Abstract

This study reports on silicide coating on Ti6Al4V alloy realized by pack siliconizing method at 1000°C for 8, 10 and 12 h using Si as Si source, Al2O3 powder as filler and NH4Cl as an activator. The morphology and presence of Ti3Si5, TiSi2, TiN and non-stoichiometric TiO compounds formed on surface of Ti6Al4V alloy was actualized by using classical metallographic techniques and X-ray diffraction analysis (XRD). A dense, compact silicide layer with a thickness of changing between 7.5- 9.7 μm were detected. Dispersion of the elements in the coating layer were investigated by using electron microscope (SEM) and elemental analysis (EDS). Hardness of silicide layer measured by using Vickers indenter was determined that the hardness was over 2000HV.

1. Introduction

Titanium and its alloys are promising materials because of their excellent properties, such as high specific strength, light weight and excellent corrosion resistance at relatively low temperature making them of interest for many automotive, military, aerospace and chemical industries [1- 4]. However, titanium alloys exposed to rapid oxidation at elevated temperatures and also has poor surface wear properties [1, 2]. This limits the highest operating temperature for structural components of Ti-based alloys [3]. Among various methods used for improving the oxidation resistance and wear properties of Ti-based alloys surface siliconizing has been extensively studied. Siliconizing is one of the surface hardening process where silicon atoms diffuse into solid metal at elevated temperature. It has been shown in many papers that the addition of Si produces hard silicide layers and increases the thermal, chemical, wear and creep resistance of these alloys [2, 3, 5- 7]. There are several methods modifying the surface of titanium with silicon. Laser surface alloying, silicon ion implantation, pack siliconizing, liquid phase siliconizing and vapour phase siliconizing have been extensively studied [2, 8]. The silicide layers are adherent and hard and can prevent oxidation of the metallic surface up to 950°C [9]. Pack siliconizing has distinctive advantages such as able to produce uniform coating of the substrate, easily controllable thickness, excellent adhesion between the coating and the substrate, minimum cleaning of parts after treatment, being applicable for a wide range of shapes and size, low environmental impact and low capital investment and low operation cost [5, 8]. In our work we focused on pack siliconizing method to fabricate hard silicide coating on Ti6Al4V alloy. Effect of siliconizing time on morphology, microstructure and microhardness of Ti6Al4V alloy was investigated.

2. Experimental Procedure

Ti6Al4V alloy in the form of annealed bars (10 mm in diameter) was used as the substrate for siliconizing. The samples of 5 mm in height were cut from these bars. Before siliconizing, the surfaces of the substrates were mechanically ground on SiC papers up to 1200 grit and polished with 1μm Al2O3 suspension, then washed and dried. Pack siliconizing powder mixtures mainly consisted of silicon source (pure silicon), activator (ammonium chloride) and filler material (Al2O3). The samples, embedded in silicon powder mixture and filled with graphite powder to prevent oxidation, were placed into the open atmospheric furnace in an alumina crucible for 8, 10 and 12 h at 1000°C then removed from the furnace and cooled in air. Microstructure studies of siliconized samples were performed by using a light microscope and scanning electron microscope (SEM). The adequacy of silicide coatings was also verified by microhardness measurements. The phases, formed on the surfaces of the coated samples, were identified with a Rigaku X-ray diffractometer using the Cu Kα radiation with a wavelength of 0.15418 nm over a 20 range of 10° to 90°.
and HCl at temperature higher than 340°C as presented in reaction 1. Then HCl reacts with Si powder and SiCl\(_4\) pass into the vapour phase with the reaction 2. SiCl\(_4\) gaseous diffuses to the substrate surface and reacts with Ti forming atomic Si as shown in reaction 3. Thus solid state diffusion of the coating element of Si on the surface of substrate occurs. Total reaction was given in reaction 4.

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\begin{align*}
\text{NH}_4\text{Cl(s)} & = \text{NH}_3(g) + \text{HCl(g)} \quad (1) \\
4\text{HCl} + \text{Si} & = \text{SiCl}_4(g) + 2\text{H}_2 \quad (2) \\
\text{SiCl}_4 + \text{Ti} & = \text{TiCl}_2 + \text{Si} \quad (3) \\
\text{Ti} + 2\text{SiCl}_4 + 4\text{H}_2 & = \text{TiSi}_2 + 8\text{HCl} \quad (4)
\end{align*}
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**Figure 1.** Optical microstructures of Ti6Al4V alloy pack siliconized at 1000°C for a) 8, b) 10 and c) 12 hours.

SEM-Map images of siliconized Ti6Al4V alloy in Fig.2 revealed that the coating having 8μm thickness includes N, Si, Ti and V elements. Si did not detect in the matrix and there is no diffusion zone beneath of coating.

**Figure 2.** SEM-Map images of Ti6Al4V alloy pack siliconized at 1000°C for 8 hours.

EDS analysis given in Fig.3 showed that the coating layer are consisting of Ti, Si and N. Presence of nitrogen in the coating layer probably caused from the NH\(_4\)Cl used as activator.

**Figure 3.** SEM- EDS analysis of Ti6Al4V alloy pack siliconized at 1000°C for a) 8, b) 10 and c) 12 hours.

Porosity was observed at the interface of coating and matrix material siliconized at 1000°C for 12 h. The probably reason is vapourizing of Cl gases with increasing siliconizing time. Also titanium and titanium alloys oxidizes easily in normal atmosphere and formed oxides on the surface of samples before siliconizing heat treatment maybe causes formation of porosity. In other to avoid from these oxides and gas vacancies, siliconising heat treatment must be in vacuum or controlled atmosphere. XRD analysis studies indicated that dominant phases formed in coating layer are Ti\(_5\)Si\(_3\), TiSi\(_2\), TiN and TiO and SiO\(_2\) (Fig. 4). Ti/Si oxide on the coating surface prevent the oxidation and wear of the coatings and also prevented the diffusion of the O towards to the matrix [4].
Layer thickness increased with increasing time but growth rate of layers progressively reduced with siliconizing time. Vojtech et al. claimed in their study that reducing growth rate of layer thickness with increasing time is in accordance with the parabolic law [4]:

\[ L^2 = K_P \cdot \tau \]  

where \( L \) is layer thickness, \( K_P \) is parabolic rate constant and \( \tau \) is siliconizing time. This means that the layer growth is governed by a slow solid state inward diffusion of Si and outward diffusion of Ti atoms. This equation can show that long duration of siliconizing time is not efficient on growth rate of layer thickness. It is seen from Fig. 1 and Fig. 3 that 12h siliconizing time increased the layer thickness slowly and the coating layer get more porous (Fig. 5a). Average microhardness of the coating layer was over 2100 HV which is nearly six times than that of matrix (330 HV) and increased with increasing siliconizing time. Such a considerable increase could be attributed to Ti-Si intermetallic compounds and TiN phases (Fig. 5b).

4. Conclusion

In the present study it was observed that the powder siliconizing at 1000°C for 8, 10 and 12 hours resulted in hard multi-phase surface layers composed of Ti-Si intermetalics such as Ti₅Si₃, TiSi₂, TiN phase, TiO and SiO₂ which confirmed by XRD analysis. The thickness of silicide layer appeared in white color ranged from 7 to 10 μm with increasing process time. There is nearly a parabolic relationship between layer thickness and process time in siliconizing heat treatment being a diffusional process. It was found that compound coating layers are very hard, possessing hardness values up to 2100 HV.

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References