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Influence of heat treatment on microstructure of slurry aluminide coatings type TiAlSi obtained on TiAlCrNb alloy

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ABSTRACT

Purpose: Influence of heat treatment on microstructural changes in slurry TiAlSi coating deposited with 12.5% Si concentration on Ti48Al2Cr2Nb intermetallic alloy and investigation of the influence of Si addition on the structure of obtained coatings is a purpose of this paper.

Design/methodology/approach: The research allowed identifying microstructural changes that took place during annealing at 950°C of the TiAlSi coating for 2 to 10h exposure in air. A scope of the research encompassed a microstructural analysis with the use of macro and micro investigation - LM, SEM microscopy, XRD phase analysis and EDS analysis.

Findings: The investigation has shown that the thickness of the TiAlSi coatings in initial conditions and after a test was in a range from 30 to 40 μm. The structure of the silicon-modified aluminide coatings is as following: the outer zone consisting of the $TiAl_3$ phase and titanium silicides / the middle zone consisting of columnar titanium silicides in phase $TiAl_3$ matrix / the inner zone consisting of $TiAl_2$ phase. Basic changes were related to differences in thickness in sublayers.

Research limitations/implications: The discussed research proves that main reason of much better protection of TiAlSi coated base alloy is related to high microstructure stability of Si modified in $TiAl_3$ phases. In addition silicon decreases activity of titanium, and in consequence the susceptibility of Al to selective oxidation is much stronger. The presence of Si due to Ti-Si phase generation with high oxidation resistance is presented.

Practical implications: The slurry method can be applied in aerospace and automotive industry as low-cost technology in production of aluminide coatings on intermetallics.

Originality/value: New method of aluminide coatings deposition on TiAl alloys.

Keywords: Thin and thick coatings; Aluminides; Microstructural stability

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1. Introduction

At present, oxidation resistance constitutes a major problem restricting the application of Ti-Al alloys. This problem is particularly acute in the elements designed for work conditions requiring prolonged exploitation at cyclically fluctuating temperature circa 700^{o}C, and undergoing mechanical stress for periods ranging from 500 to 5000 hours. The given times correspond to the periods of work of aircraft engines, civil and military respectively. The heat resistance of γ -TiAl based alloys is higher than titanium alloys; they cannot, nevertheless, compete with nickel superalloys or NiAl phase-based alloys [1,2]. The possible solution to this problem is the development of protective coatings characterized by sufficient plasticity and adherence as well as good oxidation and corrosion resistance [3]. As far as these properties go, interesting results have been obtained for $TiAl_3$ based, silicon-modified alloys, created by Arc-PVD method [4-6]. The literature data indicate clearly that the addition of silicon is an efficient way to improve oxidation resistance of Ti-Al alloys. During the early oxidation stages the presence of titanium silicides Ti_5Si_3 in the scale has been noted, as well as the existence of $Ti_7Al_5Si_{12}$ silicide [7,8]. Initially, these silicides form a barrier for oxygen diffusion and prevent internal oxidation of aluminium by means of decreasing the diffusion in the base alloy. However, the silicides in question are oxidised to the $Si0_2$ form, which can be placed in the base forming a continuous layer. The presence of either amorphic or crystalline form of the SiO_2 layer works as diffusion barrier, hindering the oxidation process at its initial stage [9]. In addition to this, the presence of Si as well as W hampers creates the TiN and Ti_2AlN nitrides, decreasing the susceptibility of scale off-dropping [7]. Dip painting followed by diffusion treatment seems to be a comparatively rare method of obtaining aluminide coatings. This technology, when used for the formation of aluminide coating on Ni superalloys, enables arbitrary content of the substances in the slurry to be used for the modification. As the slurry composition is modifiable to a large extent, so the influence of the silicon content in a structure and oxidation resistance of the aluminide coatings on the high-niobium TiAl alloy can be investigated. [10,11]. The automotive industry employs the TiAl alloys to produce valves and turbine wheels [12-15].

