

MICROSTRUCTURAL INVESTIGATION OF THE COATINGS PREPARED BY SIMULTANEOUS ALUMINIZING AND SILICONIZING PROCESS ON γ -TiAl

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Abstract

In this research, formation of aluminide/silicide diffusion coatings on γ -TiAl[Ti-48Al-2Nb-2Cr (at.%)] alloy using gas-phase diffusion pack cementation process has been investigated. The application of powder mixtures with various chemical compositions in the pack cementation process performed at 1000°C for 6 hours in order to achieve simultaneous diffusion of Al and Si, showed that the composition of the powder mixture could have a significant effect on the structure and thickness of the aluminide/silicide coatings. The identification and analysis of aluminide/silicide microstructures formed as a result of simultaneous diffusion of Al and Si, which was comprehensively and qualitatively done for the first time in this study, showed that the sequential mechanism is dominant in the formation of the above-mentioned coatings. Furthermore, Kirkendall phenomenon and volumetric changes caused by the formation of Ti_3Si_3 and Ti_3Si_4 , were considered as the two dominant mechanisms in the formation of porous segregated structure in these coatings. In this study, the effect of decreasing the activity of Si, through two approaches of reducing the amount of Si in the powder mixture and using Al-20wt.%Si alloyed powder instead of pure Al and Si depositing elements, on the microstructural modification coatings was investigated. The results showed that reducing the Si activity at the surface of the coating and, consequently, reducing the flux of active silicon atoms (J_{Si}), has a significant effect on the formation of coating with an ideal structure.

Keywords: γ -TiAl Alloy; Pack Cementation Process; Aluminide/Silicide Diffusion Coatings

1. Introduction

Gamma TiAl intermetallic compound is a low density material, which has been widely used for its high specific strength, good oxidation and creep resistance at fairly high temperatures [1-5]. These attractive properties make the material work in the aerospace and automotive industry as well as use in manufacture of low-pressure turbine blades [4-9]. But this alloy is not sufficient oxidation protection above 800°C [10, 11]. This is explained by the fact that γ -TiAl intermetallic compounds could not form a protective and dense Al_2O_3 layer, but form a brittle, porous and non-protective $TiO_2 + Al_2O_3$ mixed layer on their surfaces at oxidation environment at higher temperatures [9, 12-14]. For this reason, widespread use of γ -TiAl alloy has been restricted.

So far, various methods have been used to improve the oxidation resistance of this alloy at high temperatures. One of these approaches is the use of

alloying technique [15-18]. This method is based on the suppression of rutile formation that accounts for most of the mass gain of γ -TiAl due to oxidation. Park et al. [17] developed Ti-46Al-6Nb-0.5W-0.5Cr-0.3Si-0.1C alloy and found out that its oxidation resistance is superior mainly due to alloying elements such as Al, Cr, Nb, W, and Si, which beneficially enhanced the formation of alumina and suppressed the formation of rutile in the scale. Yoshihara et al. [15] and Jiang et al. [16] also used Cr and Nb as alloying elements and observed their beneficial effects on the improvement of oxidation resistance of the γ -TiAl alloy. However, the use of this method often leads to losing properties such as ductility at room temperature and creep resistance. Therefore, improving the oxidation resistance of γ -TiAl by using alloying elements for practical applications is not always beneficial [18].

Another approach to improve the high temperature oxidation resistance of these alloys, is their surface modification, which is known as the best method [19].

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All coating methods can be placed in this category. Nishimoto et al. [20] prepared two-step Cr and Al diffusion coating on TiAl, Jung et al. [21] have prepared an Al+Y coating by a single EB-PVD process, and Taniguchi et al. [22] have also deposited thin Al₂O₃ layer by chemical vapor deposition (CVD). A large number of other methods of coating for various other compounds have also been studied by various researchers for surface modification of TiAl alloy to improve its high temperature oxidation resistance [23-28].

Among the methods mentioned above, the production of coating by pack cementation method, with consideration of its numerous advantages, can be considered as the most suitable method for the surface modification of the γ -TiAl alloy in order to increase its high temperature oxidation resistance. These advantages include [29, 30]: (i) The ability to produce a large volume of diffusion coatings with controllable thickness up to 200 μm ; (ii) Possibility of co-deposition of numerous elements such as Al, Si, Cr, Y; (iii) Excellent adhesion between coating and substrate; (iv) Practicable for various shapes and sizes, without limitation for coating of out sight zones; and (v) Low environmental effects.

Several researchers have prepared aluminide coatings on γ -TiAl alloy [6, 30-33]. The Si-modified aluminide coatings are also prepared on γ -TiAl alloys by pack cementation method to form titanium silicide layers on them. Based on thermodynamics, all titanium silicide phases (Ti₃Si₃, Ti₅Si₄, TiSi and TiSi₂), except Ti₃Si, can form a protective SiO₂ layer on γ -TiAl alloy surface [34-36]. In addition, various intermetallic titanium silicide compounds have good properties for high temperature applications.

Xiang et al. [37] studied the possibility of the co-deposition of aluminum and silicon and the formation of aluminide/silicide compounds on the alloy surface using pack cementation process, in their research. They found that by using the powder mixture of [Al(1-4wt.%)+Si(1-6wt.%)+AlCl₃(1-5wt.%)+Al₂O₃(balance)], the co-deposition of Al and Si on the γ -TiAl is possible. They reported that a dense double layer coating consisting of a silicide and an aluminide layer formed on the γ -TiAl surface, which resulted in a significant increase in the high temperature oxidation resistance of the alloy.

However, recent research has shown that the main disadvantage of titanium silicide compounds is its high brittleness [38]. In this investigation, it is decided to study the morphology, microstructure, and phase composition of the layers formed as a result of the simultaneous siliconizing and aluminizing process.

2. Experimental

In this study, γ -TiAl substrates with a chemical

composition of Ti-48Al-2Nb-2Cr (at.%) were used. The substrates were the coupons of size 10×10×2 mm³ which were cut from an ingot. The substrate surfaces were ground with SiC paper up to 1000 grit and then ultrasonically cleaned in ethanol and dried in air.

