Improvement of the High Temperature Oxidation Resistance of γ-TiAl by means of Si-based Coatings

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In this study the oxidation resistance of γ-TiAl was increased by using titanium silicides as top coat material. Silicon was deposited on the γ-TiAl base material by means of magnetron sputter techniques. To induce the formation of silicides, the coating system was pre-treated by air exposure for 100h at 750°C or annealed in vacuum (pressure of 10^{-6} mbar) for 100h at 1000°C. The oxidation resistance of the pre-treated coatings was tested at 900°C and 950°C using a cyclic testing procedure: lh heating and 10 min cooling down to 60°C. After 1000 cycles or failure the samples were investigated by means of SEM and EDX to analyse the microstructural evolution and phase formation. After pre-treatment under high vacuum conditions the stable Ti-Si phase, Ti_5Si_3, was formed. It resulted in a minimum lifetime of the coating systems of 1000 cycles at 900°C and 950°C. The samples pre-oxidised at 750°C showed Ti_5Si_4 phase formation. Additionally, a thick oxide scale was formed which grows much slower during cyclic testing. Despite a higher oxidation rate of the pre-oxidised samples, only one specimen failed after 440 cycles when exposed at 950°C.

Keywords: γ-TiAl, oxidation resistant coatings, titanium silicides

1. Introduction

Recent trends in aerospace as well as in automotive industry have led to the use of light weight materials especially applied in highly stressed components[1-4]. Thereby γ-TiAl becomes more and more interesting because of the attractive mechanical properties, such as low density, high stiffness, high yield strength and good creep resistance under service conditions at temperatures up to 900°C. Owing to these advantages titanium aluminide alloys appear to have the potential to partly replace heavy steels and nickel-based alloys presently used in aeroengines. Titanium aluminides based on γ-TiAl have proven suitability as construction material for parts of automotive engines[3,4] and have been successfully tested as low pressure turbine blades in aeroengines[5]. However, the oxidation resistance of γ-TiAl alloys decreases rapidly at temperatures above 750°C due to the formation of fast growing TiO_2[6-10]. Reducing the formation of non-protective titanium oxide is the primary objective to improve the resistance of titanium aluminides against oxidation.

The main approach is the formation of a continuous protective Al_2O_3 scale by means of coatings[6,11-13]. One possibility is the deposition or formation of aluminum rich top coats[13-15]. Besides this most suitable approach, coatings with chromium and/or further elements added can provide moderate oxidation protection[16-20].

In this study titanium silicides formed on TiAl base material should increase the oxidation resistance of the coating system.

2. Experimental Setup

Extruded gamma titanium aluminide alloy Ti-45Al-8Nb (in at%) provided by GfE, Germany, was used as substrate material. Disk-shaped specimens were machined being 15 mm in diameter and 1 mm in thickness. The surfaces of the specimens were polished and ultrasonically cleaned prior to coating deposition.

The Si coating was produced by magnetron sputtering in a laboratory coater installed at DLR[17,21]. This coating was deposited using an elemental silicon target on a RF-source while the specimens rotated in the center of the vacuum chamber. The Si layer was 10 μm in thickness.

Prior to testing the coating was annealed to form thermodynamically stable phases. Two processes had been chosen. Firstly, specimens were exposed in air at 750°C for 100h. The second pre-treatment was performed under high vacuum conditions (10^{-6} mbar) at 1000°C for 100h.

Cyclic oxidation tests were performed in automated rigs in air at 900°C and 950°C. One cycle consisted of 1 h at temperature and 10 min cooling down to 60°C. Specimens were periodically weighed and visually inspected during testing up to 1000 1-h cycles (equal to 1000 hot hours).

Post-oxidation investigations of the microstructure were performed using a LEO Gemini field emission gun scanning electron microscope (SEM) equipped with an Oxford energy-dispersive X-ray spectrometry (EDS) detector attached. Elemental compositions were determined using semi-quantitative analysis for spot and line scan measurements.

