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The formation of Si-aluminide coating formed by plasma spraying and subsequent diffusion annealing on Ti-Al-7Nb intermetallic alloy

M. Góral [a,*], P.C. Monteiro [b], P. Sosnowy [c], M. Woźniak [a], T. Kubaszek [a], B. Kościelniak [a]

[a] Research and Development Laboratory for Aerospace Materials, Rzeszow University of Technology, ul. Powstańców Warszawy 12, 35-959 Rzeszów, Poland
[b] Department of Materials and Ceramic Engineering, University of Aveiro, Campus Universitário de Santiago, Aveiro, 3810-193, Portugal
[c] Pratt Whitney Rzeszow, ul. Hetmańska 120, 35-959 Rzeszów, Poland
* Corresponding e-mail address: mgoral@prz.edu.pl
ORCID identifier: https://orcid.org/0000-0002-7058-510X (M.G.)

ABSTRACT

Purpose: In the article, the kinetic growth phenomena of aluminide coating formed by plasma spraying pure Al-Si powder and subsequent diffusion annealing on TiAl intermetallic alloy in inert atmosphere were investigated.

Design/methodology/approach: The Al-Si powder was thermal sprayed (APS) on TiAl7Nb intermetallic alloy and annealed in Ar atmosphere during 5, 15, 30, 60, 240 and 480 min. The kinetic growth of the coating was observed using the scanning electron microscopy method (SEM), and chemical composition was analysed using the EDS method.

Findings: The Kirkendall Effects pores formation, as well as titanium silicides on the grain boundary of $TiAl_3$, was found.

Research limitations/implications: The oxidation resistance of the developed coating might be analysed in further work.

Practical implications: The developed coating might be used for the production of protective aluminide coatings on TiAl intermetallic alloys.

Originality/value: The description of aluminide coating formation in a new technological process.

Keywords: TiAl, Intermetallics, Aluminide coatings, Plasma spray, $TiAl_3$, Kinetic

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MATERIALS

1. Introduction

TiAl intermetallics are a promising material for high-temperature in applications for aerospace and automotive industries. According to their insufficient oxidation resistance, different types of the coating were developed [1]. The one typically used is aluminide coatings based on $TiAl_2$ [2] and $TiAl_3$ [3] coatings produced by pack cementation [4] or gas-phase (VPA) methods [5]. Alam et al. developed the $TiAl_3$ coating on lamellar TiAl intermetallic alloy [6]. The oxidation resistance of aluminide coatings might be improved by forming SiO_2-modified composites $7O_2$-deposited coating [8]. Malecka et al. [9] proposed the deposition of Al_2O_3 coating for oxidation resistance improvement of TiAl at 950°C. Ebach-Stachl and Frolich [10] developed the $PtAl_2$ coating with YSZ (yttria-stabilized zirconia) ceramic topcoat for high-temperature protection of TiAl intermetallics. The titanium silicides obtained on TiAl alloy allow the privileged formation of alumina oxide [11]. The similar effect was observed in other refractory disilicide coatings on TiAl surface [12].

The better improving in oxidation resistance was observed in Si-modified aluminide coatings deposited by the pack cementation method [13]. This type of coating might also be formed using different methods such as magnetron sputtering [14], dip coating [15], pack cementation [16,17], paste [18], slurry [19,20], HS-PVD [21], magnetron sputtering with SiO_2 deposition [22] and by Arc-PVD [23].

The aluminide coatings modified by Si addition are one of the most effective in protecting TiAl intermetallics against oxidation. They permit the formation of pure alumina oxide on the surface and the bonding of the titanium by the formation of silicides. In our previous research, we analysed the influence of silicon content on the structure of aluminide coating obtained on TiAl intermetallics [20, 23-26]. The concept of the thermal spray of Al-Si powder by cold [27] and warm [28] spray and subsequent diffusion treatment was developed. In the present article, we proposed the use of the atmospheric plasma spraying (APS) process for Al-Si coating deposition and subsequent diffusion treatment.

