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Effect of Temperature on Pack Siliconizing of Ti6Al4V Alloy

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ABSTRACT

This study aims to investigate the temperature effects on silicide coating formed by pack siliconizing method on Ti6Al4V substrate. Pack siliconizing process was conducted out for 2h at 1000°C, 1100°C, 1200°C, in vacuum atmosphere, by using Si as Si source, Al_2O_3 powder as filler and NH_4Cl as an activator. The presence of the formed phases such as Ti_5Si_3, TiSi, $TiSi_2$ on coating, and non-stoichiometric Al_20_3 compound from the pack mixture was actualized by X-ray diffraction analysis (XRD). It was observed that the silicide coating on Ti6Al4V substrate is compact, dense and the coating thickness varies between 10.5-30.4 µm depending on the treatment temperature. The morphological features of the coating and dispersion of the elements in the silicide layer was examined by using electron microscope (SEM) and elemental analysis (EDS). Hardness of silicide layer measured by Vickers method and determined that the hardness ranges between 1170 $Hv_{0,025}$ to 1450 $HV_{0,025}$.

Keywords: Pack cementation, surface modification, silicide coating, intermetallic coating.

1 Introduction

In the last century, pure titanium and its alloys have been attracting both industrial and academic attention due to its superior properties such as good strength weight ratio, high ductility, good biocompatibility, high corrosion resistance [1]. While pure titanium can easily match desired design properties for low strength applications , for higher strength applications and more severe conditions, titanium alloys can perform better [2]. Accordingly, major titanium alloys such as Ti6Al4V, Ti-5Al-2.5Sn, Ti8Al-1Mo-1V, Ti6Al-2Sn-4Zr-2Mo, Ti6Al-2Sn-4Zr-Mo, Ti-8Mo-8V-2Fe-3Al have been used in higher technology applications in aerospace, biomedical, automotive industry. Even tough, titanium alloys exhibits challenging corrosion resistance until 550°C in engineering applications, due to $Ti0_2$ formation then surface would be prone to hot corrosion failure [3]. Therefore, material scientists have focused on surface modifications in order to improve both hot corrosion resistance and wear resistance. Many surface modifications such as CVD, PVD, thermal spray coatings, ion implantation, pack cementation method developed to answer this need [4–7]. Among these methods, pack cementation is known to be one of the

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most economic and capable of producing smooth and uniform final surface properties.

The most common pack cementation applications are aluminizing, chromizing, siliconizing in which source of coating material is aluminum, chrome, silicon respectively. These pack cementation methods are mainly used in aerospace and automotive engines as hot oxidation and wear resistant coatings. Comparing to the other coatings, which are used in hot engine sections of aerospace and automotive systems, such as thermal barrier coatings and CVD coatings, pack cementation methods appear to be one of the most cost-effective solutions for serial production. On the other hand, processs flow is much more easy and doable than other refractory coatings, even tough some scientists call pack cementation method as in-situ CVD due to its similarity in the process [6]. In previous papers, it can be noticed that mainly the focus has been on pack aluminizing and chromizing rather than siliconizing [8,9]. Nevertheless, in some aspects, pack siliconizing is more promising application for high temperature environments where the substrate can be exposed to high temperature oxidation and wear. Since coating would made of hard and stable intermetallic titanium silicides such as Ti_5Si_3, $TiSi_2$, TiSi, it can bear excessive temperatures up to 2000°C without substrate being effected by heat [10]. These properties may aid titanium to be used in applications that normally it cannot be used by its own nature. Authors aim to contribute to the literature by applying pack siliconizing on Ti6Al4V alloy in optimum process period of 2 hours for different temperatures of 1000°C, 1100°C and 1200°C in order to understand the formation morphology, temperature-time correlation on layer growth and the mechanical properties.

2 Experimental Procedure

Ti6Al4V plates to be coated, were cut into 20x20x2 mm square shape. Since titanium is very active metal, substrate plate surfaces have been grinded with 120, 240, 320, 600, 800, 1000, 1200 grit sand paper before pack process in order to remove either oxides or impurities on surface.

Pack has been prepeared with the stoichiometrically arranged powder mixtures of NaH_4Cl as activator, pure silicon as silicon source and Al_20_3 as reactive. Surface grinded samples were embedded into the pack mixture in an alumina crucible and covered with graphite to prevent oxygen diffusion to system as shown in Figure 1.