3. Experimental Results and Discussion

In the literature titanium silicides were successfully applied on γ—TiAl[22-26] by using different procedures. Obviously, the formation process needs a high amount of energy. In Figure 1 the results of two different pre-treatment processes are presented. In one case the Si coated TiAl sample was exposed under high vacuum conditions (10^{-6} mbar) for 100h at 1000°C (Figure 1a). The second pre-treatment process was performed in air at 750°C for 100h (Figure lb). In the first case the stable Ti_5Si_3 phase was formed through interdiffusion between substrate and Si coating. Presumably, the silicon rich phases were formed first and finally transformed into the Ti rich Ti_5Si_3 phase.

At 750°C in air "only" the Ti_5Si_4 phase could be formed with a mixed oxide scale on top consisting of TiO_2, SiO_2 and Al_2O_3. Here spallation of the coating occurred during pre-treatment due to the very low thermal

expansion of pure silicon. Therefore, the oxide scale found on top grew after spalling. Due to interdiffusion and Ti-Si phase formation a thin titanium depleted zone, namely $TiAl_2$, was formed underneath the titanium silicide on the pre-oxidised sample (Figure lb).
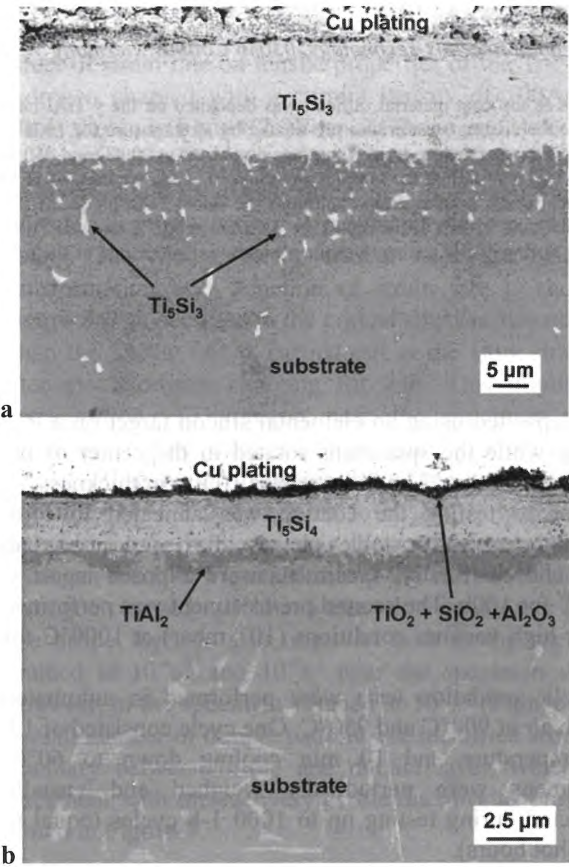

a

b

Figure 1. Micrographs of Si coated TiAl substrates pre-treated under high vacuum conditions (10^{-6} mbar) after 100h at 1000°C (a) and in air at 750°C for 100h

In Table 1 elemental analysis of the formed structures of both differently pre-treated coatings is presented. The aluminum content in both silicide phases is negligible. Despite such low solubility of Al, the alumina content in the oxide scale of the pre-oxidised specimen is relatively high. This indicates that in the first stages of phase formation the diffusion of aluminum through the coating was higher. In both pre-treated coatings titanium is partly substituted by niobium. The content of the latter element is near to that of the substrate composition.

The high temperature oxidation resistance of the coated samples was tested at 900°C and 950°C and compared with the oxidation behaviour of bare γ—TiAl. In Figure 2 the oxidation kinetics of the coated and uncoated specimens are plotted. The bare substrate exhibits a short lifetime due to spallation of the formed oxide scale (900°C: 700 cycles; 950°C: 40 cycles) whereas the Si coated samples reveal excellent oxidation resistance. The coating systems annealed under high vacuum conditions show the lowest oxidation rate at both exposure temperatures. Thus, the Ti_5Si_3 phase has higher oxidation

resistance than the Ti_5Si_4 phase. But the latter one, formed on the pre-oxidised specimens, also provides oxidation protection. The pre-oxidised sample failed after 440 cycles at 950°C caused by spallation of the oxide scale formed during pre-treatment.
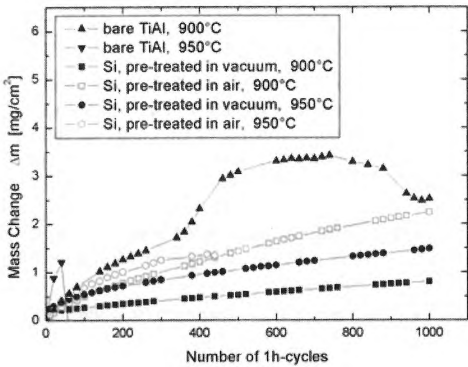