The simultaneous aluminizing and siliconizing process was then used to form a Si-modified aluminide coatings onto the γ -TiAl substrates. This process was carried out by burying the γ -TiAl coupons in 60g (for each sample) powder mixture consisting of aluminum and silicon depositing elements, AlCl₃ as an activator, and Al₂O₃ (with maximum particle size of 50 μm) as a filler material. It should be noted that in some coating processes, pure Al (<65 μm) and Si (<5 μm) were used as a source of depositing elements, and in some experiment runs, Al-20wt.%Si alloy powder was used. Chemical composition of the powder mixtures used in pack aluminizing-siliconizing process of γ -TiAl specimens is shown in Table 1.

Table 1. The chemical composition of the powder mixtures used in pack aluminizing-siliconizing process

Specimen	Pack Composition (wt.%)				
	Depositing elements			Activator	Filler
	Al	Si	Al20wt.%Si	AlCl ₃	Al ₂ O ₃
Al(0.5)Si(0.5)	0.5	0.5	-	1	98
Al(1)Si(1)	1	1	-	1	97
Al(2)Si(2)	2	2	-	2	94
Al(4)Si(4)	4	4	-	4	88
Al(8)Si(8)	8	8	-	8	76
Al(10)Si(10)	10	10	-	10	70
Al(2)Si(1)	2	1	-	2	95
Al(2)Si(0.5)	2	0.5	-	2	95.5
Al(2)Si(0.3)	2	0.3	-	2	95.7
Al(2)Si(0.1)	2	0.1	-	2	95.9
Al-20%Si(2)	-	-	2	1	97
Al-20%Si(4)	-	-	4	2	94
Al-20%Si(10)	-	-	10	5	85

The pack was heated in an alumina crucible under flowing Ar (%99.99) atmosphere from room temperature to 1000°C at heating rate of 4°C/min and then kept at 1000°C for 6 h. The crucible was sealed with an alumina lid and cement. At the end of the coating period, the crucible was cooled in the furnace to room temperature while maintaining the Argon gas flow. The samples were then extracted from the powder mixture and rinsed with tap water and washed with distilled water for 10 minutes under ultrasonic conditions.



In order to estimate weight changes of the specimens after the coating process, weight of all the specimens was measured before and after the above process with the precision of 0.01 g.

The cross-section of the coatings was analyzed by a field emission SEM (Σ IGMA VP, ZEISS Germany) equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS) detector and back scattered electron imaging facilities.

3. Results and discussion

According to Fig. 1(a) and Table 2, it can be seen that the specimen which was coated with a powder mixture of 0.5wt.%Al + 0.5wt.% Si + 1wt.% AlCl_3 and balance Al_2O_3 by simultaneous aluminizing and siliconizing process, has been subjected to weight loss ($\Delta w/w_0(\%) = -1.39$). This indicates the degradation of this sample under condition of using low percentage of depositing elements of pure aluminum and silicon.

In the Al(1)Si(1) specimen (Fig.1(b)), by using a powder mixture of 1wt.%Al + 1wt.%Si + 1wt.% AlCl_3 and balance Al_2O_3 , a very thin coating with a two-

layer structure was obtained. The coating has a silicide TiSi outer layer with a thickness of 2-3 μm and an inner layer of aluminide TiAl_3 with a thickness of 5-6 μm .

By increasing the content of depositing elements of pure aluminum and silicon and activator in the powder mixture (Al(2)Si(2) specimen (Fig.1(c)), with powder mixture of 2wt.% Al + 2wt.% Si + 2wt.% AlCl_3 and balance Al_2O_3), a coating with a three-layer structure has been obtained. These three layers are:

- 1-The outer layer of relatively dense and thin TiSi
- 2-Two-phase zone characterized by TiAl_3 matrix and secondary phase of Ti_5Si_3
- 3-The continuous inner layer of TiAl_2 .

Given the Al(4)Si(4), Al(8)Si(8) and Al(10)Si(10) specimens (Figs.1(d) to 1(f)), it can be seen that the structure of the coatings obtained in these samples consists of four separate layers which include:

- 1-The outer layer of relatively dense TiSi_2
- 2-The TiSi intermediate layer
- 3-Two-phase zone containing TiAl_3 matrix and Si-rich Ti_3Si_4 and Ti_5Si_3 lamellas
- 4-The continuous inner layer of TiAl_2 .

The morphology is almost identical in the Al(4)Si(4), Al(8)Si(8) and Al(10)Si(10) specimens. In general, the morphology of the coatings obtained in these specimens consists of two types of structures:

- 1-Initial compact coating structure
- 2-Porous breakaway structure.

It is very difficult to detect the two above-mentioned structures in Fig. 1(d), because the porosity in this coating is very low, but by increasing the amount of depositing elements of pure aluminum and silicon and AlCl_3 as an activator in powder mixture (Al(8)Si(8) and Al(10)Si(10) specimens), the two above-mentioned structures are clearly visible.

According to Figs. 1(b) to 1(f), it can be seen that, in general, silicide phases are formed in the outer layers and aluminide phases in the underlying layers of the coatings. This indicates that the diffusion of aluminum and silicon must have occurred in a sequential manner. According to Fig.2, it can be seen that in the temperature range of the simultaneous aluminizing and siliconizing process, the partial pressure of the silicon chlorides resulting from the reaction between silicon depositing element and AlCl_3 activator is much less than the partial pressure of Aluminum chloride (AlCl) resulting from the reaction of the aluminum depositing element with AlCl_3 activator. Therefore, during the early stages of simultaneous aluminizing and siliconizing through the pack cementation process, the aluminum in the powder mixture and around the sample should react with AlCl_3 activator and form the TiAl_3 aluminide layer. Subsequently, when the content of aluminum in the powder mixture, and especially around the sample, decrease significantly as a result of reaction

