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Original Research

Growth Kinetics of a Silicon-Modified Aluminide Coating on a TiNM-B1 Intermetallic Alloy

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Abstract

TiAl-based intermetallic alloys are used as a structural material in high-temperature applications such as aircraft and turbine engines. To improve the mechanical properties of TiAl, it is often modified by adding other elements such as niobium or chromium. The one of disadvantages of TiAl alloys is not sufficient oxidation resistance. The pack cementation process is one well-known method of modifying TiAl, which involves coating the surface of the alloy with a special mixture containing silicon, to enrich it with this element. As a result of this process, Si-modified aluminide coating is formed, which exhibits improved resistance to high temperatures, making it ideal for use in the aerospace and turbine industries. The study was conducted on a substrate of one of the latest generation of TiAl alloys which we have not yet analyzed. The powder used in the pack cementation process consisted of 20 wt.% Si, 20 wt.% Al, 2 wt.% NH_4Cl activator, and the rest Al_2O_3, as well as 40 wt.% Si, 40 wt.% Al, 1-2% NH_4Cl activator, and the rest Al_2O_3 calculated for 100 g of powder. The process was carried out at a temperature of 950°C for 2, 4, and 6 hours. The following analyses were performed after the pack cementation process: scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) attachment for microanalysis, as well as X-ray diffraction (XRD). Test results indicated a coating structure typical of silicon-modified coatings including the presence of titanium silicides. It was found that increasing the silicon content causes a significant increase in coating thickness.

Keywords: TiAl, intermetallics, aluminide coatings, pack cementation

1. Introduction

Titanium aluminides (TiAl) have garnered significant attention in recent years due to their exceptional combination of low density, high specific strength, and excellent high-temperature properties (Dai et al., 2020; Sun et al., 2023; Wang et al., 2020). These attributes make TiAl alloys promising candidates for numerous applications in aerospace, automotive, and other industries where lightweight and high-performance materials are essential (Kim et al., 2014; Pflumm et al., 2015; Wu et al., 2022). The pack cementation process involves the deposition of a Si-containing compound onto the surface of TiAl alloy samples, followed by a subsequent heat treatment to promote interdiffusion between Si and the alloy constituents. This diffusion-based approach allows for the controlled introduction of Si into the TiAl matrix, resulting in the formation of Si-rich phases and the modification of the alloy microstructure (Goral et al., 2011b; Goral et al., 2022). Silicon modification on TiAl alloys is possible in many chemical and metallurgical processes such as powder metallurgy (Knaislová et al., 2021), spark plasma sintering (Knaislová et al., 2018), directional solidfication (Kim et al., 2004), pack cementation (Rubacha et al., 2022; Woźniak et al., 2023; Wu et al., 2019; Xiang et al., 2003; Zhou et, al., 2003), slurry method (Goral et al., 2007; Goral et al., 2011a; Moskal et al., 2021), magnetron sputtering (Bauer et al., 2021), and high-speed physical vapor deposition (HS-PVD) (Bobzin et al., 2018). Xiang et al. (2003) proved by

SEM analysis and X-ray diffraction (XRD) that the Si modification of the TiAl alloy resulted in different phases in the surface layer. The main phase present in the surface layer is the Ti_5Si_3 phase. Other phases in smaller amounts that have been identified are TiSi, $TiSi_2$ and Si phases. During many processes, it has also been demonstrated that Si in the coating allows selective oxidation of Al and the formation of a compact Al_2O_3-rich surface layer (Li et al., 2003; Ma et al., 2006; Xiong et al., 2004; Zhang et al., 2021). The main purpose of modifying the surface layer of a TiAl alloy is to increase the strength properties. The alloying addition of Si improves oxidation resistance and creep strength (Maki et al., 1992). Silicon also increases the thermodynamic activity of Al, which significantly increases the oxidation resistance of TiAl alloys due to the formation of an Al_2O_3 layer. The higher the Si percentage, the thickness of the oxidation layer decreases, and the oxides formed in the process become finer (Genc et al., 2022; Jiang et al., 2008). In addition, silicon has a positive effect on creep resistance, raising it (De Farias Azevado & Flower, 1999).

