

Microstructure and oxidation behaviour of TiAlSi coatings on TiAlCrNb alloy

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Properties

ABSTRACT

Purpose: Influence of slurry coating deposition TiAlSi with different Si concentration on oxidation resistance of Ti48Al2Cr2Nb intermetallic alloy and investigation of the influence of Si addition on the structure of obtained coatings.

Design/methodology/approach: The research allowed the identification of microstructural changes that take place during oxidation test of TiAlSi coating during isothermal oxidation at 900°C for 500h of exposure in air. The scope of the research encompassed a microstructural analysis with the use of macro and micro investigation - LM, SEM microscopy, XRD phases analysis and EDS analysis.

Findings: The investigation has shown that the thickness of the coatings TiAlSi was in range from 30 to 40 μm. The structure of the silicon-modified aluminide coatings is as follows: the outer zone consisting of TiAl₃ phase and titanium silicides / the middle zone consisting of columnar titanium silicides in phase TiAl₃ matrix / the inner zone consisting of TiAl₂ phase. In oxidation test, the much smaller increase of the mass has been observed, as a result of the coating deposition. The smallest mass changes have been detected in samples containing the coatings formed from 12.5 % Si slurries.

Research limitations/implications: The discussed research proves that main reason of much better oxidation resistance of TiAlSi coated base alloy is related to rich in aluminium TiAl₃ phase presents in coating modified by Si. In addition silicon decrease activity of titanium, and in consequence the susceptibility of Al to selective oxidation is much stronger. The presents of Si due to Ti-Si phase generation with high oxidation resistance.

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 aluminide coatings deposition on TiAl alloys.

Keywords: Thin & thick coatings; Aluminides; Degradation; Oxidation

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°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 TiAl₃ 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 Ti₅Si₃ 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 SiO_2 form, which can be placed in the base forming a continuous layer. The presence of either amorphous or crystalline form of 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 the creation of 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 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. [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 Ti-48Al-2Cr-2Nb type alloy. The silicoon-modified aluminide coating was obtained by slurry method, utilising aluminium and silicon powder slurries in the water solution. The mixtures containing aluminium and 5%, 12.5% and 20% of silicon were employed. 100% aluminium and silicon content slurries have also been used to form the coatings. The procedure of coating deposition was as follows: the preparation of samples according to Testcorr requirements ($15 \times 10 \times 4$ mm); sample grinding (maximum gradation 600 paper); sand-blasting with corundum of 150-220 mesh granularity; ultrasound degreasing in tri-chloro-ethylene; soaking at $350^\circ C$ 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 $80^\circ C$, soaking for 30 min. at $200^\circ C$ - $220^\circ C$; diffusion treatment at $950^\circ C$ for 2 and 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 isothermal oxidation tests have been performed at $900^\circ C$ for 500 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 diffractometer. 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

The conducted tests have testified the differences in the structure of the obtained coatings depending on the Si content in the slurry. The principal differences are connected with the thickness of the obtained layer and its chemical and phase content. The slurry containing aluminium content created a coating made up of the outer $TiAl_3$ phase zone and the middle $TiAl_2$ phase zone. In the base alloy, the presence of an aluminium-rich TiAl phase below has been noted, in which the lamellar structure of the base alloy is present ($Ti_3Al + TiAl$). The addition of silicon and the increase of its content up to 5, 12.5 and 20 % have caused the appearance of silicide phases in the structure of Ti-Si type and varied morphology. Their presence was detected in the outer layer, in the form of equiaxed particles placed mainly on the borders of three grains. Another type of silicon particles was discovered above the transition zone: it took the form of columnar mole ecules, elongated in the direction of the base alloy. Their appearance seems to be the 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. In case of the coating deposited in the slurry containing 100% Si a different type of layer was obtained. No zone organisation was encountered; only a thin layer of silicides was present. A juxtaposition of the essential information on the thickness of the outer zone – O, the transition zone together with the columnar silicide zone – T and the inner zone – I 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

| Coating | Thickness O [μm] | Thickness T + (Ti-Si) [μm] | Thickn. I [μm] | Phases content |
|---------|-------------------------------|--|-----------------------------|---------------------------------------|
| 100%Al | 78 | 8 | 6 | $TiAl_3$ |
| 5% Si | 45 | 9 | 6 | $TiAl_3$ |
| 12.5%Si | 69 | 7 + 4 | 7 | $TiAl_3$, Ti_5Si_4 , Ti_5Si_3 |
| 20%Si | 60 | 5 + 14 | 5 | $TiAl_3$, Ti_5Si_4 , Ti_5Si_3 |
| 100% Si | 18 | - | - | TiAl, Ti_5Si_3 |

