

Si-modified aluminide coating deposited on TiAlNb alloy by slurry method

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Received 04.11.2006; accepted in revised form 15.11.2006

Manufacturing and processing

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 was 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.

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 Si modified 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 800°C), 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 L_{12}), is employed to prevent it [12]. Besides chromium, aluminide coatings are modified with silicon.

Silicon is an element which greatly increases the TiAl alloys oxidation resistance. This property of silicon is related to its ability of forming titanium silicides of the types TiSi_2 , Ti_5Si_3 , Ti_5Si_4 and TiSi , that exhibit high oxidation resistance. As well as this, it forming of silicides slows down the process of forming

rutile during oxidation (as a result of binding titanium), and thus increasing the activity of aluminium [15].

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 $\text{Ti}_7\text{Al}_5\text{Si}_{12}$ 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 Taniguchi [15] to use the pack cementation method. As a result of holding the samples of TiAl alloy in silicon powder at a temperature of 800-1000°C, 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 900°C 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 aluminide 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. Experimental

TiAlNb alloy, (7% at Nb) produced by Mitsubishi Heavy Industries, has been used as the base material for the coatings. Samples measuring 12x7x1 mm have been cut out of the delivered ingot. The samples have been grinded up to 600 SiC paper sanded and degreased. The water slurry (with small amount of chromic and phosphoric acid) which contained 12.5% wt Si and Al (bal.) powder has been prepared. The samples have been covered by a single-time immersion in slurry, and drayed at temperature of 80°C in air. The diffusion treatment has been done in Ar atmosphere (950°C/4h). During the final stage, the samples have been cleaned by ball penning.

A Hitachi S-3400 equipped with Noran Voyager EDS was used for surface morphology and microstructure observation. The XRD phase content analysis has been conducted with JEOL JDX-7S.

The isothermal oxidation test has been carried out in the temperature of 900°C in air. The mass of the sample has been measured at the beginning and at the end of the test.

The cyclic oxidation tests were conducted in static air. One cycle considered of heating to 950°C holding for 23 h and cooling to room temperature in air. The specimens were weighed at each interval when cooled to room temperature. The oxidation test was finished after 690 hours (30 cycles).

3. Results

3.1. Structure and chemical composition

The microphotographs of the cross-section of the coating after the diffusion treatment have been presented in Fig. 1. The results of the chemical composition analysis of the selected areas have been presented in Table 2. The deposited coating was 40 μm average thickness and a triple-zone structure. No fractures in the cross-section of the coating have been observed. The outer zone was about 30 μm thick, while the middle zone exhibited columnar grains and was about 8 μm thick, and the inner zone, containing no grains, was only 2 μm thick.

In the matrix of the coating's outer layer (Fig. 1, point 2), high titanium and aluminium content has been detected (Ti:Al at. ratio roughly equaled 1:2). Bright silicon-rich grains have also been discovered (point 1), containing as much as twice the amount of niobium present in the matrix.

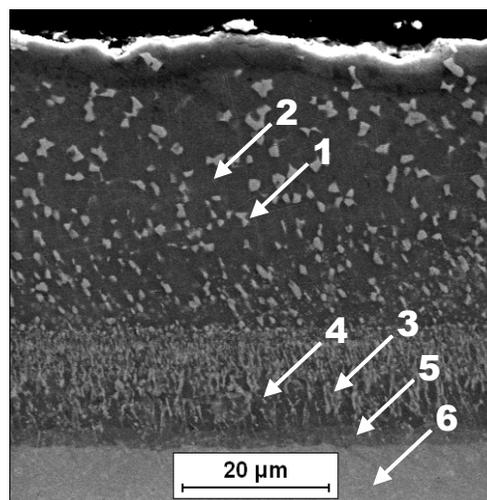


Fig. 1. The structure of the Si-modified aluminide coating deposited on TiAl7Nb alloy by slurry method

The middle zone was built from thickly packed columnar grains with high niobium content (point 3). The chemical composition of the matrix in that zone was close to the one observed in the outer zone (point 4). The inner zone was characterized by the increasing of aluminium content along with a complete lack of silicon (point 5). Below that zone, the chemical composition was similar to the base alloy (point 6).

The XRD phase analysis of the coating's surface as well as each of its zones has been performed. Gradual removal of the

zones by means of grinding has been used to enable it. The results showed the following phase composition of the coating's zones: (a) the outer zone consisting of $TiAl_3$ phase and titanium silicides type Ti_5Si_3 ; (b) the middle zone containing $TiAl_3$ and the silicides Ti_5Si_3 , which, formed columnar grains, (c) the inner zone, consisting of $TiAl_2$ phase.

