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The effect of different methods to add nitrogen to titanium alloys on the properties of titanium nitride clad layers

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A R T I C L E I N F O

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In this investigation, titanium nitride (TiN) reinforcements are synthesized *in situ* on the surface of Ti–6Al–4V substrates with gas tungsten arc welding (GTAW) process by different methods to add nitrogen, nitrogen gas or TiN powder, to titanium alloys. The results showed that if nitrogen gas was added to titanium alloys, the TiN phase would be formed. But if TiN powder was added to titanium alloys, TiN + TiN_x dual phases would be presented. The results of the dry sliding wear test revealed that the wear performance of the Ti–6Al–4V alloy specimen coated with TiN or TiN + TiN_x clad layers were much better than that of the pure Ti–6Al–4V alloy specimen. Furthermore, the evolution of the microstructure during cooling was elucidated and the relationship among the wear behavior of the clad layer, microstructures, and microhardness was determined.

1. Introduction

Titanium alloys are widely applied in aerospace, chemical, petrochemical and marine industries because of their prominent properties of high specific strength, excellent corrosion resistance and high temperature properties. However, their poor wear resistance and high galling tendency, both of which prevent them from being widely applied as engineering tribological components [1,2]. Therefore, the surface modification of titanium alloys such as Ti–6Al–4V is necessary to improve their wear resistant properties for tribological applications. The literature reveals that a range of surface modification techniques have been applied to titanium alloys, including conventional thermochemical processes such as carburizing, nitriding, and boronizing all of which were developed approximately 60 years ago [3]. However, these processes have limited application because of high temperatures, long treatment time and nonuniformity of microstructure. In addition, problems correlative with significant reductions in fatigue limit and poor ductility have also been reported in the literature [4].

Recently, surface modification using a concentrated heating source such as laser or electron beam radiation permits the nitrogen into the titanium alloy surface melted zone to produce a hard and wear resistant layer of titanium nitride (TiN). Laser surface nitriding was initiated by the work of Katayama et al. [5] and since then there have been a number of researches, e.g. Refs. [6–10]. These treatments are accomplished through laser surface melting of the alloy in a nitrogen environment, which forms TiN. The melted zone consists of dendritic structures of TiN which are responsible for the high hardness at the surface. The laser nitrided commercial purity titanium (CP-Ti) is reported to produce surface hardness of about 2000 HV [11].

The electron and laser beam surface processing time is very short; however, they are limited by several factors, such as need for vacuum chamber, costly manufacturing procedure, and expensive initial investments. Moreover, the surface with some cracking in the laser nitrided layers being reported [12]. Weerasinghe et al. [13] showed that this surface cracking could be eliminated by preheating the substrate before laser melting. This has the effect of reducing the steep temperature gradients and, therefore, the thermal stresses generated during laser processing. However, preheating the substrate before laser melting is inconvenient.

Substitute heat sources, which can provide melting, such as gas tungsten arc welding (GTAW), which is utilized to form clad layers on the surface of metal substrates, is a less expensive method and has larger productivity comparing to the electron and laser beam surface processing because no special surface treatment is further required for the GTAW.

This study is an extension of earlier work [14], which has shown that, TiN powder was used as a nitrogen source; it was then clad onto a Ti–6Al–4V substrate by GTAW and while a shielding gas of argon was supplied. During the cladding process, the TiN + TiN_x reinforcing phase was formed *in situ* within the clad layer. Since the TiN + TiN_x reinforcing phase exists within the clad layer, the hardness of the clad layer is double that of the substrate. Wear test results reveal that the wear resistance of TiN clad layer is up to ten

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times more resistant than the Ti–6Al–4V substrate. In this study, the nitrogen source would be changed from the other way which was a shielding gas of nitrogen. The effects of the processing parameters on the microstructural evolution, mechanical properties and wear behavior in the Ti–6Al–4V surface are presented.

2. Experimental method

The Ti–6Al–4V was selected as substrate materials with the dimensions of $100 \times 19 \times 22\ \text{mm}^3$. Before the cladding process, the substrate surface that was to be clad was polished using sand paper to ensure that the surface was suitable for cladding. Fig. 1 schematically depicts the GTAW process and Table 1 specifies its parameters. The specimens were held stationary under the moving electric arc while a shielding gas of pure nitrogen was supplied. The GTAW equipment has an automatic traversing arm. The heat input of the process depends on the current used and it was calculated using the following equation [15]:

$$\text{Heat input} = \frac{\text{Current(A)} \times \text{Voltage(V)} \times 60}{\text{Electrode travel speed(cm/min)}} \quad \text{(J/cm)} \tag{1}$$

