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Review on coloring effect & Physical Properties of Anodized Titanium and its Alloy

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ABSTRACT
Titanium and its alloy are expected to suitable for aerospace and biomedical application. Various techniques have been used for its surface properties improvement. The impact of anodizing parameters on surface behavior has been studied. This review examines the effect of bath parameters of anodized Titanium and its alloys on coloring behaviour & physical properties. The influence of electrolyte, anodizing time, voltage and concentration of electrolyte, on the coating characteristics like color spectrum, film thickness, surface roughness, hardness, crystal structure etc. is discussed in this article. Finally, the article concluded by examination of key properties including corrosion aspects in aerospace and biomedical field.

Keywords – Anodizing parameters, corrosion, titanium, and its alloy, tribological property.

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I. INTRODUCTION

Aerospace industries increase the use of titanium alloy because of excellent mechanical properties that can be provided at a critical load-carrying location in the military and commercial aircraft [1-2]. It has a characteristic of high corrosion resistance, non-toxicity and mechanical properties compatible with bones that is why it is commonly used in implants [3] [4]. The primary reasons for using titanium in the aerospace are weight saving, space limitation, operating temperature, corrosion resistance and composite compatibility [5]. It has been noticed that titanium has poor tribological properties. It is prone to high surface friction, low surface hardness, and poor wear resistance. Freshly exposed titanium tends to react with the oxygen in the atmosphere to form titanium dioxide, which prevents corrosion of material [6]. However, a small thickness of oxide layer and its amorphous structure cannot meet all the requirement [7]. The natural oxide layer can be easily damaged during a application. Anodizing process in which the thickness of this oxide layer can be modified with varying parameters [8]. By controlling the anodizing potential difference, a specific thickness of the oxide layer is produced [9-10]. Resistance against corrosion can be increased by increasing the thickness of oxide. The presence of alloying element can affect the response of the material to the anodizing process, but it can be applied to the most grade of titanium [11].

1.1 Anodizing of Titanium and alloy

Anodizing is an electrochemical process which is used to produce a thin oxide layer on the surface of the material. Anodized titanium can be used for various applications [12-13]. Anodizing of titanium can be used to provide decorative finishing [14-15], To protect the metal from atmospheric, corrosion. To reduce the friction between sliding surfaces, to provide thermal control. By varying anodization process parameter like temperature, voltage, the concentration of bath, type of electrolyte, anodizing time results may be altered. In the present overview paper anodizing of titanium and its alloy, and the effect of parameters is described. Xuanyong Liu et al. [16] had explained anodic oxidation is the combine process of electric field driven metal and oxygen diffusion leading to the formation of oxide film on the surface. He also suggested that It can also be used to increase the oxide thickness to increase corrosion protection and decrease ion release, coloration, and porous coatings.

Variation in the structural and chemical properties can be observed over a wide range by altering the anodizing parameters such as anode potential, electrolyte composition, temperature, and current. if, the anodizing process will be carried out above breakdown voltage. At such high voltage, increasing of gas evolution and frequent sparking is observation [17-18]. This type of anodizing is often referred to as spark anodizing that typically leads to less uniform and more porous oxide films. Anodic spark oxidation is also called micro-arc oxidation (MAO) or plasma electrolytic oxidation. Xuanyong Liu [16] had summarized that anodization is a simple and effective method to modify the surface of titanium and its alloys for better biocompatibility and bioactivity.

II. LITERATURE REVIEW

EFFECT OF PROCESS PARAMETERS ON ANODIZATION

2.1 Voltage

2.1.1 Color spectrum

To identify the effect of voltage on color spectrum, Lynne Bartlett [15] had anodized pure titanium in ammonium sulfate at intervals of 5V from 25 to 80 V. shows the colored samples and shows the variability of the coloring especially at the higher voltages. The color spectrum is shown in Fig. 2.1

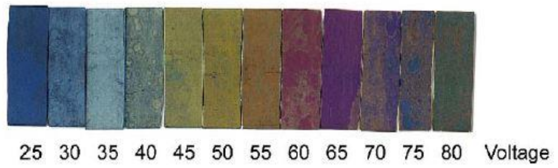


Fig. 2.1: Anodized samples of unpolished scrap CP Ti [15].