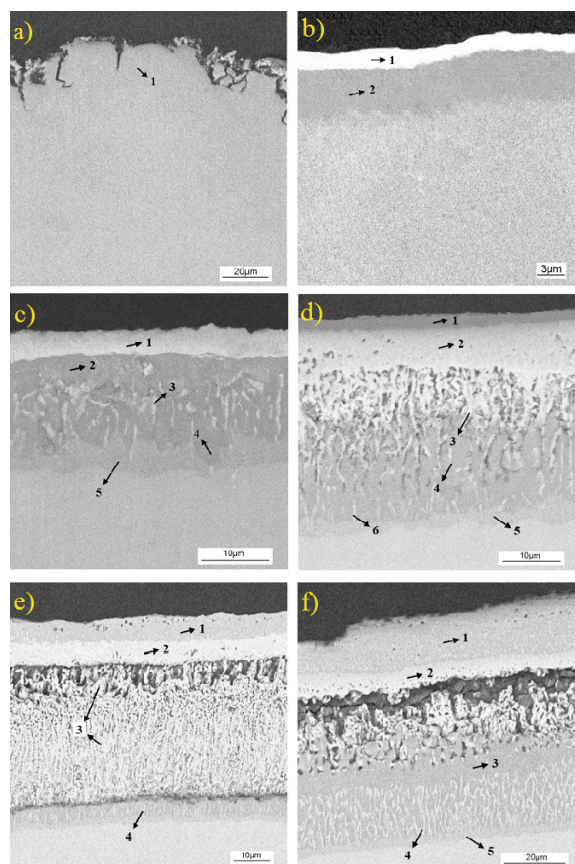


Figure 1. SEM cross-sectional micrograph of different samples after simultaneous aluminizing and siliconizing process at 1000°C for 6h a) Al(0.5)Si(0.5), b) Al(1)Si(1), c) Al(2)Si(2), d) Al(4)Si(4), e) Al(8)Si(8), and Al(10)Si(10)

Table 2. The EDS analysis of the positions marked in Figs.1(a) - 1(f) and weight changes of Al(0.5)Si(0.5), Al(1)Si(1), Al(2)Si(2), Al(4)Si(4), Al(8)Si(8), and Al(10)Si(10) samples after aluminizing-siliconizing process

Position	Chemical composition (at. %)					Deduced phases	$\Delta w/w_0(\%)$
	Al	Si	Ti	Cr	Nb		
1 in Fig. 1(a)	45.50	—	50.73	1.89	1.88	γ -TiAl	-1.39 [for Al(0.5)Si(0.5) sample]
1 in Fig. 1(b)	0.59	46.81	44.28	6.91	1.41	TiSi	+0.35 [for Al(1)Si(1) sample]
2 in Fig. 1(b)	72.88	0.33	24.47	0.46	1.86	TiAl ₃	
1 in Fig. 1(c)	0.06	49.10	43.49	5.96	1.38	TiSi	+1.01 [for Al(2)Si(2) sample]
2 in Fig. 1(c)	73.98	0.81	23.76	0.04	1.40	TiAl ₃	
3 in Fig. 1(c)	32.47	23.98	39.87	2.37	1.30	Ti ₅ Si ₃	
4 in Fig. 1(c)	72.51	0.45	24.39	1.11	1.54	TiAl ₃	
5 in Fig. 1(c)	65.56	—	30.85	1.70	1.88	TiAl ₂	
1 in Fig. 1(d)	3.79	61.48	29.32	4.21	1.20	TiSi ₂	+1.27 [for Al(4)Si(4) sample]
2 in Fig. 1(d)	1.14	48.10	46.24	3.15	1.37	TiSi	
3 in Fig. 1(d)	1.81	41.78	52.59	2.71	1.10	Ti ₅ Si ₄	
4 in Fig. 1(d)	72.60	0.89	24.81	0.21	1.49	TiAl ₃	
5 in Fig. 1(d)	66.30	—	30.73	1.14	1.82	TiAl ₂	
6 in Fig. 1(d)	31.41	24.08	40.10	2.90	1.50	Ti ₅ Si ₃	
1 in Fig. 1(e)	6.51	60.31	27.84	4.09	1.25	TiSi ₂	+1.30 [for Al(8)Si(8) sample]
2 in Fig. 1(e)	1.22	48.23	46.21	3.03	1.31	TiSi	
3 in Fig. 1(e)	0.94	41.61	53.48	2.68	1.29	Ti ₅ Si ₄	
4 in Fig. 1(e)	65.26	—	33.06	0.10	1.58	TiAl ₂	
1 in Fig. 1(f)	6.80	60.70	28.85	2.41	1.23	TiSi ₂	+1.34 [for Al(10)Si(10) sample]
2 in Fig. 1(f)	1.41	48.35	46.89	1.94	1.41	TiSi	
3 in Fig. 1(f)	72.43	1.10	24.56	0.42	1.48	TiAl ₃	
4 in Fig. 1(f)	29.61	24.01	41.80	2.75	1.82	Ti ₅ Si ₃	
5 in Fig. 1(f)	66.81	—	30.40	1.08	1.71	TiAl ₂	

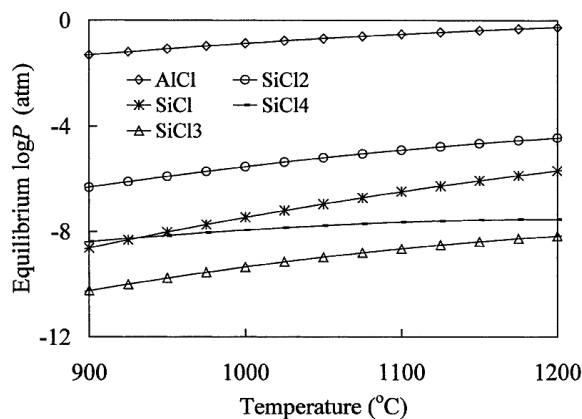


Figure 2. Comparison of partial pressure of aluminum chloride and silicon vapor in powder mixture with the composition of 5wt.%Si + 2wt.%Al + 2wt.%AlCl₃ + 91wt.%Al₂O₃ [37]

between the activator and Al and the formation of aluminum chloride vapor, then the depositing element of silicon contained in the powder mixture react with AlCl₃ activator and silicide layers forms by silicon diffusion into the TiAl₃ aluminide layer.