The microstructures and chemical compositions of the clad layers were observed with a field-emission scanning electron microscope (FE-SEM), energy dispersive spectroscope (EDS) and electron probe microanalysis (EPMA) device. The compounds and the phases of the clad layer were primarily examined with an X-ray diffractometer (XRD). Before the wear test, a Vickers microhardness test was carried out to measure the hardness along the direction deep into the clad layers and a nanoindenter was used to measure the hardness and elastic modulus of the phases in clad surfaces. The microhardness is measured in accordance with ASTM: E 384-11e1. ASTM: E 384-11e1 is the standard test method for Vickers Hardness. A pin-on-disc rotating type tribometer was used to evaluate the wear resistance capacity. A rotating upper specimen (pin) and a fixed lower specimen (disc) were mounted at the ends of a driving shaft and a fixed base, respectively. During dry sliding wear test, a personal computer was connected with a data acquisition system, which continuously monitored and recorded the coefficient of friction and normal force between the upper and lower specimens. The disc specimen was made of hardened AISI 52100 bearing steel with hardness of 63 HRC approximately, which is used as a standard counter specimen for wear performance evaluation. The Rockwell Hardness is measured in accordance with ASTM: E 18-11. To evaluate the wear resistance of the specimens, the wear test was performed under specific conditions, as listed in Table 2. Before wear tests, the contact surface of each disc specimen was polished using SiC abrasive paper of 600-grit to a surface roughness (Ra) of 0.06 μm. After the wear test, the worn surfaces of the specimens were observed by the FE-SEM. Then, the width of the wear scar on the worn surface was measured under a microscope and utilized to calculate the volume wear loss that was used to evaluate the wear resistance of the specimen. Each experiment was done three or more times in order to reduce the occurrence of errors.

Table 1
The GTAW process parameters.

Specimen	Current (A)	Voltage (V)	Travel speed (cm/min)	The method to add nitrogen
S1	60	8	16	N_2 gas
S2	60	8	8	N_2 gas
S3	120	16	16	N_2 gas
S4	120	16	4	TiN powder

Table 2
Dry sliding wear test conditions.

Parameter	Condition
Load (N)	40
Sliding speed (m/s)	0.9
Sliding distance (m)	540
Temperature (°C)	Room temperature

3. Results and discussions

3.1. Effect of processing parameters on TiN formation

The arc current, arc voltage, and electrode travel must be carefully coupled and adjusted to obtain TiN in the microstructure of the titanium alloy surface. The heat input is found to affect the thickness of the TiN clad layer as shown in Fig. 2. The results in Fig. 2 show that, melting of preplaced TiN powder along with a thick layer of base metal causes surface alloying and produce around 4 mm thick clad layer. Under all processing parameters used in this investigation, the clad layer thickness was observed to increase with increasing the heat input. It is because that cladding with higher heat inputs in nitrogen environment allows more nitrogen to dissolve and diffuse into the liquid melt and thus forms increased amount of TiN. The other reason is the formation of TiN occurs by exothermic reaction and the heat released from this chemical reaction increases the melt pool temperature, which is believed to be responsible to increase clad layer thickness.

3.2. Microstructural characteristics of the TiN clad layer

The X-ray diffraction patterns taken at the surface of the each clad layer are presented in Fig. 3, respectively. The results in this

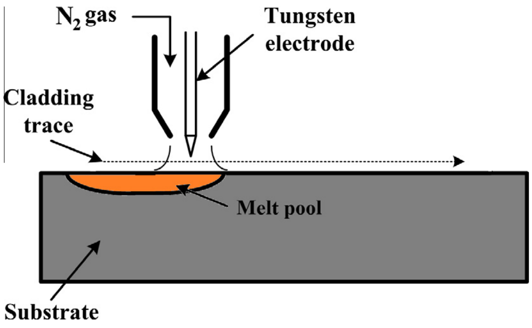

Fig. 1. Schematic illustration of the GTAW method.

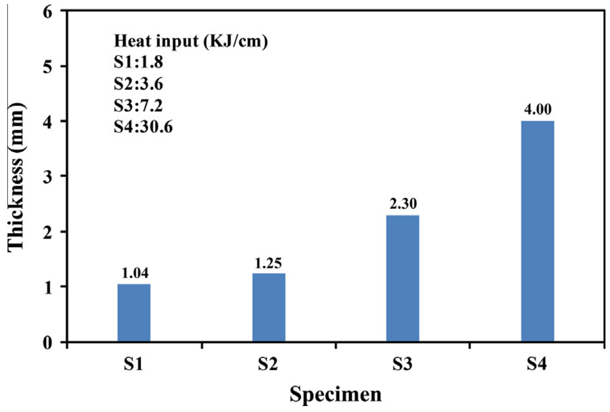

Fig. 2. Thickness of the clad layers for various heat input.