Short Communication

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

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A B S T R A C T

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 μm and a
micro hardness of 1850HV and low fracture toughness of boride layer Ti6B. 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 its good mechanical properties, good resis-
tance 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
[1–3]. Titanium alloys employed in many applications;
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 8h, 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 reserved 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

| Table 1 – Chemical composition of titanium alloy Ti-6Al-4V. |
|---------------------|--------|------|------|-----|-----|-----|-----|
| Element | Al | V | Fe | O | C | N | Ti |
| % | 6.15 | 4.0 | 0.27 | 0.20 | 0.04 | 0.03 | Balance |
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 (I) 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;

$$K_C = 0.048(\nu/a) - 1/2(HV/E\phi) - 2/5((HV a1/2)/\phi)$$  \hspace{1cm} (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 $\mu$m. The dendrite form was also observed due to the heterogeneous of the phase formed and the microstructure in the directional solidified Ti-64Al alloy. Nevertheless, the borides formed on the stainless steel substrate have a smooth and flat morphology when compared to borides formed on the surface of titanium alloy Ti-6Al-4V and SEM cross-sectional
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 Ti2B 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**


**4. Conclusions**

Ti-6Al-4V alloy was successfully borided with electrochemical boriding technique, it can be performed in 30 min at 950 °C, with electromagnetic frequency in the range of 100–500 kHz during. Microstructure, micro hardness, fracture toughness and some mechanical characterization of boride layers of that alloy were evaluated. The following conclusions can be drawn from this investigation:

The results obtained showed a very fast formation of boride layer, for a few minutes, of a mono-phased layer in a nominal boride layer thickness about 55 μm. The boride layers formed by electrochemical boriding were less thickly compared to the boride layers formed by past boriding of carbon steel. However, the formed boride layers in this study were much harder than the presence of the boride layer formed on the surface of titanium alloy. While the micro hardness of boride layers on steel ranged between 1400 and 1800 HV as it has been reported in the literatures [25–27].

The surfaces of the cracks shown a typical transcolony fracture pattern, which is often found in titanium lamellar microstructures. The transcolony fracture is referred to as crack paths either crossing the lamella or parallel to the lamellae direction [28]. When the direction of crack propagation is perpendicular to αl lamellaires, crack would cross a and l laths successively. The increase of the growth rate leads to the solute enrichment due to the decrease of the diffusion ability, leading to the fully β phase solidification changing to the peritectic solidification, and congruently the microstructure of lamellar structure.

Fracture toughness of titanium boride coatings (Ti$_2$B) obtained on the surface was evaluated, agreeing with the crack parameters achieved from Vickers indentation test, the boride layer obtained reveals radial-median crack mode and not an intermediate crack mode as obtained in the boride layers (Fe$_5$B) of carbon steel [29]. The results shown a low fracture toughness of titanium boride coatings ranging from 5.5 to 10.8 MPa/m$^{1/2}$. It should be noticed that the fracture toughness influenced by the morphology, microstructural boride layers formed on the surface of titanium alloy.

**Fig. 6 – Variation of the Vickers hardness as function of the depth into the substrate.**

Micro hardness of boride Ti$_2$B (HV)