Considering that in the simultaneous diffusion of aluminum and silicon in diffusion pack cementation process using AlCl₃ activator, gas phase transfer is a process controller, therefore, any factor that increases the partial pressure of aluminum and silicon chloride vapor inside the chamber can affect the microstructure and phase structure of the coatings obtained. One of the factors affecting the partial pressure of aluminum and silicon chloride vapor is the chemical composition of the powder mixture. According to Figs.1(b) to 1(f), it can be seen that in general, by increasing the content of depositing elements of pure aluminum and silicon in the powder mixture, the partial pressure of the chlorides vapor produced as a

result of reaction between above mentioned elements and AlCl_3 activator inside the chamber increases and leads to increase the flux of active aluminum and silicon atoms on the surface of the specimen and as a result, the overall thickness of the aluminide/silicide coatings is increased.

The chemical composition of the powder mixture also affects the phase structure of the coatings; as in Figs. 1(b) and 1(c), the first silicide phase formed on the outer layer is TiSi , while with the increase of silicon content in the powder mixture, the outer silicide layer is TiSi_2 as shown in Figs. 1(d) to 1(f). In fact, these microstructures show that the amount of flux of active silicon atoms on the surface of the $\text{Al}(1)\text{Si}(1)$ and $\text{Al}(2)\text{Si}(2)$ specimens is not enough to provide the required concentration for the formation of the richest titanium silicide phase (TiSi_2) and therefore, the first phase is formed on the outer layer of these specimens is TiSi . On the other hand, by increasing the content of the depositing element of silicon in the powder mixture ($\text{Al}(4)\text{Si}(4)$, $\text{Al}(8)\text{Si}(8)$ and $\text{Al}(10)\text{Si}(10)$ specimens), the amount of flux of active silicon atoms on the surface of these samples is sufficient to reach the required concentration for the formation of the TiSi_2 titanium silicide phase.

According to the sequential mechanism, in the early stages of the cementation process, a TiAl_3 layer forms on the surface of the $\gamma\text{-TiAl}$ alloy. Further, by decreasing the concentration of aluminum in the powder mixture, and especially around the specimen, the silicon depositing element reacts with the AlCl_3 activator in the powder mixture. Regarding the morphology of the coatings, the first step of siliconizing should include the diffusion of the silicon into the TiAl_3 layer and the formation of TiSi_2 and TiSi layers. If the amount of Si in the powder mixture is low (Fig. 1(c)), the first phase formed will be TiSi , and if the amount of silicon element is high in the powder mixture (Figs. 1(d) to 1(f)), the first phase formed will be TiSi_2 .

In general, the solubility of Al in all titanium silicides is very limited and less than 2 at.%, while the solubility of Si in the TiAl_3 has been reported to be about 7 at.% [38, 39]. Due to the solubility limitation of Al in TiSi_2 and TiSi , the aluminum is released into the TiAl_3 phase and on the $\text{TiSi}/\text{TiAl}_3$ interface during

the formation of the above mentioned layers on TiAl_3 (Fig. 3(a)). This leads to the formation of an aluminum atomic flux (J_{Al}) toward the TiAl_3 layer. Also, due to the reaction of silicon in the powder mixture with AlCl_3 and the formation of silicon chlorides, there is naturally a silicon atomic flux (J_{Si}) on the surface and towards the TiAl_3 layer. After the initial stages of siliconizing and formation of TiSi_2 and TiSi layers, the silicon atomic flux (J_{Si}) to the $\text{TiSi}/\text{TiAl}_3$ interface is decreased compared to the early stages of siliconizing, because: 1- the amount of silicon contained in the powder mixture and around the specimen is decreased with time, and 2- the active silicon atoms introduced on the surface should pass through the TiSi_2 and TiSi layers for reaching to the $\text{TiSi}/\text{TiAl}_3$ interface. Considering the fact that the diffusion rate of Si through the TiSi and TiSi_2 layers is higher than the diffusion rate of Al within the TiAl_3 layer [40, 41], qualitatively, an inward flux imbalance between aluminum and silicon atoms is formed ($J_{\text{Si}} > J_{\text{Al}}$) (Fig. 3(b)).

By reducing the flux of active silicon atoms in the $\text{TiSi} / \text{TiAl}_3$ interface, as a result of the formation of TiSi_2 and TiSi layers on the TiAl_3 layer, the arrival of active silicon atoms to the front of the $\text{TiSi} / \text{TiAl}_3$ interface at this stage leads to the formation of Ti_5Si_3 or Ti_5Si_4 layers in contact with TiAl_3 . In the absence of sufficient flux of the active silicon atoms toward the $\text{TiSi}/\text{TiAl}_3$ interface, a large part of the titanium silicide phase formed in the two-phase region will be Ti_5Si_3 (Fig. 1(c)), and if the flux of the active silicon atoms toward the $\text{TiSi}/\text{TiAl}_3$ is high, a major part of the titanium silicide phase formed in the two-phase region will be Ti_5Si_4 (Fig. 1(e)). It is clear that the amount of flux of active silicon atoms toward the $\text{TiSi}/\text{TiAl}_3$ interface is directly related to the amount of silicon depositing element used in the powder mixture.