The research aimed to analyse the microstructural and phase phenomena occurring during diffusion annealing in the inert atmosphere of these coatings.

2. Experimental

The TNB intermetallic alloy containing 7 wt.% of Nb was used as a base material. The flat samples 2 mm thick were cut from the bar. The Al-Si coating was thermal sprayed using the atmospheric plasma spraying method (APS) by F-1 plasma torch (Oerlikon-Metco) using low-energy plasma (Tab. 1) and Metco 52C-NS powder (Oerlikon-Metco). The diffusion annealing was conducted in an argon atmosphere (Ar flow 0.5 NLPM, Normal Litres Per Minute) at 1000°C during different periods: 5, 15, 30, 60, 240 and 480 min in a tube furnace (XERION).

Table 1.
Plasma spraying parameters of Al-Si powder

Parameter	Value
Power Current/Voltage	250 A/ 60V
Ar flow, NLPM	55
H_2 flow, NLPM	11
Spray distance, mm	55
Powder feed rate, g/min	15

After diffusion treatment, the metallographic samples were prepared. The coating microstructure the was observed using the scanning electron microscopy method (Phenom XL microscope), and chemical composition was analysed using Energy-dispersive X-ray spectroscopy method (EDS).

3. Results and discussion

The as-sprayed Al-Si coating was characterized by a typical lamellar structure and average thickness about 150-170 μm (Fig. 1a). The porosities and oxides were available in coating structure. The results of chemical composition analysis confirmed presence of aluminium (96.2 at.%) and silicon (3.8 at.%) in the coating (Fig. 1a, Table 2). In the base material, the main components of intermetallic alloy were detected: Ti, Al and Nb (Fig. 1b, Tab. 2). After a short time of diffusion annealing (5 and 15 min), the formation of porosities as a result of Kirkendall effect was observed (Fig 2a,b), like reported by Sienkiewicz et al. [28].

Table 2.
The results of chemical composition analysis from areas marked on Figures 1a,b

Area	Element amount, at.%				
	Ti	Nb	Al	V	Si
1	-	-	96.2	-	3.8
2	47.8	-	45.2	0,2	-
3	52.6	6.8	8.7	0.34	-
4	40,0	54.7	5,0	0,3	-
5	62.4	21.9	10.1	5.7	-
6	45.0	49.6	5.3	0.2	-
7	68.4	14.6	16.7	0.3	-

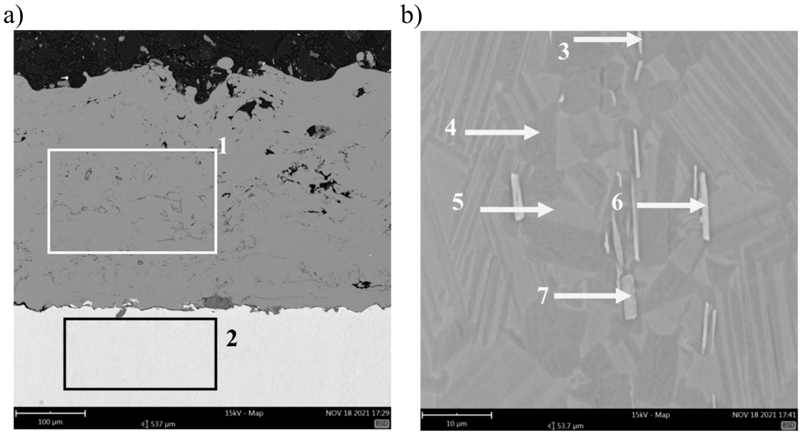

Fig. 1. The microstructure of as-sprayed Al-Si coating and base TiAlNb alloy with marked areas of chemical composition analysis