Figure 2. Oxidations kinetics of Si coated TiAl samples tested at 900°C and 950°C compared to oxidation data of bare TiAl

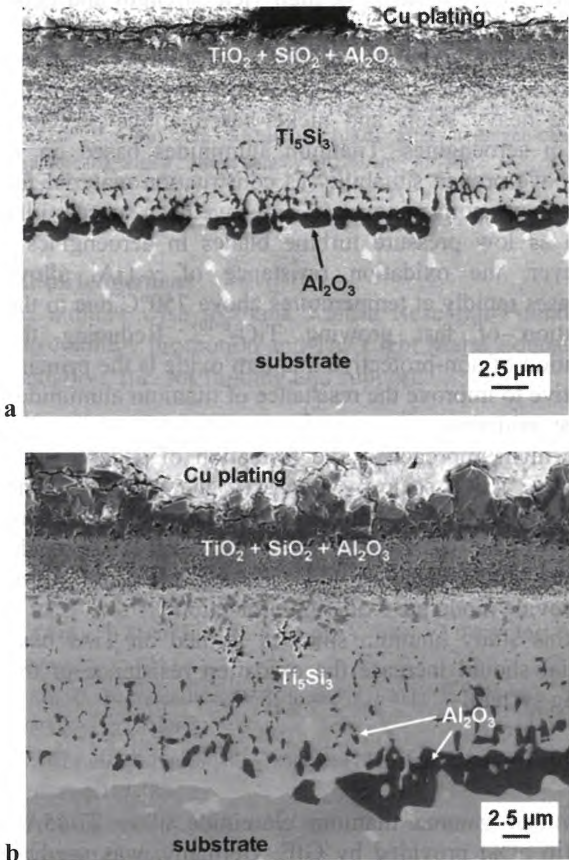Two micrographs of samples exposed at 950°C are presented in Figure 3.

a

b

Figure 3. Micrographs of at 950°C exposed Si coated TiAl substrates after 1000 cycles (pre-treated under high vacuum conditions) (a) and after 440 cycles (pre-oxidised in air)

Table 1. Composition of different phases measured by EDS: the phase identification was confirmed by XRD analysis

System	Zone	Composition c [at%]					Phases
		O	Al	Si	Ti	Nb	
Si coating annealed under vacuum conditions	Coating	-	0.5	36.6	55.6	7.4	Ti_5Si_3
(Figure 1a)	Precipitates	-	25.5	20.6	43.7	10.1	$\gamma + Ti_5Si_3$
Si coating pre-treated in air	Oxide scale	67.4	16.2	7.2	8.6	0.6	Oxides
(Figure 1b)	Coating	-	-	45.0	47.8	7.2	Ti_5Si_4
	Ti depleted	-	60.4	1.9	32.1	5.6	$TiAl_2$
Si coating annealed under vacuum conditions	Oxide scale	68.9	0.4	5.2	25.3	0.3	Oxides
after 1000 cycles at 950°C (Figure 3a)	Coating	-	0.4	38.0	54.7	6.8	Ti_5Si_3
	Interface	65.3	33.2	0.2	1.1	0.1	Al_2O_3
Si coating pre-treated in air after 440 cycles	Oxide scale	70.1	3.2	7.2	18.4	1.1	Oxides
at 950°C (Figure 3b)	Coating	-	2.7	37.4	51.2	8.8	Ti_5Si_3
	Interface	61.7	35.9	0.4	1.9	0.2	Al_2O_3
Subsurface region of Si coating annealed under	Top layer	74.4	0.9	0.9	23.4	0.4	TiO_2
Vacuum conditions after 1000 cycles at 950°C	Reaction zone	70.0	0.3	4.4	25.0	0.3	$TiO_2 + SiO_2$
(Figure 4)	Precipitates	60.8	-	8.3	28.7	2.2	TiO_2

On the vacuum pre-treated system and on the air pre-oxidised sample a mixed oxide scale was formed mainly consisting of titania and lower amounts of silica and alumina, respectively (see Table 1). The composition of the Ti_5Si_3 phase formed on the vacuum pre-treated system did not change during exposure at 950°C. The solubility of aluminum is still low. But the Ti_5Si_4 phase has changed into the stable Ti_5Si_3 phase after 440 cycles at 950°C, apparently induced by thermal activation through the exposure.