In a previous publication (Woźniak et al., 2023), we presented preliminary results on the growth kinetics of Si-modified aluminide layers on TNM-B1 alloy substrates. In the present publication, we present the results of kinetics of growth of layers modified with higher amounts of silicon (20 and 40% by weight in powder).

2. Experimental

The base material used in the pack cementation process was TNM-B1 intermetallic alloy which composition is shown in Table 1.

Table 1. TNM-B1 alloy content (wt.%).

Elements	**Ti**	**Al**	**Nb**	**Mo**	**B**
Contents	bal.	28.6	9.2	2.3	0.026

The prepared samples were grinded with waterproof paper to a gradation of 500. The prepared samples were placed in a metal box made of stainless steel and mounted into Ar-protective atmosphere tube furnace (Xerion, Germany). Two types of powders were prepared (Table 2).

Table 2. Composition of powders for pack cementation process (wt.%).

Component	**Si**	**Al**	**Al_2O_3 (filler)**	**NH_4Cl (activator)**
Contents	**20**	20	bal.	2
	40	40	bal.	2

The experiment was conducted at 950°C. The duration of the process was 2, 4 and 6 hours respectively. The pack cementation process was carried out under a protective argon atmosphere with a flow of 0.5 NLPM (Normal liters per minute). The temperature and process time were selected from previously published articles (Woźniak et al., 2023).

Metallographic samples were etched with a pre-prepared solution of 30 cm^3 $C_3H_6O_3$, 15 cm^3 HNO_3 and 5 cm^3 HF. The microstructure was analyzed using Phenom XL scanning electron microscope equipped with EDS detector used for elemental mapping. The thicknesses of the coatings formed during aluminizing were also measured using a program built into the Phenom XL software.

Phase composition analysis of the coatings was performed using an ARL X'TRA X-ray diffractometer (Thermo Scientific Corporation, Waltham, MA, USA) (Cu Kα radiation Bragg–Brentano geometry, value of the angle 20°–90°). For identification of the phase components, the ICDD-PDF4-2023 crystallographic database from the International Centre for Diffraction Data was used.

3. Results

The pack cementation process was conducted at 950°C for two different Si contents of 20 wt.% and 40 wt.% respectively. After two hours of the pack cementation process, the thickness of the coating produced for 20 wt.% Si was on average 22.8 µm and for 40 wt.% Si 40.36 µm. After four hours the thickness was similar for samples after 2 hours of cementation. A 6-hour aluminizing process allowed the layer to grow to about 90 µm for the 40 wt.% Si sample and 35 µm for 20 wt.% Si sample (Fig. 1).

Titanium alloys on γ-TiAl intermetallic phase matrix modified with silicon in the pack cementation process after 2, 4 and 6 hours formed a dense surface layer consisting of two intermediate layers. The first layer adjacent to the substrate is a columnar layer rich in titanium and silicon (Fig. 2, 3, 4). It is likely that a TiSi phase was formed, which was observed by XRD analysis (Fig. 5, 6). The outer zone formed after the process was mainly composed of titanium, aluminium and silicon at the grain boundaries during diffusion (Table 1). After a 2-hour process, the thickness of the surface layer was twice as thick for TiAl 40 wt.% Si compared to 20 wt.% Si. Similar results were obtained for the 4 and 6 h process. For the 6-hour process, the formation of a Kirkendal-Frenkel effect in the outer zone was noted. XRD analysis showed that the main phase present in the alloy is $TiAl_3$ and the triple phase TiAlSi (Fig. 6). Other phases included in the alloy are TiO_2, TiAl and TiSi. During the aluminizing process, oxidation of the coating surface was noted, resulting in the appearance of TiO_2.

