

## Gas phase aluminising of TiAl intermetallics

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### Manufacturing and processing

#### ABSTRACT

**Purpose:** Increasing oxidation resistance of TiAl intermetallic alloy by gas phase aluminising.

**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 was 10  $\mu\text{m}$ . The structure of the silicon-modified aluminide coatings is as follows: the outer zone consisting of  $\text{TiAl}_3$  phase (on the TiAl7Nb alloy only), the middle zone consisting  $\text{TiAl}_2$  phase, the inner zone consisting of TiAl 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.

**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; TiAl intermetallics

### 1. Introduction

The studies and experiments conducted so far clearly show that TiAl alloys are materials which, on account of their resistance properties in a wide range of temperatures, could be applied in aircraft or automotive engines. The main restriction in introducing those materials on a mass scale is, apart from the high production costs, their relatively low oxidation resistance at temperatures above 800°C. This is connected with the susceptibility of the materials in question to the creation of scale which is a mixture of titanium and aluminium oxides. The oxidation resistance could be obtained by means of increasing Al content, which would induce the production of  $\text{Al}_2\text{O}_3$  scale, thus creating the barrier for the further progress of the corrosion [1, 2].

The  $\text{TiAl}_3$  phase is the richest in aluminium in the whole TiAl system. During the oxidation process, it enables the production of the continuous layer of  $\text{Al}_2\text{O}_3$ . The primary procedure of creating  $\text{TiAl}_3$  based coatings is the contact out of pack method in which the coating is created as a result of inward diffusion of aluminium from the powder in which the samples are placed, while employing the

halogenide activator. The obtained layers consist of the outer zone, made up of  $\text{TiAl}_3$  phase, and the intermediate layer, including a relatively thin  $\text{TiAl}_2$  phase. In the coatings, fractures have been observed, created during the cooling from the deposition temperature, which is the consequence of the brittleness of  $\text{TiAl}_3$  phase [3]. Xiang and Rose have proved that employing  $\text{AlCl}_3$  as an activator permits the control of the layer development kinetics as well as the avoidance of micro-fractures.

Gauthier et al. [5] studies on aluminide coatings oxidation resistance at temperatures ranging from 800 to 1000°C a strong growth of the transitory zone made up of  $\text{TiAl}_2$  at the expense of the  $\text{TiAl}_3$  area. After 300h of testing at 900°C, the  $\text{TiAl}_3$  area has completely disappeared. However, the scale, which did not exceed the thickness of 2  $\mu\text{m}$ , still consisted of aluminide oxide. Further oxidation tests of the samples covered with Ti-Al phases rich in aluminium have revealed the creation of  $\theta\text{-Al}_2\text{O}_3$  oxide on the surface, which exhibits lower thermodynamic stability than  $\alpha\text{-Al}_2\text{O}_3$  oxide present on the surface of  $\text{TiAl}_2$  phase. A longer period of time (exceeding 100h) is necessary for the conversion of  $\theta\text{-Al}_2\text{O}_3$  oxides into  $\alpha\text{-Al}_2\text{O}_3$  oxides. The authors suggest that  $\text{TiAl}_2$  phase might be a more attractive covering preventing

oxidation on account of the creation of the stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxide in the first stages of oxidation.

Aluminide coatings are also manufactured using magnetron sputtering method. The tests of the sample surface with TiAl<sub>2</sub> coating created with this method have shown the presence of both types of aluminide oxide ( $\theta$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) after 924h/900°C cyclic oxidation tests. The existence of micro-fractures in the TiAl<sub>2</sub> coating has also been revealed [6]. The aluminide coating may as well be produced by aluminium spraying followed by diffusion treatment in order to obtain a coating.

The properties of diffusive aluminide coatings are strongly influenced by the chemical content of the alloy matrix. Jung [8] has proved the positive effect of chromium in the TiAl alloy on the improvement of coating plasticity. As the chromium content increased (from 1 to 6% at), the size of the grains in the alloy and the amount of micro-fractures decreased. Furthermore, the chromium addition reduces the hardness of the coating as compared to the pure TiAl<sub>3</sub> coating obtained on TiAl without alloy additions. In case of high chromium content in TiAl<sub>3</sub> phase, a significant improvement of its plasticity has been observed. This is connected with the capability of creating (Al,X)<sub>3</sub>Ti phases, whose cubic net of L<sub>12</sub> type is less brittle than the DO<sub>22</sub> net of the TiAl<sub>3</sub> phase.