2. Description of experiments, methodology and materials

The study has been done on the Ti-48Al-2Cr-2Nb type alloy. The silicon-modified aluminide coating was obtained by slurry method, utilizing aluminium and silicon powder slurries in the water solution. The mixtures containing aluminium and 12.5% silicon were employed. The procedure of coating deposition was as following: the preparation of samples (15×10×4 mm); sample grinding (maximum gradation 600 paper); sand-blasting with corundum of 150-220 mesh granularity; ultra-sound degreasing in tri-chloro-ethylene; soaking at 350°C for 30 min in argon; thorough mixing of the slurry, immediately preceding the immersion, in order to place the solid particles evenly in the solution; drying of the samples in free air, until a bright-grey layer was obtained, drying for additional 60 minutes; drying for 15 min. at 80^{o}C, soaking for 30 min. at 200°C-220°C; diffusion treatment at 950°C for 4 hours in the atmosphere of argon; ball-peening (balls sized 320-140 mesh in diameter); sand-blasting with electro-corundum 150-220 mesh. The heat treatment at 950°C lasted for 2-10 hours. The phase content analysis and the chemical content analysis have been done preceding and following the tests. In addition to that, microstructural analysis has been done. The qualitative phase analysis has been conducted by X-ray diffraction method. The tests were done at JDX-7S JEOL diffract meter. The phase content analysis has been done both on the surface and after removing consecutive layers in order to display the inner zones of the scale and the coating. The chemical content microanalysis has been done by EDS method using Six Sigma system attached to Hitachi 3400N microscope.

3. Description of achieved results of own researches

After o process of deposing a coating, structural investigations were carried out and an analysis of chemical composition and phase composition were carried out as well. Microscope investigations, carried out on a sample, which was sunk once after 4 hour preliminary diffusive treatment, proved that a got coating was characterized by thickness approx. 45 μm. Presence of cracks, running right through the coating, was stated (Figure 1).

An analysis of a phase composition proved that the $TiAl_3$ phase in a main component of the TiAlSi coating (Figure 2). No presence of tungsten silicides, tantalum silicides and chromium silicides, of which a possibility to occur is shown by an instruction to get a coating. An analysis of covering microstructure, by means of a scanning microscope, was carried out. Presence of numerous and bright precipitates was stated (Figure 3 p. 1). The carried out analysis of chemical composition in micro-areas proved that these precipitates were rich with titanium and silicon of atom proportion of both components as 5:3, what can determine probable presence of the Ti_5Si_3 silicides of very strong resistance on oxidation. An analysis of chemical composition, carried out directly in covering area (Figure 3 p. 2), proved considerable less content of silicon approx. 4.25% at. Presence of chromium and niobium, coming from a substrate material of concentration approx. 1% at. was stated.

Presented results of the phase analysis and analysis of chemical composition proved presence of the $TiAl_3$ phase, as a main phase component of the coating. The SEM investigations also proved presence of transitive area between covering and substrate of aluminium content considerably lower than in a coating (Figure 3 p. 3). A linear analysis of chemical composition is presented in Figure 4. It proved presence of a layer rich with silicon and titanium at reduced content of aluminium. Presence of three zones of different aluminium content is also visible. The first of them corresponds to substrate alloy, the second one lies between a silicide layer and substrate (phase $TiAl_2$), and the third one is an outer layer, which corresponds to the $TiAl_3$ layer. In order to define kinetics in growth of aluminiate layer of the TiAlSi coating and phenomena occurring during annealing process, further diffusive treatment of the coating in duration of next 2, 4, 6, 8 and 10 hours was carried out. Totally, taking into consideration 4h diffusive treatment of the coating, the treatment lasted 14 h in temperature 950°C in argon atmosphere. Having finished this process, structural investigations were carried out in order to define kinetics in growth of the layer and changes in chemical and phase compositions of diffusively treated coating.

Firstly, quality tests of phase composition were carried out by the X-ray method on all diffusively annealed samples. Results of these tests are shown in Figs. 5 and 6 for selected parameters of this treatment i. e. 2 and 10 h annealing.

The got results show no changes in a phase content of coating area, independently of treatment time. Also in indirect stages i. e. after 4, 6 and 8 hours, diffraction patterns are similar. Distinct presence of the dominating $TiAl_3$ phase and Ti_5Si_3 titanium silicides were stated, while they were not observed directly after having got a layer.