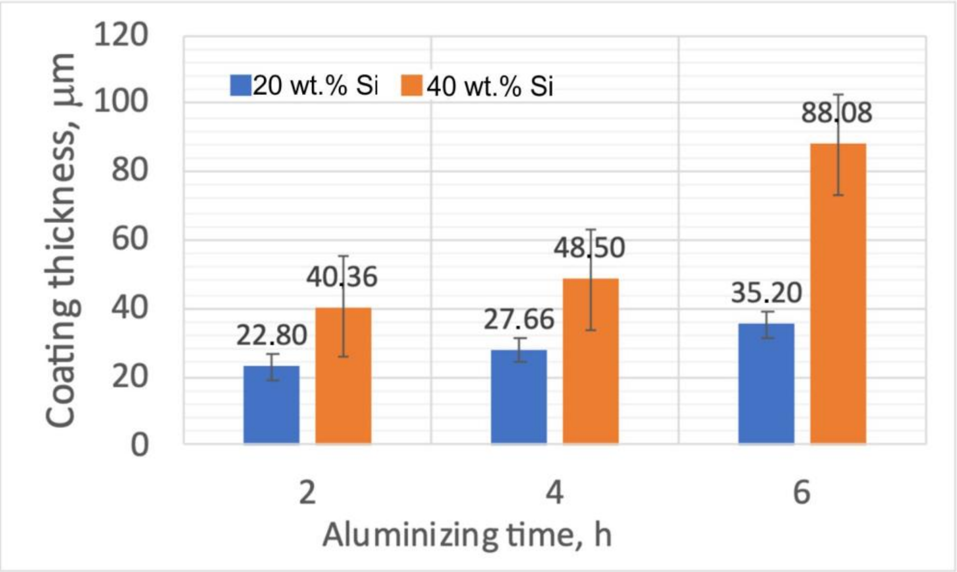

Fig. 1. Coating thickness after pack cementation for different times of pack cementation at 950°C using powder contains 20 and 40 wt.% of silicon.

Table 3. Elemental content in wt.% for all pack cementation processes.

Powder type	TiAl 20%Si 950°C 2h	TiAl 20%Si 950°C 4h	TiAl 20%Si 950°C 6h	TiAl 40%Si 950°C 2h	TiAl 40%Si 950°C 4h	TiAl 40%Si 950°C 6h
Element						
Aluminium	42.26	48.19	46.83	22.00	21.28	30.13
Titanium	19.10	21.87	19.54	22.28	23.12	21.65
Silicon	4.52	5.83	5.55	16.66	14.38	13.65

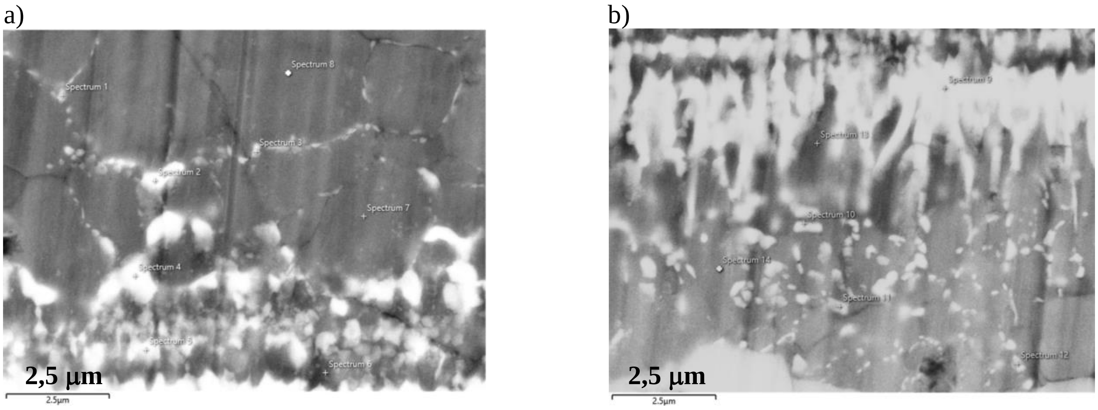
a) b)

Fig. 2. SEM spot analysis of an aluminium coating containing 20 wt.% a) and 40 wt.% b) of Si after 4-hours process of pack cementation cementation at 950°C.