During anodizing of commercially pure titanium Z. Liu [19] has observed an influence of voltage on the color spectrum. Anodizing of commercially pure titanium in NaTESi electrolyte had done with varying voltage between 5-40V. Due to the interference effect, the coloration of specimen undergoes changes in the sequence: pale gray-brown–blue–dark gray for 5, 10, 20 and 40 V as shown in Fig. 2.2

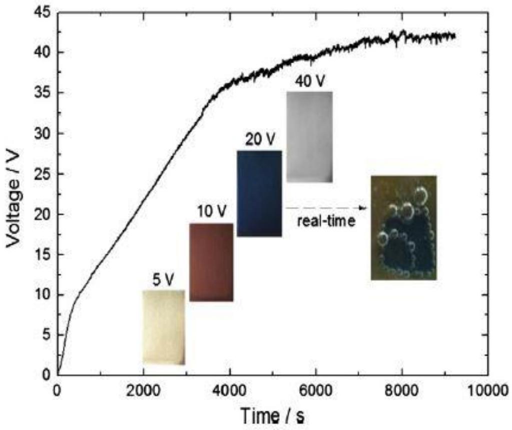


Fig **2.2:** Effect of Voltage on the color spectrum [19]

M. Manjaiah [20] had performed anodizing of pure Titanium grade 4 with the 20% diluted H_2SO_4 electrolyte. Anodizing was conducted for constant 3 minutes for potential difference varying between 5 to 90 V. As a function of different anodizing voltages, the colors as obtain from the anodizing process is shown in Fig. 2.3

Voltage (V)	Colours	Image	Voltage (V)	Colours	Image
5	Tiny yellow		50	Yellow green	
10	Dull golden		55	Violet	
15	Purple		60	Purple	
20	Dark blue		65	Electric blue	
25	Shallow blue		70	Bluish green	
30	Sky blue		75	Darksea green	
35	Greyish yellow		80	Wine red	

Fig. 2.3: The correlation of colors to volts of anodized titanium [20]

Sunil Kahar [22] has performed anodization with 10% KOH electrolyte at an interval of 20-72 V for 10 seconds. He had observed different color on anodized Titanium sample for different applied voltage as shown in fig. 2.4

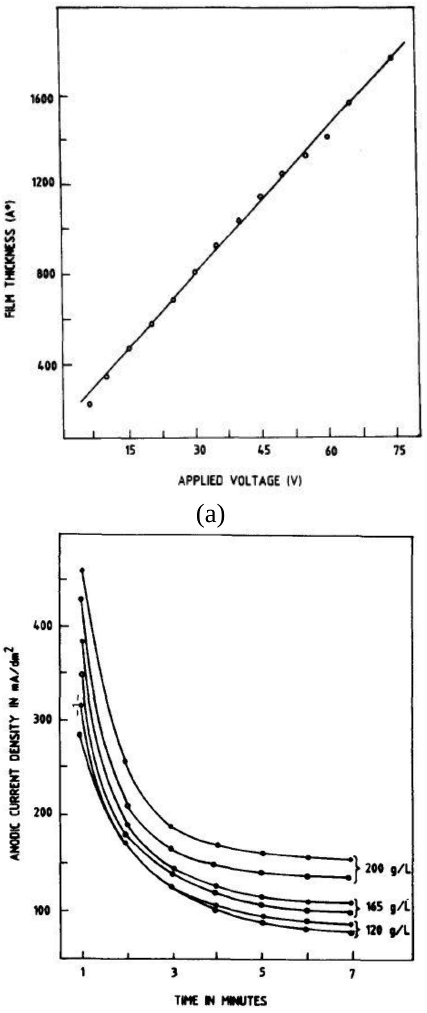
Fig. 2.4: Titanium Spectrum at different voltage ranges in KOH bath [22]

A.K. Sharma [14] had mentioned that when Ti-6Al-4V was anodized in the H_2SO_4 electrolyte, different color spectrum has been observed. The various color produced on anodized titanium sample, depending on applied voltage. After the anodizing process, the colors that are produced on titanium sample are known as interface color.

2.1.2 Current density and film thickness

A.K. Sharma [14] observed that apart from varying of voltage, type of electrolyte has also an influence on the color spectrum. With different electrolyte but the same voltage and material have a different color spectrum.

He has also observed that with increasing applied voltage, the anodic current density is also increased. Initially, the rate of reduction in current density was very fast but, it slows down gradually and on a later stage, it becomes near to constant. Streaking and pitting of the coating was observed greater than 80 V. It is also observed that coating thickness is increasing with increasing of the applied voltage.