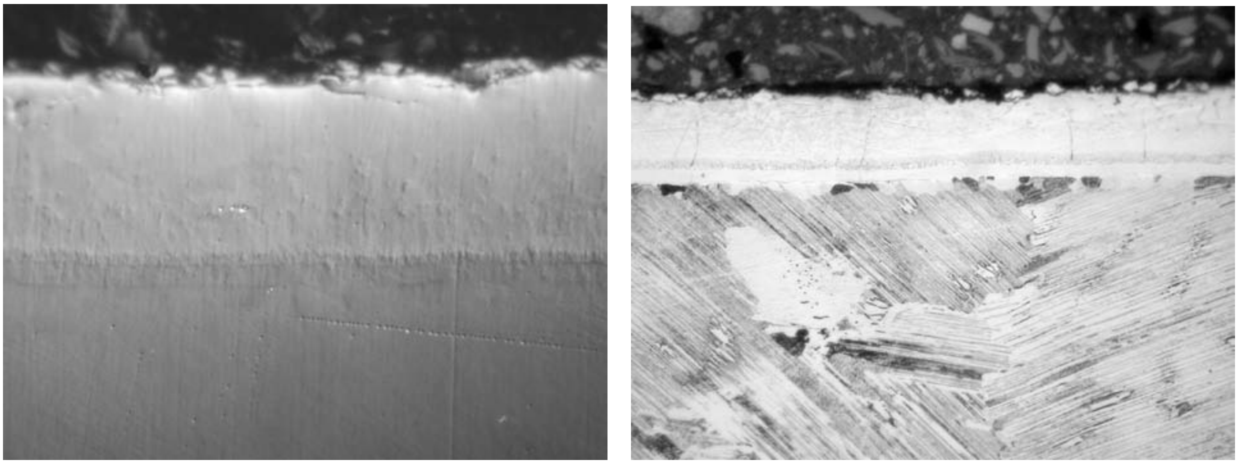

Fig. 1. Microstructure of an exemplary layer type TiAlSi in an output state – mag. 400x

