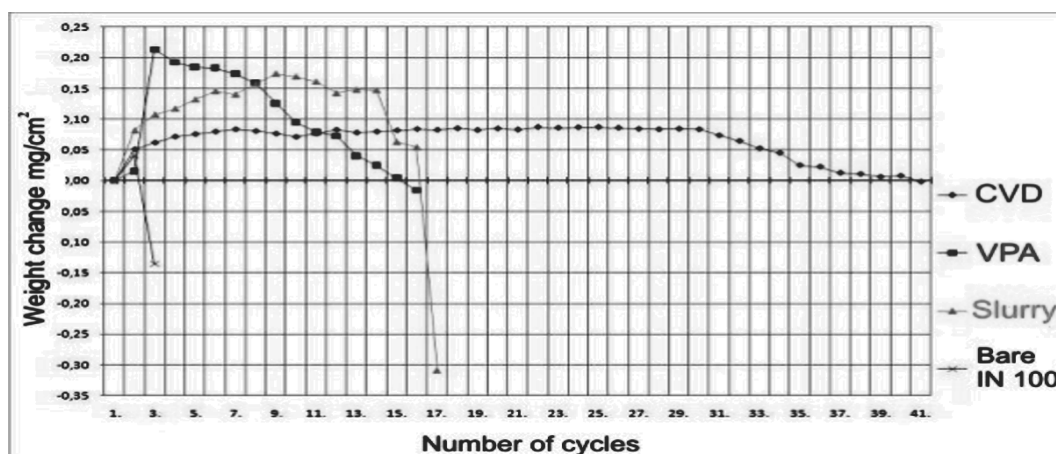


Fig. 3. The changes of the samples mass after the cyclic oxidation tests in the temperature of  $1100^\circ\text{C}$

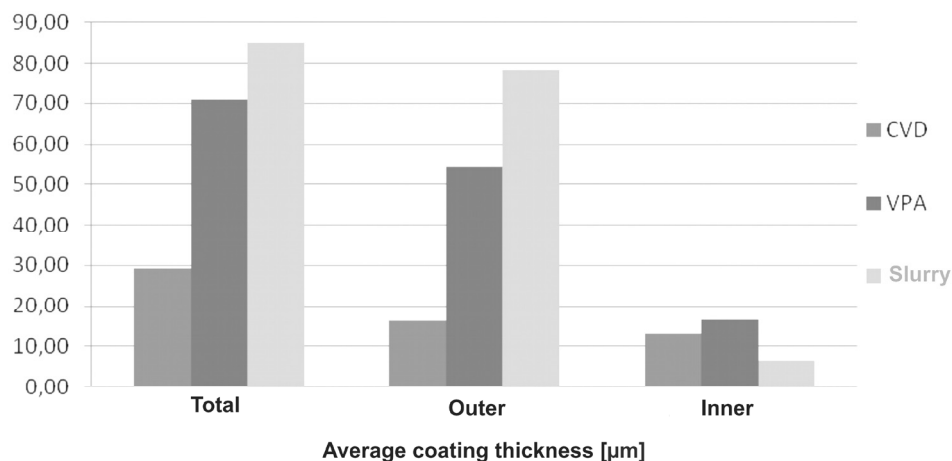


Fig. 4. The comparison of average values of the coating thickness (inner-, outer- and total thickness) depending on the deposition method

The largest value of this ratio is obtained for the slurry method and the smallest value for the CVD method. The obtained coatings are characterized by the thickness diversity along the sample surface. The largest differences were observed in the coating made using the slurry method. The smallest differences were obtained with CVD and VPA method. The microstructure of formed coatings differs between the presented coating method. There are also the differences in chemical composition, the coating homogeneity and the presence of separations. The separations in the inner zone are characteristic for coatings obtained using the slurry method and CVD method. In case of the VPA method the separation are visible in the whole coating. For the slurry method and the VPA method small cracks in the outer zone were observed. In all cases the boundary between the inner- (diffusion-) and the outer coating was visible. The chemical composition analysis indicates that for all methods the outer part of the coating consists of the  $\beta$ -NiAl phase. The aluminium content decreases towards the base material for all analysed methods. The largest drop of aluminium content was observed for the coating obtained using the CVD method (47.55% at. for the outer coating). The aluminium content in the outer coating is approx. 40-45% at. for the slurry method and of approx. 53% at. for the VPA method.

The uncoated samples as well as the samples with coatings formed by application of different methods were submitted to cyclic oxidation in the temperature of 1100°C and the air atmosphere. The largest mass gain was obtained for samples with aluminide coating formed during respectively the VPA-, slurry- and CVD method. While analysing the graph, one can observe that the larger mass gain for samples with protective coatings results in its faster failure. The sample with aluminide coating formed during the CVD process was characterized by the best oxidation resistance.

## Acknowledgements

Financial support of Structural Funds in the Operational Programme - Innovative Economy (IE OP) financed from the European Regional Development Fund - Project "Modern material

technologies in aerospace industry", No. POIG.01.01.02-00-015/08-00 is gratefully acknowledged.

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