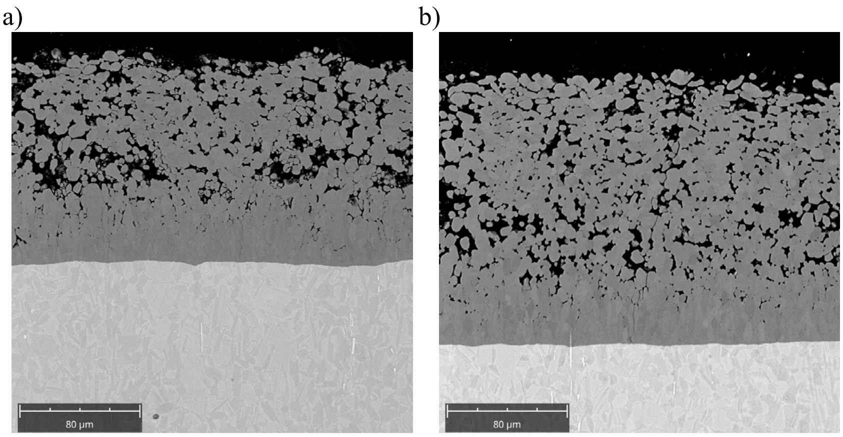

Fig. 2. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after a) 5 min, b) 15 min of annealing in Ar atmosphere at 1000°C

The Kirkendal effect and increase of coating porosity were also observed after 30 min of diffusion treatment (Fig. 3). The initiation of diffusion zone formation was observed as well (Fig. 4). The chemical composition analysis of this zone showed the nucleation of titanium silicides (area 1 on Fig. 4, Tab. 3). The small concentration of Si in the $TiAl_3$ phase was also detected (area 2 on Fig. 4). Near the diffusion zone the titanium silicides were probably formed on the grain boundary area of $TiAl_3$ phase (area 3 in Fig. 4). Below, the columnar structure of titanium silicides in $TiAl_3$ matrix was formed (area 4 on Fig. 4) similarly to observe in previously investigated slurry coatings [25]. In the area marked ”5” (Fig. 4), silicon was not detected. This suggests the formation of the $TiAl_2$ phase characterized by the very low solubility of Si [26].

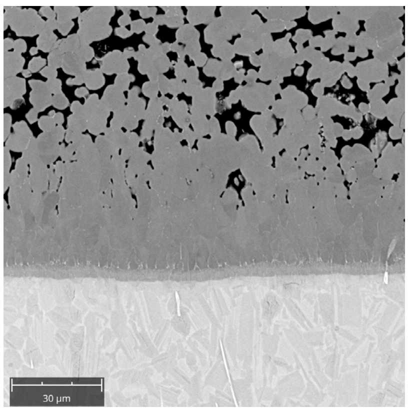

Fig. 3. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 30 min of annealing in Ar atmosphere at 1000°C

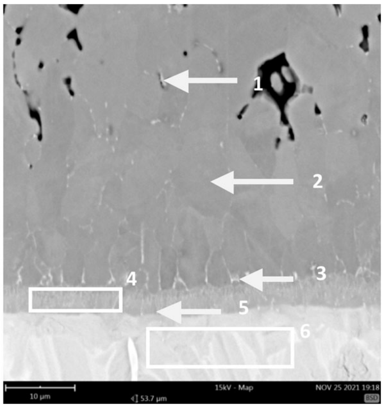

Fig. 4. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 30 min of annealing in Ar atmosphere at 1000°C with marked areas of chemical composition analysis

Table 3.
The results of chemical composition analysis from areas marked in Figure 4

Area	Element Mount, at.%			
	Ti	Nb	Al	Si
1	34.2	2.3	50.5	13.0
2	19.2	2.2	74.7	4.0
3	26.1	1.9	62.4	9.6
4	23.3	2.6	71.0	3.1
5	27.2	2.7	70.1	-
6	42.7	4.9	52.2	-

The presence of Kirendall effect pores was also observed after 60 min of diffusion annealing (Fig. 5). The thickness of the diffusion zone increased to 4.65 μm (Fig. 6).