Furthermore, at the interface of both systems alumina was formed. This inner oxidation is a result of oxygen diffusion through the coating. Obviously, the oxygen did not react with the Ti_5Si_3 phase but a closer look on the subsurface region revealed a reaction zone below a relatively dense titania scale (see Figure 4).
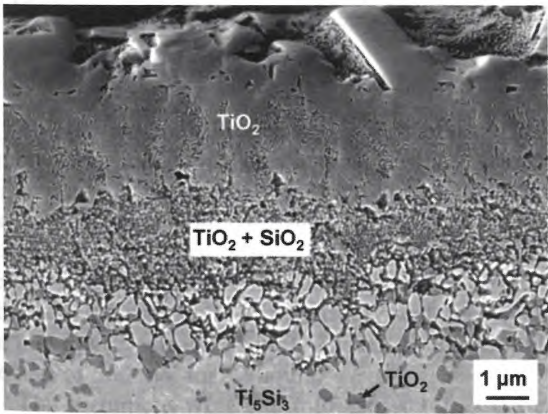

Figure 4. Micrograph of the subsurface region of a vacuum pre-treated Si coated system after 1000 cycles at 950°C

Underneath the TiO_2 layer a porous oxide scale containing silica and mainly titania has grown (see Table 1). Furthermore, the silicide phase below seems to be oxidised at the grain boundaries indicating that oxygen

diffused along the grains. This procedure starts at earlier stages, as it can be seen in Figure 5, where the cross-section of a vacuum pre-treated sample after 10 cycles at 950°C is shown. Already after this short exposure time oxidation along the grain boundaries in a small subsurface zone was observed.
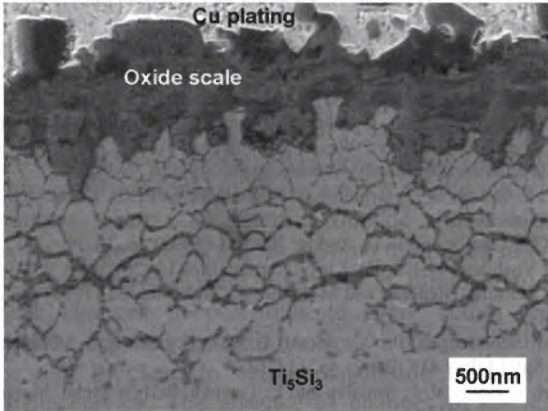

Figure 5. Micrograph of the subsurface region of a vacuum pre-treated Si coated system after 10 cycles at 950°C

After a longer test period of 1000 cycles further inner oxidation took place. Within the Ti_5Si_3 coating titania precipitates could be observed (see Figure 4 and Table 1).

Apparently, at the beginning of testing mainly titania was formed on the surface of the vacuum pre-treated systems. With increasing exposure time oxygen diffused through the oxide scale and along the grain boundary of the silicide phases where both, TiO_2 and SiO_2, were formed. Finally, the grains oxidised completely forming a porous inner oxide scale consisting of silica and mainly titania. The outer TiO_2 scale grew simultaneously.

The pre-oxidised samples reveal the same microstructure in the subsurface region. Here a comparable oxide growth process can be assumed.

During exposure no formation of nitrides on the titanium silicides could be observed like reported elsewhere[27].

Despite of the formation of mainly titania the oxidation resistance of the titanium silicide coatings is high especially compared to the oxidation behaviour of the TiAl base material.

4. Conclusions

Titanium silicides were successfully applied on γ—TiAl to increase the oxidation resistance. Cyclic testing at 900°C and 950°C showed excellent oxidation resistance of the coating systems. Especially the Ti_5Si_3 phase oxidised only slightly.

On the coating surfaces mainly titania was formed. Along the grain boundaries of the intermetallic layer oxygen diffused and reacted with the material. The whole oxidation process is not well understood, yet.

The results show that the titanium silicides reveal a high potential as oxidation protection on γ—TiAl for long term use.

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