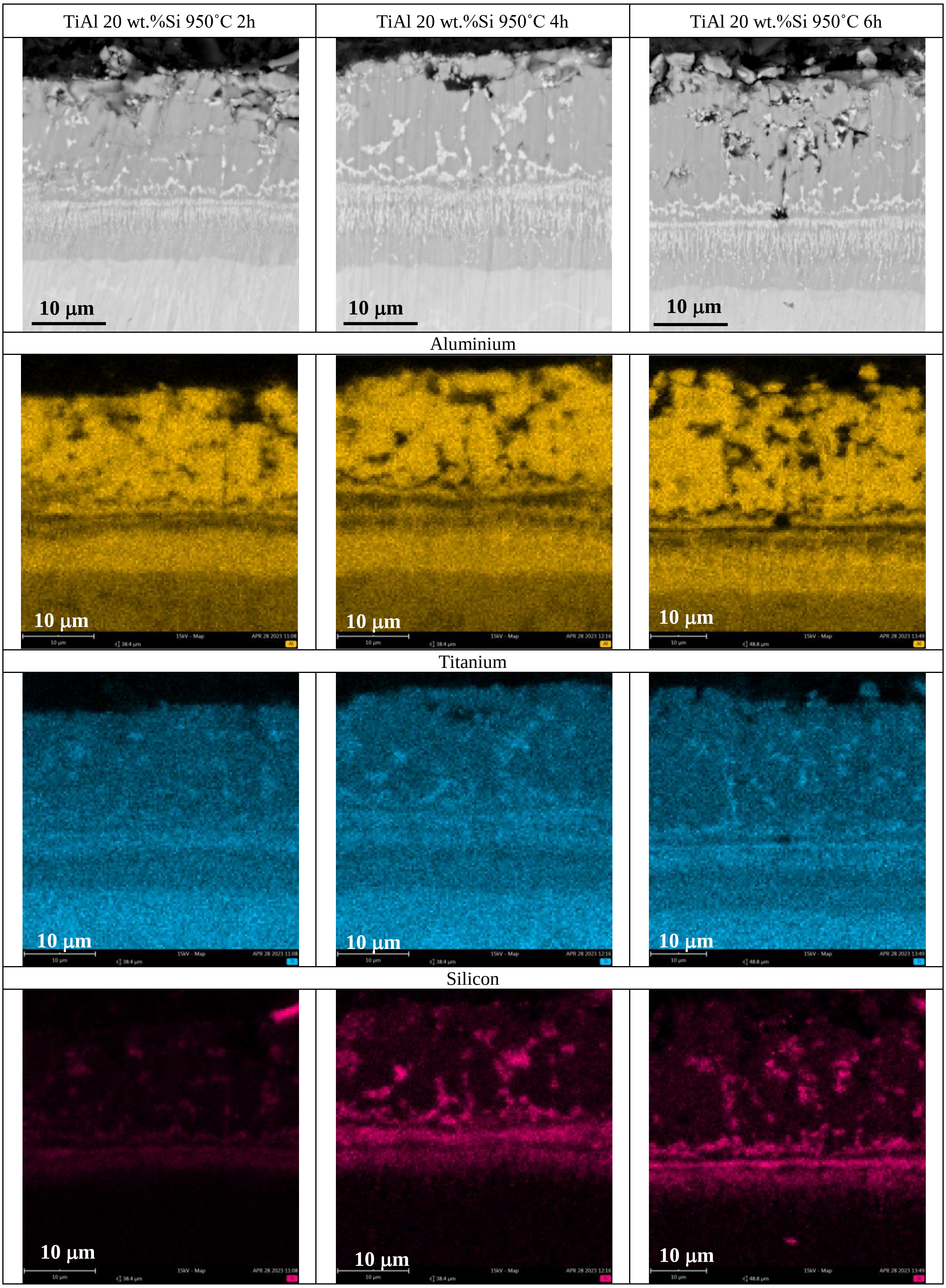

Fig. 3. The microstructure of whole coating of aluminide coating formed from powder containing 20 wt. % of Si and elemental mapping of of Al, Si and Ti for 2, 4 and 6 hours of pack cementation at 950°C.

