Fe-C-Si ternary composite coating on CP-titanium and its tribological properties

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Abstract. This study focused on the development of ternary composite coating through incorporation of Fe-C-Si ternary powder mixtures on CP-Ti substrate and characterizes the microstructure, hardness and wears behavior in presence of Jatropha oil. In this work, the surface of commercial purity titanium (CP-Ti) was modified using a tungsten inert gas (TIG) surface melting technique. The wear behavior of coated CP-titanium was performed using pin-on-disk machine. The results showed that the melt track has dendritic microstructure which was homogenously distributed throughout the melt pool. This Fe-C-Si ternary composite coating enhanced the surface hardness of CP-Ti significantly from 175 HV for the untreated substrate to ~800 HV for the Fe-C-Si coated CP-Ti due to the formation of intermetallic compounds. The wear results showed that less wear volume loss was observed on the composite coated CP-Ti in presence of Jatropha-biodiesel compared to uncoated CP-Ti. The achievement of this hard Fe-C-Si composite coating on the surface of CP-Ti can broadened new prospect for many engineering applications that use biodiesel under different tribological variables.

1. Introduction
Titanium is one of the few allotropic metals that exist in two different crystallographic forms. At room temperature, it has a close-packed hexagonal structure, designated as the alpha phase whereas, at around 884 °C, the alpha phase transforms into a body-centred cubic structure, known as beta phase which is stable up to titanium’s melting point of 1677 °C. Alloying elements promote the formation of one or the other of the two phases. Carbon, for example, stabilizes the alpha phase which means it raises the alpha to the beta transformation temperature. Iron, copper, chromium and vanadium are beta stabilizer which lowers the transformation temperature, therefore allowing the beta phase to remain stable at lower temperatures, and even at room temperature. Thus, titanium’s mechanical properties are closely related to these allotropic phases. For example, the beta phase will be much stronger but more brittle than alpha phase. Commercially pure titanium (CP-Ti) is unalloyed titanium characterized by an alpha phase hexagonal close-packed crystal structure. Commercially pure titanium is over
99.6% titanium with traces of carbon, iron, nitrogen, oxygen, and hydrogen [1]. However, CP-Ti has poor tribological properties due to lower hardness and high friction coefficient [2]. Therefore, it is utmost important to improve the tribological properties of CP-Ti especially under biodiesel lubricated condition through surface modification to increase the performance of the engineering components and extend their service life.

TIG welding was introduced as a surface alloying and modification technique in the late 19th century as an effective nitriding technique [3]. It was used as a reliable nitriding technique for the improvement of wear resistance of Ti-6Al-4V alloy. Later, several researches have been conducted addition research on the surface modification by cladding or surface alloying using this concept for ferrous material substrate [4]. Eroglu and Ozdemir [6] investigated the TIG surface alloying with preplaced graphite, chromium and high-carbon ferro-chromium powders on SAE 1020 steel. The result showed remarkable enhancement in wear resistance and corrosion resistance without impairing bulk properties.

Biodiesel is chemically comprised of alkyl mono-esters of fatty acids originally derived from vegetable oils or animal fats [7, 8]. “Biodiesel” is well known chemically as the mono-alkyl esters of long-chain fatty acids and is produced from several types of conventional and non-conventional vegetable oils and animal fats including those of used oils from the frying industry, soybean oil, rapeseed oil, tallow, rubber seed oil and palm oil [9, 10]. Biodiesel have better lubrication behaviour rather than diesel, which lubrication behaviour plays vital roles in pumping and injecting the fuel. It acts as an alternative green fuel which offers some technical advantages. The advantages of using biodiesel as a diesel engine fuel because it has the biodegradability, higher cetane number, and higher flashpoint and reduced greenhouse gases (GHG) emission [11]. It is very important to study the effect of biodiesel on the tribological behaviour of composite coated CP-Ti which is not available in literature. Therefore, the main aim of this work is to form a ternary composite coating layer via surface modification process under TIG torch melting and study the wear behaviour in jatropha biodiesel oil.

2. Processing route for hard surface layer

2.1. Materials
Commercially purity titanium (CP-Ti) plate was used with the dimension of this specimen was 50 mm x 40 mm x 12 mm. The specimen was abraded with coarse emery paper to remove the oxide layer as well as to obtain an even surface finish and degreased by using acetone clean from any dirt such as oil and dust. The Fe-C-Si ternary powder mixture was prepared using polyvinyl acetate (PVA). The biodiesel used in this research was synthesized from crude jatropha curcas oil (JCO) that was supplied by UNMAS, Malaysia. The chemical compositions of the free fatty acids in the crude jatropha oil.

2.2 Powder Preparation
Iron (Fe), silicon (Si) and carbon (C) ternary mixture were used with the composition 94%, 4% and 2% respectively. After measuring the powders (Fe, Si, and C) according to their compositions, it was gone through ball milling process. These powders were mixed for one hour of a speed of 200 rpm in order to make it homogenous mixture. The amount of Fe-C-Si powder mixture to be placed on the surface of CP-Ti was according to the ratio 1 mg/mm2. After the calculation, the amount of powder need to be placed on sample is 2g. For the pre-placement of powder, the binder PVA, distilled water and alcohol (ethanol) were used. The powder was first placed on the sample and makes slurry. Then, the powder was mixed with water and ethanol and binder (PVA). The binder is used in order to prevent the powder from blown away during the TIG melting process. The binder was mixed thoroughly with the powder until a paste like mixture was obtained. The specimen then dried in the oven at 80°C for 60 minutes.
2.3 Coating with Tungsten Inert Gas (TIG) Melting

In this experiment, TIG torch or arc was used as a heat source to melt the powder mixture in order to form a composite coating layer on the CP-ti substrate. TIG uses a non-consumable tungsten electrode to produce the torch. The melt area is protected from oxidation by a shielding gas. The shielding gas used is argon at a rate of 20 l/min.. The samples position was adjusted at 1 mm below the electrode tip. The arc voltage and current were, 30 V and 100 A respectively. Once the arc is struck, the torch in a small circle to create a melting pool, the size of which depends on the size of the electrode and the current. Then, the molten single track is allowed to be solidify at room temperature. The energy input for melting was calculated using an expression: \[ H = \eta \cdot V \cdot I / S \] where \( \eta \) is heat absorption efficiency equal to 0.45.