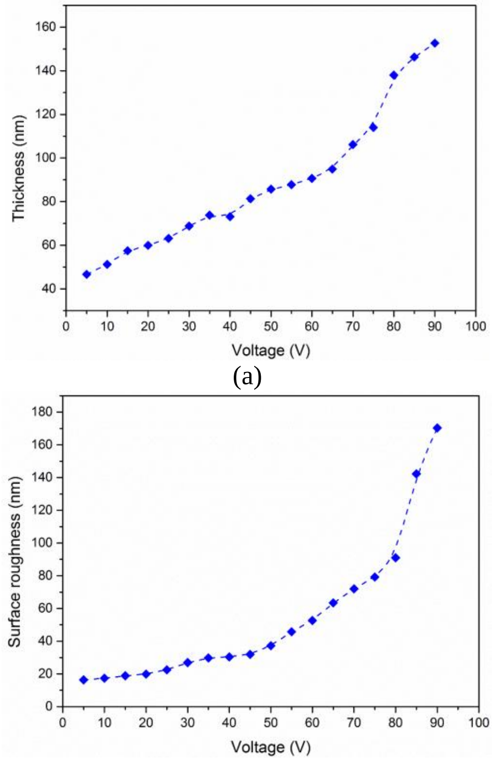
(a)

(b)

Fig. 2.5: (a)Variation of anodic current density with time for various applied voltages (b) Variation of anodic film thickness with time for various applied voltages: electrolyte 165 gl-1 H_2SO_4, temperature 23℃ [14]

2.1.3 Oxide thickness and surface roughness

M. Manjaiah [20] had performed anodizing of pure Titanium grade 4 with the 20% diluted H2SO4 electrolyte. He measured the thickness of the oxide layer is measured indirectly by the spectral reflectance of a wavelength (nm) and the refractive index. It has been observed that with increasing of voltage oxide thickness is also increases. The oxide layer increases in thickness due to an increased oxygen ion diffusion towards the anodizing interface along with a migration of Ti^{+4} ions from the titanium substrate. Also, he discussed that an increase in anodizing voltage increases the roughness because of an increase in the size and number of pores.



(a)

(b)

Fig. 2.6: (a) Variation of the oxide layer thickness for different applied voltages (b) Variation of surface roughness (Sa) a function of anodizing voltage [20].

M. Nakajima [18] studied of Spark anodizing of titanium, Ti–6Al–4V and Ti–15V–3Al–3Cr– 3Sn in 0.15 mol dm^{-3} $K_2Al_2O_4$ + 0.03 mol dm^{-3} Na_3PO_4 + 0.015 mol dm^{-3} NaOH alkaline solution at 293 K. He explained that thickening of the anodic film is also dependent on the substrate composition. He observed that the thickness of anodic films formed by anodizing to the peak voltage of 410 V is 20– 23 µm.

Z.J. Liu [10] has performed anodization processes on Ti6Al4V. Ti6Al4V alloy was anodized in the aqueous NaTESi electrolyte, with a set of 10, 20 30 and 40 V. He observed the thickness on film

~15nm at 10 V, which was increased up to ~250 nm after anodizing at 40 V.

2.1.4 Crystal structure

During the anodization of Ti-6Al-4V, Tiago Augusto Soares [23] had observed dielectric rupture, which occurs following a sudden increase in current, starts at approximately 65 V. He noted that during anodic polarization of up to 132 V, no new crystal structure could be significantly detected. A small amount of phase anatase and rutile was detected between 132V to 156V. With the increase of the voltage, almost only the rutile phase could be identified.

M. Nakajima [18] observed that sparking commences at ~110 V, but the highly crystalline oxides are not formed up to 300 V for Ti-6Al-4V. He suggested that high voltages for intense sparking are apparently vital for a growth of highly crystalline oxide film.

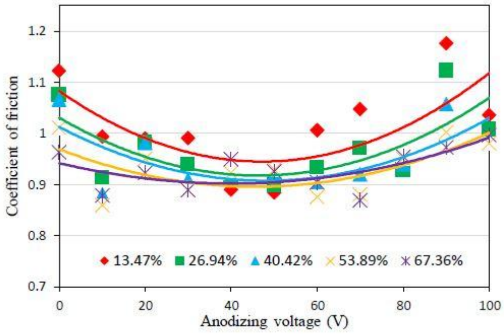
Bangcheng Yang [17] had studied anodic oxidation treatment on pure titanium metal. Anodization process has been carried out in 1 M H_2SO_4 electrolyte. Samples were immersed in an electrolyte-contained glass chamber and subjected to anodic oxidation by applying DC for 1 min at room temperature at different DC voltages of 90, 155 and 180V under a constant electrolyte concentration of 1 M. At 90 V, on the surface of titanium metal he observed anatase structure. At 155 V anatase and rutile, both phases were formed and only rutile appeared at 180 V. He also explained that amount of titania with the structure of anatase and/or rutile on the titanium surfaces increased with increasing voltage.

