Effects of electrochemical boriding process parameters on the formation of titanium borides

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In this study, the boriding of titanium via molten salt electrolysis was investigated in borax based electrolyte at various current densities (50–700 mA/cm^2), temperatures (900–1200°C) and process durations (1 min to 4 h). Thin film XRD results revealed that two main titanium boride phases TiB$_2$ and TiB was formed even after 1 minute of process time. Scanning electron microscopy (SEM) images conducted on the cross–sections demonstrated a bilayer boride structure composed of a continuous uniform TiB$_2$ phase and TiB whiskers that grew below the TiB$_2$ layer toward the substrate. Dependence of boride layer thickness and morphology on the process parameters was evaluated. The results of the study showed that temperature of boriding was the most critical parameter both on boriding rate and morphology of the boride layer. It was possible to grow 8 µm thick TiB$_2$ layer on titanium in 30 minutes of boriding at 1200°C.

INTRODUCTION

The demand for the development of new methods and alternative materials have been increasing in parallel to the industrial development and ever increasing concerns on energy and environment. Titanium and titanium alloys with their exceptional strength-to-weight ratios (even at high temperatures), high stiffness, toughness, and excellent biocompatibility [1–4] became one of the most important structural materials for a variety of demanding applications. However, poor friction and wear behavior of titanium and its alloys limits their usage for tribological applications [5–9]. Different surface treatments have been applied to titanium for improving their tribological behavior including thermo diffusion processes such as nitriding and pack boriding. Pack boriding has been applied to iron and steel parts for a long time resulting in very positive contributions on the working efficiency and service life [10, 11]. Since transition metal borides have attractive properties such as high melting points and high hardness at elevated temperatures, researches for the boriding of transition metals have been accelerated in last decade; particularly for the applications in cutting tools, automotive, casting, textile, food, and ceramic industries that friction dependent huge energy losses and intensive corrosion and wear occurs [12, 13]. At the moment pack boriding which uses solid precursors in the form of powder or paste, is the most widely used industrial boriding technique. However, this process is not as extensively used as other thermo diffusion processes because of the limitations (generation of significant amounts of solid wastes and toxic gaseous emissions and long duration) of the technique mainly because of its long duration of pack boriding extending to 40 hours of pack boriding process [10, 11, 14, 15]. Basically, boriding is a thermal diffusion process in which boron atoms diffuse into the work piece to form a range of metal boride phases [10, 11, 14–18].

Another alternative for boriding is electrochemical boriding, which provides a considerably fast growth rate for the formation of boride layers in an environmentally clean way without any ecological issues as experienced in the conventional pack boriding [16–22]. Potential of this technique has been clearly demonstrated with previous studies conducted by our research group [16, 19–22].

A previous study conducted in our research group on electrochemical boriding of titanium has shown that the growth rate of titanium boride layers on titanium substrate is higher than conventional pack boriding [19]. In this study, the effects of the other critical parameters such as current density and electrolyte temperature were examined in a systematic manner for evaluating their effects on the chemistry, morphology and thickness of boride layers. The knowledge gained with this work may offer a different perspective on the unexplored part of the electrochemical boriding of titanium.

1. MATERIAL AND METHODS

1.1. Experimental procedure

Mirror polished CP-Ti Grade 2 plates (size 10×50×1 mm) are used as a substrate material. Prior

to the electrochemical boriding experiments, they were ultrasonically cleaned in acetone.

Electrochemical boriding experiments were carried out at current densities ranging between 50–700 mA/cm^2, at electrolyte temperatures between 900–1200°C and for electrolysis durations of 1 min. to 4 h in a borax based electrolyte composed of 15% sodium carbonate (Na_2CO_3) and 85% borax ($Na_2B_4O_7$). A high frequency induction furnace (180 kHz, 5 kW, 7 A) was employed to heat electrochemical cell consisting of graphite crucible acting as an anode where the titanium substrate was polarized as a cathode (Fig. 1). During electrolysis, the temperature of the molten electrolyte was both measured by a Pt-PtRh13 thermocouple and an IR pyrometer.

Once electrochemical boriding was completed, the Ti samples were drawn out of the electrolyte and left in air to cool down then washed with boiling water to dissolve the solidified electrolyte on them.