Moreover, the aluminide chromium-modified coatings can be created utilising the contact out of pack method from the mixture of Al and Cr powders as well as Al<sub>2</sub>O<sub>3</sub> as a filler and NH<sub>4</sub>Cl as an activator. Furthermore, magnetron sputtering from Al-21Ti-23Cr targets in which a two-phase structure has been detected has been used [10]. The aluminide chromium-modified coatings may also be obtained by means of plasma spraying [11, 12].

Niobium has a beneficial influence on the structure and diffusion properties on the TiAl<sub>3</sub> aluminide coatings gained by means of pack cementation method. The coatings obtained on TiAlNb alloys have been characterised by considerably higher oxidation resistance than the coatings obtained on TiAl alloys without any additions. This property increased as the niobium content grew in the matrix. Niobium causes the coatings obtained with the same deposition parameters to be thicker, which is the consequence of the decrease in the grain size. The grain size reduction, especially in the TiAl<sub>3</sub>/TiAl<sub>2</sub> transition area, along with the presence of niobium aluminide issues, moderates the inward diffusion of Al. Simultaneously, the niobium in the coating enhances its mechanical properties by reducing its micro-hardness, intensifying its resistance and limiting the number of fractures [13].

In aircraft industry, out of pack aluminising method is employed for manufacturing aluminide coatings. This method enables the acquirement of high-quality aluminide coatings, as required in that sector of commerce. The application of oxidation resistant coatings should permit, when foundry engineering technology has developed, a wider use of alloys Ti-Al [14].

## 2. Experiments

As the matrix for the manufactured coatings, the alloys provided by ALD and MHI companies have been used, Ti48Al2Cr2Nb and TiAl7Nb (7% at Nb) respectively. The samples measuring 12x7x1 mm have been extracted, ground with the use of waterproof paper of maximum gradation 600 and degreased. Employing the out of pack method, the samples have been set in a container containing the activated aluminium powder, the filler and

the activator. The process has been conducted for 4 hours in Ar atmosphere at a temperature of 1050°C.

## 3. Results

The average chemical analysis of the surface of the sample with the aluminide coating based on the TiAl7Nb alloy (Fig. 1) showed high titanium content and lower aluminium content as represented by the atomic ratio Ti:Al, equaling 3:1 (Table 1).

XRD phase analysis from the top of the coating deposited on TiAl7Nb alloy (Fig. 2) has indicated the presence high-aluminium TiAl<sub>3</sub> and TiAl<sub>2</sub> phases, as well as TiAl and Ti<sub>3</sub>Al phases, which formed the base alloy. In addition to that, niobium aluminides of Al<sub>3</sub>Nb type and a triple TiAl<sub>2</sub>Nb phase have been observed.

The SEM investigations and the EDS analysis of the aluminide coating on the TiAl7Nb alloy have proved its triple-zone structure. On the top of the coating, the proportions of Ti to Al corresponded to Ti<sub>3</sub>Al phase (Fig. 3a, point 1), which agreed with the chemical content analysis of the surface of the coating (Fig. 2, Table 1). Below, the presence of a thin (about 1  $\mu$ m) layer consisting of TiAl<sub>3</sub> phase (Fig. 3b, point 2) has been detected. In this zone, the niobium content exceeded that of the matrix alloy, which proves that an outward diffusion towards the outer zone of the coating had taken place. The middle zone exhibited the percentage of Ti to Al indicating TiAl<sub>2</sub> phase (Fig. 3b, point 3). The niobium content of this zone equals about 8% wt. The inner zone (Fig. 3b, points 4, 5) shows a composition which is almost identical to the matrix alloy. The difference was only in the niobium content reduced from 14 to 10% wt.