However, since the silicon flux within the (Ti_5Si_3 or Ti_5Si_4)/ TiAl_3 interface is much faster than the migration rate of the above mentioned interface, the amount of silicon exceeds the solubility of silicon in TiAl_3 and leads to interface instability (Fig. 3(c)). In this case, since $D_{\text{Si}} > D_{\text{Al}}$, any instability in the interface leads to the development of a non-planar interface, which further, forms a two-phase region consisting of

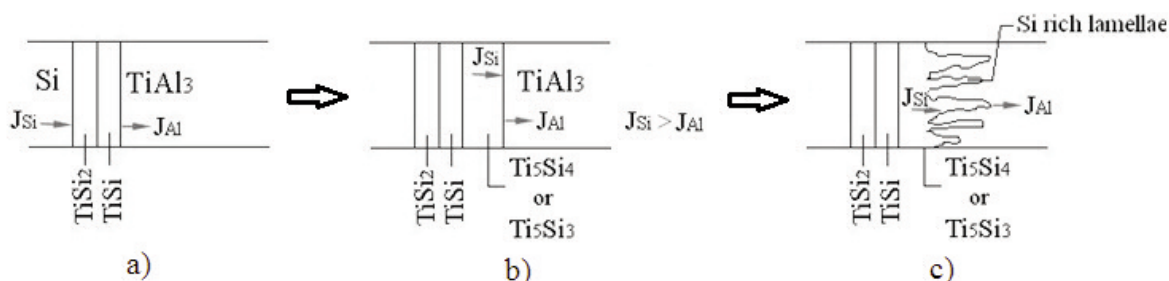


Figure 3. Schematic illustration of the stages of development of the aluminide/silicide coating on the $\gamma\text{-TiAl}$ alloy substrate

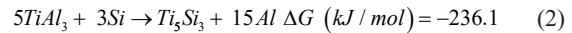
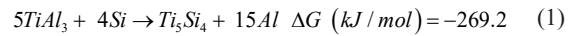
columnar layers of Ti_5Si_3 or Ti_5Si_4 within the $TiAl_3$ phase due to the growth process (Fig. 3(c)). The growth of the two-phase zone mentioned above is accompanied by the phenomenon of silicon segregation from the $TiAl_3$ phase in the Si-rich foreground regions, and Si-rich lamellas (Ti_5Si_3 phase) are formed within the $TiAl_3$ phase (point 4 in Fig. 1(f)).

According to Figs. 1(c) to 1(f), the formation of Ti_5Si_4 and Ti_5Si_3 phases inside the $TiAl_3$ phase is accompanied by the formation of porosities that in fact have made the two-phase porous separated structure. Furthermore, it can be seen that with increasing the percentage of depositing elements present in the powder mixture, the porosities made in the two-phase structure of coating have been increased significantly. Two possible mechanisms for porosity formation in the two-phase zone of the aluminide/silicide coating are the Kirkendall mechanism and the volume change mechanism.

As already mentioned, in the formation of an aluminide/silicide coating through the pack cementation process, there are always certain inward fluxes of depositing elements of aluminum and silicon (Fig. 3). However, during the progression of the Ti_5Si_4 and Ti_5Si_3 porous phases into the $TiAl_3$ phase, the inward flux of silicon and aluminum should be balanced by counter flux of vacancies. These vacancies tend to be absorbed in the interphase boundaries and eventually merged into cavities. The possible model for the nucleation of cavities at the (Ti_5Si_3 or Ti_5Si_4)/ $TiAl_3$ interface is shown in Fig. 4.

Regarding Figs. 1(c) to 1(f), another mechanism that could contribute to porosity formation in the two-phase zone of Ti_5Si_4 and Ti_5Si_3 within the $TiAl_3$ phase seems to be volume changes during the formation of Ti_5Si_4 and Ti_5Si_3 phases. According to the reactions 1 and 2, and $TiAl_3$, Ti_5Si_4 , Ti_5Si_3 , Si, and Al (Table 3), it can be seen that during the formation of the Ti_5Si_4

phase in the $TiAl_3$, the volume expansion is about %59.29, while this value was calculated to be %14.44 for the formation of the Ti_5Si_3 phase in the $TiAl_3$.



Based on the calculations, it can be concluded that significant volume changes can occur in the Ti_5Si_4 / $TiAl_3$ interface, which can lead to further stresses at this interface and formation of porosities. The amount of volume changes and consequently the resulting stress, caused by the formation of the Ti_5Si_3 phase in $TiAl_3$ is much less. Therefore, it can be concluded that during the formation of aluminide/silicide coatings, as the Ti_5Si_3 phase is formed and the Ti_5Si_4 phase is prevented, it actually decreases the porosity caused by volumetric changes.

According to Figs. 1(c) to 1(f), it can be seen that by reducing the amount of Si in the powder mixture and consequently reducing the flux of the active silicon atoms, the formation of the Ti_5Si_3 phase will be dominant and the total porosity formed in the two-phase zone will be decreased.

As previously noted, in the Al(0.5)Si(0.5), Al(1)Si(1), Al(2)Si(2), Al(4)Si(4), Al(8)Si(8) and Al(10)Si(10) specimens (Figs. 1(a) – 1(f)), J_{Si} was greater than J_{Al} and this led to the limitation of the rate of development of Ti_5Si_4 and Ti_5Si_3 by the rate of aluminum release, and then any instability in the (Ti_5Si_3 or Ti_5Si_4)/ $TiAl_3$ interface resulted in the non-planar development of interface and the formation of an non-ideal structure in the coating.

With the application of approaches to make J_{Si} closer to J_{Al} , it is possible to prevent the formation of non-uniform coatings. There are two strategies for this: 1- reducing the flux of Si; and 2- increasing the flux of Al.

In the present study, both solutions have been adopted simultaneously to improve the microstructure of aluminide/silicide coatings. The use of depositing element of Al in the powder mixture already increased the flux of Al atoms before the siliconizing process begins. In order to reduce the flux of the Si atoms, two approaches have been adopted: 1- reducing the Si activity by improving the chemical composition of the powder mixture; 2- reducing the Si activity by using Al-20wt. %Si powder alloy in the powder mixture.

In the Al(2)Si(1), Al(2)Si(0.5), Al(2)Si(0.3), and Al(2)Si(0.1) specimens (Figs. 5(a) to 5(d)), the reduction of Si activity was achieved by reducing the amount of pure Si in the powder mixture. In each case, the results of EDS analysis are also presented in Table 4.