1.2. Boride layer characterization

After the boriding treatment, titanium samples were sectioned and polished metallographically then etched by Kroll's solution to reveal the microstructure. The cross sectional morphology, thickness and chemical analyses of boride layers were inspected with SEM and EDS investigations (JSM-7000F Model Field Emission SEM and Oxford instrument INCA x-sight EDS unit capable of analyzing light elements).

The phase composition of the boride layer was characterized by the thin film X-ray diffraction analysis using CuKα radiation and with the grazing angle of 2° (XRD-Philips Model PW3710, 40 kV–40 mA).

2. RESULTS AND DISCUSSION

2.1 Effect of current density

Contrary to conventional boriding processes in which reduction of boron oxides is achieved through chemical reducing agents, in our case the reduction of boron oxides to atomic boron is realized through electrons produced during cathodic polarization of the substrate [10, 11, 22]. In electrochemical systems, in which reaction rate is controlled with charge transfer step, the magnitude of applied current is the major parameter for determining the thickness of the coated or modified layer. According to Faraday's first law, the amount of electrochemical decomposition is proportional to the quantity of electricity passed in electrolytic processes; hence the amount of reduced boron, and consequently the thickness of boride layer should be the function of the applied current. Within this perspective, current density experiments were conducted at various current densities (50–700 mA/cm^2) at a constant temperature (1000°C) and time (30 min.) in order to investigate the effect of current density on the structure and thickness of titanium borides.

The cross sectional SEM images of borided titanium at various current densities revealed the uniformly thick TiB_2 layer formations at all applied current densities (Fig. 2). A relatively low current density of 50 mA/cm^2 was sufficient to grow a compact TiB_2 layer. As observed in previous studies [19, 23–25] a whisker like growth of TiB phase took place below the TiB_2 layer. The magnitude of the applied current did not alter the appearance of TiB whiskers. Accordingly, the morphology of TiB exhibited the same needle structure at all current densities used in this study.

The current density dependent thickness variations of titanium boride layers (Fig. 3) showed that the applied current did not lead to a noteworthy alteration in the thickness beyond 100 mA/cm^2. The reason of the unremarkable influence of current density on thickness higher than 100 mA/cm^2 could be explained by the limiting effect of boron diffusion into the structure. Even though we increased the amount of reduced boron on the substrate surface with increasing current density, only limited amount of boron atoms was able to diffuse into the structure that was controlled by kinetics of boron diffusion into the TiB_2 layer.

The results of thin film XRD analysis of the borided surfaces at different current densities were given in Fig. 4. Only TiB_2 peaks were detected at all applied current densities due to the low penetration depth of X-rays with a glancing angle 2°.

As expected, the cell potential, thus the energy consumption of electrochemical cell, was getting higher with rising current densities (Fig. 5).

Overall, it could be deduced that the increase in the current densities did not trigger any major modifications in both the thickness and the morphology of boride layers, TiB_2-TiB.

2.2 Effect of electrolyte temperature

Boriding process temperature was investigated in a systematic manner to explore its effects on the growth of titanium boride layers. Since boriding is a diffusion based process, the temperature of boriding is one of the significant parameter to be considered. Temperature dependent experiments were carried out for a constant duration of 30 minutes, a current density of 300 mA/cm^2 and at temperatures ranging between 900–1200 °C.

