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# The influence of Si on structure of aluminide coatings deposited on TiAl alloy

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## ABSTRACT

**Purpose:** Increasing oxidation resistance of TiAl intermetallic alloy by depositing aluminide coating by slurry method and investigation of the influence of Si addition on structure of obtained coatings
**Design/methodology/approach:** The structure of coatings was investigated by light scanning microscopy. The chemical composition of coatings was investigated by EDS method and XRD phase analysis was used as well
**Findings:** The investigation has showed that the thickness of the coatings ranged from 30 to 40 µm. The structure of the silicon-modified aluminide coatings is as follows:
- the outer zone consisting of $TiAl_3$ 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

The analysis of the average chemical composition of the outer zone exhibited the gradual increase of the silicon content along with the increase of this element in the slurry. The phase analysis has confirmed $Ti_5Si_3$ creation and, in case of the high silicon content in slurry, also other silicides: types $Ti_5Si_4$,$TiSi_2$,TiSi
**Practical implications:** The slurry method can be applied in aerospace and automotive industry as low-cost technology of producing of aluminide coatings on intermetallics
**Originality/value:** New method of depositing of aluminide coatings on TiAl alloys
**Keywords:** Surface treatment; Aluminide coatings

## 1. Introduction

The alloys based on the intermetallic phases from Ti-Al system are materials which, due to their high specific strength in a wide range of temperatures (up to 800ºC), can be used in automotive and aerospace applications [1,2].
The automotive industry employs the TiAl alloys to produce valves and turbine wheels [3,4].
One of the major problems connected with the application of these alloys is their insufficient oxidation resistance, which can be improved by the usage of protective coatings.[5-10] The recent research focuses on aluminide and silicide coatings.

The high-aluminide coatings from Ti-Al system ($TiAl_2$ and $TiAl_3$) are produced by pack cementation method. The $TiAl_3$ phase exhibits high hardness and embrittlement, which, however, results in the possibility of fracturing [11]. The addition of chromium, which causes a change in the crystalline structure of the phase $TiAl_3$ (from the brittle $DO_{22}$ into the more plastic $L1_2$), is employed to prevent it [12]. Besides chromium, aluminide coatings are modified with silicon.

Xiang [13] has obtained aluminide coatings employing by the pack cementation method. The 30 µm thick coating consisted of the outer, continuous titanium silicide ($Ti_5Si_3$) layer and the inner layer, composed of $TiAl_3$ phase and silicide grains.

In China, immersing the TiAl alloy samples in liquid siluminum of eutectic composition has been employed. The layer was made up both by TiAl system phases and titanium silicide grains. The triple $Ti_7Al_5Si1_2$ phase has been detected as well [14].

The good oxidation resistance has been observed in case of the pure silicon coatings. The positive results of modification of the outer zone of TiAl alloy achieved by means of ion implantation have encouraged Taniguhi [15] to use the pack cementation method. As a result of holding the samples of TiAl alloy in silicon powder at a temperature of 800-1000ºC, titanium silicide $Ti_5Si_3$ coating, whose thickness didn't exceed 6 µm, has been obtained.

Due to the outward diffusion of titanium from the alloy base below the coating, an aluminium-enriched zone has been formed. The cyclic oxidation tests at the temperature of 900ºC in the air or in the atmosphere simulating combustion gases have proved the coating to be highly resistant, despite it being relatively thin.

So far, the research of the alunimide coatings presented in literature has centered on silicon modification with no more than 25% wt. Si content. This has been due to the siluminum use in the coatings deposition, which restricted the practical possibility of increasing the silicon content above the mentioned level.

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 used for the modification. As the slurry composition is modifiable to a large extent, the influence of the silicon content on the structure and oxidation resistance of the aluminide coatings on the high-niobium TiAl alloy can be investigated.