In the Al(2)Si(1) specimen (1wt.% Si in the powder mixture), the aluminide/silicide coating from the outer surface to the substrate consists of a thin outer layer of TiSi, a two-phase layer containing very

Table 3. The unit cell volume of the phases involved in reactions 1 and 2 [42]

Phase	V(nm ³)
$TiAl_3$	0.1276
(Si)	0.1600
Ti_5Si_4	0.6602
Ti_5Si_3	0.2835
(Al)	0.0664

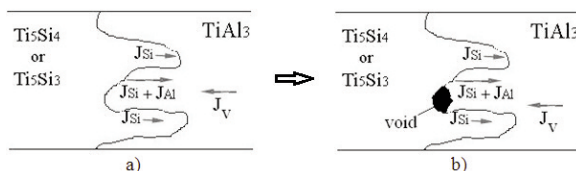


Figure 4. The model represents the porosity formation mechanism in the columnar structure

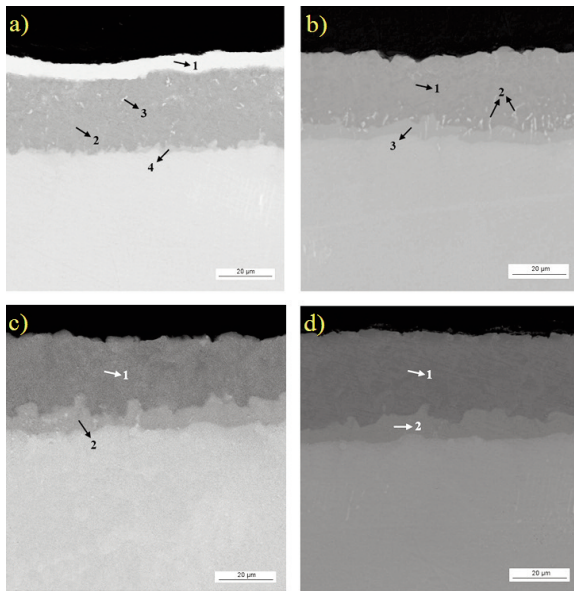


Figure 5. SEM cross-sectional micrograph of different samples after simultaneous aluminizing and siliconizing process at 1000°C for 6h a) Al(2)Si(1), b) Al(2)Si(0.5), c) Al(2)Si(0.3), and d) Al(2)Si(0.1)

thin lamellas of Ti_5Si_3 within the $TiAl_3$ phase and a continuous, very thin $TiAl_2$ inner layer, respectively.

By decreasing the weight percentage of pure Si from 1 wt.% to 0.5 wt.% in the Al(2)Si(0.5) specimen, the structure of the dense coating of titanium silicide in the outer layer is no longer observed and the resulting coating contains a $TiAl_3$ layer with Si solubility of 1.06 at.% and a continuous, very thin inner layer of $TiAl_2$. Indeed, in this specimen, due to the low amount of Si in the powder mixture, the Si activity on the surface of the coating and, consequently, the flux of the Si, decreased in the

specimen, and by decreasing the amount of Si, a certain amount of dissolution between Si and $TiAl_3$ occurred and an alloy phase of Ti (Al,Si)₃ formed on the surface of the coating. Of course, during the counter diffusion of silicon, in some areas where the amount of silicon in them is greater than the solubility of Si, very thin Si-rich lamellas are formed in the $TiAl_3$ phase shown in Fig. 5(b) with point 2. By decreasing the amount of pure silicon in the powder mixture to 0.3 wt.% and 0.1 wt.% in the Al(2)Si(0.3) and Al(2)Si(0.1) specimens respectively, it is observed that the coating structure contains a thick layer of Ti (Al,Si)₃ alloy phase and thin, continuous inner layer of $TiAl_2$.

In the Al-20%Si(2), Al-20%Si(4), and Al-20%Si(10) specimens (Figs. 6(a) – 6(c)), Al-20wt.%Si alloyed powder is used instead of the depositing elements of aluminum and pure silicon in the powder mixture and a different structure was formed in which the chemical composition of each of its layers is shown in Table 5 for each specimen, respectively.

The structure of the coatings obtained in the above specimens is similar to Al(2)Si(0.3) and Al(2)Si(0.1) specimens, and consists of a thick outer layer of $Ti(Al,Si)_3$ alloy phase and a very thin, continuous $TiAl_2$ inner layer. The absence of separate titanium silicide layers in the outer layers as well as Si-rich lamellas within the $TiAl_3$ phase in the above specimens indicates that by using the above-mentioned alloyed powder as a depositing component in the powder mixture, the flux of Si is so low that causes small amount of counter diffusion of Si inside the $TiAl_3$ layer. As a result, only an alloy phase of $Ti(Al,Si)_3$ with a small dissolution of silicon is formed.

Table 4. The EDS analysis of the positions marked in Figs.5(a) - 5(d) and weight changes of Al(2)Si(1), Al(2)Si(0.5), Al(2)Si(0.3), and Al(2)Si(0.1) samples after aluminizing-siliconizing process

Position	Chemical composition (at. %)					Deduced phases	$\Delta w/w_0(\%)$
	Al	Si	Ti	Cr	Nb		
1 in Fig. 5(a)	0.69	47.57	43.59	6.72	1.43	TiSi	+1.19 [for Al(2)Si(1) sample]
2 in Fig. 5(a)	72.48	46.023	24.77	0.08	1.41	$TiAl_3$	
3 in Fig. 5(a)	33.20	23.76	39.49	2.24	1.31	Ti_5Si_3	
4 in Fig. 5(a)	65.40	—	30.84	1.86	1.90	$TiAl_2$	
1 in Fig. 5(b)	70.41	6.01	21.16	1.11	1.31	$TiAl_3$	+1.23 [for Al(2)Si(0.5) sample]
2 in Fig. 5(b)	34.72	22.84	37.92	3.11	1.41	Ti_5Si_3	
3 in Fig. 5(b)	66.10	1.74	29.65	0.65	1.86	$TiAl_2$	
1 in Fig. 5(c)	70.88	3.96	22.66	1.08	1.42	$TiAl_3$	+1.48 [for Al(2)Si(0.3) sample]
2 in Fig. 5(c)	66.86	1.93	28.58	0.74	1.89	$TiAl_2$	
1 in Fig. 5(d)	70.47	2.15	24.86	1.22	1.30	$TiAl_3$	+1.64 [for Al(2)Si(0.1) sample]
2 in Fig. 5(d)	67.09	0.87	29.05	1.04	1.95	$TiAl_2$	