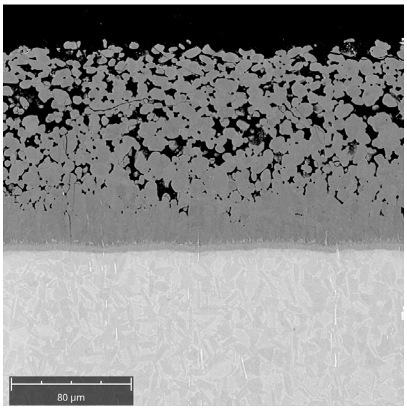

Fig. 5. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 60 min of annealing in Ar atmosphere at 1000°C

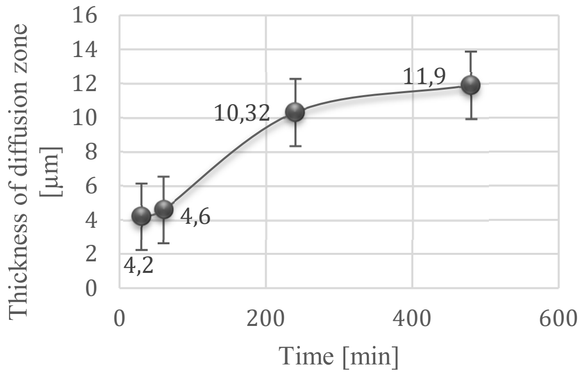

Fig. 6. The influence of annealing time to diffusion zone thickness in plasma sprayed Al-Si coating

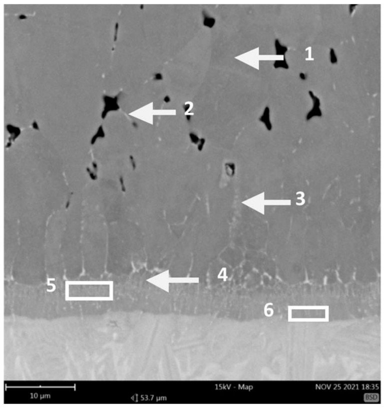

Fig. 7. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 60 min of annealing in Ar atmosphere at 1000°C with marked areas of chemical composition analysis.

The analysis of the chemical composition of the coating annealed during 60 min (Fig. 7, Tab. 4) showed similar results observed after 30 min of annealing (Fig. 6, Tab. 4). In area 1 (Fig. 7, Tab. 4), the presence of silicon was observed.

Table 4.
The results of chemical composition analysis from areas marked in Figure 7

Area	Element Mount, at.%			
	Ti	Nb	Al	Si
1	19.3	2.0	73.9	4.9
2	22.2	2.1	67.0	8.7
3	22.0	2.3	72.3	3.4
4	26.7	2.2	61.9	9.3
5	28.1	2.5	67.1	2.3
6	27.0	3.1	70.0	-

In area 2 (Fig. 7, Tab. 4), near porosity, the higher Si concentration and lower Al content was detected. It might suggest the formation of titanium silicides. The lower amount of silicon was observed in area 3 (Fig. 7, Tab. 4) – the $TiAl_3$ containing Si was probably formed. In area 4 (Fig. 7, Tab. 4) the higher Si and lower Al content was measured. Below in the diffusion zone, the Si concentration was lower than 2.5 at. %. In area 6 (Fig. 7) silicon was not detected.

The microstructure of the Al-Si coating was significantly changed after 240 min of annealing in Ar atmosphere (Fig. 8). The porosity in the outer area was decreased and more silicides were formed on the grain boundary of $TiAl_3$ phase (area 1-4 in Fig. 8, Tab. 5). Below the columnar silicides were formed (area 5 in Fig. 8, Tab. 5).