The cross sectional SEM images of borided titanium substrates at various process temperatures showed that the boriding temperature caused considerable effects in the thickness of TiB_2 layer and the
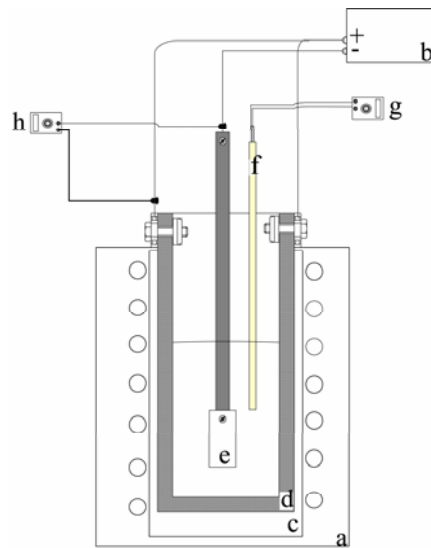
Fig. 1. Schematic drawing of the electrochemical boriding setup. *a* – High frequency furnace; *b* – Direct current source (±0.001mA); *c* – Alumina protector crucible; *d* – Graphite crucible acting as an anode; *e* – Cathode; *f* –Thermocouple in alumina protection tube; *g* – Multimeter (for temperature measurement); *h* – Multimeter (for cell potential measurement).
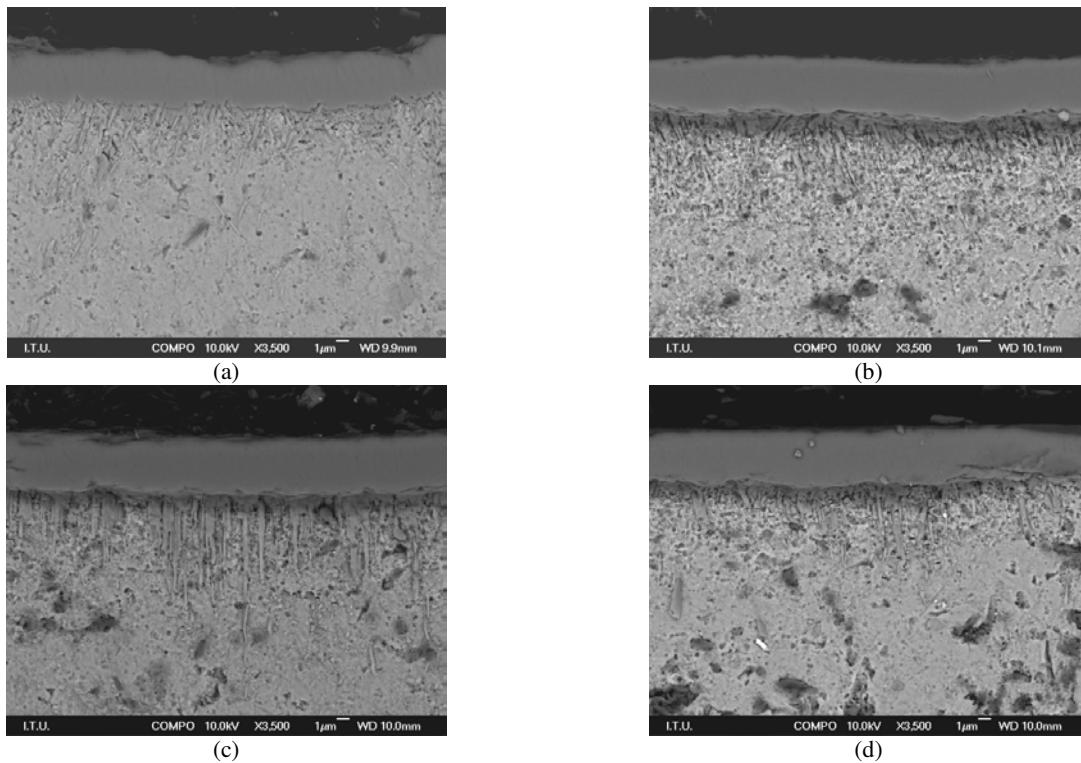

Fig. 2. Cross-sectional SEM images of boride layer produced at different current densities: (a) 50 mA/cm^2, (b) 100 mA/cm^2, (c) 200 mA/cm^2, (d) 700 mA/cm^2, [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 1000°C, 30 min.].
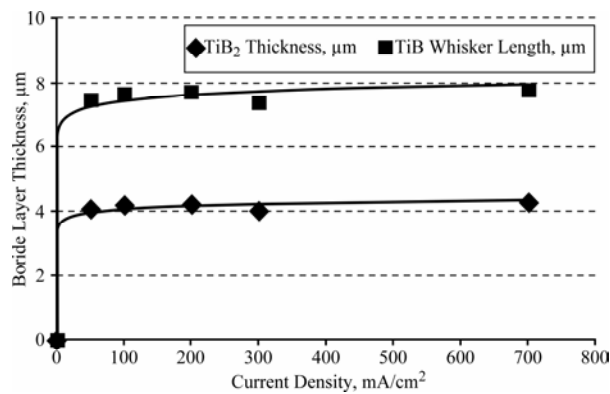