2.4 Material Surface Preparation

The CP-titanium plates were cut into required size and dimension using an EDM wire cut machine (model: W11FX2 K). A standard metallographic technique of grinding, polishing, and etching was used to prepare the samples for microstructure investigation and coating. Final polishing was done using diamond polishing paste. Then the cross sections of the coated materials were chemically etched for revealing their microstructure. The etching solution was prepared using 50% hydrofluoric acid (HF), 30% nitric acid (HNO3) and 20% of distilled water. The surface grinding process was done on the coated CP-Ti.

3. Results and Discussion

3.1 Microstructural Morphology

Figure 1 shows the microstructure of the coated layer which showed dendrites and are strongly bonded to the substrate after melting the Fe-C-Si particles which re-precipitated after being solidified. The melt microstructure also consisted of same unmelted Fe-C-Si particles (refer to Figure 1 (b)) along with the dendrites precipitates (Fig. 1 (a). The presence of particles always present at the bottom of the melt pool due to the mechanism of heating, stirring, and solidification [2].

Table 1 shows the matrix of the advantages and disadvantages of melting and diffusion processes on materials of the surface modification. It is important to understand of the process and to choose the best method in the application.

![Figure 1](image_url)

Figure 1. (a) Dendrites microstructure observed by SEM; (b) formation of unmelted Fe-C-Si particles (x200 magnification)

3.2 Microhardness of the Coated CP-titanium

The depth hardness profile was measured from the top surface of composite coating to the bottom of the composite coating layer and the hardness values are plotted against melt depth as shown in...
Figure 2. It can be seen from the profiles that the hardness through the pool is not stable. It is increasing and decreasing due to the different distribution of Fe-C-Si ternary powders. However, it can be seen that the hardness of the coated layer increased in comparison with that of the substrate. The diagram also shows that maximum hardness value in profile is near the surface and they gradually decrease towards the substrate. This is related to the concentration of the phases present in the modified layers. According to hardness profile, the maximum hardness was more than 800HV. This result showed that the surface hardness was significantly enhanced from 175 HV for the untreated substrate to 800 HV for the coated surface, due to the formation of intermetallic compound such as TiC and Fe3C in the modified layers.

![Microhardness Profile](image)

**Figure 2.** Microhardness profile across the coated layer via replacing powder of Fe-C-Si

### 3.3 Wear of Coated CP-Ti with and without Jatropha biodiesel

In this work, wear test was done for 10 minutes at a speed of 2.36 cm/s and load of 25N using wear testing machine. After the wear testing, the width and radius of the wear track for the sample were measured and recorded. Table 1 shows the wear test parameters and test results with and without jatropha biodiesel.

| Table 1. Wear test parameters for the samples with and without lubricants |
|-------------------------------------------------|
| Experimental Runs | Speed (cm/s) | Load (N) | Sliding distance (m) | Wear track radius (mm) | Wear tracks width (µm) | Wear volume loss (mm³) |
|--------------------|--------------|----------|----------------------|------------------------|------------------------|------------------------|
| Without lubricant  | 2.36         | 25       | 14                   | 1.5                    | 0.91                   | 727                    |
| With lubricant     | 2.36         | 25       | 14                   | 1.5                    | 0.59                   | 469                    |

From the Table 1, the difference of wear track width for each sample can be observed clearly. Moreover, when measured using Mitutoyo Surface Test SJ-400, there is a difference in wear track width between samples. It can be concluded that as for the sample under lubricated conditions, the wear track width is smaller than the one without lubricant. Figure 3 shows the depth of penetrations (Rz value) and average surface roughness (Ra value) measured by Mitutoyo Surface Test SJ-400 machine of coated CP-Titanium samples were tested under biodiesel lubricated condition and without the biodiesel lubricants.
Figure 3. Comparison depth of penetration (Rz value) and surface roughness (Ra value) for (a) sample under lubricated conditions (Rz = 4.20 um, Ra = 3.03 um) and (b) sample without lubricants (Rz = 12.48 um, Ra = 5.30 um).

The sample under the lubricated condition showed smaller Rz and Ra indicated that the presence of lubricants reduce the wear of the sample. Without lubricants, average surface roughness is larger than the one with the lubricants. The higher the Rz and Ra values leading to higher wear volume loss.

4. Conclusions

The CP-Titanium has been modified successfully by surface coating with ternary powder mixtures of Fe-C-Si using TIG melting technique in argon gas environment. This Fe-C-Si composite coating has increased surface hardness from 175 HV for the untreated substrate to more than 800 HV for the coated composite Fe-C-Si layers, due to the formation of intermetallic compound such as TiC and Fe3C in the modified layers. Then, the coated CP-Ti samples were tested for wear test under biodiesel lubricated conditions. It shows that less wear volume loss was observed on the composite coated CP-Ti in presence of Jatropha-biodiesel. Since, Fe-C-Si composite coating samples experienced less wear; it is preferable to use this material in many engineering applications that use biodiesel under different tribological variables.

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