## 2. Experiment

High-niobium content alloy, produced by Mitsubishi Heavy Industries, has been used as the base for the deposited coatings. Samples (12x7x1 mm) have been cut out of the delivered ingot. The obtained samples have been ground with the use of water-resistant paper of maximum gradation 600, sanded, and degreased. The water slurries containing Al and Si powders have been prepared with 0-100 wt % silicon content. The samples have been covered by a single-time immersion in slurry, which was followed by drying at the temperature of 80ºC. The diffusion treatment has been done in argon (Ar) atmosphere (950ºC/4h). During the final stage, the samples have been cleaned by ball peening.

## 3. Results

### 3.1. The coating obtained from pure-aluminium slurry

As a result of the diffusion treatment of the sample covered with the slurry containing only aluminium, the 15-30 µm thick coating has been deposited, exhibiting a triple-zone structure. The outer layer, not more than 20µm thick, contained 56-63% at aluminium content (Fig. 1, Table 1 the area marked as "1" and "2"). The phase composition analysis has indicated $TiAl_3$ as the major component of the outer zone, while the inner zone is dominated by $TiAl_2$ phase (Figure. 1, Table 1, area marked as "3").

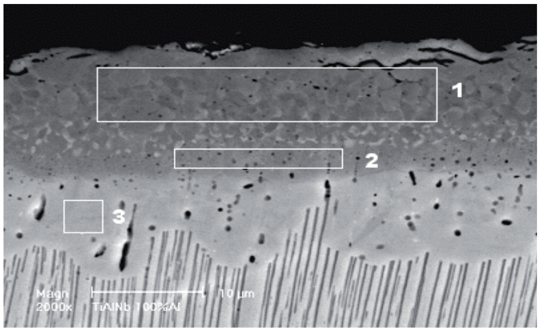


Fig. 1. The structure of the aluminide coating deposited on TiAlNb alloy from 100% Al slurry

Table 1.
The results of EDS analysis from the areas marked in Fig. 1

| Area | Al | | Nb | | Ti | |
|---|---|---|---|---|---|---|
| | %wt | % at. | %wt | % at. | %wt | % at. |
| 1 | 46,65 | 62,69 | 8,83 | 3,45 | 44,52 | 33,75 |
| 2 | 39,90 | 56,07 | 9,48 | 3,07 | 50,61 | 40,06 |
| 3 | 25,06 | 39,37 | 13,25 | 6,05 | 61,68 | 54,58 |

### 3.2. The coating obtained from slurries containing 5-20% wt of silicon

The coatings produced from slurries of low silicon content (5-20% wt) was 20-30 µm thick, with a triple-zone structure (Fig. 2). The results of EDS analysis were presented in Table 2. The matrix of the outer zone, 12-15 µm thick, was the high-aluminium phase $TiAl_3$ (Fig 2a, Table 2; the points marked as 1 and 3), on whose grain boundaries particles rich in silicon were present. The middle zone was composed of high-silicon columnar grains (Fig. 2b, Table 2). The thickness of this zone grew as the silicone content in the slurry increased (up to 11 µm in the coating from 20% wt Si slurry). The inner zone, the thickness of which didn't exceed 3µm, consisted of $TiAl_2$ phase; no silicon has been detected there. The XRD phase analysis of the coating has exhibited, besides the high-aluminium phases of Ti-Al system, the presence of titanium silicides (type $Ti_5Si_3$).

Table 2.
The results of EDS analysis from the areas marked in Fig. 2

| Point/ Area | Al | | Si | | Nb | | Ti | | Cr | |
|---|---|---|---|---|---|---|---|---|---|---|
| | %wt | % at. | %wt | % at. | %wt | %at | %wt | % at. | %wt | %at. |
| 1 | 48,12 | 64,12 | - | - | 8,41 | 3,25 | 43,47 | 32,63 | - | - |
| 2 | 27,60 | 38,53 | 13,81 | 18,52 | 8,00 | 3,24 | 49,13 | 38,64 | 1,46 | 1,06 |
| 3 | 46,06 | 61,64 | 1,58 | 2,03 | 8,44 | 3,28 | 42,87 | 32,32 | 1,05 | 0,73 |
| 4 | 42,75 | 57,98 | 3,21 | 4,19 | 9,13 | 3,60 | 43,81 | 33,47 | 1,09 | 0,77 |
| 5 | 35,45 | 49,58 | 6,19 | 8,32 | 9,98 | 4,06 | 47,26 | 37,23 | 1,12 | 0,81 |

