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Original Research

The Formation of Al-Si Aluminide Coatings by Pack Cementation Method on TNM-B1 Intermetallic Alloy

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Abstract

The TiAl intermetallics are the promising material for aerospace application. According to its insufficient oxidation resistance above 900oC the using of protective coatings is necessary. The diffusion aluminide coatings based on TiAl2 or $TiAl_3$ phases permits to formation of alumina scale on the surface of TiAl alloys. The pack cementation with Si doping is one of the most popular methods of this type of coatings production. In present article the influence of Si content in the pack, process time and temperature during pack cementation process were investigated. The thickness of obtained coating was in range 20-50 µm. When Si content was higher the formation of titanium silicide's was observed using almost all analysed values of process parameters. The results showed that using of 24 wt. % Si containing pack and process parameters: 4h/950°C enables to obtain the coating characterized by optimal thickness and structure. The porosity and cracks in coatings according to TiAl phases brittleness was observed.

Keywords: pack cementation, TiAl, aluminide coatings, Al-Si coatings, oxidation

1. Introduction

The Ti-Al system includes intermetallic phases, which are characterized by high operating temperature (up to 800˚C), good oxidation resistance, high plasticity, high Young's modulus and low weight. Due to such properties of the intermetallics, they might be used in aerospace and automotive applications (Goral et al., 2007; Rubucha et al., 2022; Wu et al., 2006; Novak et al., 2009). For increase the operating temperature and oxidation resistance of the TiAl alloy, it is possible to introduce alloying elements into the base material by diffusion treatment (Jiang et al., 2008). The main elements modifying the surface layer of the Ti-Al intermetallics are: Si (Musi et al., 2022), Nb (Jiang et al., 2002), W (Wendler & Kaczmarek, 2005) or Mo (Chlupová et al., 2020). Above a temperature of 800˚C, the material begins to oxidize quickly, which leads to a reduction in mechanical properties. Mainly titanium and aluminium oxides mixture, are formed on the surface of TiAl alloy. Additionally, nitride oxides TiN / Ti_2AlN or Ti_3AlN might appear at the interface. The oxides of these elements do not protect the TiAl against oxygen, which causes a rapid weight gain (Knaislová, 2021; Locci, 2001; Swadźba et al., 2020a). Many methods and technologies were developed for increasing oxidation resistance of TiAl intermetallics. Wang at al. (2015) showed that a silicon-rich coating significantly inhibits oxygen diffusion into the layer, resulting in better oxidation resistance of the alloy. The silicon protective layer can be obtained by various processes. Goral M. (2011) and Moskal et al. (2009) proposed a slurry diffusion coating and Arc-PVD deposition of Al-Si and formation of Si-rich titanium silicides into aluminide coating (Bauer et al., 2022; Bobzin et al., 2018) investigated the HS-PVD rapid vapor deposition process in which the cathodic discharge (HCD) phenomenon occurs and gas sputtering (GFS), which allows to obtain thick coatings Earlier research shows the effect of silicon on TiAl material. Swadźba et al. (2020b) showed that silicon significantly affects the working time of the material at the temperature of 850˚C. The substrate of the material without silicon modification after the oxidation process formed a thick oxide scale, which did not protect the substrate against corrosive gases. By modifying of the TiAl substrate with silicon, a continuous scale was formed, protecting the base material. Jiang et al. (2002) after high-temperature oxidation confirmed that silicon has a positive effect on the substrate. Studies have shown that dense Al_2O_3 is formed inside. Moreover, TiAl alloys produce a Ti_5Si_3 phase. In this phase, after the high-temperature oxidation process, the TiO_2 phase is formed. They used the pack cementation method to introduce silicon by inward diffusion to base material. A coating thickness of up to 30 μm was obtained. The coating consisted of two outer and inner layers. The inner layer contained $TiAl_3$ and the outer layer slilicide (Xiang et al., 2003). It has also been shown that during very long heating, two phases of $TiAl_3$ and $TiAl_2$ are formed. Additionally, silicon can bind titanium and niobium, where the aforementioned Ti_5Si_3 phase is formed on the thin phases of $TiAl_3$ and $TiAl_2$ (Swadźba et al., 2020b).

The pack cementation is the main method of Si-modification of TiAl aluminides (Novák et al., 2009) In present article the kinetics growth of Si-modified aluminide coatings on TNM-B1 alloy was presented.