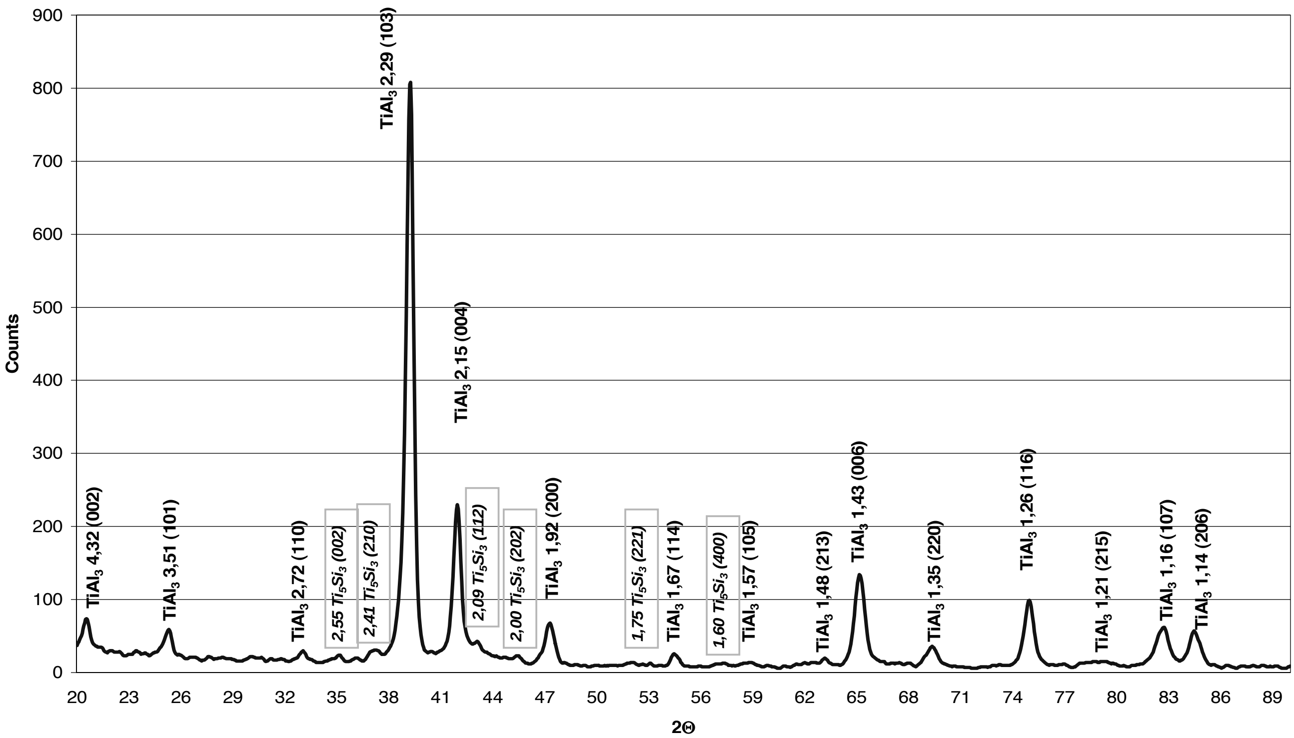

Fig. 2. Results o fan analysis of phase composition of a sample with slurry covering in an input state