Z.J. Liu [10] has performed anodization processes on Ti6Al4V. Ti6Al4V alloy was anodized in the aqueous NaTESi electrolyte, with a set of 10, 20 30 and 40 V. With increasing of voltage amorphous-to-crystalline transition was observed. He mentioned that the degree of crystallinity of the film was more plentiful as the anodic voltage increased.

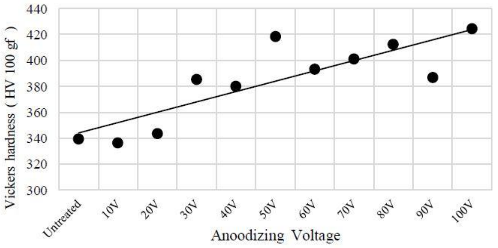
2.1.5 Hardness and coefficient of friction

Dirk J van Vuuren [29] anodized Grade 4 commercially pure Titanium using 20% sulfuric acid solution as an electrolyte at ambient temperature. A variable voltage is applied across the electrodes using an analog dc power supply.

He presented the variation of surface friction coefficient as a function of anodizing voltage for various proof loads (applied torque). He has observed that the Coefficient of friction decreased with an increase in anodizing voltage to attain a minimum at between 40V and 50V. At voltages above this, the oxide layer thickness increased dramatically and the decrease in Coefficient of friction was less apparent compared to untreated samples. He had also observed that the hardness increased with an increase in anodizing voltage.



(a)



(b)

Fig. 2.7: (a) Variation of surface friction coefficient as a function of anodizing voltage (b) Vickers hardness as a function of anodizing voltage [29].

2.1.6 Corrosion resistance

Sunil kahar [21] had performed anodization process on pure titanium with a set of the voltage of 10-62 V and for the duration of 10 S. Anodized Ti samples were studied for corrosion behavior as per ASTM G 5 standards in 3.5% NaCl solution and 0.1N H_2SO_4 solution using potentiostat Gamry Reference 600. He observed Anodized done at 60-62V exhibits best corrosion resistance compare to anodized below 50-55V range in 0.1N H_2SO_4 and 3.5% NaCl solutions.

It has been also observed that film formed at 60V is compact and more uniform and higher capacitance compares to film formed below 50-55V.

2.1.7 Bonding strength

Z.J. Liu [10] has performed anodization processes on Ti6Al4V. Ti6Al4V alloy was anodized in the aqueous NaTESi electrolyte, with a set of 10, 20 30 and 40 V. For measuring a bond strength, the single-lap shear bonding test method was adopted. The result showed that the shear bonding strength increased with increasing anodic voltages. It was concluded the thicker anodic films showed a better adhesion performance compared with the thinner anodic TiO_2.

2.1.8 Surface morphology

N.R. Rodrigues [24] had performed anodization of Ti6Al4V in a mixture of 1 M H_2SO_4 and 0.08 M HF electrolyte. He observed the formation of randomly organized nanotubes when the anodic voltage was set to 20 V for 5 min, whereas increasing the time to 60 min led to the formation of a self-organized nanotubular structure with increased pore diameter.

When Z.J. Liu [10] has performed anodization processes on Ti6Al4V with NaTESi electrolyte, he observed that formation of pores within the anodic oxide film formation was started from 20 V, and the pore population density increased with increase in anodic voltage.

Bangcheng Yang [17] observed that pure titanium metals surfaces become porous during anodization in 1 M H_2SO_4 electrolyte at DC voltage from 90 to 180V and spark discharge happened when the DC voltage was higher than 105 V. The porosity and the pore size increased with increasing voltage from 90 to 155V.

2.2 Electrolyte

2.2.1 Crystal Structure

Naoya Masahashi [25] had performed anodization process on Ti6Al4V. Anodization was performed in a sulfuric acid electrolyte ranging from 0.02 to 1.2 M with a current density of 50 mA/cm^2 for 0.5 h. It has been observed that in an electrolyte of 0.02 M sulfuric acid is anatase, while it is replaced by rutile with increasing the concentration up to 1.2 M.