2. Experimental

The TNM-B1 type intermetallic alloy with composition (wt. %): Al-28.6% Nb-9.2% Mo-2.3% and Ti-bal. was used as a base material. Samples were 10 mm × 20 mm. The samples were cut to rectangular from cylindrical bar. The surface was grinded using waterproof paper to gradation Mesh 500. The sample were put into metallic box and mounted into Ar-protective atmosphere tube furnace (Xerion, Germany). The two types of powder were prepared (wt. %):

- Si-14%, Al-14%, $AlCl_3$-2%, Al_2O_3- bal,
- Si-28% Al-14%, $AlCl_3$-2%, Al_2O_3- bal.

In experimental three values of temperature (900/950/1000ºC) any time (2/4/6h) were used. The duration of the aluminizing process and the temperature were selected from previously published scientific articles. Etching of metallographic samples was carried out in a solution of the following chemical composition: 30 cm^3 $C_3H_6O_3$, 15 cm^3 HNO_3 and 5 cm^3 HF. The process was conducted in Ar flow 0.5 NLPM (Normal litres per minute). The microstructure was analysed 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. Qualitative phase analysis was performed from the surface of the samples by X-ray diffraction.

3. Results and discussion

3.1. The coating formed from powder containing 14 wt. % of Si

The temperature had strong influence on microstructure of Si aluminide coating formed after 4h of deposition time. In lower temperature (900ºC) the measured coating was about 30 μm (Fig. 1a). Thin (about 2 μm) layer was observed on the interface with base material. In higher temperature (950ºC) thicker (about 35 μm) with presence of small precipitation zone (about 5 μm thick) in the inner zone (Fig. 1b). According to Goral et al. (2007) the columnar titanium silicide grains were formed in $TiAl_3$ matrix. In highest analysed temperature (1000ºC) the coating's thickness decreased to about 20 μm (Fig. 1c) and silicide precipitations were not observed in the structure (Goral et al., 2011). It was connected probably with oxidation of surface layer and non-homogenized powder structure used for experimental.

After 2h of pack aluminizing process conducted at 950ºC the thin columnar inner zone was formed (Fig. 2a). Based on Goral et al. (2011) and Moskal et al. (2009) and elemental mapping (Fig. 2b-e) the titanium silicides in $TiAl_3$ matrix were formed. Extending the process to 6 hours resulted in the formation of a coating devoid of silicon precipitates (Fig. 3a). During aluminizing, oxidation of the coating surface was observed, which resulted in the appearance of titanium nitrides and oxides on the surface. On the elemental mapping (Fig. 3b-e) on the surface, an increased content of these elements was observed on the surface. The crack seen in Fig.1a may be caused by the pressure set too high when the samples were incubated. Further testing was corrected, and a lower pressure was set.

An analysis of a phase composition proved that the $TiAl_3$ phase in a main component of the aluminide coating formed from powder containing 14 wt. % of Si during 4h pack aluminizing (Fig. 4). In addition, a TiN phase was found to be present in the surface layer. The TiN phase may have been formed by oxygen access to the vacuum furnace during the aluminizing process. Phase analysis confirmed the presence of an AlN and Al_2O_3 phase. The Al_2O_3 phase increases oxidation resistance and improves the mechanical properties of the surface layer (Lu et al., 2020). Zhao et al. (2023) showed that the addition of Si significantly affects the formation of the Al_2O_3 phase (Yang et al. 2023). The AlN phase can significantly improve corrosion resistance. At 900˚C, AlN can be oxidised to Al_2O_3 (Yang et al., 2023).