Pack siliconizing process was performed in vacuum atmospheric furnace with argon gas to prevent oxidation at the temperatures of 1000, 1100 and 1200°C for 2 hours and cooled in the furnace till to room temperature. After siliconizing process cross-sections of surface coated samples were prepared metallographically for microstructural studies.

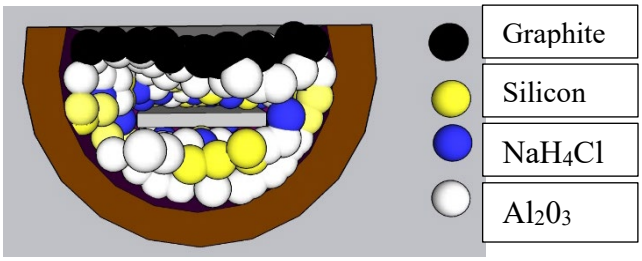


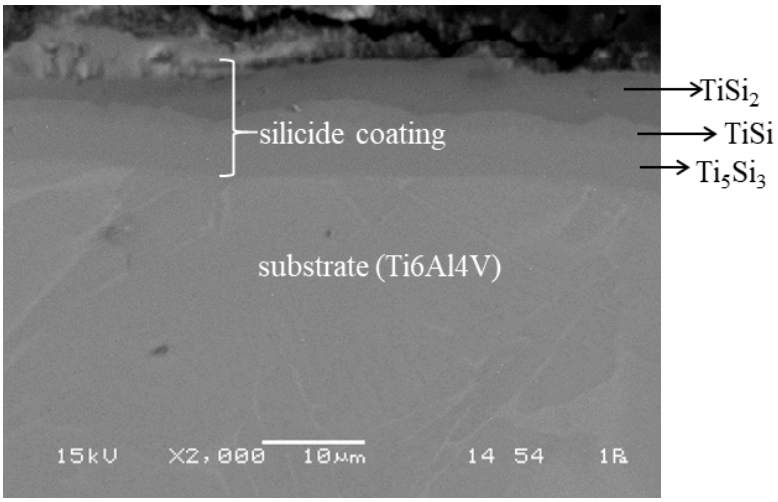
Figure 1 Schematic illustration of pack mixture for pack siliconizing process of Ti6Al4V

Microstructure examination of siliconized Ti6Al4V specimens were performed by JOEL JSM-5600 model scanning electron microscope (SEM). Microhardness tests were conducted out by EMCOTEST DUROSCAN-70 to understand mechanical properties of the Silicide layers (Vickers Hv0.025). The

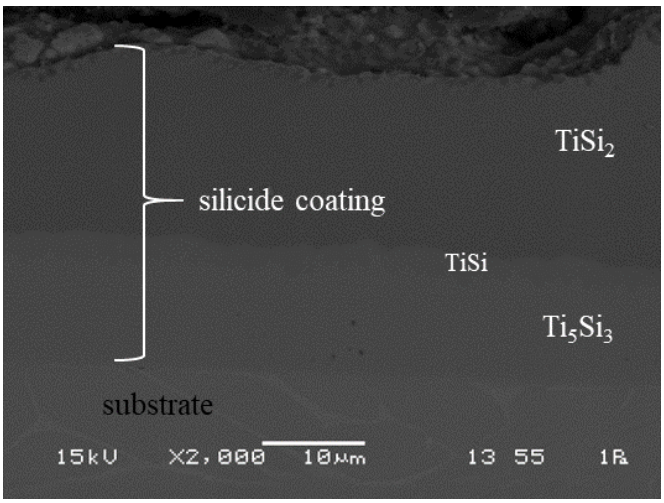
dominant phases, formed on the coating were identified by Rigaku X-ray diffractometer using CuKα radiation with 1,54056 A° wave length and 2 θ angle selected between 20° and 90°.