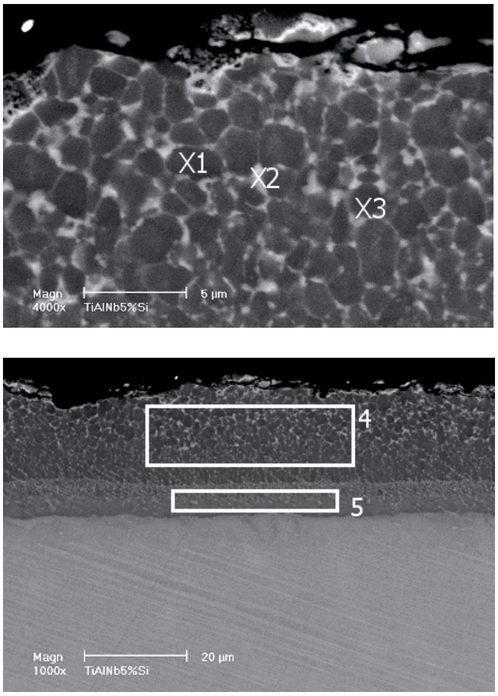


Fig. 2. The structure of aluminide coatings obtained from slurry containing 5% wt Si

## 3.3. The coating obtained from slurries containing 40-80% wt of silicon

The coatings deposited from high-silicon content slurries (40-80% wt) exhibited, similarly to the coatings mentioned before, a triple-zone structure. The structure of aluminide coating obtained from slurry containing 40% wt Si was presented on fig. 3 and the results of EDS analysis was presented in Table 3. The increase in the amount and size of the silicide grains, which has been proved to characterize those coatings, had, however, a coagulating effect on them and led to the creation of a continuous silicide zone in the coating deposited from the 80% wt Si slurry. The thickness of the columnar silicide zone grew until it reached the thickness of the outer zone: about 11 µm (Fig. 3; the area marked as 2). The presence of the high-aluminium phases $TiAl_2$ and $TiAl_3$ has been, correspondingly to the coatings made from low-Si slurries, observed in the phase content.

The differences in the types of the silicides formed: apart from the $Ti_5Si_3$ type, types $Ti_5Si_4$, TiSi and $TiSi_2$ have been found.

Table 3.
The results of EDS analysis from the areas marked in Fig. 3

| area | Al | | Si | | Nb | | Ti | | Cr | |
|---|---|---|---|---|---|---|---|---|---|---|
| | %wt | % at. | %wt | % at. | %wt | % at. | %wt | % at. | %wt | % at. |
| 1 | 34,68 | 48,18 | 8,10 | 10,81 | 9,76 | 3,94 | 46,40 | 36,31 | 1,05 | 0,76 |
| 2 | 32,44 | 45,21 | 9,40 | 15,59 | 9,04 | 3,66 | 49,11 | 38,55 | - | - |

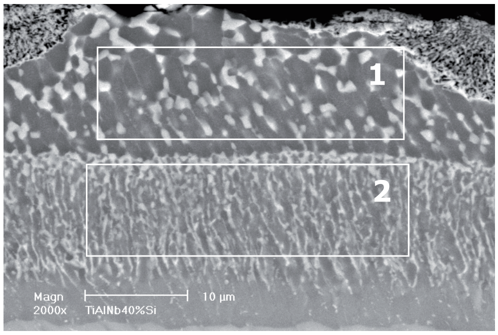


Fig. 3. The structure of aluminide coating obtained from slurry containing 40% wt Si

## 3.4. The coating obtained from pure-silicon slurry

The coating deposited from the slurry containing only silicon exhibited quite different structure. First of all, it was thin (10-11 µm), in comparison to the other coatings. Secondly, its structure was only double-zone. The linear chemical analysis (Fig. 4) and the X-ray phase analysis has shown that the outer zone was composed of titanium silicides, while the inner zone exhibited high aluminium content. The phase content of the silicides in the inner zone was similar to the coatings created from high-silicon content slurries (40-80% wt Si) – types $Ti_5Si_3$, $Ti_5Si_4$, TiSi and $TiSi_2$ were present.