Fig. 3. Thickness variations of boride layers as a function of applied current densities [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 1000°C, 30 min.].
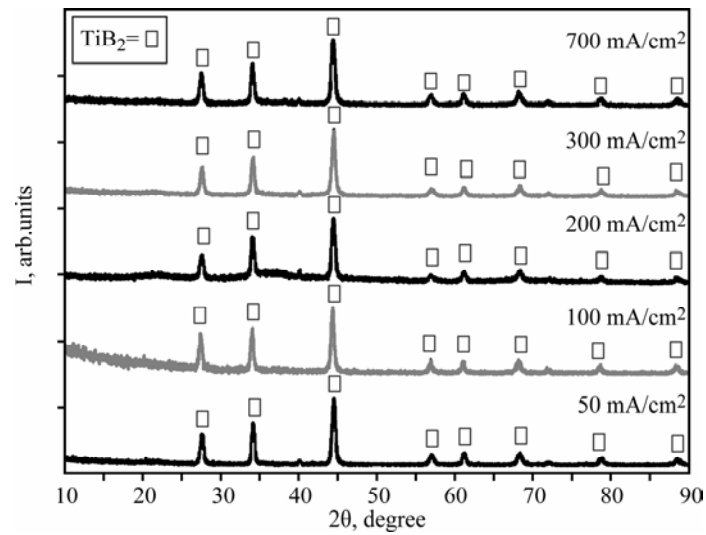
Fig. 4. XRD diffraction pattern of boride layers obtained at different current densities [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 1000°C, 30 min.].
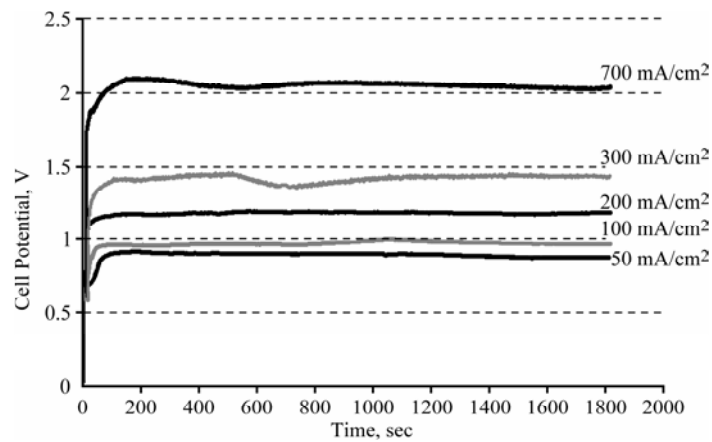

Fig. 5. Variation of cell potential at different current densities [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 1000°C, 30 min.].
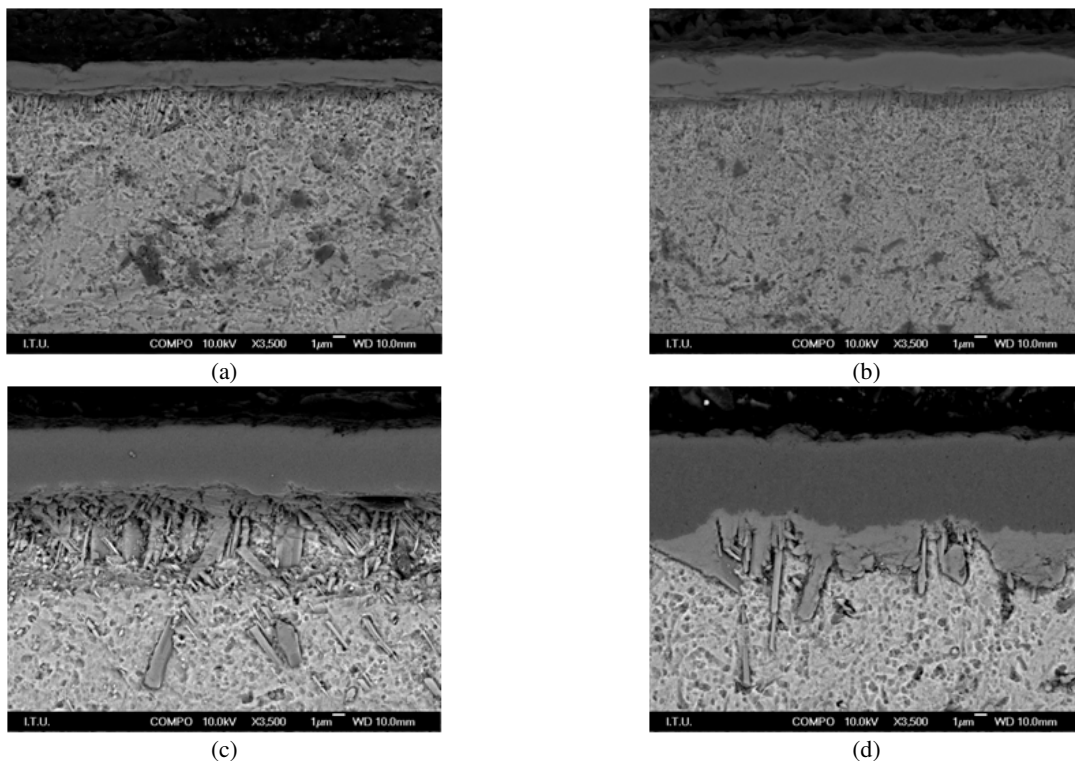