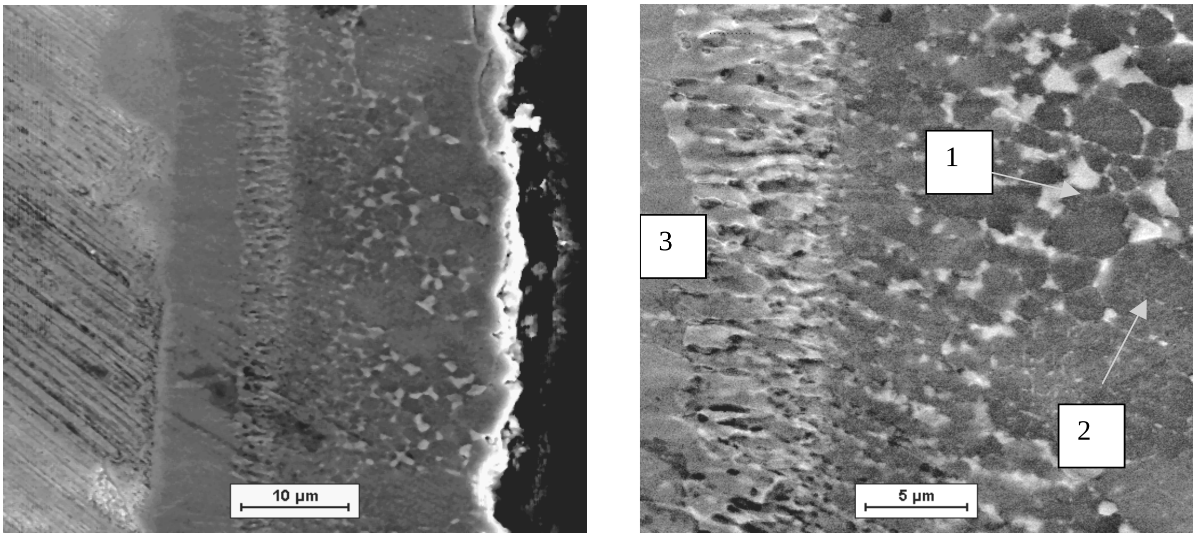

Fig. 3. SEM microstructure of the analysed TiAlS coating and in an output state

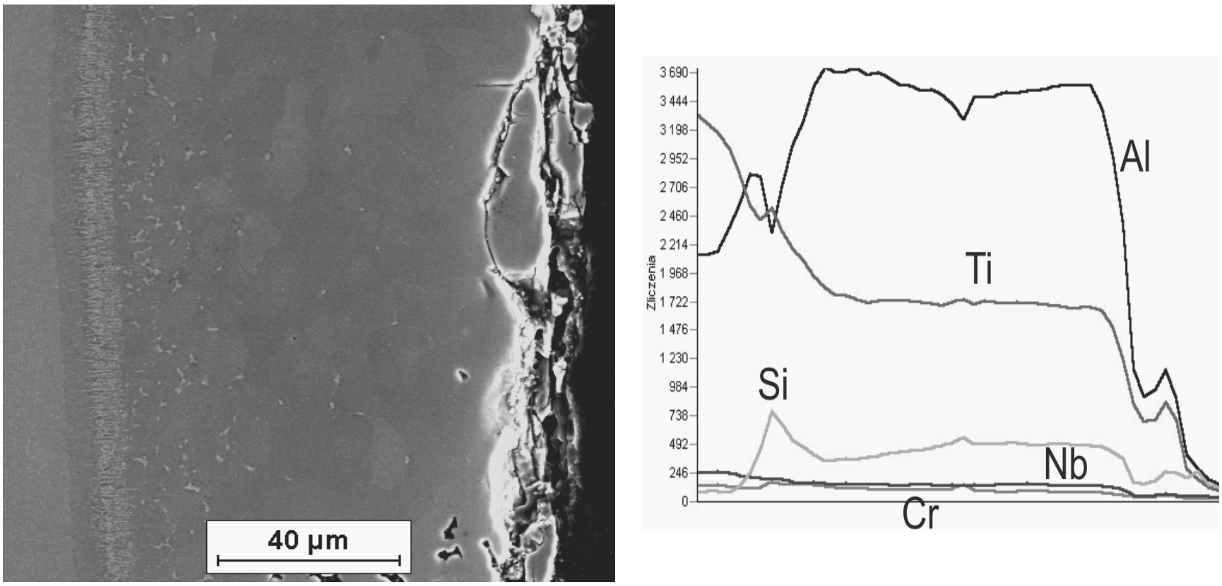

Fig. 4. Results of linear micro-analysis of chemical composition on the tested coating

Microscope investigations proved presence of three characteristic areas in layout coating – substrate. Analogically, as sooner, presence of an outer layer, transitive layer and layer constructed of equiaxed grains, was stated. An outer layer was rich with precipitations, especially near transitive area. The used Nomarski's contrast enabled to observe post morphology of grains in a transitive zone. Comparing to an input state, growth in thickness of the transitive area was noticed. Similar growth was observed also in a case of other layers of a coating. Microstructure of the TiAlSi layer after 2, 4, 6, 8 and 10h of diffusive annealing are shown in Figure 7. Distinct differences in individual areas of a coating are visible.