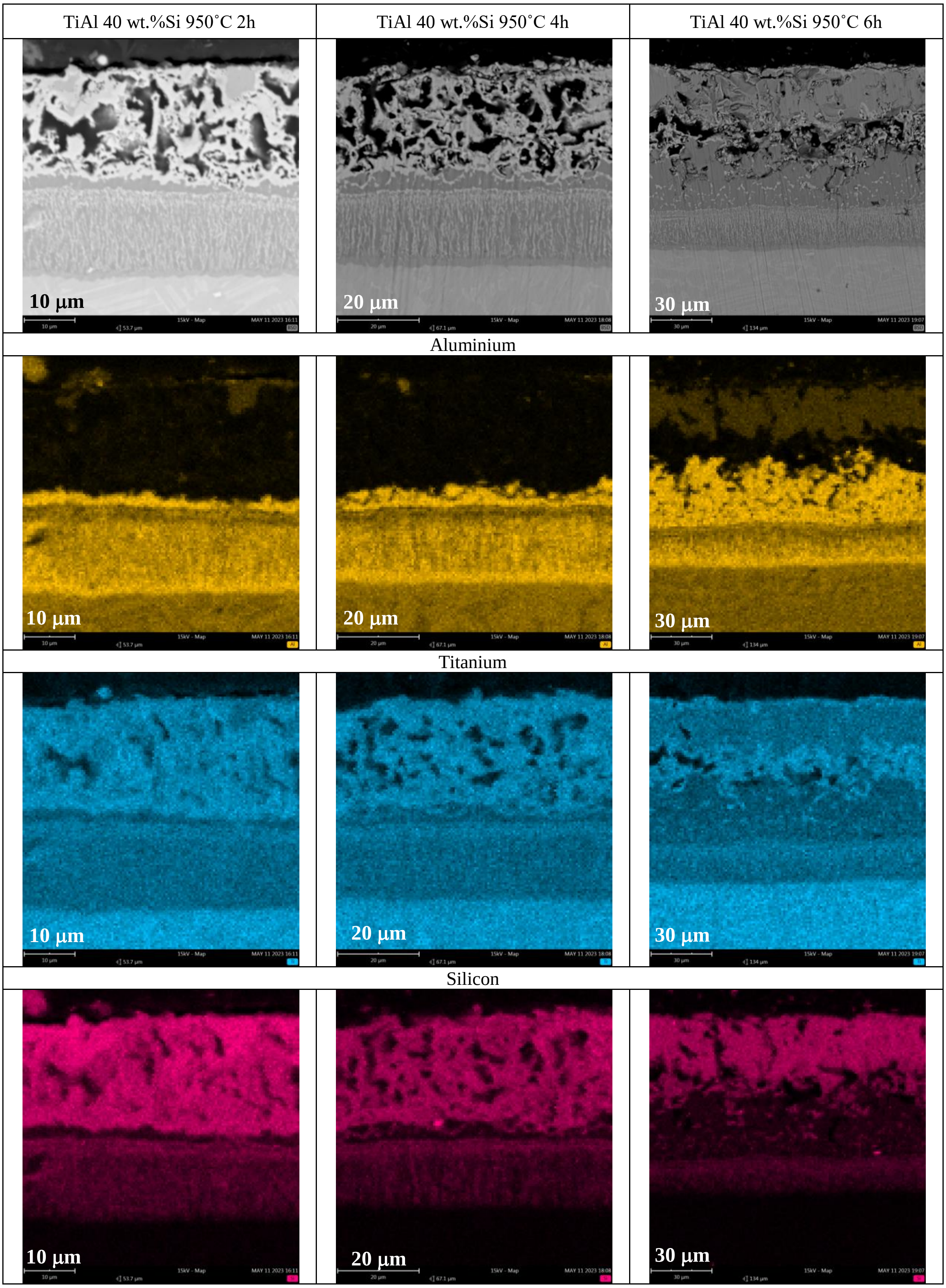

Fig. 4. The microstructure of whole coating of aluminide coating formed from powder containing 40 wt. % of Si and elemental mapping of Al, Si and Ti for 2, 4 and 6 hours pack cementation at 950ºC.