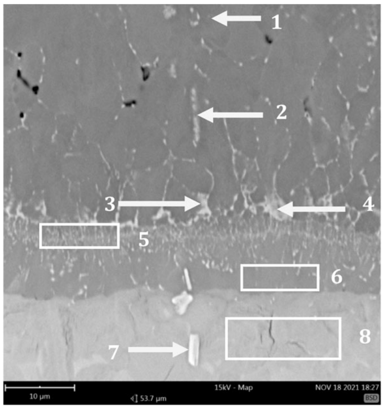

Fig. 8. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 240 min of annealing in Ar atmosphere at 1000°C with marked areas of chemical composition analysis

Table 5.
The results of chemical composition analysis from areas marked in Figure 8

Area	Element Mount, at.%			
	Ti	Nb	Al	Si
1	40.8	2.5	38.1	18.7
2	28.3	2.1	59.2	10.2
3	31.7	2.0	47.0	19.3
4	38.4	2.3	33.8	25.5
5	25.7	3.3	66.2	4.8
6	26.7	2.9	70.4	-

After the next 4 hours (total annealing time 480 min), the presence of porosity in the outer area was observed (Fig. 9). In the inner area of the coating the further increase of diffusion zone in the coating (Fig. 10) and formation of columnar silicides grains were observed. The results of chemical composition analysis in areas 1 and 4 (Fig. 10, Tab. 6) showed a high concentration of Al and the presence of Si. It suggests presence of silicon in $TiAl_3$ phase solid solution [26]. The high amount of Si in area 2 (Fig. 10, Tab. 6) and lower Al indicate the formation of titanium silicides – typically Ti_5Si_3 [24,25]. The titanium silicides were also formed on grain boundaries (areas marked 2 and 3 in Fig. 10, Tab. 6). The columnar grains silicides were also detected into the inner diffusion zone (areas 5 and 6 in Fig. 10, Tab. 6). The low concentration of Si was also observed in area 7 (Fig. 10). Below, in area 8 (Fig. 10), the $TiAl_3$ phase without Si was observed. In area 9 (Tab. 6) the chemical composition was similar to that measured in the base material.

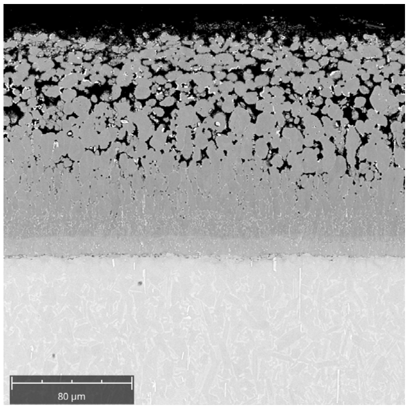

Fig. 9. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 480 min of annealing in Ar atmosphere at 1000°C with marked areas of chemical composition analysis.

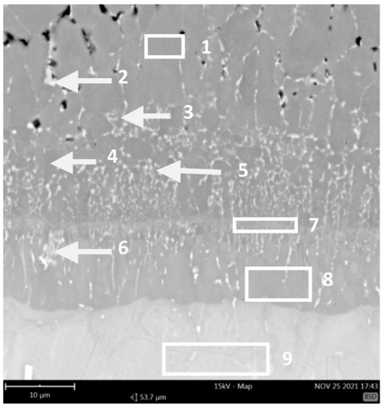

Fig. 10. The microstructure of Al-Si plasma sprayed coating on TiAl7Nb alloy after 480 min of annealing in Ar atmosphere at 1000°C with marked areas of chemical composition analysis