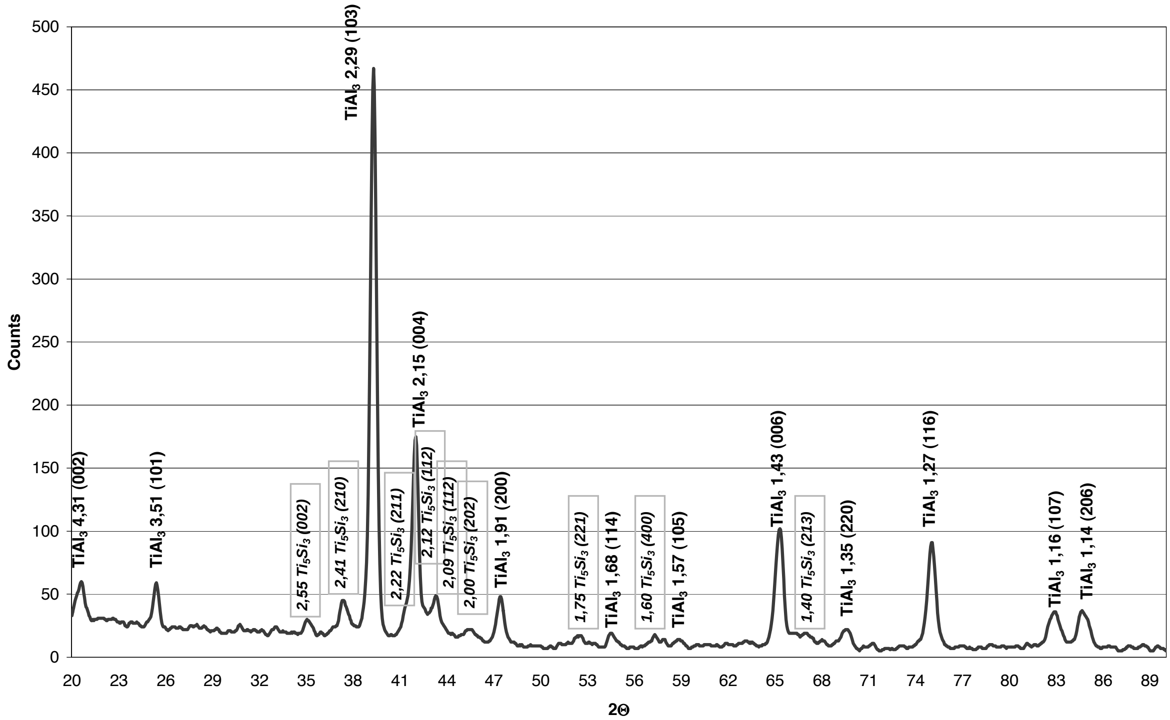

Fig. 5. Results of analysis of phase composition of a sample with the TiAlSi slurry covering after 2 h diffusive treatment in temperature 950°C

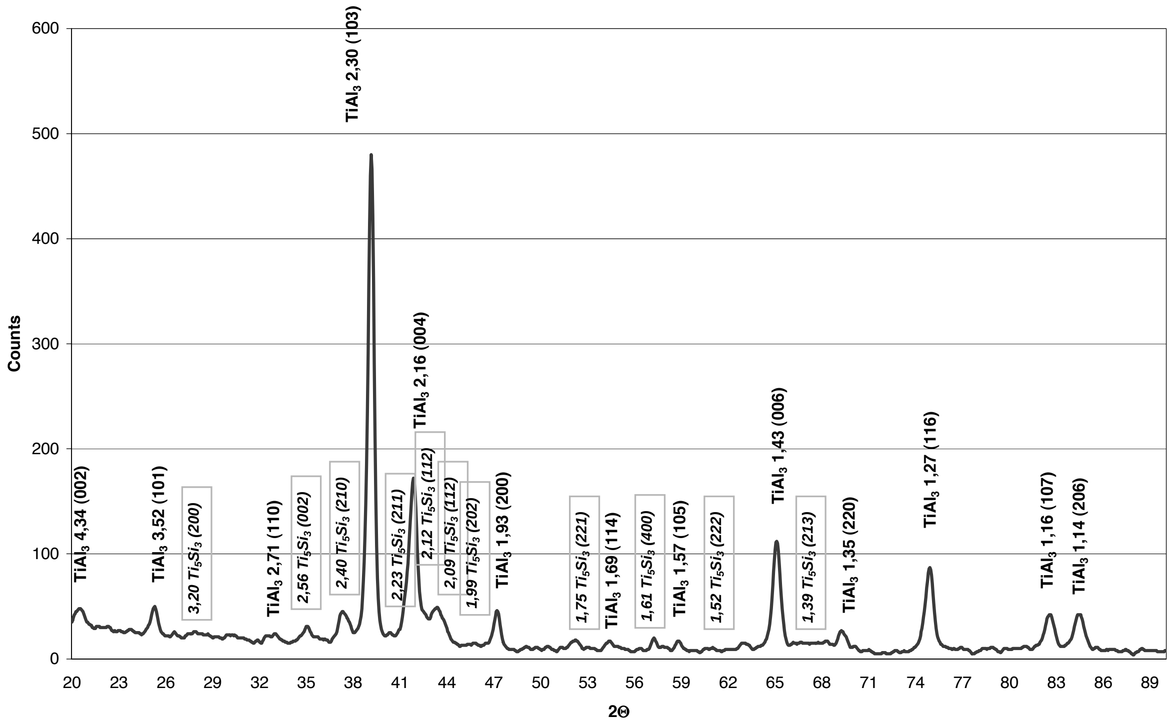

Fig. 6. Results of analysis of phase composition of a sample with the TiAlSi slurry covering after 10 h diffusive treatment in temperature 950°C