3 Results and Discussion

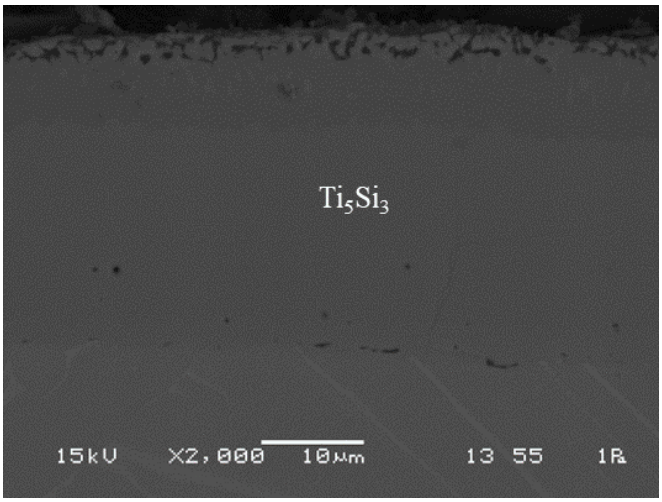
According to SEM examination given in Figure 2, it can be clearly noticed that formed coating surface has smooth morphology. In section-cut samples siliconized at 1000 and 1100°C there are mainly four obvious layers (Fig.2a, b). Based on XRD analysis, these layers are TiSi, $TiSi_2$, Ti_5Si_3 phases and the matrix (Fig. 3). On the other hand, EDS analysis revealed that Si concentration is more intense in outer layer than inner layers, shows that the first formed layer is $TiSi_2$ and turned into TiSi and Ti_5Si_3 with increasing treatment temperature (Fig. 4).



a)



b)



c)

Figure 2. SEM morphologies of Ti6Al4V alloy pack siliconized at a) 1000°C, b) 1100°C and c) 1200°C for 2 hours.

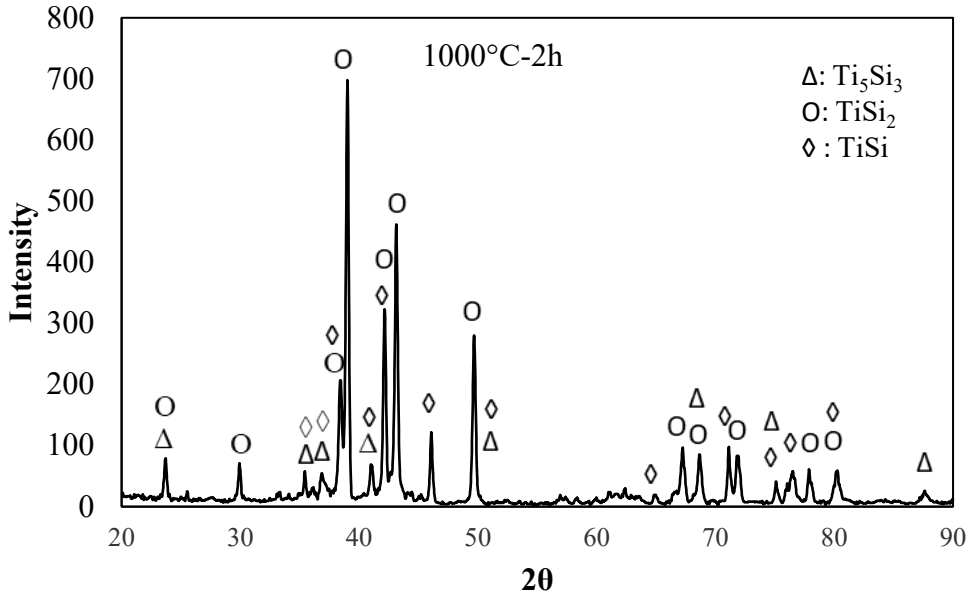
The reactions in the pack are basically so similar to CVD coating processes. Primarily, the reactions begin with the dissociation of the activator NH4Cl into NH_3 and HCl in temperatures more than 340°C (1). Secondly, HCl reacts with Si to form gaseous $SiCl_4$ (2). As gaseous SiCl4 contacts titanium substrate, the reaction between Ti and $SiCl_4$ leads into atomic Si formation in order to further solid state diffusion occurs on surface so that TiSi intermetallic multilayer coating forms (3) [11].

