

Boriding titanium alloys at lower temperatures using electrochemical methods

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Abstract

In this study the boriding of titanium alloys was attempted with the use of electrochemical methods at room temperature followed by a tempering process at much lower temperatures than those reported in literature. The electrochemical boriding process with tempering at 500 °C resulted in the formation of compact TiB and TiB₂ layers.

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1. Introduction

Boriding is a surface treatment process of diffusion and chemical reaction of elemental boron into the substrate at elevated temperatures which results a refractory coverage with superior mechanical properties and corrosion resistance [1]. Boriding process can be carried out by both chemical and electrochemical means. One needs an activator (which is a reducing agent such as hydrogen) in a chemical process as well as a boriding agent. Activator and boriding agent (which is generally a boron halide) react to give elemental boron which diffuses into the metal surface. There are various chemical and physical boriding techniques such CVD (chemical vapor deposition) [2], PACVD (plasma-assisted CVD) [3] and PVD (physical vapor deposition) [4]. Apart from these, boriding can also be carried out by heating the boron-yielding agents or elementary boron in air-free media at elevated temperatures which results in diffusion of boron on the surface. In electrochemical method the metal 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. Kaptay et al. have explained the electrochemical boriding process in detail [5].

Due to their corrosion resistance and mechanical strength, Ti alloys have diverse applications such as implants in medicine and dentistry. Boriding procedure results in the formation of TiB and TiB₂ on Ti alloys depending upon the conditions used. Both these compounds have refractory character and are stable at high temperatures [1].

The establishment of a boron film upon the surface is of great importance due to its superior mechanical, thermal and corrosion resistance properties [6,7]. Kamimura et al. formed a α -rhombohedral boron layer upon the surface by the pyrolysis of decaborane at 1000°C [8].

Boriding procedure is dependent on boriding agent, boriding type, boriding temperature and boriding time. Boriding temperature is the biggest factor which affects the cost of the process and choice of the substance to be borided. Elevated temperatures may be detrimental to the mechanical properties of the substrate. Ricceri et al. [9], obtained TiB₂ nano particles by mixing powdered B₂O₃, TiO₂ and Mg with ball milling. This study disproves the wide spread belief that the boriding procedure should be carried out at elevated temperatures. The fact that the resulting particles are at nano dimensions is another

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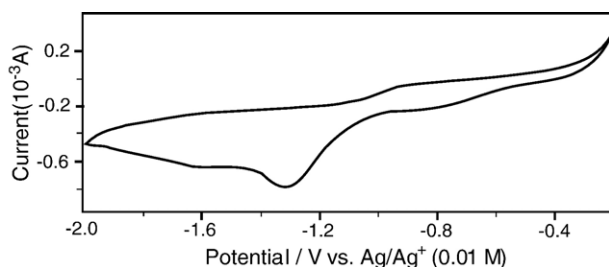


Fig. 1. The cyclic voltammogram of 0.1 M BBr_3 boriding agent in DMF solution containing 0.2 M tetrabutylammonium tetrafluoroborate supporting electrolyte at scan rate of 50 mV/s.

advantage. It is obvious that boriding process can be carried out at much lower temperatures.

Jain et al. [10] borided 0.2% soft carbon steel using a boriding agent with different particle size ranging 2–25 μm in dimension. They observed that the use of 10 μm diameter particles resulted in the formation of FeB and FeB_2 layers upon the surface and the thickness of the boride layer remained unchanged with increase in the size of the particles. This study contradicts the general belief that the smaller particles diffuse much better into the surface of the substrate. On the contrary bigger particles result in a much homogenized coverage.

There are no studies related to the formation of a boron films on metal surface by the cathodic reduction of boron at room temperature. The purpose of this study was to bring the boriding of Ti alloys, which are generally carried out at temperatures of 1000–1200 $^\circ\text{C}$ [5,11], to lower temperatures. In this study the surface of Ti6Al4V alloy discs were electrochemically borided at room temperatures by the use of BBr_3 and the surfaces were tempered at different temperatures. This substrate was chosen due to its wide use as medical implants and its susceptibility against fretting corrosion [12]. It was thought that refractory boride layer would prevent this corrosion. The formation of TiB and TiB_2 upon the surface was monitored with X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques.