The chemical content analysis of the sample coated with aluminide based on Ti48Al2Cr2Nb alloy hasn't indicated the existence of TiAl<sub>3</sub> phase, such as has been observed on TiAl7Nb alloy. The only phases present were TiAl<sub>2</sub>, TiAl and Ti<sub>3</sub>Al.

The structure of the coating based on Ti48Al2Cr2Nb alloy displayed a double-layered structure. In the outer zone, of the greatest thickness, Al prevailed over Ti, as represented by the proportion of titanium to aluminium equalling 2:3. This proved the formation of TiAl<sub>2</sub> phase (Fig. 3b, Table 2, points 6 and 7).

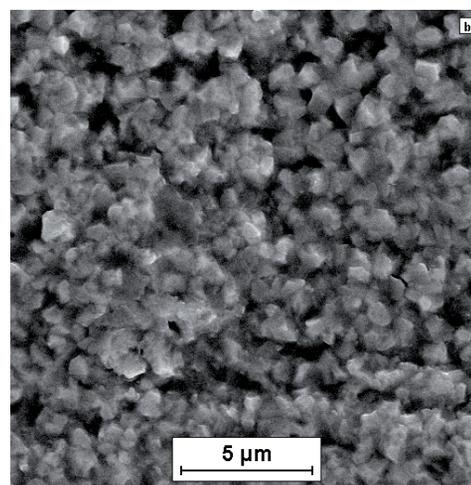


Fig. 1. Surface morphology of aluminide coatings deposited on TiAl7Nb alloy by out of pack method (SEM)

Table 1.

Results of EDS analysis from area presented on Fig 1

Element	Ti	Al	Nb
% at.	74.70	24.56	0.75
% wt.	83.02	15.37	1.61

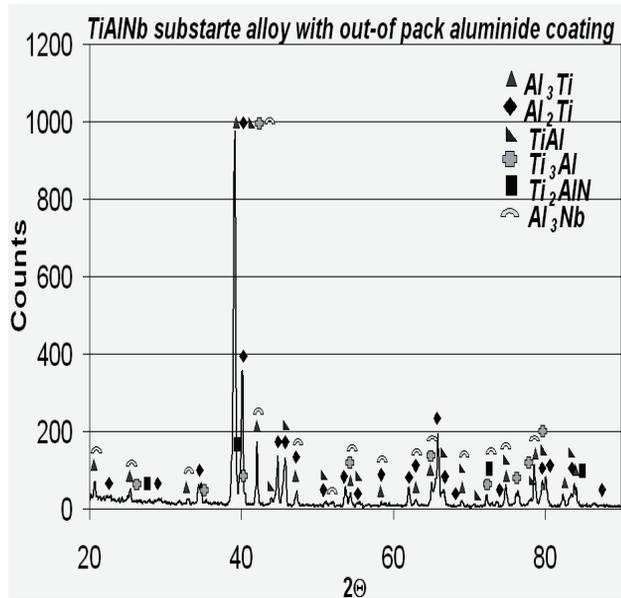


Fig. 2. Results of XRD phase analysis of TiAl7Nb alloy with aluminide coating

Table 2.

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

Point	Ti		Al		Cr		Nb	
	% at.	% wt	% at.	% wt	% at.	% wt	% at.	% wt
1	67.91	78.26	31.51	20.45	-	-	0.58	1.29
2	27.52	35.42	65.67	47.59	-	-	6.81	16.99
3	39.43	50.50	57.28	41.32	-	-	3.29	8.18
4	43.46	53.55	52.29	36.30	-	-	4.25	10.15
5	46.74	56.57	48.98	33.39	-	-	4.28	10.04
6	36.07	47.42	60.36	44.69	1.09	1.55	2.48	6.33
7	38.40	50.59	58.65	43.53	1.46	2.09	1.49	3.80
8	54.57	65.12	41.54	27.92	2.02	2.61	1.88	4.35

## 4. Discussion

The gas phase aluminising technology enables producing a relatively thin coating of 10  $\mu\text{m}$ , characterized by the multi-layer structure. In case of the coating based on high-niobium TiAl alloy the structure is as follows:

- the outer zone, consisting of  $\text{TiAl}_3$  phase;
- the middle zone, including  $\text{TiAl}_2$  phase;
- the inner zone, containing TiAl phase.