$$NH_4Cl(s)=NH_3(g)+HCl(g) \quad (1)$$

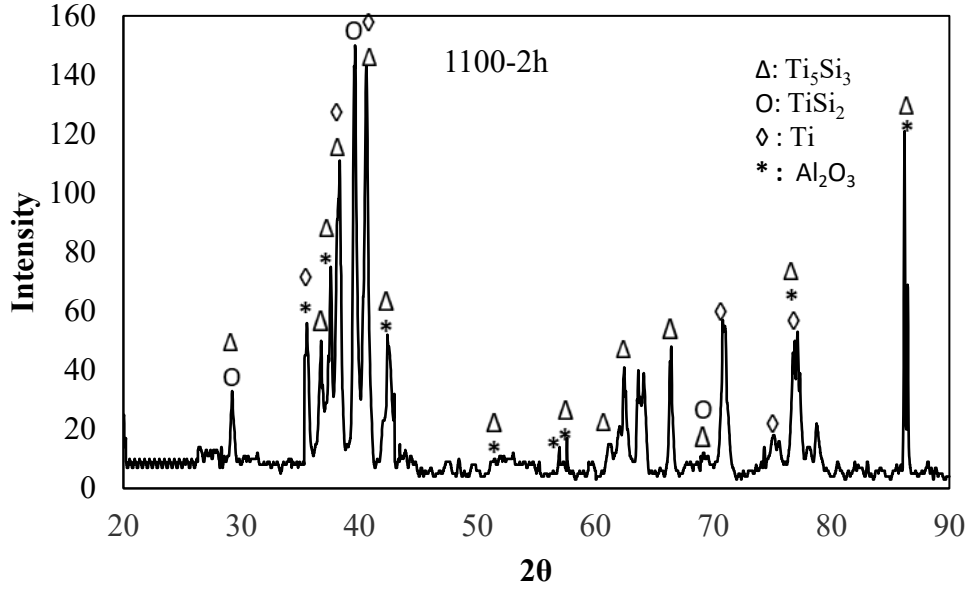
$$4HCl+Si=SiCl_4(g)+2H_2 \quad (2)$$

$$Ti+2SiCl_4+4H_2=TiSi_2+8HCl \quad (3)$$

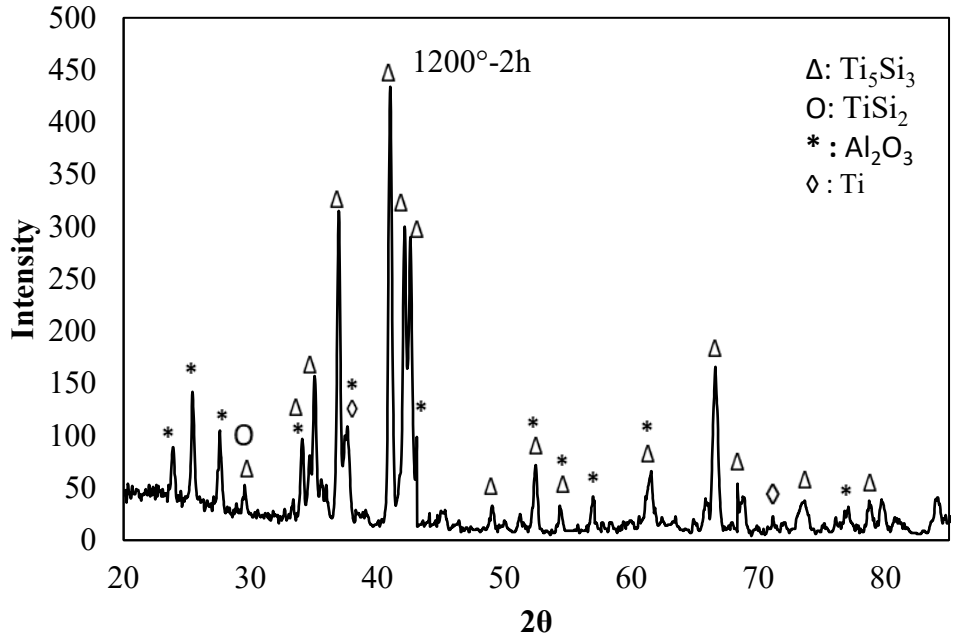
The coatings morphology is smooth and consist of multilayers as well as small amount of micro voids can be observed. The main reason why these voids form is that actually Kirkendall effect applies to the coating. Due to the difference of the mobility rates in diffusion couples such as aluminum-titanium in substrate matrix and silicon-titanium in coating, Kirkendall voids are likely to form in the system as in the process, silicon atoms move inwards meanwhile titanium atoms move outwards to form diffusion coating [12].