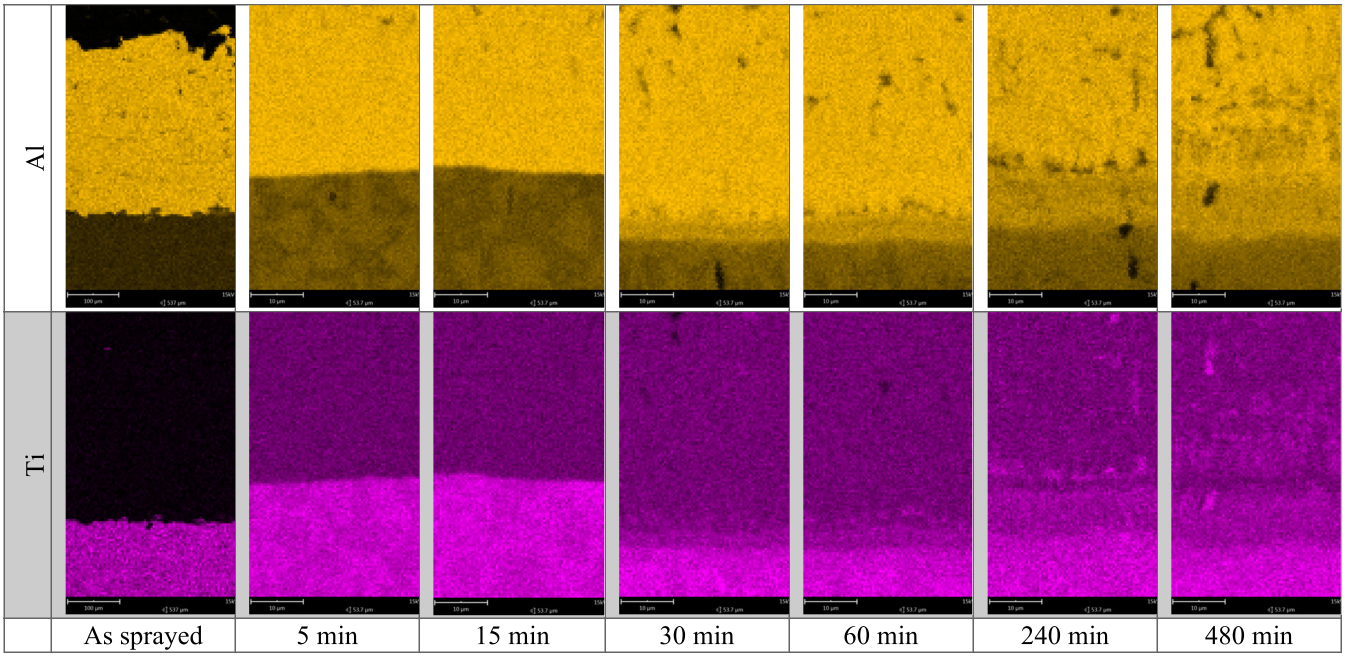

Fig. 11. The elemental mapping of Al and Ti distribution in the diffusion zone of Al-Si plasma sprayed coating during diffusion annealing

Table 6.
The results of chemical composition analysis from areas marked on Figure 10

Area	Element Mount, at.%			
	Ti	Nb	Al	Si
1	19.3	2.0	76.2	2.5
2	41.1	2,8	29.9	26.1
3	27.3	1.8	58.4	12.4
4	19.3	2.2	78.1	0.4
5	28.6	1.8	55.9	13.8
6	42.2	8.6	33.9	15.1
7	20.0	3.7	74.3	1.9
8	26,4	3.1	70.5	-
9	39.1	4.9	55.7	-

The comparison of Al and Ti elemental mapping on the Al-Si coating confirmed the formation of a diffusion zone on the interface with base materials and its thickness increases with annealing time (Fig. 11).

4. Conclusions

The diffusion annealing of Al-Si plasma sprayed coating enables to form $TiAl_3$ aluminide coating containing titanium silicides [20]. Additionally, in the outer zone of the coating, the Kirkendall effect is formed with high porosities [28]. The inward diffusion of Al and Si was the dominant coating formation mechanism.

During a short time of diffusion annealing (5-30 min) the initial formation of the diffusion zone was observed. According to the kinetic growth of Al-Si coating produced using pack cementation [16] and slurry [20, 24-26] methods the two phases was formed during diffusion annealing:

- $TiAl_3$ phase grains with silicon dissolved in solid solution;
- titanium silicides – probably Ti_5Si_3 type formed on grain boundary of $TiAl_3$ phase.

After longer time of annealing (240 and 480 min), the diffusion zone was formed. In their structure, the columnar titanium silicides were formed between grains of $TiAl_3$ phase, which not contains silicon. The niobium was presented in aluminide coating due to its diffusion from base material. The plasma spraying process enables to form Si-modified aluminide coating similar to the ones produced by cold [27] and warm spray [28] methods.

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