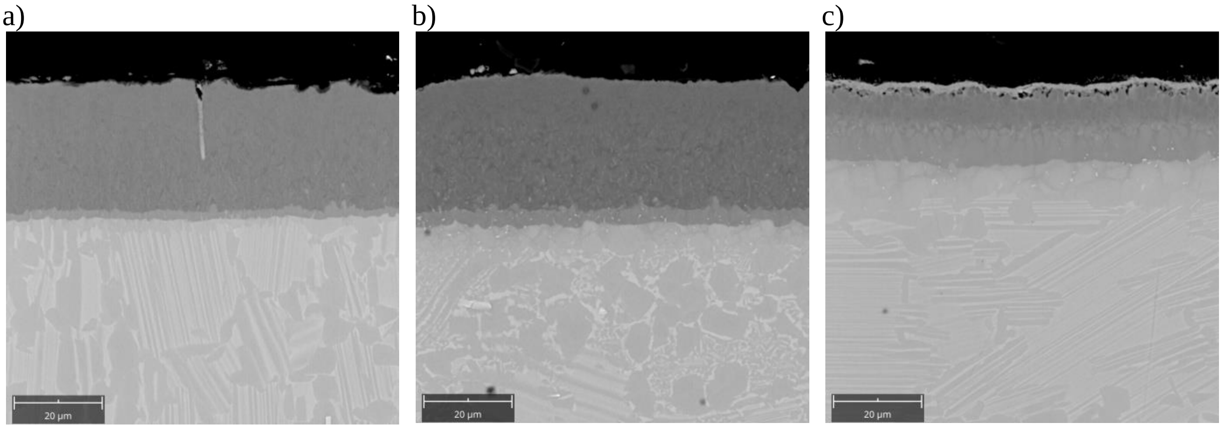

Fig. 1. The microstructure of aluminide coating formed using 14% Si containing pack at 900 (a), 950 (b) and 1000ºC (c) during 4h diffusion process

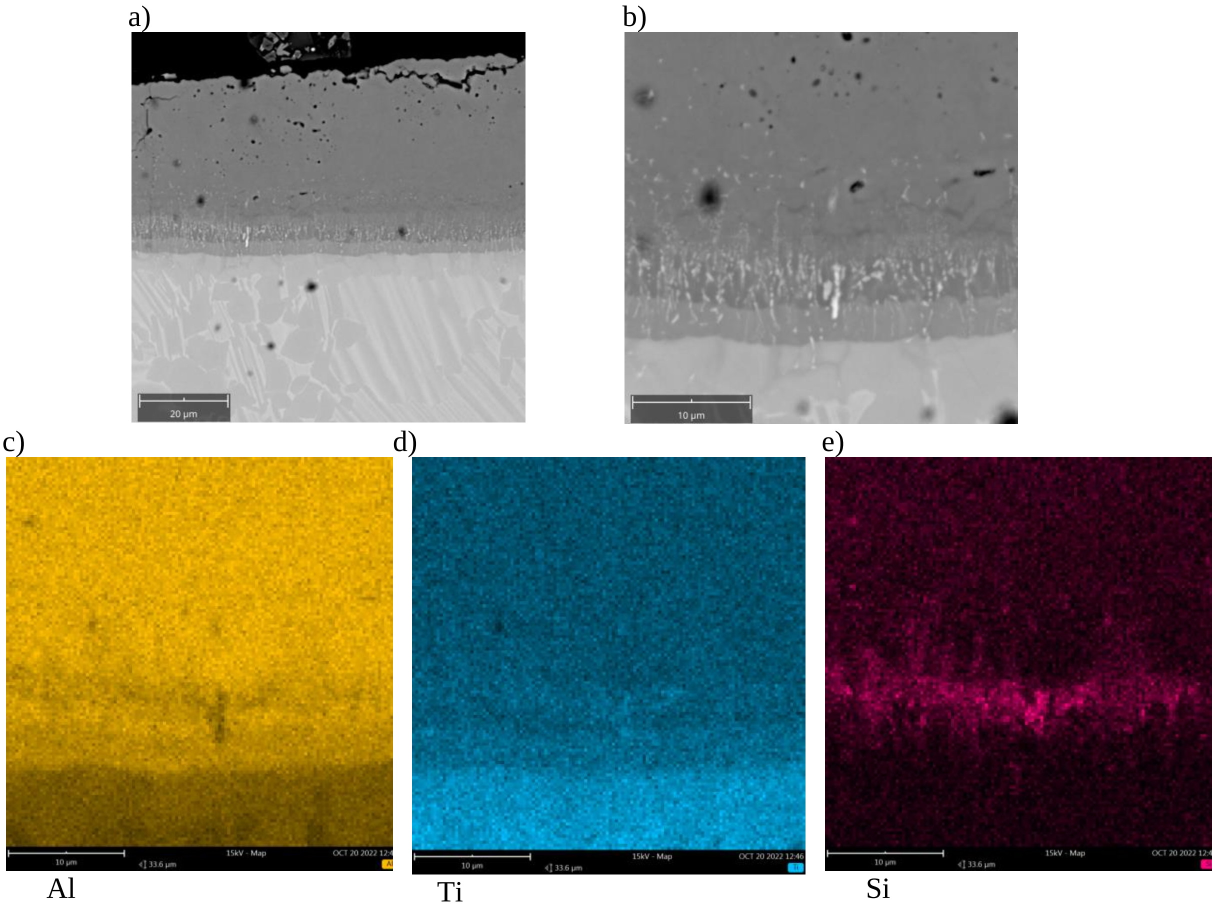

Fig. 2. The microstructure of whole coating (a) and inner zone (b) of aluminide coating formed from powder containing 14 wt. % of Si and elemental mapping of Al (c), Ti (d) and Si (e)