The results of the isothermal oxidation test conducted at $900^\circ C$ for 500h have been displayed in Figure 1. As the presented data suggests, the application of silicon-modified coatings substantially improved the oxidation resistance of the alloy. Out

of the variants analysed, the best results were achieved in case of the alloy coated in the slurry containing 12.5 % of silicon. However, there are only minor differences in the mass increase. The coating obtained from the pure silicon slurry exhibited relatively the worst results, which may be due to its comparatively lowest thickness.

The macro investigations of oxidized specimens showed that the most intensively process of surface degradation was observed in the based alloy case (Fig.2). The same condition of top layer was observed on the specimens after pure siliconizing, but in this case this effect was related to insufficient thickness of the obtained coating. In the other cases the surface of the coated specimens do not showed drastically effects of coating degradations. XRD investigations of oxides on the top layer showed that in the case of based alloy dominated TiO_2 oxides as well as on the siliconizing specimens. In the cases rest of aluminizing specimens with different contents of silicon dominated oxide is alumina (Fig.2).

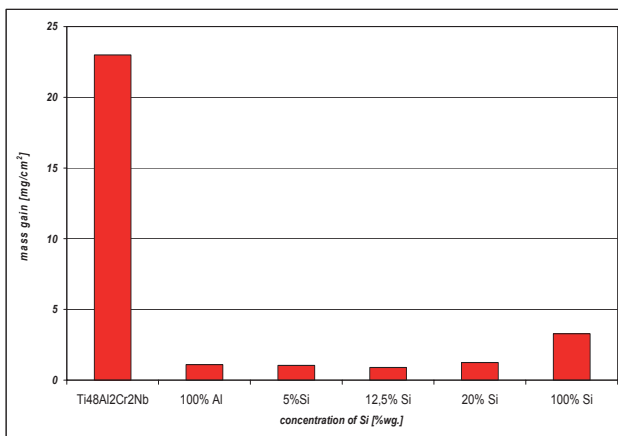


Fig. 1. Mass gain of uncoated and coated specimens during oxidation

The SEM analysis of the top-layer of the coatings has confirmed earlier observations. Visually, the variants obtained from 5 and 12.5% silicon slurries appear to be the most serviceable, which is clearly visible in Fig. 2.

The remnants of the outer layer containing titanium oxide TiO_2 and the inner layer made up of Al_2O_3 have been detected (based alloy). A 5% silicon addition influenced the morphology and the adherence of the scale remarkably. In case of the coating produced in the 12.5% silicon content, the layer of compact oxides covers the sample more tightly. When the silicon content reaches 20%, a decline in the oxidation resistance takes place, when compared to the lower silicon content. Scattered titanium-rich oxide islands were detected in the aluminium oxide scale. In case of the slurry containing 100% Si, the undesired rutile is dominant on the surface of the coating, which was confirmed by X-ray phase analysis and chemical content analysis. An additional factor hampering oxidation resistance at 900°C is the relatively low thickness of this type of coating.

