Short Communication

Electrochemical boriding of titanium alloy
Ti-6Al-4V

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\textbf{ABSTRACT} & \\
Boriding is well known as a thermochemical surface hardening method, there are several types and compositions for carrying out this treatment. In this work, a novel method based on the electrochemical boriding applied on titanium alloy at 950 °C for 30 min, this method has an electromagnetic frequency in the range of 100–500 kHz during electrolysis has been proposed and realized on Ti-6Al-4V alloy. The results obtained showed a very fast formation of boride layer, for a few minutes, of a mono-phased layer with a thickness of 55 \textmu m and a micro hardness of 1850HV and low fracture toughness of boride layer Ti3B. The chemical and phase composition of the investigated layers strongly influenced their hardness and fracture toughness. & \\
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1. Introduction

Titanium alloys are among the most important of advanced materials, due to their good properties, such as low mass density, which is approximately 60% of the value of common steels, high resistance to oxidation, lightness, stiffness, high specific modulus and creep resistance. Titanium alloy is characterized by it good mechanical properties, good resistance to corrosion in many different aggressive environments, good resistance to wear, fatigue and creep resistance, good biocompatibility and high strength at relatively high temperatures, low Young's modulus similar to that of human bone \cite{1-3}. Titanium alloys employed in many applications; in aerospace, automotive industries, chemical industries and many biomedical applications used to fabricate surgical tools and dental implants \cite{4,5}. The increasing demand of titanium alloys in world production, the refinement of the processes and the new techniques developed have allowed a reduction of the production costs and a better satisfaction of the demand. Titanium and its alloys can be produced by powder metallurgy where powders are sintered to produce near-net-shape products, by casting, primary working and machining. However, the service of titanium and its alloys still limited in high execution industries, due to the production costs of titanium compared to other metals such as steel or aluminium and due to the high extraction of this metal. Thus, titanium is an expensive metal to process and extraction due to its good affinity to oxidation. In aerospace and biomedical applications, oxidation is considered as a serious problem. The oxygen able to decline the mechanical properties of titanium, oxide layers on titanium decrease the wear

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resistance and the ductility of titanium alloy even in small amounts [6–8].

Using of a surface coating on titanium substrate prevents any reaction between the titanium alloy and the corrosive agent, this coating must at least save the interesting functional characteristics that possesses of origin the substrate, or even increase them. As widely used surface modification in titanium and its alloys progressive in last years, boriding can form the hard boride layers on the surface by the diffusion of boron atoms into the substrate during the thermochemical surface treatment process [9–11]. Boriding is well known as a surface treatment process of diffusion of elemental boron into the substrate at high temperatures. Boriding in titanium and its alloys is carried out at the temperature range of 800–1000°C at 2 for 8 h, by a several methods counting solid, liquid, gas, plasma and electrochemical boriding. Boriding can be achieved by both chemical and electrochemical means. Among these boriding methods, the last one reveals some advantages such as a good mechanical properties and fast time process. In electrochemical method titanium alloy is immersed into the melts of boron salts and boron is reduced and deposited on the surface using a suitable potential. Elemental boron then diffuses into the metal structure. Boriding procedure results in the formation of TiB and/or TiB2 on titanium alloys depending upon the conditions used.

Some recent studies have focused on the diffusion of refractory elements such as Mo and Nb on titanium alloys [12–14]. In this context, it has been detected that the diffusion of these elements into the surface of some titanium alloys formed layers led to improvement in their oxidation. However, in terms of mechanical properties these studies are relatively limited to the fracture toughness and hardness of the surface. Therefore, it is necessary to improve the mechanical properties of this alloy. On the other hand, there are a few studies interrelated to the diffusion of boron element on titanium substrate by electrochemical process [15–17]. This study proposes to bring the effect of electrochemical boriding on titanium alloy Ti-6Al-4V substrate. The formation of boride layers formed on the surface was confirmed by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. This work study also the relation between the fracture toughness, micro hardness values and microstructural parameters, such as the grain size, the morphology and the thickness of grain boundary.

Thus, the main objective of this study revolved on the boriding treatment on titanium alloy Ti-6Al-4V applied with electrochemical process, and investigate some mechanical properties such as micro hardness and fracture toughness of boride layers formed on the surface. This work is analysed also the microstructure of boride layers formed on titanium alloy Ti-6Al-4V substrate and determine the phase transition and the interface morphology. Some mechanical properties were investigated such as micro hardness and fracture toughness.

2. Materials & methods

The material used is Ti-6Al-4V alloy in the form of a bar cylindrical, then cut to the desired dimensions. The nominal chemical composition of titanium alloy Ti-6Al-4V used is shown in Table 1.

Samples of Ti-6Al-4V alloy were initially polished up to 1000 grit size emery paper to achieve a nominal surface roughness and remove the oxide layers and other contaminants from the surface. The samples were ultrasonically cleaned in acetone bath and dried in air. The boriding experiments were carried out in a molten salt based on 90% borax (Na2B4O7) and 10% sodium carbonate (Na2CO3) at a constant temperature of 950°C for 30 min and a current density of 500 mA/cm2 in a stable. The electrolytic boriding cell was composed of SiC crucible, which played the role of anode while the sample was polarized as the cathode. An induction furnace at 100–500 kHz heated the electrolyte. Fig. 1 shows the schematic depiction of the electrochemical cell. After electrochemical boriding, the samples were removed from the electrolyte and let cool in the free area. Samples washed with acetone to remove any contamination.

To characterize microstructural features and mechanical properties, specimens were achieved to cross-section observations including grinding with SiC abrasive paper up to 4000, polished and etched with Kroll’s solution (10 vol.% HNO3, 5 vol.% HF, 85 vol.% H2O).