Table 5. The EDS analysis of the positions marked in Figs.6(a) - 6(c) and weight changes of Al-20%Si(2), Al-20%Si(4), and Al-20%Si(10) samples after aluminizing-siliconizing process

Position	Chemical composition (at. %)					Deduced phases	$\Delta w/w_0(\%)$
	Al	Si	Ti	Cr	Nb		
1 in Fig. 6(a)	72.95	2.30	21.72	1.39	1.64	TiAl ₃	+1.64 [for Al-20%Si(2) sample]
2 in Fig. 6(a)	66.52	1.15	29.08	1.47	1.78	TiAl ₂	
1 in Fig. 6(b)	72.11	3.02	21.79	1.36	1.72	TiAl ₃	+1.74 [for Al-20%Si(4) sample]
2 in Fig. 6(b)	65.31	1.24	29.91	1.60	1.94	TiAl ₂	
1 in Fig. 6(c)	72.16	3.27	21.33	1.46	1.78	TiAl ₃	+2.73 [for Al-20%Si(10) sample]
2 in Fig. 6(c)	65.48	1.39	29.83	1.53	1.77	TiAl ₂	

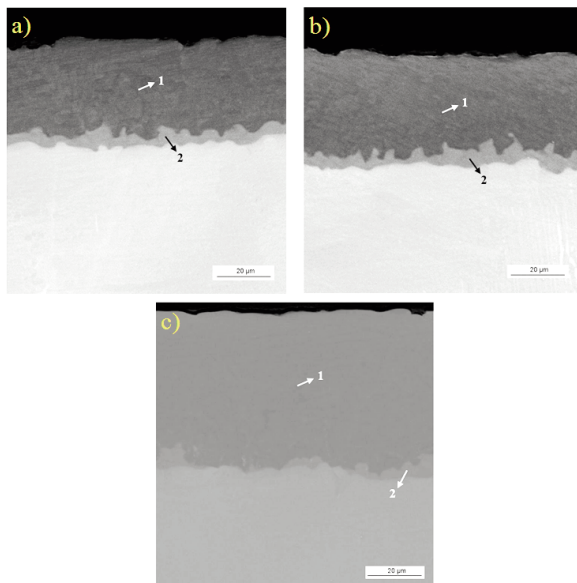


Figure 6. SEM cross-sectional micrograph of different samples after simultaneous aluminizing and siliconizing process at 1000°C for 6h a)Al-20%Si(2), b)Al-20%Si(4), and c)Al-20%Si(10)

Conclusion

1-The formation of aluminide/silicide coatings on γ -TiAl alloy through the gas-phase diffusion pack cementation method in the form of a dense outer layer of titanium silicide and a single inner layer of TiAl₃ indicates that the sequential mechanism is dominant in the formation of the above-mentioned coatings.

2-Qualitative study of morphology and phase structure of aluminide/silicide coatings showed that the Kirkendall phenomenon and volumetric changes could be considered as the two dominant mechanisms in porosity formation in the two-phase porous segregated region of the coating structure.

3-Reduction of silicon activity by reducing the amount of Si in the powder mixture or using Al-20wt.%Si alloyed powder has a beneficial effect on eliminating of porous structures in aluminide/silicide coatings. If 0.5 or 1 wt.% silicon is used in the powder mixture together with a constant amount of 2 wt.% aluminum, the aluminide coatings with small amounts of titanium silicide compounds are formed. In the case of using 0.1 and 0.3 wt.% Si in addition to a constant amount of 2 wt.% Al, or using Al-20wt.%Si alloyed powder in the powder mixture, two-layer aluminide coating is obtained, in which the outer layer is a thick layer of TiAl₃ with small amount of dissolved Si and the inner layer is a thin layer of TiAl₂.

References

- [1] G. Yang, H. Kou, J. Yang, J. Li, H. Fu, Acta Mater., 112 (2016) 121-131.
- [2] B. Bewlay, S. Nag, A. Suzuki, M. Weimer, Mater. High Temp., 33 (2016) 549-559.
- [3] F. Muhammad, E. Basuki, M. Juliansyah, Indones. J. Phys., 26 (2016) 13-16.
- [4] J.-C. Han, S.-L. Xiao, J. Tian, Y.-Y. Chen, L.-J. Xu, X.-P. Wang, Y. Jia, S.-Z. Cao, Rare Met., 35 (2016) 26-34.
- [5] R. Swadźba, L. Swadźba, B. Mendala, B. Witala, J. Tracz, K. Marugi, Intermetallics, 87 (2017) 81-89.
- [6] S. Nouri, S. Rastegari, S. Mirdamadi, M. Hadavi, Surf. Eng., 31 (2015) 930-933.
- [7] H. Jiang, S. Zeng, A. Zhao, X. Ding, P. Dong, Mater. Sci. Eng., A, 661 (2016) 160-167.
- [8] N. Cui, X.-P. Wang, F.-T. Kong, Y.-Y. Chen, H.-T. Zhou, Rare Met., 35 (2016) 42-47.
- [9] K. Bobzin, T. Brögelmann, C. Kalscheuer, T. Liang, Surf. Coat. Technol., 332 (2017) 2-11.
- [10] S. Nouri, S. Mirdamadi, S. Rastegari, M. Hadavi, Metallography, Microstructure, and Analysis, 4 (2015) 109-113.
- [11] J.-Q. Wang, L.-Y. Kong, T.-F. Li, T.-Y. Xiong, T. Nonferr. Metal Soc., 26 (2016) 1155-1162.