1000°C-2h
Δ: Ti_5Si_3
O: $TiSi_2$
◊ : TiSi
Intensity
2θ

a)


1100-2h
Δ: Ti_5Si_3
O: $TiSi_2$
◊ : Ti
* : Al_2O_3
Intensity
2θ

b)



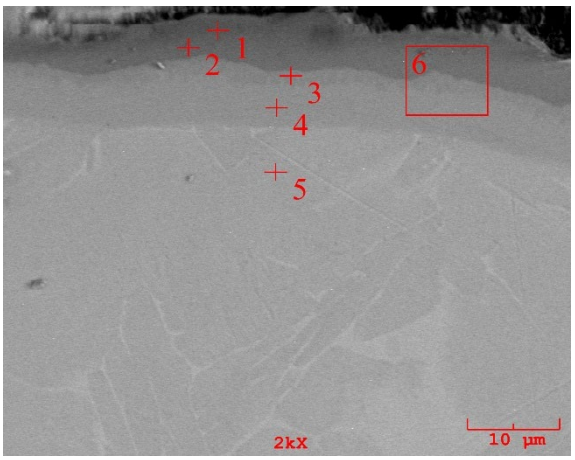
c)

Figure 3. XRD analysis of Ti6Al4V alloy pack siliconized at a) 1000°C, b) 1100°C and c) 1200°C for 2 hours.

As known from the previous works, thermochemical coatings such as chromizing, aluminizing, siliconizing etc. the layer composition and growth behaviours can be affected from both the substrate compositions and pack composition [13]. Since the siliconizing process driven by solid state diffusion, in order to understand the growth behaviour, it is highly important to understand the diffusion phenomena [14]. In diffusion coatings usually Arhenius equation applies and coating growth expected to be parabolic as function of time and temperature. It is highly mentioned that as temperature and time raises, the coating would be thicker. The equation is:

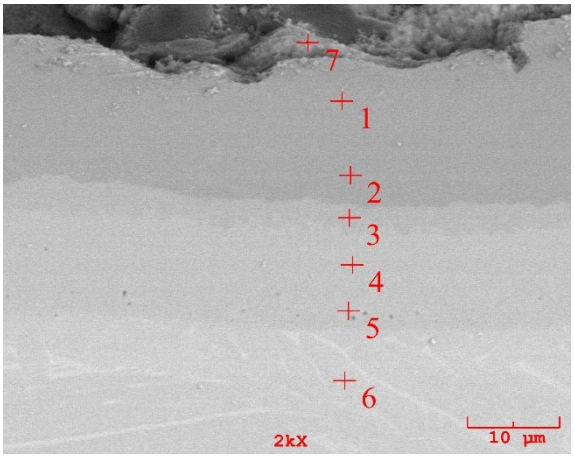
$L2 = KP \times t$

where L is layer thickness, KP is parabolic rate constant and t is siliconizing time [15].



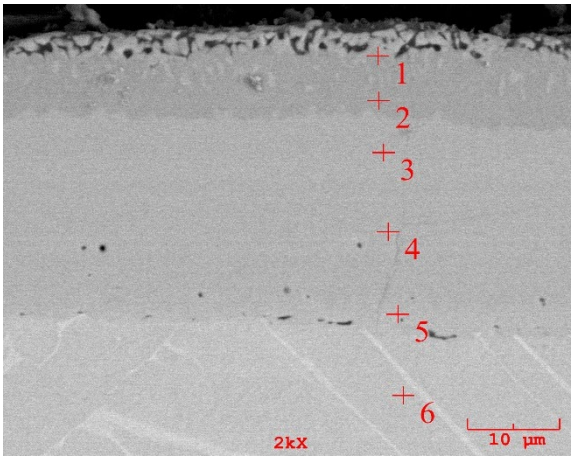
Marks	Elements, Conc. %				
	O	Al	Si	Ti	V
1	0.000	30.90	42.65	25.18	1.257
2	0.000	5.82	59.13	33.76	1.27
3	1.498	0.159	47.24	49.93	1.158
4	2.332	0.350	40.32	56.18	0.810
5	2.169	12.618	0.749	81.717	2.747
6	0.000	0.125	50.50	47.69	1.669

a)