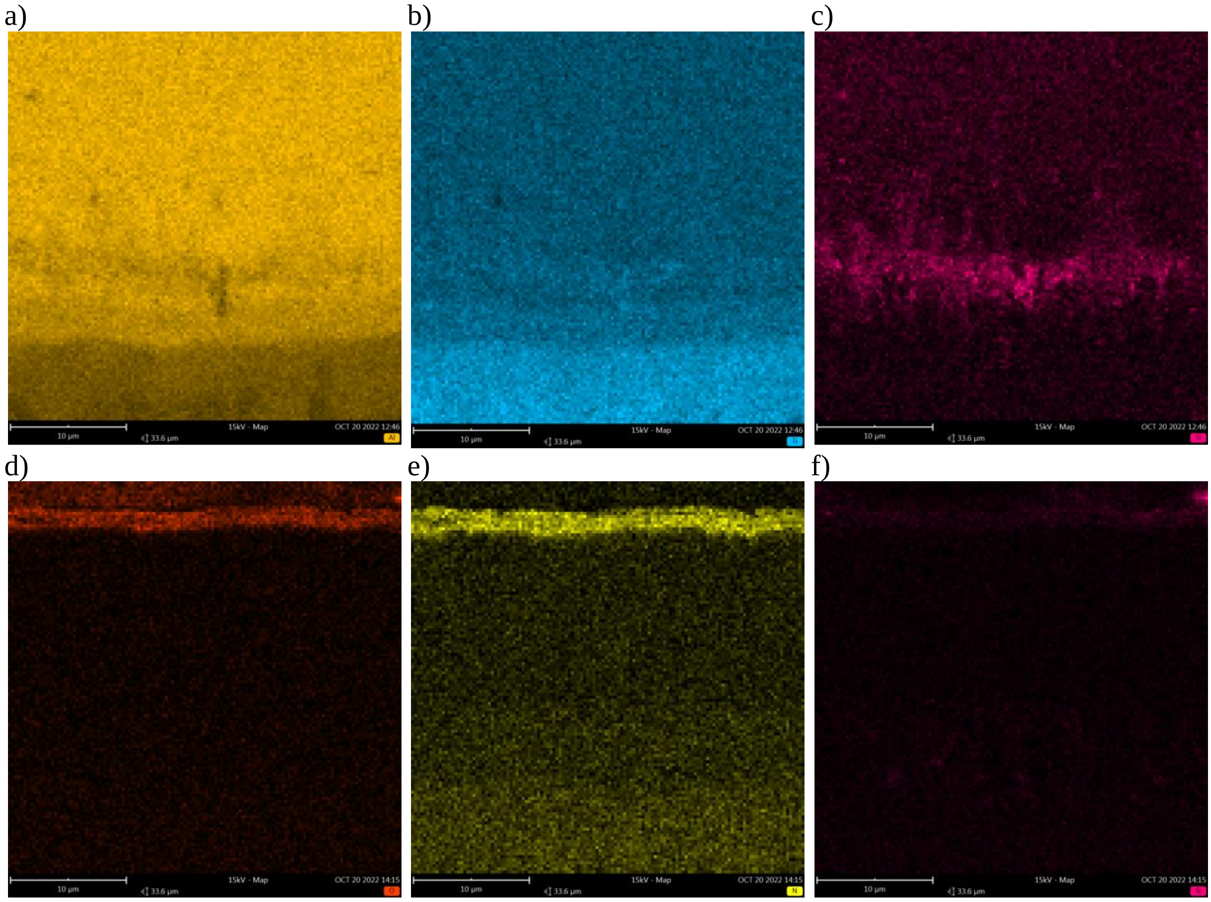

Fig. 3. The microstructure of aluminide coating formed from powder containing 14 wt% of Si (a) and elemental mapping of Al (b)., Ti (c) O (d), N (e) and Si (f)