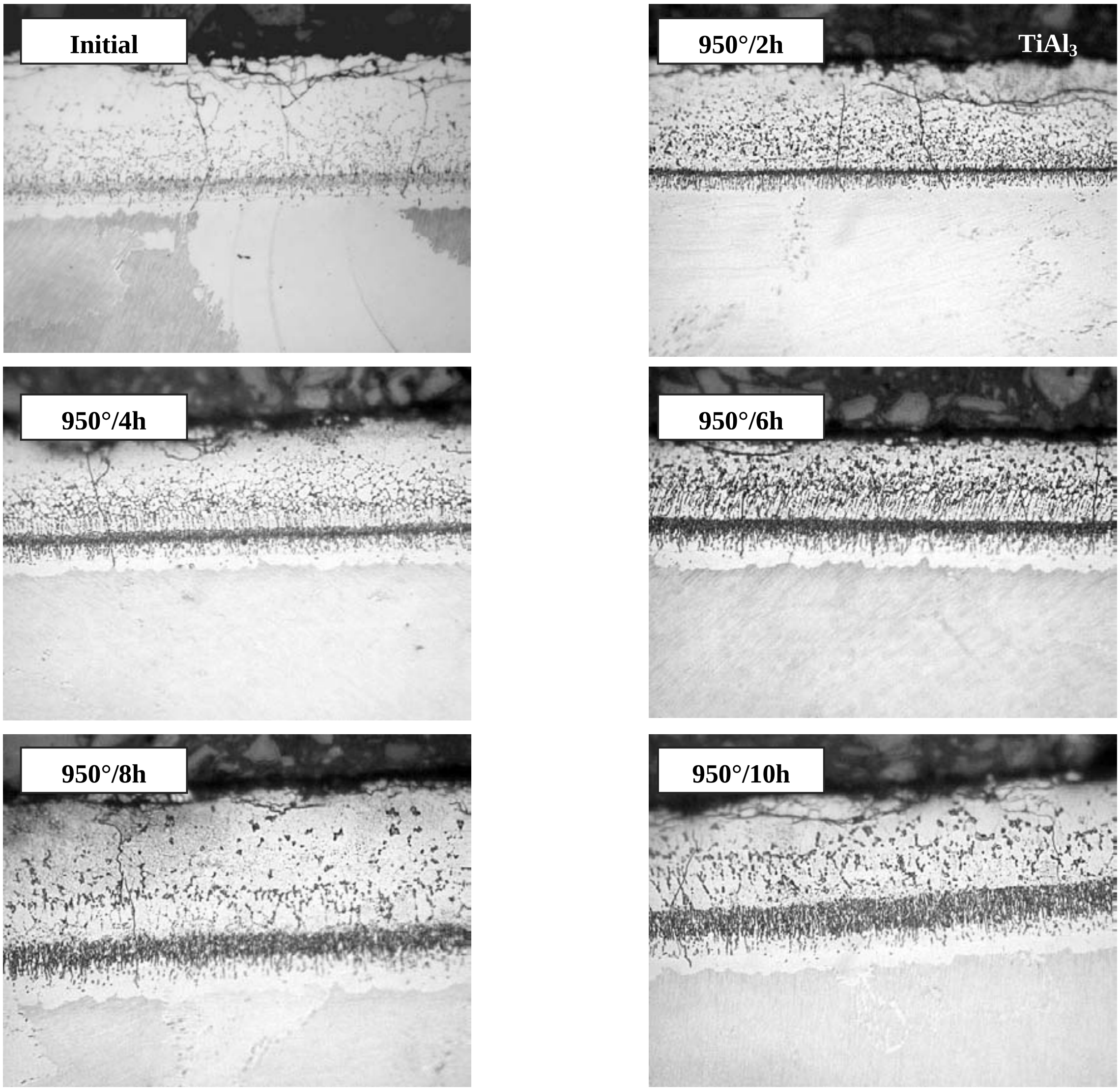

Fig. 7. Cross-section of TiAlSi coating – main view of top sublayer with precipitates, transition sublayer and base alloy with equiaxed grain sublayer – LM, mag. 400×