Marks	Elements, Conc. %				
	O	Al	Si	Ti	V
1	1.783	0.268	59.69	38.25	0.000
2	1.450	0.238	60.46	36.26	1.575
3	2.229	0.138	42.909	53.256	1.468
4	1.657	0.288	38.09	58.46	1.494
5	1.423	0.086	37.22	59.09	2.178
6	1.046	9.991	1.329	85.80	1.825
7	4.013	1.766	59.37	34.84	0.000

b)



Marks	Elements, Conc. %				
	O	Al	Si	Ti	V
1	2.044	1.808	37.973	57.269	0.90
2	0.359	0.307	42.670	56.417	0.24
3	2.217	0.068	37.409	59.501	0.80
4	0.572	0.266	38.408	59.006	1.74
5	0.557	1.255	29.709	67.326	1.15
6	0.273	8.942	1.049	87.981	1.75

c)

Figure 4. SEM- EDS analysis of Ti6Al4V alloy pack siliconized at a) 1000°C, b) 1100°C and c) 1200°C for 2 hours.

The coating thicknesses respectively measured through SEM and were obtained 10.5, 27.45, 30.4 µm as result and given in the Figure 5. As temperature raised, the thicker coating layer has been obtained. It is seen that increasing temperature made the diffusion easer and the coating layer has grown parabolically similar to study done by Cotell et al [16].

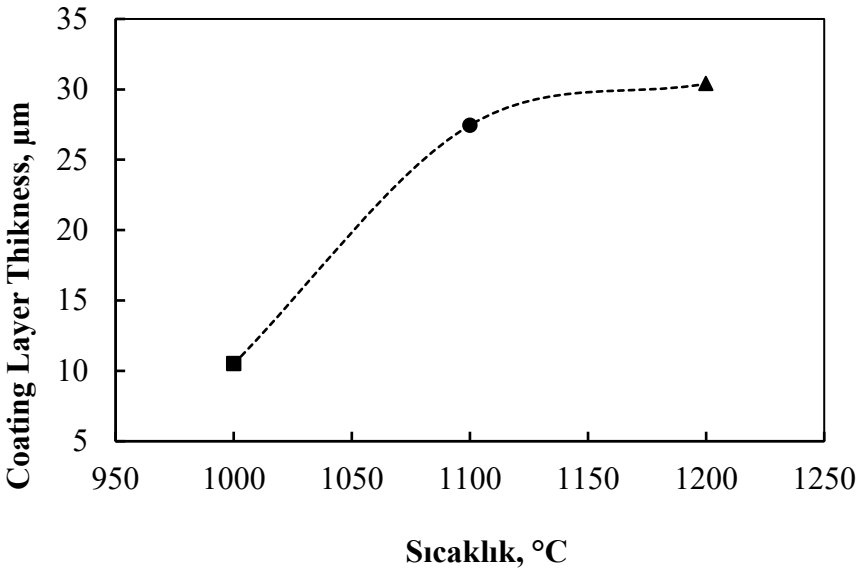


Figure 5. Variation of coating layer thickness of pack siliconized Ti6Al4V alloy versus treatment temperature.

By taking low silicon solubility in α-titanium into consideration, it can be revealed that β-titanium and silicon deposit, initiates a solid state reaction. Primarily, silicon diffuses into the substrate until it reaches to the critical point where titanium rich Ti3Si silicide begins to precipitate in Ti/Si interface near to substrate [17]. The solid-state reactions between substrate and silicon transforms into multilayer compact coating consist of various Ti_XSi_Y phases. Also, in another word, titanium has rather low mobility so that the first layer of the coating expectedly becomes titanium rich layer consist of equilibrium Ti_5Si_3 or Ti_2Si phases and then silicon rich phases such as TiSi, $TiSi_2$ will be formed according to TiSi phase diagram.

The obtained results indicate that the diffusion through the Ti_5Si_3 phase detected by XRD nevertheless some other titanium silicides are expected to present, but since their volume fractions are smaller than the detection limit of XRD, they could not be detected.

Above mentioned all diffusion-based reactions continues until all silicon source is ran out in the system. It can be also noted that in greater temperatures the number of layers significantly reduces.[18] The authors thinks that the underlying reason of this case is that the more temperature leads into the more interdiffusion between each layer.