(a)

(b)

(c)

(d)

Fig. 6. Cross-sectional SEM images of boride layer formed on titanium substrate at different process temperature: (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 200 mA/cm², 30 min.].
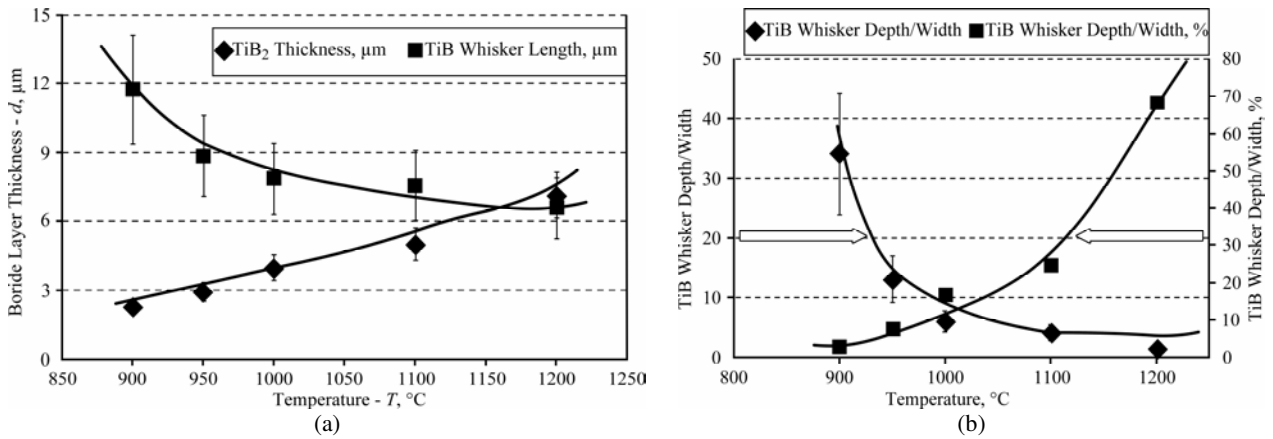
Fig. 7. (a) – variations of boride layers thicknesses with respect to boriding process temperature; (b) – the ratio of depth to width of TiB whiskers as a function of temperature [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 200 mA/cm^2, 30 min.].
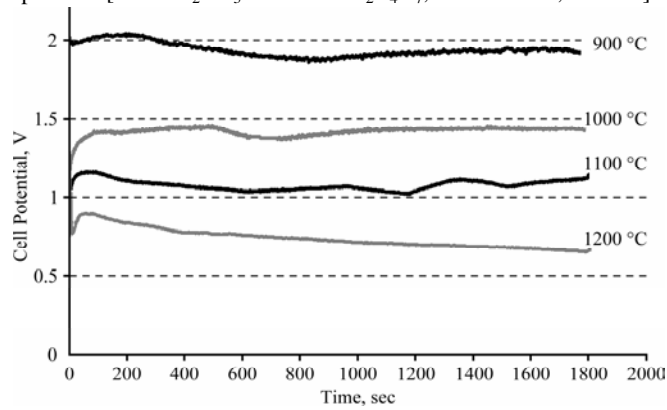