Table 1.
The results of EDS analysis from area presented on Fig 1

Point	Al		Si		Ti		Nb	
	% wt	% at	% wt	% at	% wt	% at	% wt	% at
1	22.27	33.10	12.66	18.08	51.09	42.78	13.99	6.04
2	50.85	66.94	-	-	39.72	29.45	9.42	3.60
3	16.17	23.20	21.61	29.77	53.97	43.60	8.25	3.44
4	43.46	58.54	3.67	4.75	43.60	33.08	9.27	3.63
5	40.95	56.94	0.61	0.82	49.14	38.49	9.30	3.75
6	23.59	37.59	-	-	62.16	55.81	14.25	6.60

3.2. Oxidation resistance

The mass change after the isothermal oxidation test has been presented in Fig. 2. The sample without the coating showed a large mass decrease (o 15,3 mg/cm²), whereas the sample with the aluminide coating obtained from the Al-Si slurry showed a minor mass increase which didn't exceed 2,5 mg/cm². On the surface of the TiAlNb alloy sample without the coating, the remains of the dark gray dropping scale were present, while on the surface of the aluminide-coated sample only dark-yellow thin tarnish could be seen. The examination of the morphology and the chemical composition of the samples' surface after cyclic oxidation test has shown the double-layered structure of the scale. The outer layer was characterized by high titanium content (Fig. 3 point 1) while the inner layer the titanium content prevailed remarkably (Fig 3 point 2).

The XRD phase analysis of the sample surface has indicated the presence of the corrosion products in the forms of aluminium and titanium oxides. In addition to that, the phase contents of the coating were detected – aluminium-rich $TiAl_3$, $TiAl_2$ and titanium silicide Ti_5Si_3 .

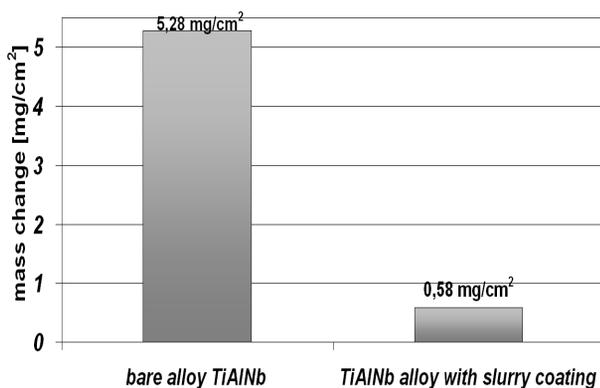


Fig. 2. Mass change in the samples after the isothermal oxidation test 900°C/500h

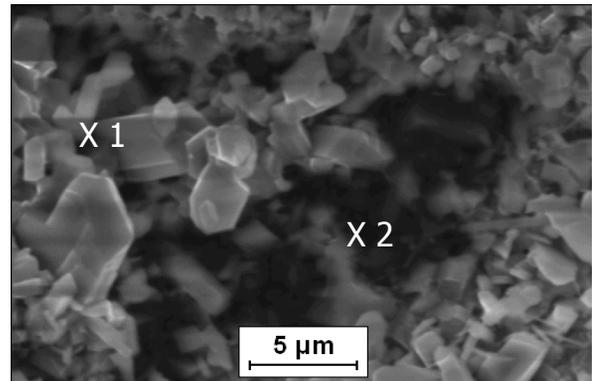


Fig. 3. Surface morphology the coating after isothermal oxidation test 900°C/500h

4. Discussion

The employment of the dip-painting method using Al and Si slurries, followed by diffusion treatment enables the formation of coatings without fractures, of the average thickness of 40 µm. The structural, chemical and phase composition investigations 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 $TiAl_3$ -type Ti_5Si_3 ;
 - the middle zone containing the same phase components with the matrix $TiAl_3$ and the silicides Ti_5Si_3 , which formed columnar grains;
 - the inner zone, 2 µm thick, consisting of $TiAl_2$ phase;
- Presence of niobium content has been detected in the coatings (3-6% at). This is the effect of the outward diffusion of this element from the base alloy (containing about 7% at Nb), which also improves the coating's oxidation resistance.

The major problem in the coatings obtained from the slurries is the possibility of fractures in the layer, resulting in the damage of the protective coating and, consequently, in the decline of the oxidation resistance ensuing from the pinhole corrosion. Hence the demand for the precise selection of the coating's thickness to eliminate the hazard.

The isothermal test showed a remarkably higher oxidation resistance of the TiAlNb alloy with the protective coating in comparison with the uncoated sample. A double-layered scale formed on the surface of the coating, was built from aluminium and titanium oxides. It exhibited a limited thickness and good adhesion to the samples' surface. The scale spallation was observed only on uncoated sample

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

Ti₅Si₃, characterized by high oxidation resistance. As well as this, the grains creation has slowed the process of rutile scale production.

5. Conclusions

1. The obtained coating was 40 μm thick and had a triple-zone structure.
2. The phase and chemical content analyses have proved that the main content of the coating's matrix is aluminium-rich TiAl₃ phase; a lot of titanium silicide grains of Ti₅Si₃ type have been detected as well. In the outer zone, they formed particles within the borders of the matrix grains, in contrast to the middle zone, where they formed columnar grains.
3. The presence of niobium has been observed, resulting from the outward diffusion from the base alloy.
4. On the surface of the sample of the TiAlNb alloy without the coating, the scale saplled from the surface. The scale spallation wasn't observed on coated sample
5. The scale obtained on the surface of the aluminide-coated sample has a double-layered structure: rutile was discovered on the top, whereas aluminium oxide was detected below.

Acknowledgements

The authors would like to acknowledge the financial support of this research by the Polish Ministry of Education and Science.

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