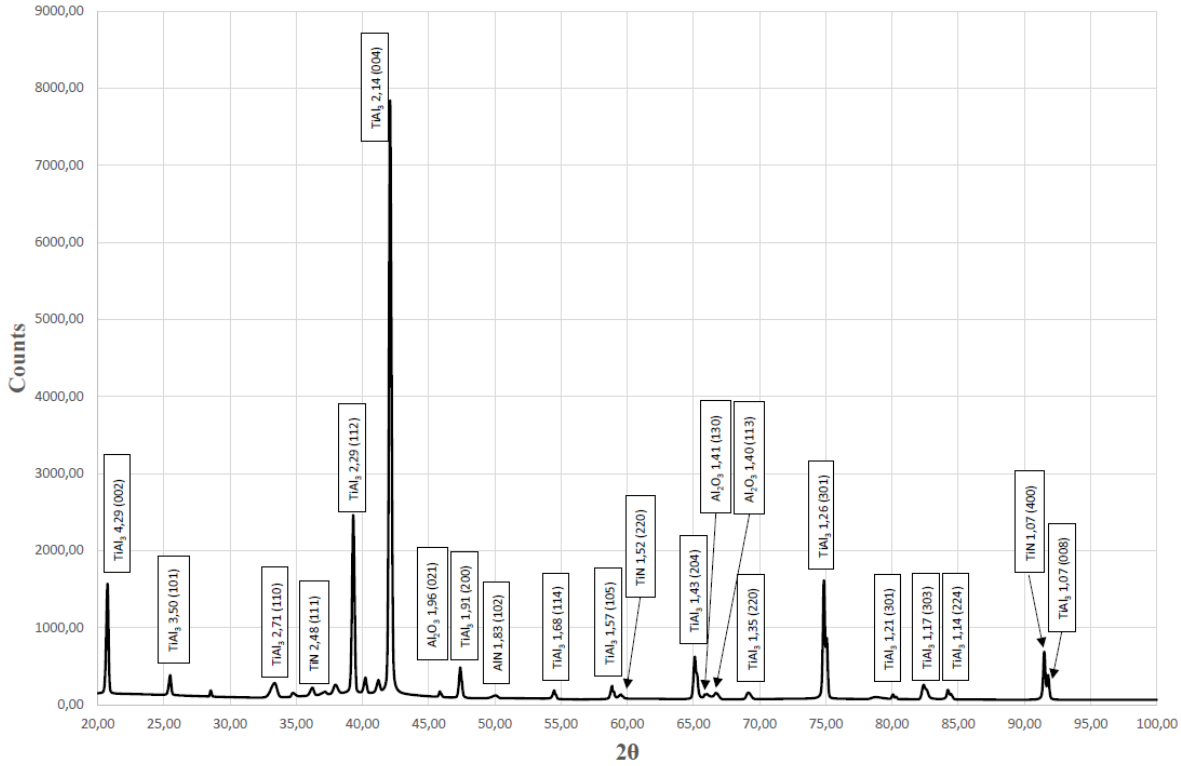

Fig. 4. Results of analysis of phase composition of a sample aluminide coating formed from powder containing 14 wt. % of Si after 4h

3.2. The coating formed from powder containing 28 wt.% of Si

The increase in the silicon content in the powder resulted in the formation of silicide precipitates in all the analysed coatings during pack aluminizing process (Fig. 5a-c). The temperature had a strong influence on coating thickness. In lowest temperature (900°C) the coating thickness did not exceed 30 µm (Fig. 5a). The presence of cracks in the coating is related to the high brittleness of the $TiAl_3$ phase from which it is composed. Increasing the aluminizing temperature to 950°C doubled the thickness of the coating (to over 40 µm, Fig. 5b). The microstructure showed not only cracks but also porosity, which might be caused by the Kirkendall effect. Similar phenomena were observed in the coatings studied by Rubacha et al. (2022). In the coating obtained at the highest temperature (1000°C) of similar thickness, a zone of columnar precipitations of titanium silicides was formed (Goral et al., 2007). Rich precipitates also appeared on the grain boundaries of the $TiAl_3$ phase – elemental mapping Fig. 5c-f. A similar structure was observed in coatings made of suspensions containing from 5 to 20% Si (Goral et al., 2007).