- [12] W. Li, M. Chen, M. Wu, S. Zhu, C. Wang, F. Wang, Corros. Sci., 87 (2014) 179-186.
- [13] M. Jovanović, B. Dimčić, I. Bobić, S. Zec, V. Maksimović, J. Mater. Process. Tech., 167 (2005) 14-21.
- [14] H.G. Jung, D.J. Jung, K.Y. Kim, Surf. Coat. Technol., 154 (2002) 75-81.
- [15] M. Yoshihara, K. Miura, Intermetallics, 3 (1995) 357-363.
- [16] Z.-H. Jiang, C.-Z. Zhao, H.-X. Zhang, II International Conference on Materials Engineering and Nanotechnology, 12-14 May 2017, Kuala Lumpur, Malaysia, 2017, pp. 012003.
- [17] S.Y. Park, D. Seo, S.W. Kim, S.E. Kim, J.K. Hong, D.B. Lee, Intermetallics, 74 (2016) 8-14.
- [18] V. Haanappel, J. Sunderkötter, M. Stroosnijder, Intermetallics, 7 (1999) 529-541.
- [19] H. Du, A. Aljarany, P. Datta, J. Burnell-Gray, Corros. Sci., 47 (2005) 1706-1723.
- [20] T. Nishimoto, T. Izumi, S. Hayashi, T. Narita, Intermetallics, 11 (2003) 225-235.
- [21] H. Jung, D. Wee, M. Oh, K. Kim, Oxid. Met., 55 (2001) 189-208.
- [22] S. Taniguchi, T. Shibata, K. Takeuchi, Mater. Trans., JIM, 32 (1991) 299-301.
- [23] H.-E. Zschau, M. Schütze, H. Baumann, K. Bethge, Intermetallics, 14 (2006) 1136-1142.
- [24] S. Taniguchi, T. Shibata, T. Yamada, X. Liu, S. Zou, ISIJ Int., 33 (1993) 869-876.
- [25] X.-B. Liu, R.-L. Yu, J. Alloys Compd., 439 (2007) 279-286.
- [26] V. Gauthier, F. Dettenwanger, M. Schütze, Intermetallics, 10 (2002) 667-674.
- [27] Z. Tang, F. Wang, W. Wu, Mater. Sci. Eng., A, 276 (2000) 70-75.
- [28] R. Yankov, A. Kolitsch, J. von Borany, A. Mücklich, F. Munnik, A. Donchev, M. Schütze, Surf. Coat. Technol., 206 (2012) 3595-3600.
- [29] P. Datta, J. Burnell-Gray, K. Natesan, Intermetallic Compounds-Principles and Practice: Progress, 3, (2002) 561-588.
- [30] Z. Xiang, S. Rose, P. Datta, Surf. Coat. Technol., 161 (2002) 286-292.
- [31] T. Sasaki, T. Yagi, Surf. Eng., 32 (2016) 809-815.
- [32] C. Zhou, H. Xu, S. Gong, K.Y. Kim, Mater. Sci. Eng., A, 341 (2003) 169-173.
- [33] M. Goral, G. Moskal, L. Swadzba, Intermetallics, 17 (2009) 669-671.
- [34] A. Rahmel, P. Spencer, Oxid. Met., 35 (1991) 53-68.
- [35] B.V. Cockeram, R.A. Rapp, Metall. Mater. Trans. A, 26 (1995) 777-791.
- [36] K.L. Luthra, Oxid. Met., 36 (1991) 475-490.
- [37] Z. Xiang, S. Rose, P. Datta, Mater. Sci. Eng., A, 356 (2003) 181-189.
- [38] J.S. Park, J.M. Kim, Materials, 3 (2010) 264-295.
- [39] F. Van Loo, G. Rieck, Acta Metall., 21 (1973) 61-71.
- [40] T. Munro, B. Gleeson, Metall. Mater. Trans. A, 27 (1996) 3761-3772.
- [41] F. Van Loo, J. van Beek, G. Bastin, R. Metselaar, Oxid. Met., 22 (1984) 161-180.
- [42] J. Park, J. Cho, B. Hur, J. Perepezko, Met. Mater. Int., 13 (2007) 1.

ISPITIVANJE MIKROSTRUKTURE PREVLAKA NA LEGURI γ -TiAl DOBIJENIH POSTUPKOM ISTOVREMENOG OBLAGANJA ALUMINIJUMOM I SLICIJUMOM

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Apstrakt

U ovom radu je ispitivano formiranje aluminidnih/silicidnih difuzijskih prevlaka na γ -TiAl[Ti-48Al-2Nb-2Cr (at.%)] leguri postupkom pakujuće cementacije. Primena smeša u prahu različitog hemijskog sastava tokom postupka pakujuće cementacije na 1000 °C tokom 6h da bi se postigla istovremena difuzija Al i Si, pokazala je da sastav smeše utiče na strukturu i debljinu aluminidnih/silicidnih prevlaka. Utvrđivanje i analiza aluminidnih/silicidnih mikrostruktura nastalih kao rezultat istovremene difuzije Al i Si, koja je prvi put urađena sveobuhvatno i kvalitativno tokom ovog istraživanja, pokazala je da je sekvencijalni mehanizam dominantan tokom formiranja gore navedenih slojeva. Osim toga, Kirkendalov efekat i zapreminske promene, do kojih je došlo zbog stvaranja Ti_5Si_3 i Ti_3Si_2 , smatraju se dominantnim mehanizmima za formiranje porozne segregatne strukture u ovim slojevima. U ovom radu su korišćena dva pristupa za ispitivanje uticaja smanjivanja aktivnosti Si na mikrostrukturne modifikacije prevlaka, a to su smanjenje količine Si u smeši u prahu, kao i korišćenje Al-20wt.%Si legiranog praha umesto čistih Al i Si elemenata. Rezultati su pokazali da smanjenje aktivnosti Si na površini sloja, kao i smanjenje kretanja aktivnih atoma silicijuma (J_{Si}), ima značajan uticaj na formiranje prevlaka sa idealnom strukturom.

Ključne reči: γ -TiAl legura; Pakujuća cementacija; Aluminidne / silicidni difuzorske prevlake.