2. Experimental details

The boron coating solution was prepared by the addition of 0.1 M BBr_3 to 50 mL 0.2 M NaBF_4 supporting electrolyte (a highly ionizable compound used to increase the conductivity of the non-aqueous or aqueous solutions with low conductivities) containing DMF solution. All the reagents used were analytical grade (Merck).

The substrate to be coated with boron was 1 cm diameter Ti6Al4V discs. The surfaces of the discs were mechanically polished with 80 grade rough and 300 and 500 grade fine sand papers. The polished surfaces were then washed with bi distilled water and acetone before being inserted into the electrochemical cell. If the polishing was finer than that it was observed that the elemental boron did not adhere on the surface and dispersed into the solution.

The XRD apparatus was Bruker V8 Discover with a $\text{Cu K}\alpha$ source at a wavelength 1.540 Å . JEOL field emission SEM was employed for the characterization of the covered boride layers.

2.1. Electrochemical boron coating process

The electrochemical boron coating process was carried out by the use CH Instruments 660B computer controlled potentiostat system using a three electrode cell. The reference electrode was Ag/Ag^+ (0.01M) 0.2 M TBABF_4 (tetrabutylammonium tetrafluoroborate)/DMF and the counter electrode was the spiral Pt wire placed opposite to Ti alloy disc working electrode. The solution was purged with argon to remove the residual oxygen. The cyclic voltammetric scan carried out to determine the deposition potential is given in Fig. 1. The deposition potential used in this study was -1.6 V (Ag/Ag^+ (0.01 M) 0.2 M TBABF_4 -DMF).

2.2. Tempering process

The boron coated discs were taken out of the deposition solution and the residual solvent was removed by washing with

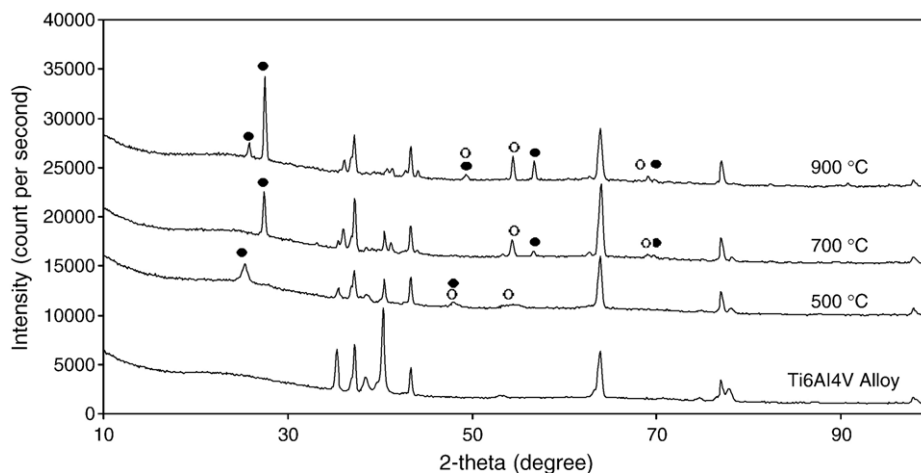


Fig. 2. XRD pattern of borided and non-borided Ti6Al4V alloys by tempering for different temperatures (○: TiB and ●: TiB_2).

dichloromethane and heating at 100 °C. Finally the discs were tempered at 500, 700 and 900 °C for 2 h under argon atmosphere to form a boride layer on the substrate surface. The tempering process below these temperatures did not yield satisfactory results. The borided discs were slightly wiped with 1200 grade sand paper, washed with acetone and dried under air and subjected to XRD analysis. The XRD results were given in Fig. 2.

The SEM micrographs of borided discs subjected and not subjected to tempering process and the discs which were not

subjected to any boriding process were taken after being slightly wiped with fine emery paper and washed with acetone. The micrographs were taken with BES mode (Back Scattering Mode) and presented in Fig. 3.