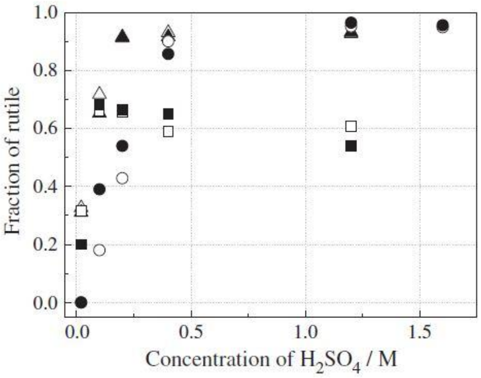


Fig. 2.8: Plots of the rutile fraction in the as-anodized (○, Δ, □) Ti6Al4V (□, ■) against the sulfuric acid concentration in the electrolyte [25].

2.2.2 Breakdown voltage

Laís T. Duarte [26] had anodized Ti-6Al-4V in pH 5 buffer electrolyte (0.252 mol/L Na_2HPO_4, 0.115 mol/L Na_2HPO_4) at various constant current densities and he had found that 130V is the breakdown potentials for the same. It has been observed that increasing the value of voltage larger that breakdown potentials resulted in larger pores.

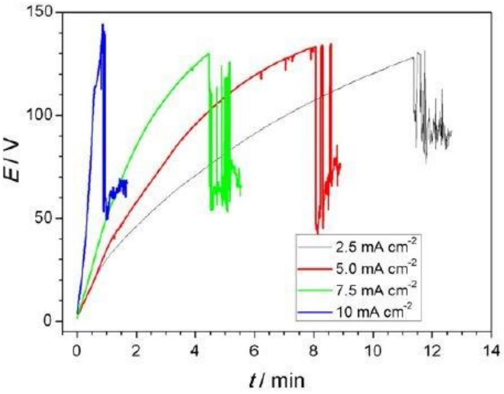


Fig. 2.9: Potential vs. time profiles for the anodization of Ti-6Al-4V in a phosphate buffer solution (pH 5) at various current densities [26].

M.V. Diamanti [27] has treated the surface of the Ti6Al4V alloy by the anodizing process. the specimen was anodized in a calcium glycerophosphate solution with a growth rate of 1 V/s, up to a cell voltage of 350 V, anodizing electrolytes were kept at a temperature of 5 °C. By doing so, slightly decreased surface hardness and stiffness compared to the metallic substrate and increased scratch and fretting wear resistances significantly with reducing of friction coefficient, the value of the hardness to modulus ratio is improved.

Spark anodizing of commercial titanium, Ti–6Al–4V and Ti– 15V–3Al–3Cr–3Sn was carried out by M. Nakajima [18] in alkaline aluminate electrolyte to evaluate the influence of substrate composition on the anodic film formation. The electrolyte used was a 0.15 mol dm^{-3} $K_2Al_2O_4$ + 0.03 mol dm^{-3} Na_3PO_4 + 0.015 mol dm^{-3} NaOH alkaline solution at 293 K up to a maximum peak voltage of 400 V. He observed Light emission due to dielectric breakdown initiates when the peak voltage of each specimen reaches ~100 V.

Laís T. Duarte [26] studied the growth of oxides on the surfaces of pure Ti, Ti–6Al–4V and Ti-6Al-7Nb by micro-arc oxidation (MAO) in a pH 5 phosphate buffer electrolyte. He concluded that the oxides are grown by micro-arc oxidation (MAO) on pure Ti and its alloys Ti-6Al-4V and Ti-6Al-7Nb in a pH 5 phosphate buffer unveiled breakdown potentials (Eb) of about 200 V, 130 V, and 140 V, respectively.

2.2.3 Bond strength

Z.X. Chen discussed that titanium metal and its alloys are used in dental and orthopedic implants because of their excellent corrosion resistance, biocompatibility, and osseointegration behavior. Four different electric currents were applied in sulfuric or phosphoric acid electrolytes for the fabrication of the surface oxide films.

The ANO-S2, ANO-S4, ANO-S12, and ANO-S20 sample groups were fabricated in 1 M H_2SO_4 electrolyte by supplying constant electric currents of 2, 4, 12, and 20 mA/cm^2, respectively. The ANO-P1, ANO-P2, ANO-P12, and ANO-P20 sample groups were fabricated in 1 M H_3PO_4 electrolyte by supplying constant electric currents of 1, 2, 12, and 20 mA/cm^2, respectively. The duration of anodization was 120 s for all the sample groups.