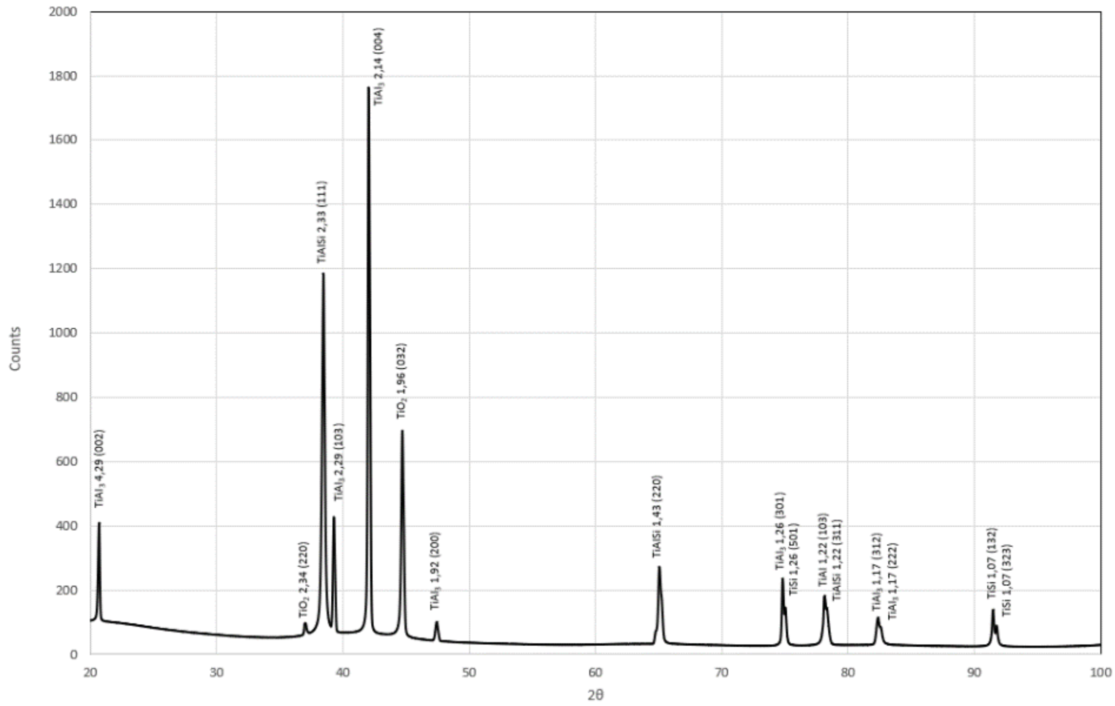

Fig. 5. Results of analysis of phase composition of a sample aluminide coating formed from powder containing 20 wt. % of Si after 4h of pack cementation at 950°C.