Fig. 8. Variation of cell potential at different process temperature during a 30 min long boriding experiment [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 200 mA/cm^2, 30 min.].
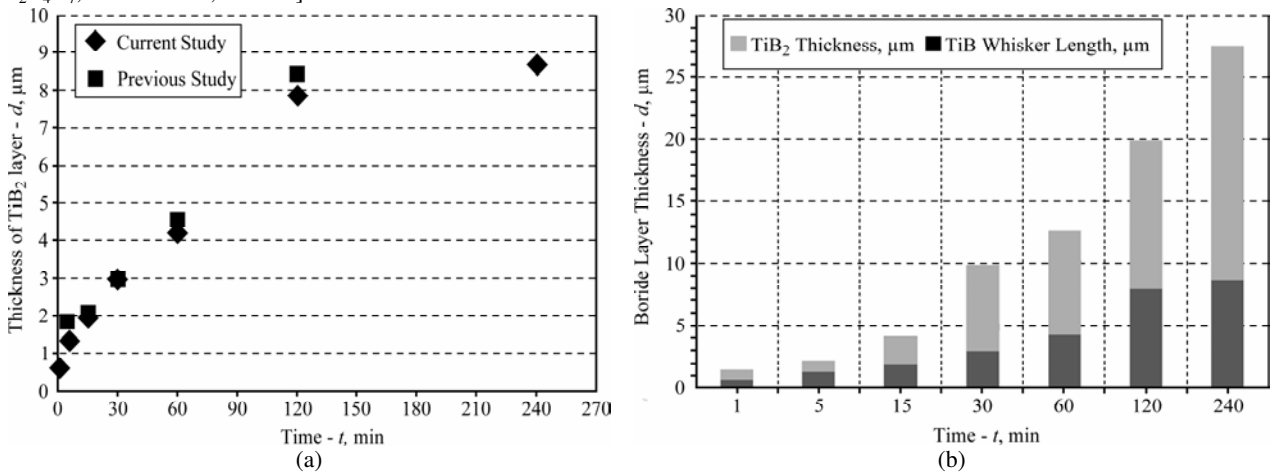

Fig. 9. (a) – comparison of TiB_2 thickness values obtained from the current study and the previous study; (b) – variations of boride layers thickness [μm] with time [min] [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 200 mA/cm^2, 950°C].
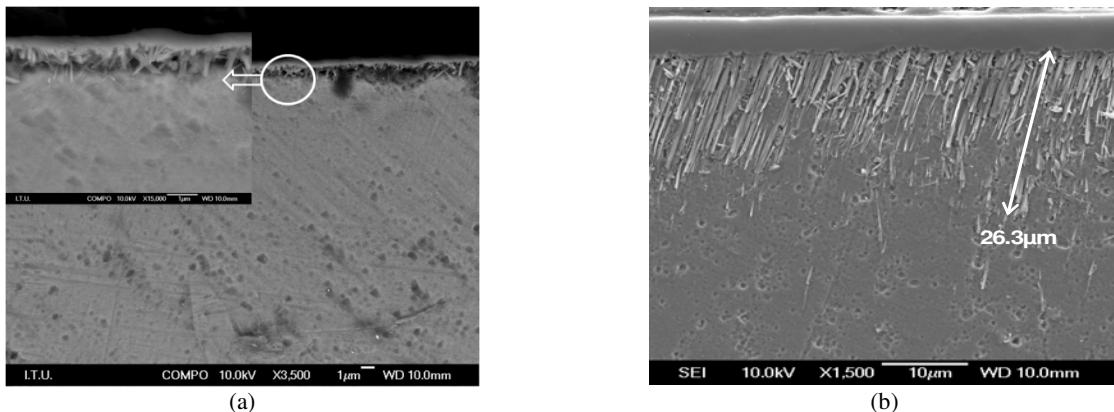

Fig. 10. Cross-sectional SEM images of borided titanium sample in 1 min. (a) and 4 h (b) [15% Na_2CO_3 and 85% $Na_2B_4O_7$, 200 mA/cm^2, 950°C].

morphology of TiB structure. The growth of TiB$_2$ was promoted with the increase of temperature as expected. Increasing boriding temperature from 900°C to 1200°C resulted in 5 µm increase in the thickness of TiB$_2$ layer (Fig. 6).

The thickness variation of TiB$_2$ layers and the penetration depth of TiB whiskers as a function of electrolyte temperatures revealed that there was a linear correlation between the thickness of TiB$_2$ and process temperature (Fig. 7a) which is an expected outcome of diffusion controlled processes [11, 16, 26].