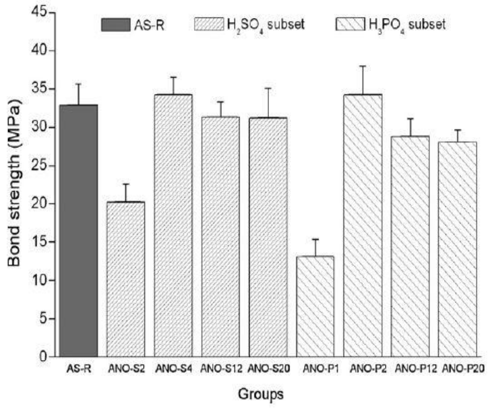


Fig 2.10: Bond strengths (Mpa) of oxide films to substrate metals

By making a variation in the electrolyte used for the anodization, the thickness of the oxide film changed, which in turn affected the bond strength. The porosity, crystalline structure, and bond strength of the oxide films on the titanium substrate could be adjusted by changing the electrolyte solution and the current densities applied during the anodic oxidation treatment.

2.3 Anodizing time

TiO_2/Al2O_3 composite coatings were prepared on the surface of the Ti-6Al-4V alloy by micro-arc oxidation in the Na_2SiO_3-$(NaPO_3)_6$-$NaAlO_2$ solution by Shen Yizhou[28]. He observed that growth of TiO_2/Al2O_3 oxide film was very fast at initial and starts to decrease in the subsequent period. After the 20 in of oxidation thickness of the film was reached 15.4µ. Thus, at constant voltage thickness of coatings continues to increase with reference of time.

Shen Yizhou[25,28] observed that after the anodizing process the coatings are mainly composed of anatase TiO_2, rutile TiO_2, and α-Al_2O_3. For the composite phase MAO coatings, the intensities of these phase peaks increase gradually with the extension of oxidation time. When oxidation time was kept for 8 min., the coating was not so thick so, only Ti substrate peak was found.

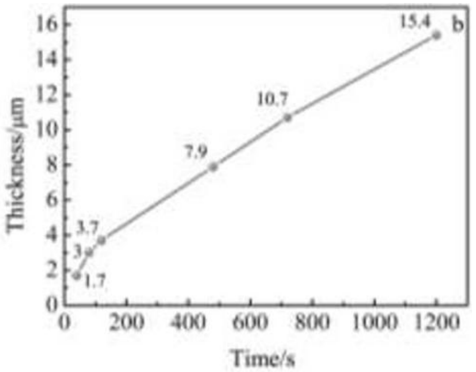


Fig. 2.11: thickness varied with the oxidation time [28].

Shen Yizhou[25 ,28] has also studied that hardness in HV was rapidly increased by 1.5 times than that of Ti-6Al-4V substrate when the time was increased from 5 min. to 12 to 20 minutes as shown in figure 2.12.

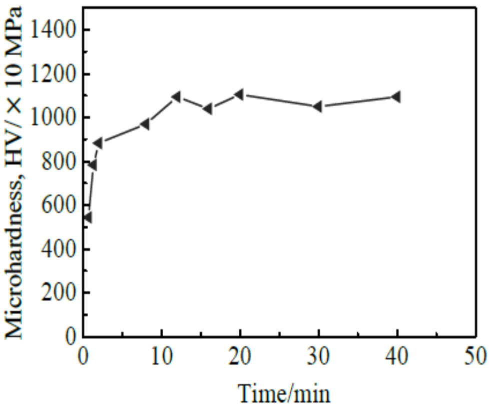


Fig. 2.12 Effect of the oxidation time on the hardness of the TiO_2/Al2O_3 composite coatings [29].

III. CONCLUSION

This feature article discusses recent development in the properties of anodized Titanium and its alloys. The conclusion has been drawn as follow.

1. A strong prominence is placed on how the process parameters like Voltage, Electrolyte and its concentration, and time affect the coating characteristics including morphology, coating properties, color spectrum, and crystal structure.
2. By increasing anodic voltage during anodization, change in the color spectrum of Titanium and its alloy has been observed. It is also studied that the increase in film thickness, corrosion resistance, capacitance, and hardness is increased with increasing the voltage. Moreover, the porosity and the pore size increased with increasing voltage has been observed. By increasing the anodic voltage

amorphous to crystalline transition and anatase to rutile transition was observed.

3. It is studied that by changing the types of electrolyte and change in concentration of the electrolyte, crystal structure, bond strength and breakdown voltage for oxide film can be modified.
4. By increasing the anodization time, thickness of oxide film can be increased.

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