3. Results and discussion

The boron coverage is clearly apparent when we compare the SEM micrographs of the surfaces of non-coated and electrochemically boron coated substrates (Fig. 3A and B). Surfaces of

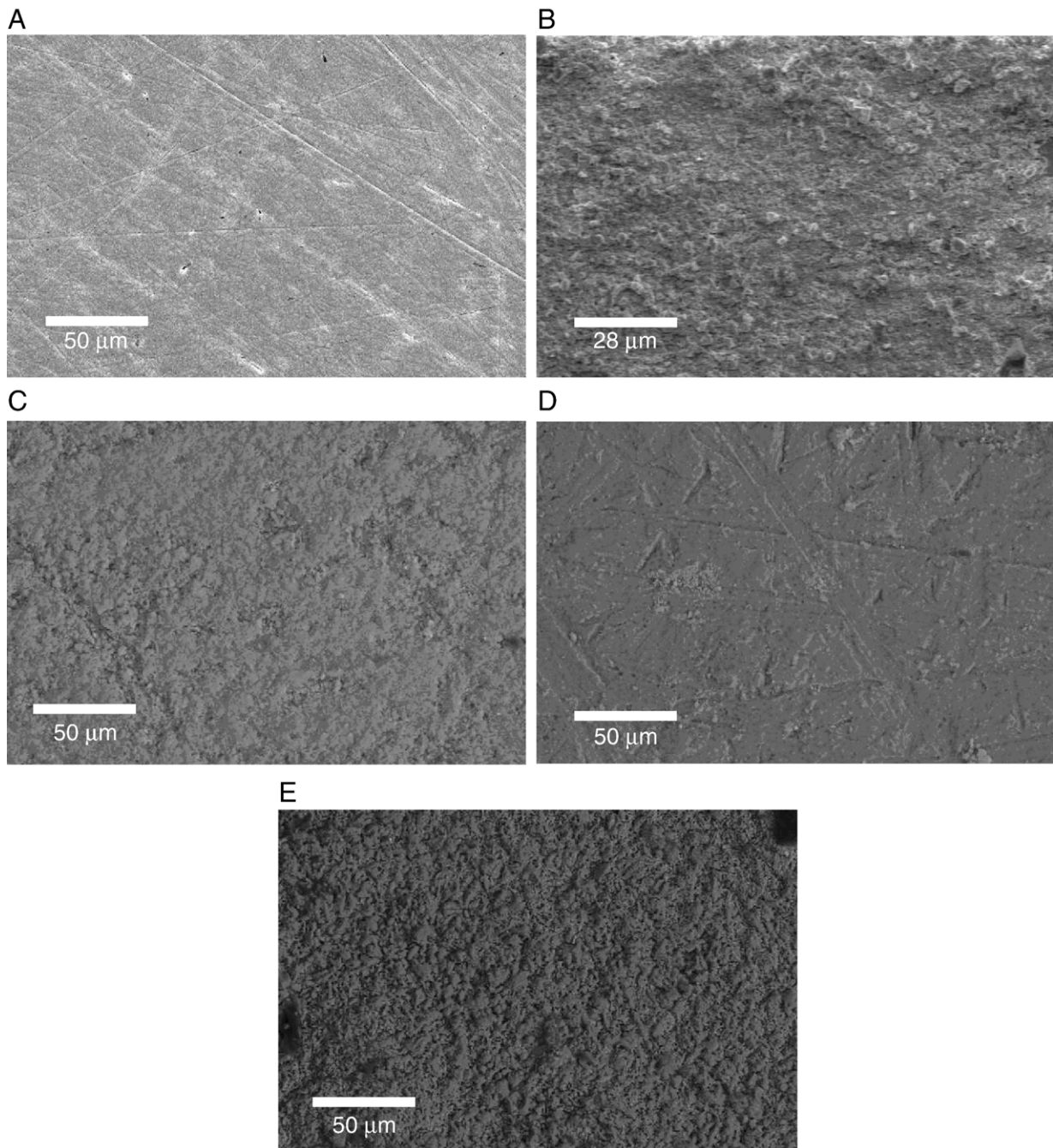


Fig. 3. Back scattered images of Ti6Al4V alloys: A) clean surface B) boron coated (untempered) surface C) borided at 500 °C D) borided at 700 °C E) borided at 900 °C for 2 h.

the substrate in our study revealed that the resulting boride layers are composed of very fine boron particles with the size of 5 μm . The interruption of the applied potential resulted in dispersion of the covered boron particles into the solution. The decrease in the particle size facilitates easier diffusion of the particles toward the surface. The electrochemical boriding process is carried out with melts at elevated temperatures for the diffusion of the cathodically formed boron to the surface. The process which take place during the electrolysis can be summarized as follows [5,11,13]:



Step (1) requires elevated temperatures. The formation of small sized particles upon the surface in our study decreases the energy demand of step (2) compared with other techniques. Ricceri et. al [9] reduced boron on Ti surface with the use of reducing properties of Mg at room temperature and obtained elemental boron and TiB_2 upon the surface. The reaction of Ti and B to form titanium boride is a thermodynamically demanding in other words high enthalpy process. The elevated temperatures facilitate the diffusion of boron and the small sized particles are much easier to diffuse into the structure of the substrate. Fig. 2 shows the XRD patterns of the borided Ti6Al4V alloy treated at different temperatures. The peaks observed at 2-Theta=44, 36, 65, 77 and 79° in the XRD pattern of Ti6Al4V alloy are characteristic for both TiB and TiB_2 . 2-Theta=26–27° peaks on the other hand is typical for TiB_2 . The peak heights show a linear increase with temperature (Fig. 4). This peak shows that TiB_2 formed a hexagonal crystal structure. All peak intensities in Fig. 4 were scaled according to the peak with the highest intensity. 2-Theta=49° peak is characteristic for TiB_2 and TiB and the peaks 54° and 69° are characteristic for TiB and the peaks 56° and 70° are characteristic for TiB_2 .

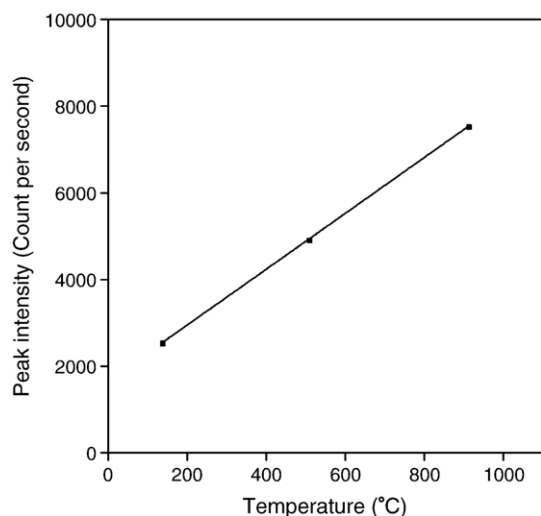


Fig. 4. The relative change of the amount of TiB_2 (2-Theta=26–27° peaks) into the substrate surface with temperature (the magnitude of the biggest peak $T=900^\circ\text{C}$ was taken as unity and the other peaks were given against it).

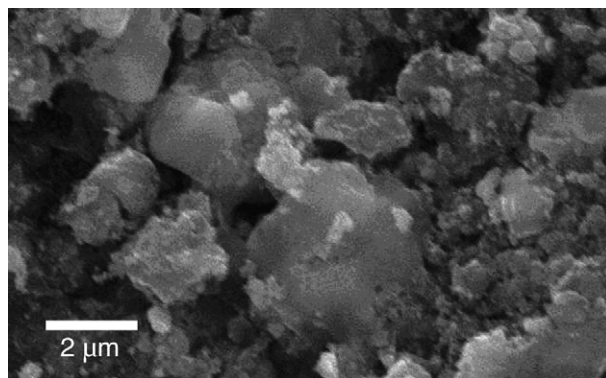


Fig. 5. Back scattered image of borided disc tempered at 500 $^\circ\text{C}$ for 2 h ($\times 10,000$).

Fig. 3 shows the back scattered and 500 times magnified SEM images of borided alloy discs tempered at 500, 700 and 900 $^\circ\text{C}$ for 2 h. The investigation of these images revealed that the crystal structures of the alloys change with temperature. Fig. 5 is 10,000 magnified surface picture of borided alloy tempered at 500 $^\circ\text{C}$ for 2 h. The detailed investigation of the surface reveals a heterogeneous structure as larger particles piled up with the smaller ones.

4. Conclusions

Electrochemically deposited boron layers were amorphous. The tempering process resulted in the formation of TiB and TiB_2 following the diffusion of boron into the structure of the alloy. Electrochemical boriding process of Ti alloys with melts has been carried out at 1000–1200 $^\circ\text{C}$ in literature. Instead of this single step process, the boriding process was electrochemically carried out at room temperature for covering the surface with elemental boron and the tempering process was carried out at low temperatures. The study revealed that even 500 $^\circ\text{C}$ is enough to form compact boride layers. The change of 2-Theta=27° peak reveals the deposition of boride layers on the surface. This two-step electrochemical boriding process may provide a cost effective way for the formation of refractory boride layers upon the metal surface.

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