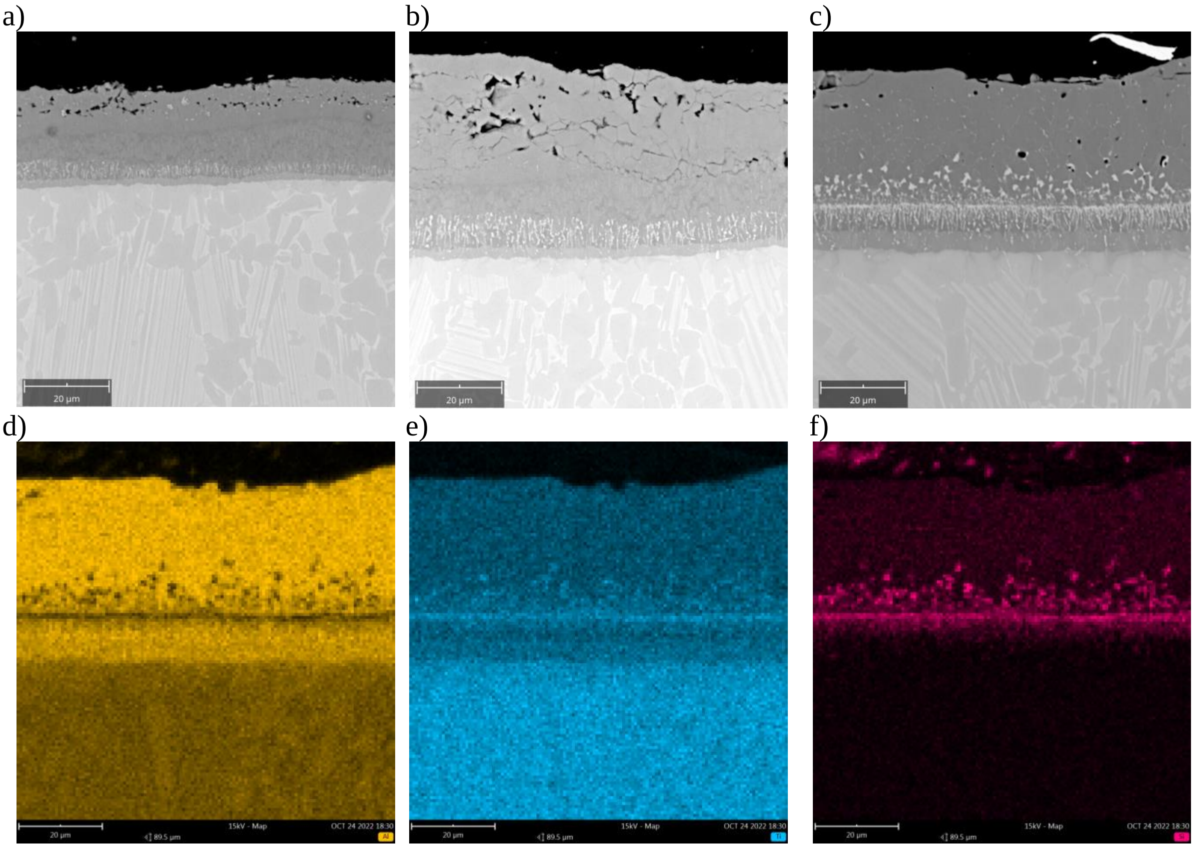

Fig. 5. The microstructure of aluminide coating formed from powder containing 28 wt% of Si at 900 (a)/950(b)/1000h(c) during 4h pack aluminizing and elemental mapping of Al (d), Ti (e) and Si (f) of coating produced at 1000°C

The influence of process time on structure of Si aluminide coating at 950°C was also observed. After 2 hours of pack aluminizing porous outer layer was formed (Fig. 6a). Below the titanium silicides formed on grain boundary of $TiAl_3$ phase and formed columnar layer on coating/base material interface which were visible on elemental mapping (Fig. 6d,e) When pack aluminizing time was extended to 4 hours the increasing of coating thickness above 40 µm was observed (Fig. 6b). In microstructure lower porosity and presence of cracks I inner layer were observed. The precipitations of titanium silicides on grain boundary were not detected probably as a result of their dissolution in $TiAl_3$ phase. In result of long-time pack aluminizing process the very small number of pores were observed (Fig. 6c). Additionally the smaller precipitations in inner zone were replaced the columnar zone formed during 2 and 4 h pack aluminizing process.

An analysis of a phase composition proved that the $TiAl_3$ phase in a main component of the aluminide coating formed from powder containing 28 wt% of Si during 4h pack aluminizing (Fig. 7). The diffractogram is like the X-ray diffraction shown for 14 wt% Si. The main phase present in the TiAl surface layer is $TiAl_3$. The appearance of titanium nitrides is also noted on the surface layer. TiN in the present study is not the phase of interest. In addition, the formation of $TiSi_2$ and Ti_4O_7 phases was noted.