The intermetallic multilayer coating mainly consist of Ti_5Si_3, Ti_2Si, TiSi, $TiSi_2$ phases is relatively almost 4 times harder than substrate Ti6Al4V material. While the substrate hardness was tested around 420 $HV_{0,025}$ the coating layer could reach up to 1450 $HV_{0,025}$. Hard coating layer exhibits hardness similar to TiN layers and it is highly wear resistant by its structure. It is also important to point it out that, coatings of the greater pack siliconizing temperatures, the harder both coating and substrate material became.

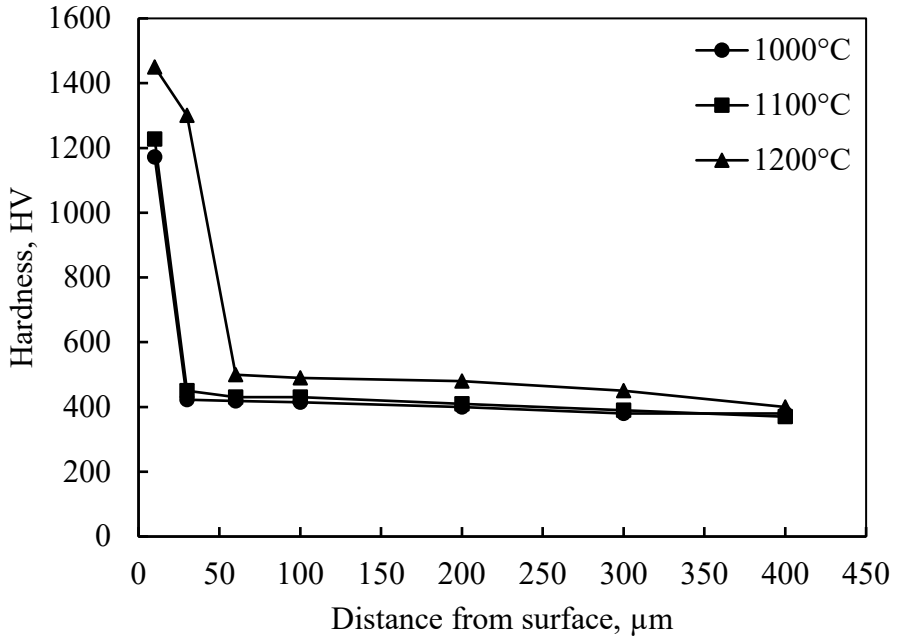


Figure 6. Microhardness distribution of silicide layer formed on Ti6Al4V alloy surface versus distance from the surface for 1000°C, 1100°C, 1200°C

4 Conclusions

In the present study following conclusions can be made:

1. The intermetallic compact silicide layers formed on Ti6Al4V are almost uniform and smooth.

2. There is a good bonding between the coating layers with the substrate material without any debonding.

3. The thickness of coating layer ranged from 10.5 to 30.4µm with increasing process temperature.

4. The coating layers confirmed by XRD and SEM analysis consists of multi phases such as $Ti5Si_3$, Ti_2Si TiSi and $TiSi_2$.

5. It was founded that the coating hardness increases for the coatings formed in higher temperatures and the hardness values ranges between 1170 $Hv_{0,025}$ to 1450 $HV_{0,025}$

6. It is concluded that process is highly depended on temperature. The coating layer grows almost parabolic and Arhenius law applied.

5 Declarations

5.1 Acknowledgements

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University of Applied Sciences, Faculty of Technology, Metallurgical and Materials Engineering Laboratory where the experimental studies carried out.

5.2 Funding source

No funding source.

5.3 Competing Interests

There is no conflict of interest in this study.

5.4 Authors' Contributions

1. Eşref Furkan TEPE: Contribution to the article. (Performing experimental study, organizing and reporting the data, taking responsibility for the literature review during the research, taking responsibility for the explanation and presentation of the results, taking responsibility for the literature review during the research.)

2. Tuba YENER:, Contribution to the article. (Taking responsibility for the creation of the entire manuscript or the main part organizing and reporting the data reworking not only in terms of spelling and grammar but also intellectual content or other contributions.)

3. Corresponding Author Gözde ÇELEBİ EFE: Contribution to the article. (Developing ideas for the research, planning the materials and methods to reach the results, taking responsibility for the experiments, taking responsibility for the explanation and presentation of the results, taking responsibility for the creation of the entire manuscript or the main part.)

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