# 4. Discussion

The employment of the dip-painting method using Al and Si slurries, followed by diffusion treatment enables the generation of coatings without fractures, of the average thickness of 30 µm. The structural research and chemical and phase analysis done on the coatings has led to the distinction of three major zones in their structure:

- the outer zone consisting of $TiAl_3$ phase and titanium silicides formed on the matrix grain boundaries composed of $TiAl_3$ (in case of the coatings obtained from the slurry containing 5-20% Si – type $Ti_5Si_3$; additionally, $Ti_5Si_4$, TiSi, $TiSi_2$ types in case of the coatings acquired from the slurries of 40-100 wt. % Si content),
- the middle zone containing the same phase components with the matrix $TiAl_3$ and the silicides $Ti_5Si_3$, which, however, formed columnar grains,
- the inner zone, 2 µm thick, consisting of $TiAl_2$ phase.

In the pure-silicon slurry, a coating composed of the inner zone (containing titanium silicides) and the outer zone (enriched with aluminium) has been created. This structure resembles the ones obtained by Taniguchi [15]. The coatings obtained from the 40-60% Si slurries exhibited, nevertheless, the structure similar to the coatings investigated by Xiang [13], who also used the pack cementation method.

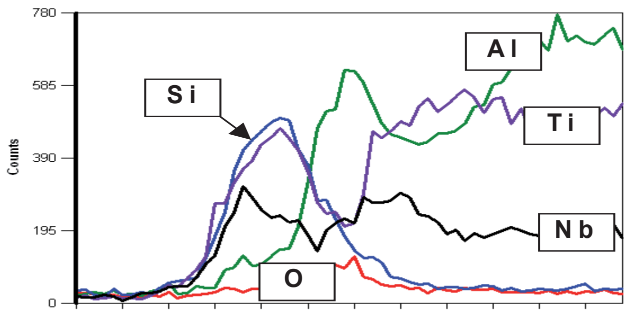


Fig. 4. The linear EDS analysis of the cross-section of the coating deposited from 100% Si slurry

In all coatings, the high niobium content has been detected (3-6% at). This is the evidence of the outward diffusion of this element from the base alloy (containing about 6% at Nb), which also improves the coating's oxidation resistance.

Taking into consideration the primary function of the obtained coating, which is the increased oxidation resistance of the TiAl alloys, it possesses beneficial phase and chemical contents. The major component – the high-aluminium phase $TiAl_3$ – exhibits a much higher oxidation resistance than the base alloy. The product of the oxidation of the $TiAl_3$ phase is aluminium oxide, which creates a barrier for further corrosion. In addition, the silicon component of the slurry has created grains of titanium silicides $Ti_5Si_3$, characterized by high oxidation resistance [16]. As well as this, the grains creation has slowed down the process of rutile scale production.

## 5. Conclusions

1. The thickness of the coatings deposited in Al And Si slurries ranged from 20 to 30 μm.
2. The silicone-modified coatings exhibited a triple-zone structure.
3. The chemical and phase analysis have showed the presence of Ti-Al system phases and titanium silicides.
4. The phase analysis has revealed that in case of 5-20% Si content in the slurries, titanium silicides of the type $Ti_5Si_3$ are formed, whereas in case of Si 40, 60 and 80 wt % content, titanium silicides of the type $Ti_5Si_4$, $TiSi_2$ and TiSi was found as well.

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