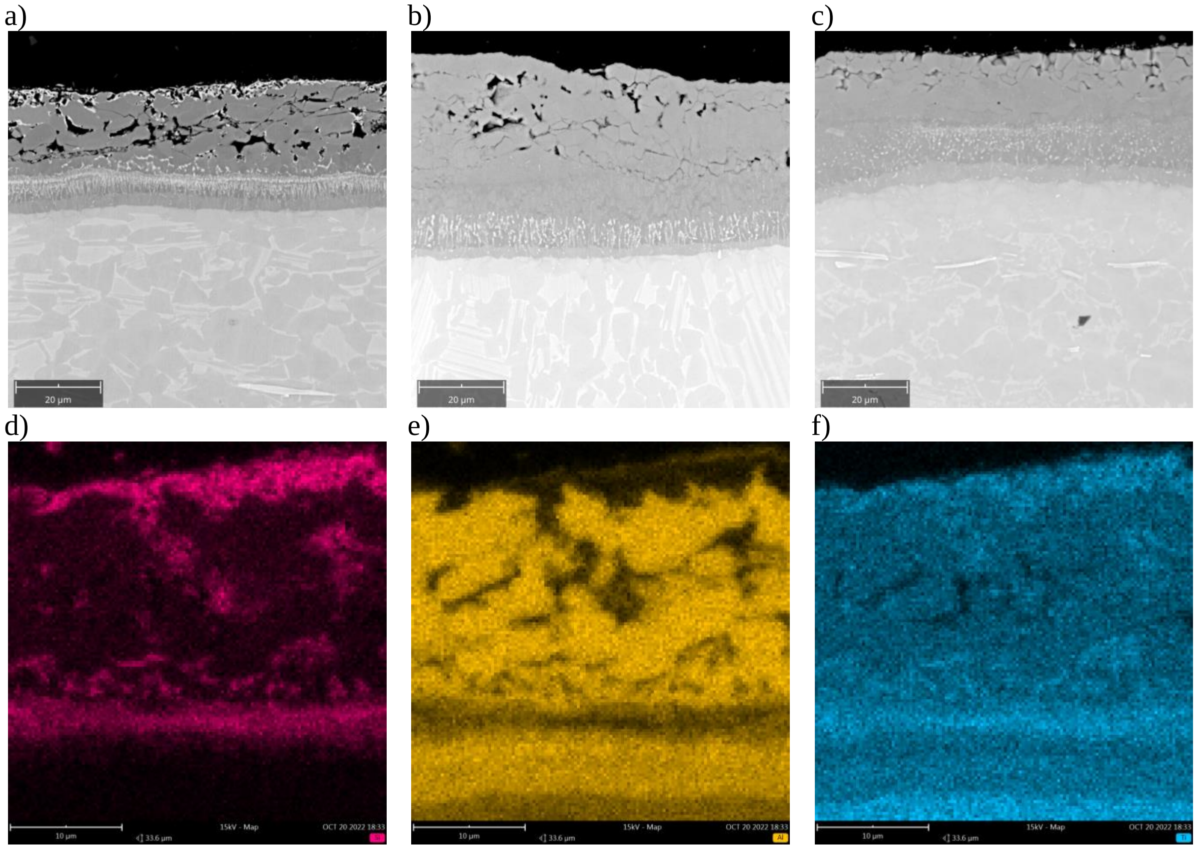

Fig. 6. The microstructure of aluminide coating formed from powder containing 28 wt. % of Si after 2 (a)/4(b)/6h(c) of pack aluminizing and elemental mapping of Al (d), Ti (e) and Si (f) of coating after 2h of the process