Moreover, the boriding temperature also showed an appreciable influence on the morphology of TiB whiskers. The tiny-hairy TiB whiskers formed at 900°C started to thicken at 1100°C and eventually the needle structure of TiB was converted into an almost continuous layer at 1200°C (see Fig. 6a-d). This remarkable tendency observed in the structure of TiB was presented in Fig. 7b. The average depth to width ratios (d/w ratio) of TiB whiskers gradually decreased with the increase in boriding temperature. It is known that the dendritic-whisker like growth of mono-boride form of titanium (TiB) is related to the preferential diffusion of boron in [010] direction in the crystal lattice of titanium [23, 24, 27], which means that the activation energy for boron diffusion into interstitial lattice sites is low in this direction. By the increase of boriding temperature, energy supplied to the system, it is possible to reach the activation energy levels required for diffusion in other directions in the titanium lattice. Hence the loose of directionality and broadening of TiB whiskers can be attributed to the increase of activation energy for diffusion in other directions in the lattice leading to a 3 dimensional growth of the TiB phase.

In order to investigate the cell potential variation depending on boriding temperature, cell potentials at different boriding temperatures were recorded (Fig. 8). As expected, cell potential decreased with increasing temperature. This effect could be explained by the increase in the conductivity of the electrolyte and the decrease in the activation energy of ionic sodium reduction.

Although an increase in boriding temperature provides positive contributions on the thickness of TiB$_2$ layers, the high temperature corrosion of metallic parts in the cell assembly starts to become a serious problem above 1000°C. Thus for practical purposes boriding at elevated temperatures may not be preferred.

2.3 Effect of electrolysis duration

The effect of electrochemical processing time on boriding of titanium was previously studied in our research group [19]. In this work, the same experiments were repeated with the addition of two new durations (1 min and 4 hours). Other than TiB$_2$

thickness, the penetration depth of TiB was also inspected for all boriding durations. The previous and current results are consistent with each other (Fig. 9a), which further verified the repeatability of the experiments.

The time dependent variation of the total boride layers were given with height bars where the thicknesses of TiB$_2$ and penetration depth of TiB were represented separately (Fig. 9b). The duration of boriding had a positive contribution on the growth of both TiB$_2$ and TiB. After 4 hours of boriding, 8.7 µm thick TiB$_2$ layer was achieved, whereas the length of TiB whiskers reached to 30 µm.

At the beginning of the boriding treatment, the formation rate of TiB$_2$ was very fast, and exhibited an almost linear correlation with electrolyses time until 1 hour. However, beyond one hour, the growth rate started to follow a parabolic relation as in other diffusion controlled processes due to the thickening of TiB$_2$ (Fig. 9c). The parabolic dependence of the boride layer thickness on time also revealed that the boron adsorption of the surface is the actual limiting stage of boron diffusion into the substrate or else the growth of boride layer.

The cross sectional SEM image of one minute borided titanium sample revealed that even such a short time was enough to grow a continuous and homogenous TiB$_2$ layer and whiskers of TiB underneath (Fig. 10a). The increase in process durations caused a thicker and denser TiB$_2$ on top and TiB whiskers growing deeper into the core of the titanium substrate. The length of TiB needle was reached to 30 µm after a 4 hour of process time (Fig. 10b).

3. CONCLUSIONS

The main objective of the study was to systematically investigate the electrochemical boriding parameters (time, electrolyte temperature and current density) on the thickness, morphology and phase composition of boride layers formed on the titanium substrate.

It was found that only the time and temperature of boriding process provide a major influence on the growth rate of titanium boride phases, TiB and TiB$_2$. The temperature of boriding media was the most critical parameter among the others to control the thickness and morphology of both titanium borides. It is observed for the first time that the whisker like growth of TiB gradually converted into a layer type 3D structure with the increase of boriding temperature. The magnitude of applied current density did not alter morphology of boride layers beyond a current density of 100 mA/cm^2.

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Реферат

В работе исследовался процесс борирования титана путём электролиза солевого расплава в электролите на основе бора при разных плотностях тока (50–700 мА/см^2), температурах (900–1200°С) и длительности процесса (от 1 мин до 4 ч). Результаты XRD-анализа тонких пленок показали, что две основные фазы борида титана (TiB$_2$ и TiB) образовались уже спустя 1 мин после начала процесса. Анализ сечений с помощью сканирующей электронной микроскопии (SEM) показал двухслойную структуру борида, состоящую из сплошной однородной фазы TiB$_2$ и нитевидных кристаллов TiB, которые формировались под слоем TiB$_2$ по направлению к подложке. Была оценена зависимость толщины и морфологии слоя борида от параметров процесса. Результаты исследования показали, что температура процесса является наиболее критическим параметром, влияющим как на скорость борирования, так и на морфологию слоя борида. Слой TiB$_2$ толщиной 8 µm на титане был получен за 30 мин борирования при температуре 1200°С.