The microstructures of the samples were examined using an Optical Microscope (Leica), the cross-section of the samples was characterized by Scanning Electron Microscopy (TUSCAN) coupled with energy dispersive X-ray spectroscopy (EDX). SEM analysis was carried out in order to identify and quantify the magnitude of the interaction between the diffusion of boride layers and the titanium alloy substrate. X-ray diffraction was carried out using a Siemens D5000 diffractometer with monochromatic Cu Kα radiation. XRD patterns were measured in the range of 2θ = (20–90) with a scanning rate of 0.02°/s. Prior to cutting the treated samples, a Cu layer was applied by electro deposition in order to protect the underlying coatings/oxides during metallographic preparation. Samples for OM and SEM observations were prepared according to conventional metallographic techniques. More than 20 micrographs were used to measurement the average boride layers formed on the surface.

The micro hardness analysis presents a simple method to predict the mechanical properties of boride layer formed on the titanium alloy Ti-6Al-4V. Hence, it is beneficial to study the evolution of the micro hardness with the microstructure under different conditions. Moreover, the investigation of micro hardness is necessary for the processing and potential applications of the titanium alloy.

Micro hardness measurements of boride layers from the surface to the interior of the Ti-6Al-4V alloy substrate were measured by a micro hardness tester fitted with a standardized Vickers diamond indenter under a load of 100 g and at a dwell time of 20 s on the longitudinal section. Before the measurements, samples were prepared by conventional
metallographic techniques. For each case, at least five indentations were taken from companion specimens to check the repeatability of the results. The hardness values were the average of 5 measurements.

Fracture toughness ($K_c$) of the boride layers was estimated from the micro hardness values obtained and the cracks emanating parallel to the boride surface at the corners of the indent (1) as shown in Fig. 2, considering a set of applied loads ranging between 200 and 400 mN. The fracture toughness values were calculated by using the universal crack Eq. (1) proposed by Niihara [18] for Palmqvist crack geometries;

$$K_c = 0.048(\nu/a) - 1/2(HV/E\phi) - 2/5((HVa1/2)/\phi)$$

(1)

where $\nu$ is Palmqvist crack length, $a$ is half diagonal length of indent, $HV$ is hardness, $E$ is Young’s modulus and $\phi$ is constraints factor ($\approx$3).

The fracture toughness ($K_c$) of titanium boride coatings was calculated by measurements of the crack lengths using SEM, the boride layer Ti$_2$B exhibited the radial-median cracking mode as it was mentioned before.

### 3. Results and discussions

Phase analysis of boride layer formed by the proposed electrochemical method was performed to identify phases exist on the surface of titanium alloy Ti-6Al-4V substrate. It was achieved on a cross-section of titanium alloy Ti-6Al-4V treated, optical microscopy was exposed a lamellar structure at the interface as shown in Fig. 3. Fig. 4 shows the SEM image, it was indicated a mono phase layer of Ti$_2$B with average thickness about 55 μm. The dendrite form was also observed due to

![Fig. 1 - Schematic view of the illustration boriding process via electrochemical cell.](image1)

![Fig. 2 - Cracks of the boride surface Ti2B.](image2)
Fig. 3 – Optical microscopy of boride layer on Ti-6Al-4V alloy at 950°C for 30 min.

Fig. 4 – SEM of boride layer on Ti-6Al-4V alloy.

Fig. 5 – XRD analysis of the phase on Ti-6Al-4V.

observation of borides formed on the surface of hot work tool H13 steel shown the saw tooth morphology [19,20]. No significant differences were found between the behavior of boride layers formed on the surface of hot work tool H13 steel and carbon steel with regarding to the structure [21].

The pattern indicated boron amount and a small content of aluminum. However, there was no amount of vanadium due to the lack of a distinct peak, which could correspond to this phase, it confirmed the results of phase analysis by SEM.

The microstructure is composed of the lamellar structure, which can be credited to the evaluation of micro hardness of boride layer formed. Then, the hardness values increase with the increase of the growth rate of boride layers. In addition to the study of microstructure evolution and interface morphology. The Vickers hardness values of boride layer formed on the titanium alloy Ti-6Al-4V can be characterizing the strain hardening ability, which abilities the mechanical properties of directionally solidified titanium alloy to be predicted from the Vickers hardness values [22]. The hardness measurements have been taken for different titanium alloys, and it is observed that the phase compositions in titanium alloys have different contributions to the hardness with the change of the solidification conditions [23]. Thus, the microstructures of boride titanium alloy have an effect on their mechanical properties.

XRD analysis confirmed the presence of the phase Ti3B as shown in Fig. 5, boride layers consisted primarily of titanium borides, boron atoms diffused into the titanium surface via substitution procedure. The results of investigation of boride layer phase showed significant differences in the data obtained. The presence of such significant differences can be explained by the inability of XRD method to divide phases with close values of the lattice parameter. Results of phase analysis obtained by XRD method were compared with results obtained by microstructure exam.

The micro hardness profile of samples boride layers was determined in the polished non-etched cross-section of the specimens. The micro hardness value of boride layers was decreased from the surface to substrate, which is ranging from 1440 to 2260 HV, while the hardness of titanium substrate was about 370 HV. Fig. 6 shows the variation of the Vickers hardness with the increase of the growth rate as function of the depth into the substrate. The decreasing of micro hardness gradient from the boride layer to the titanium alloy substrate of shown relatively the same profile in comparison to diffusion layer was obtained for steel substrate [24]. It should be specified that the micro hardness values were influenced by
that formed in carbon steel, which was about 1440–2260 HV and low fracture toughness of boride layer Ti$_2$B. The chemical and phase composition of the investigated layers strongly influenced their hardness and fracture toughness.

References