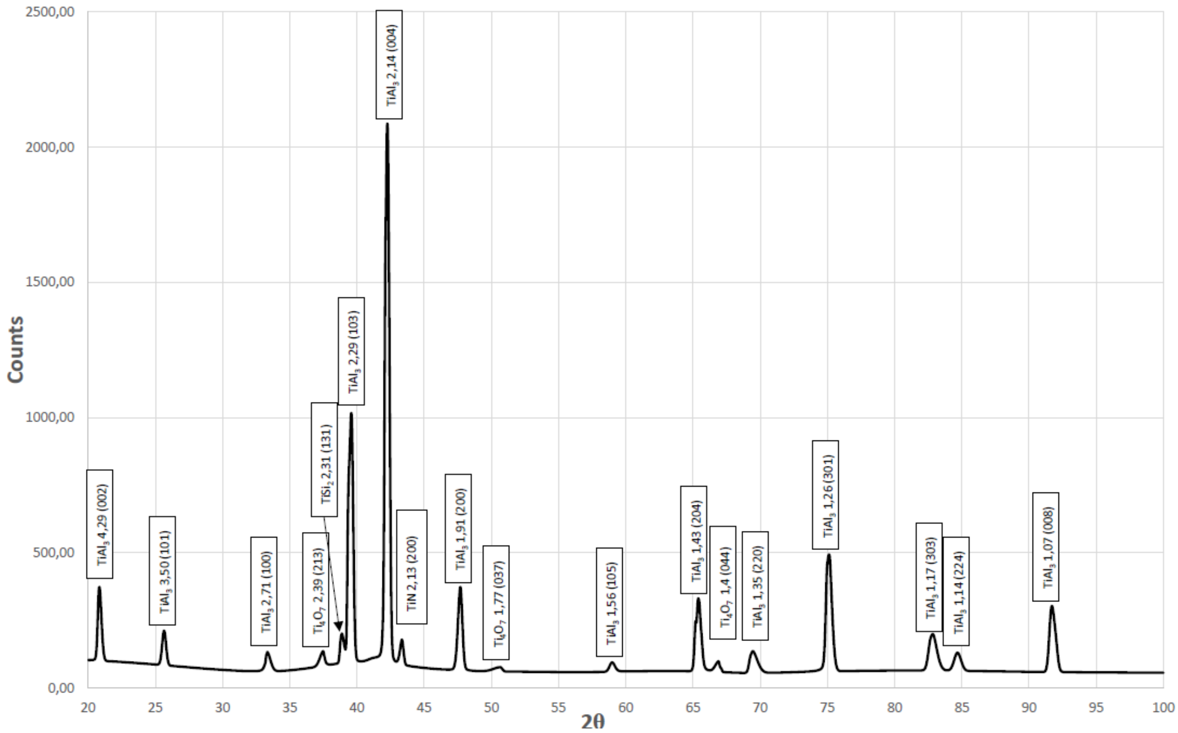

Fig. 7. Results of analysis of phase composition of a sample aluminide coating formed from powder containing 28 wt. % of Si after 4h

4. Conclusions

The conducted research showed large differences in kinetics growth of Si-modified aluminide coatings on TNM-B1 intermetallic alloy. Based on analysis of obtained results some conclusions were formed:

1) The Kirkendall effect with formation of pores was observed after short aluminizing time (2h, 4h using both types of powders).
2) There was no relationship between process time and thickness probably as a consequence of partial oxidation of coating during deposition, thin nitride layer was observed on the surface of selected sample.
3) The structure of coating was similar to formed using slurry method - columnar precipitations of titanium silicides were visible into inner area of coating.
4) The $TiAl_3$ and TiAl phases were the main components of developed coatings.
5) The using of better types of furnaces with inert atmosphere are required for further pack cementation processes.
6) Diffraction analysis showed the formation of $TiSi_2$ titanium silicide and Ti_4O_7 oxide.
7) TiN phase formed by oxidation of the sample in a vacuum furnace.

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Tworzenie się Powłok Aluminidkowych Al-Si Uzyskanych Metodą Kontaktowo-Gazową na Podłożu Stopu na Osnowie Fazy Międzymetalicznej Typu TNM-B1

Streszczenie

Fazy międzymetaliczne TiAl są obiecującym materiałem do zastosowań w lotnictwie. Ze względu na niedostateczną odporność na utlenianie powyżej 900°C konieczne jest stosowanie powłok ochronnych. Dyfuzyjne powłoki aluminidkowe na bazie faz $TiAl_2$ lub $TiAl_3$ pozwalają na tworzenie się zgorzeliny tlenku aluminium na powierzchni stopów TiAl. Aluminiowanie metodą kontaktowo gazową z wprowadzaniem Si jest jedną z najpopularniejszych technik wytwarzania tego typu powłok. W niniejszym artykule zbadano wpływ zawartości Si w powłoce w zależności od czasu trwania procesu oraz temperatury. Grubość otrzymanej powłoki zawierała się w przedziale 20-50 µm. Gdy zawartość Si była wyższa, obserwowano powstawanie krzemków tytanu przy prawie wszystkich analizowanych wartościach parametrów procesu. Wyniki pokazały, że użycie proszku zawierającego 24% wag. % Si oraz czasu i temperatury 4h/950°C pozwala na uzyskanie powłoki charakteryzującej się optymalną grubością i strukturą. Zaobserwowano porowatość i spękania powłok.

Słowa kluczowe: metoda kontaktowo-gazowa, TiAl, powłoki aluminidkowe, powłoki Al-Si, utlenianie