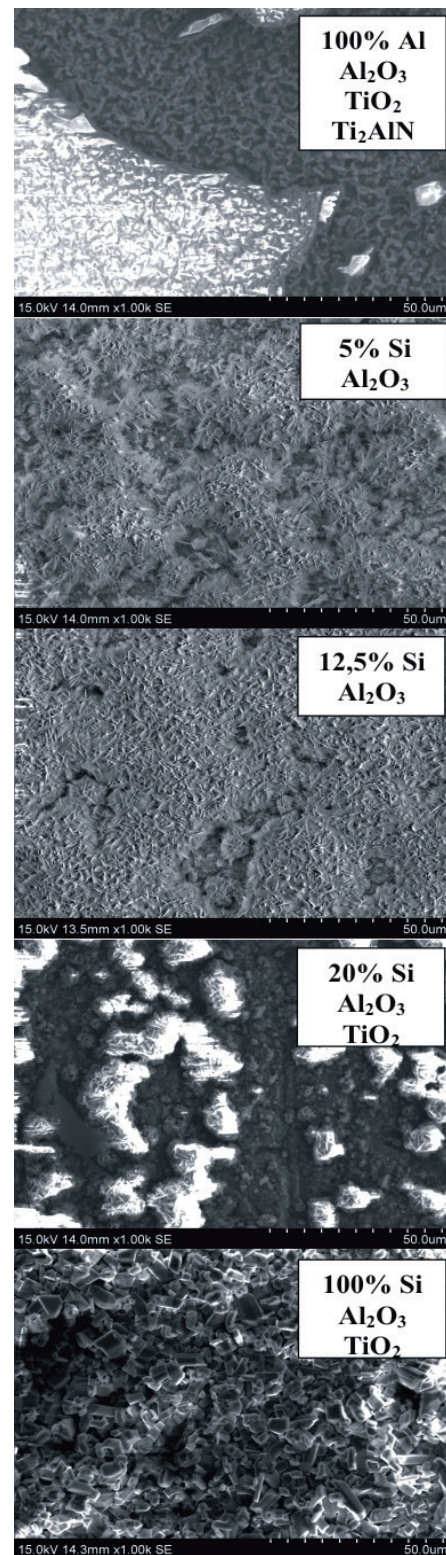


Fig. 2. Top-surface of TiAlSi coatings condition after oxidation test

4. Conclusions

The TiAlCrNb alloy can be described as insufficiently oxidation-resistant. A notably higher mass increase was detected, which results in adherence loss and chipping. This comparatively small oxidation resistance is connected to much higher kinetics of TiO₂ accretion as compared to the accretion rate of Al₂O₃. Furthermore, the presence of nitrogen induces the production of TiN nitride, hence reducing the alloy's capability to create tighter and more compact aluminium oxide scale, which could form a barrier for further oxide diffusion. Simultaneous to the progress of the oxidation process, TiN oxidation takes place, producing rutile, which has very weak protective properties. This results in the creation of the scale being a mixture of two oxides: Al₂O₃ i TiO₂ ("nitrogen effect"). The heat resistance of all coated samples deposited in TiAlSi slurries is higher than in case of the base alloy. Both silicon-modified and unmodified samples exhibit the desired high Al₂O₃ content on the surface. It is only in case of silicon-slurry-deposited coatings that the undesirable rutile prevails, which is partly due to the relative thinness of the layer. The beneficial influence of the coatings on the improvement of heat resistance of the alloy is a result of the presence of aluminium-rich silicon-modified TiAl₃ phase, which is the most oxidation-resistant phase in the TiAl system. It is characterized by a relatively high activity of aluminium (as compared to titanium), which leads to selective aluminium oxidation and, consequently, to the creation of thermodynamically durable Al₂O₃ layer. Additionally, the presence of silicon enhances the creation of SiO₂ oxide. The silicon surface modification of the investigated alloy has enabled for the intermetallic phases production from the Ti-Si system. As these silicides are produced, aluminium is released, which increases the concentration of aluminium in the layer as well as its activity and enhances Al₂O₃ production. The creation of Ti-Si type compounds results in the binding of titanium in the form of silicides and, additionally, hampers titanium activity in the coating. Silicon has notably lower enthalpy of solving in titanium (-211 kJ/mole), as compared to the analogical value for aluminium equalling -137 kJ/mole. This results in a higher capability of creating TiSiAl double-phases when compared to creating of Ti-Al phases. Only the presence of the following phases has been detected during: Ti₅Si₃ i Ti₅Si₄.

The impact of silicon on the improvement of heat resistance can also be explained by the following facts:

- silicon, the chemical element stabilising b Ti phase, in which the oxygen solubility roughly equals 4% at., whereas it equals 34%at. in a phase, lowers the deepness of oxygen penetration.

Silicon is soluble in rutile, hindering oxygen diffusion through the scale by means of reducing the amount of oxygen vacancies. This results from taking interstitial position in the rutile network by Si⁴⁺.

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