The microstructure of the surface layer for the pack cementation process for 40 wt.% Si showed that the inner zone had a greater thickness compared to the process with 20 wt.% Si. The outer zone consisted mainly of titanium and silicon as can be seen in the elemental mappings made with the EDS detector. XRD analysis showed that the main phases present in the 40 wt.% Si sample were $TiSi_2$, Ti_3Si and Ti_5Si_3. Additionally, TiAl, TiSi and TiAlSi phases were present. During aluminizing, oxidation of the coating surface was observed, resulting in the appearance of titanium oxides on the surface. The effect of process time on the structure of the silicon aluminide coating at 950°C was also observed. After 2 hours of pack aluminizing, a porous outer layer formed. Below, titanium silicides formed at the grain boundary of the $TiAl_3$ phase, and a columnar layer formed at the coating/base material interface, visible on elemental mapping.

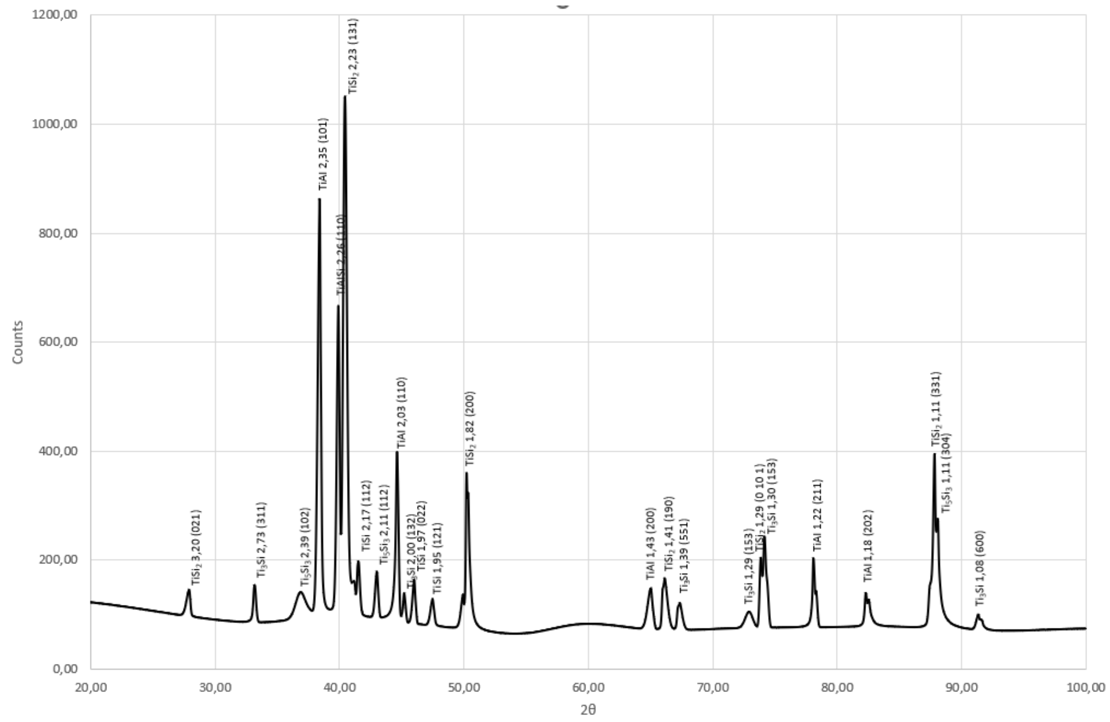

Fig. 6. Results of analysis of phase composition of a sample aluminide coating formed from powder containing 40 wt.% of Si after 4h of pack cementation cementation at 950°C.

In the first studies of silicon incorporation into the base material, TiN was present in the outer surface layer, which was not of interest. Increasing the argon flow rate and cooling the sample with gas at the end of the process avoided the formation of a TiN phase in the surface layer. White separations in the spot analysis showed the presence of aluminium and titanium in a ratio of 2:1. According to the XRD analysis, it can be concluded that a $TiAl_3$ phase was formed. The silicon content in this area was approximately 3 wt.%. The dark areas were characterised by a higher titanium and silicon content compared to the white precipitates. The aluminium content was approximately 20 wt.%. XRD analysis showed that a TiAlSi phase had formed.