4. Summary

The conducted tests have testified the differences in the microstructure of the TiAlSi coatings depending on time of annealing after deposition process. The principal differences are connected with the thickness of the obtained sublayer. The chemical and phase content in each of them is similar in initial condition and after heat treatment. In initial conditions the slurry containing aluminium and silicon content created a coating made up of sublayers as follow: the outer $TiAl_3$ (O), rich in silicon in matrix, phase zone, interface boundary rich in Ti_5Si_3 particles in $TiAl_3$ matrix (S), and the inner $TiAl_2$ phase zone (I) with very small amount of silicon in matrix but numerous particles of Ti-Si phases. In the base alloy, the presence of an aluminium-rich TiAl phase below has been noticed, in which the lamellar structure of the base alloy is present (Ti_3Al + TiAl). The addition of silicon to 12.5 % in the basic slurry have caused the appearance of silicide phases in the structure of Ti-Si type and varied morphology. In the initial conditions their presence was detected in the outer layer, in the form of equiaxed particles placed mainly on the borders of three grains and in the interface area in the form of thin layer of $TiAl_3$ rich in Ti_5Si_3 particles. The thickness of outer layer (O) was 35μm and thickness of silicon rich layer (S) was ca. 3 μm.

The basic changes in microstructure of basic coating after annealing from 2 to 10 h was related to thickness of sublayers and morphology of detected silicides. A new form of silicon particles was discovered above the $TiAl_2$ inner zone (I): it took the form of columnar molecules, elongated in the direction of the base alloy.

Their appearance seems to be a consequence of diffusion processes connected with the inward displacement of aluminium and the creation of the transition zone made up of $TiAl_2$ phase. This phase is far less soluble than $TiAl_3$ phase, which may solve substitutionally as much as 20% of Si. As the aluminium content in $TiAl_3$ phase decreases, a forced Si removal takes place, as the amount of Si atoms has to be adequate to the amount of Al in this phase. Therefore, as a result of diffusion, areas passing from $TiAl_3$ to $TiAl_2$ phase appear, as well as the neighbouring areas of $TiAl_3$ rich in silicon, which subsequently changed into $TiAl_2$ phase, containing less aluminium. The silicon removed from the solid solution binds titanium in the form of silicides, whose elongated shape is directed by aluminium diffusion. The thickness of a silicide sublayer increases with time of diffusion treatment from ca. 3 μm in initial conditions (4h of annealing during deposition of coating) to 11 μm after another 10h of exposition at 950°C.

In the same time another changes were observed in the outer layer of coating. These changes were related to formation of columnar form of $TiAl_3$ phase grain in the area near to silicides sublayer and dissolutions and coalescence of initial equiaxed particles of Ti_5Si_3 phase. Formation of $TiAl_3$ columnar grain was detected after 2h of exposition and thickness of this sublayer was ca. 2 μm. After 4 h it was 10 μm and after 10 h of annealing it was 16 μm. Independently, after 8h of exposition, process of coarsening of columnar grain and coalescences of silicide particles was observed.

A juxtaposition of the essential information on the thickness of the outer zone – O (with columnar area C), the transition zone together with the columnar silicide zone – S, the inner zone – I and rich in aluminium sublayer in basic alloy (A) as well as the phase content of each coating has been presented in Table 1.

Table 1.
The juxtaposition of geometric parameters and phase composition

Time	Thickness O (C) [μm]	Thickness S [μm]	Thickness I [μm]	Thickness A [μm]
initial	35	2	2	1
2h	35	3	5	1
4h	30 (2)	5	5	3
6h	25 (10)	6	6	6
8h	25 (13)	8	6	8
10h	20 (16)	11	5	9

5. Conclusions

- Basic changes of TiAlSi coating after diffusion treatment are related to thickness of sublayers and morphology of titanium silicides and shape of $TiAl_3$ grains.
- Thickness of each sublayers was increased during the time of treatment and but phases constituent was still the same:
  - $TiAl_3$ rich in Si outer layer;
  - Ti-Si transition sublayer;
  - $TiAl_2$ inner sublayer;
  - TiAl sublayer as a consequence of increases of Al concentration in basic alloy;
- Morphology of Ti_5Si_3 silicides was different in outer layer (equiaxed particles placed mainly on the borders of three grains) and in transition layer (columnar shape of silicides as an effect of diffusion process). The effect of coalescences of silicides was observed especially in the case of initial silicides.
- The changes of $TiAl_3$ phase grain shape to columnar form and their coarsening was observed as results of diffusion treatment at 950°C.

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