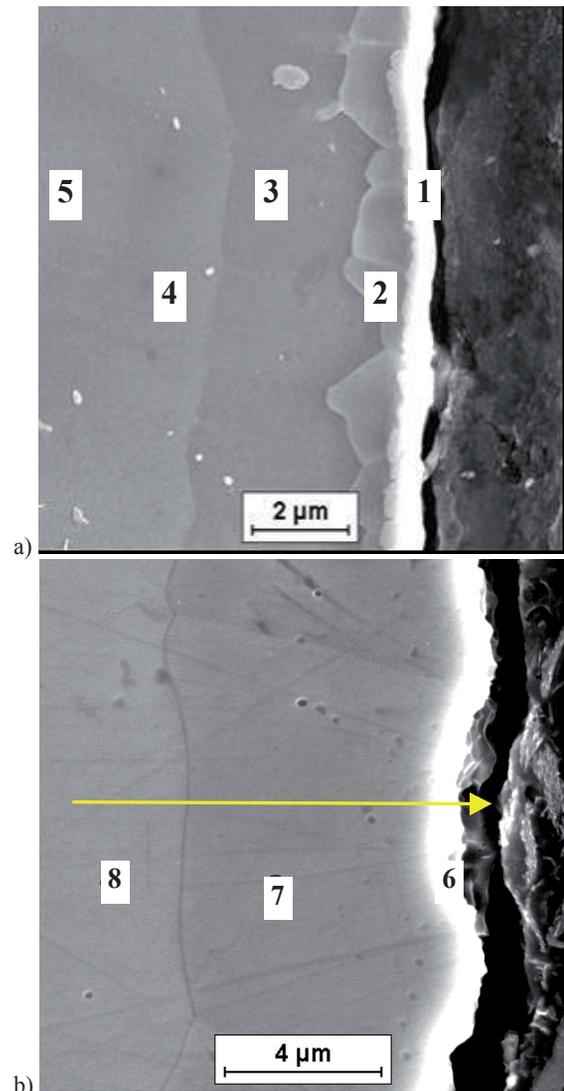


Fig. 3. The structure of aluminide coatings deposited by out of pack method on TiAl7Nb (a) and Ti48Al12Cr2Nb, (b) alloys

In case of the coating based on Ti48Al12Cr2Nb alloy the outer zone, made up of  $\text{TiAl}_3$ , hasn't been detected.

In both coatings, the outward diffusion of the alloy elements to the covering zone has been observed. In the coating based on TiAl7Nb alloy, the niobium content increased significantly in the inner zone, exceeding the content of that element in the matrix alloy. The phase analysis of that coating surface has proved the existence of niobium aluminides, which could lower the corrosion resistance, due to the peeling off and dropping of the scale containing niobium oxides [15]. The isothermal oxidation test of the aluminide-coated sample hasn't revealed any negative impact of the high niobium content in the outer layer of the coating on the oxidation resistance. In the middle layer, the amount of niobium did not exceed 10% wt. The amount of Nb and Cr in the coating based on Ti48Al12Cr2Nb alloy hasn't surpassed the niobium and chromium content in the matrix alloy.

## 5. Conclusions

1. The phase and chemical content analyses have proved that the main phase content of the obtained coating are high-aluminium TiAl<sub>3</sub> and TiAl<sub>2</sub> phases.
2. No presence of pores or fractures has been detected in the coating, and its thickness didn't exceed 10 µm.
3. The phase and chemical content analyses have shown the following structure of the coating based on high-niobium alloy: TiAl<sub>3</sub>/TiAl<sub>2</sub>/TiAl/matrix alloy.
4. In case of aluminide coating deposited on TiAlCrNb alloy no outer zone consisting of TiAl<sub>3</sub> phase has been observed.
5. The outward diffusion of Cr and Nb elements from the matrix alloy to the outer layer of the coating has been proved.
6. The application of aluminide coating deposited using out of pack method should significantly increase the oxidation resistance of the matrix alloy by means of creating Al<sub>2</sub>O<sub>3</sub> scale.

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