4. Discussion

The results of the study of the kinetics of silicon-modified aluminide coating deposited on TNM-B1 alloy showed differences in structure. The pack cementation process used to modify γ-TiAl-silicon alloy results in the formation of a compact surface layer, consisting of two intermediate layers. The first layer, adjacent to the substrate, contains a TiSi phase, rich in titanium and silicon and second with columnar Ti_5Si_3 precipitations. The structure of the coatings is similar to those obtained by the slurry method (Goral et al, 2007). The increase in silicon content resulted in the formation of the remaining titanium silicides and not only Ti_5Si_3, as well as the formation of a porous outer layer structure. In the outer zone of the coating there is diffusion of titanium, aluminium and silicon at the grain boundaries, and for the longer process time (6 hours) a Kirkendall-Frenkel effect is observed. The structure of the inner zone was analogous to previous studies (Woźniak et al, 2023) for lower Si content. The thickness of the surface layer depends on the process time and silicon content. For each process time (2, 4 and 6 hours), the layer is twice as thick for a TiAl alloy with 40 wt.% silicon compared to 20 wt.% silicon. Further analysis is required of the strong increase in thickness of the coating obtained with powder containing 40% by weight of silicon which was characterized by a much greater thickness.

5. Conclusions

Investigations on the kinetics of growth of Si-modified aluminide layers on the TNM-B1 alloy substrates modified with higher amounts of silicon allowed to draw the following conclusions. It was found that increasing the silicon content causes a significant increase in the thickness of the coating on a TiNM-B1 intermetallic alloy. As a result of the packet cementation process, a compact surface layer was obtained consisting of a layer adjacent to the substrate, rich in titanium and silicon, and an outer layer composed of titanium, aluminium and silicon at the grain boundaries.

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Kinetyka Wzrostu Warstwy Aluminidkowej Modyfikowanej Krzemem na Podłożu Stopu na Osnowie Fazy Międzymetalicznej TNM-B1

Streszczenie

TiAl to stop tytanu i aluminium, który jest wykorzystywany jako materiał konstrukcyjny w zastosowaniach wysokotemperaturowych, takich jak samoloty i silniki turbinowe. Aby poprawić właściwości mechaniczne TiAl, jest on często modyfikowany poprzez dodanie innych pierwiastków, takich jak krzem. Proces cementowania pakietowego jest jedną z metod modyfikacji TiAl, która polega na pokryciu powierzchni stopu specjalną mieszanką zawierającą krzem, w celu wzbogacenia go w ten pierwiastek. W wyniku tego procesu powstaje TiAl modyfikowany Si, który wykazuje lepsze właściwości mechaniczne i odporność na wysokie temperatury, dzięki czemu idealnie nadaje się do stosowania w przemyśle lotniczym i turbinowym. Proszek użyty w procesie cementowania pakietowego składał się z 20 % wag. Si, 20 % wag. Al, 1-2% aktywatora NH_4Cl i reszty Al_2O_3, a także 40 % wag. Si, 40 % wag. Al, 2% aktywatora NH_4Cl i reszty Al_2O_3 w przeliczeniu na 100 g proszku. Proces prowadzono w temperaturze 950°C przez 2, 4 i 6 godzin. Po procesie osadzania przeprowadzono badania za pomocą skaningowego mikroskopu elektronowego, analizę EDS, a także dyfrakcję rentgenowską (XRD). Wyniki badań wykazały strukturę powłoki typową dla powłok modyfikowanych krzemem, w tym obecność krzemków tytanu. Stwierdzono, że zwiększenie zawartości krzemu oraz czasu procesu powoduje znaczny wzrost grubości powłoki.

Słowa kluczowe: TiAl, stopy na osnowie fazy międzymetalicznej, warstwy aluminidkowe, metoda kontaktowo- gazowa