INFLUENCE OF ISOTHERMAL OXIDATION ON CORROSION RESISTANCE OF TITANIUM IN BOVINE SERUM

Benidiktus Tulung Prayoga [1,2)], Suyitno[1)], Rini Dharmastiti [1)]*
[1)]Department of Mechanical and Industrial Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia, 55281
[2)]Department of Mechanical Engineering, Vocational School, Universitas Gadjah Mada, Yogyakarta, Indonesia, 55281

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[*]Corresponding author: beni@ugm.ac.id, Tel : +62-274-548637, Department of Mechanical Engineering, Vocational School, Universitas Gadjah Mada, Jl. Grafika 2a, Yogyakarta, Indonesia 55281

Abstract
The effects of isothermal oxidation holding time on the surface properties and corrosion behavior in bovine serum of cp-Ti were studied in this paper. The isothermal oxidation was done at 700°C for 0 to 36 hours in air with natural cooling. The surface microhardness, surface roughness, wettability and polarization potentiodynamic corrosion of cp-Ti were determined. The result shows the surface microhardness, surface roughness, wettability and corrosion resistance of the cp-Ti enhanced by isothermal oxidation treatment. The presence of the oxide layer on the surface in the form of TiO_2 rutile and Ti_3O are responsible to enhance the surface properties and corrosion behavior.

Keywords: cp-titanium, isothermal oxidation, corrosion resistance, bovine serum

1 Introduction

Titanium and alloys have been known as an excellent metallic material to be used as implants [1]. They are very popular in dental and orthopedic implant material for recent years [2]. The specific advantages of titanium nature are low Young modulus, high strength, low specific gravity, excellent corrosion resistance, good biocompatible, and non-magnetic [3], [4]. The presence of spontaneous oxide film on the titanium surface is believed to be responsible for the nature of excellent corrosion resistance [5]. This passive oxide layer which makes them having a high biocompatibility [6], [7]. However, they have the limitation as very poor wear resistance due to the high and fickle friction coefficient [8]. The spontaneous oxide film is easy to exfoliate when rubbing with hard or soft tissue [9], [10]. Although Titanium showed good corrosion resistance, nevertheless corrosion still occurs at the implants that caused by the presence of bacteria in the human body [5]. This has been stimulating the research on titanium surface modification to improve the wear and corrosion resistance. Thermal oxidation treatment has been used as one of the popular methods for the surface treating of titanium material [7],[11],[12]. Due to this treatment produces a combination of a good of surface properties and enhance the biocompatibility of titanium [7], [13]. Khan et al. [14] stated that protein in the body fluid affects the corrosion behavior of the metals. Wang et al. [15] studied the effects of thermal oxidation of Ti64 on the corrosion behavior in bovine serum and reported a significant the enhancement in the corrosion resistance. Bovine serum is very famous as artificial lubricant in

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the wear test of the load-bearing implant due to the similar physical properties with synovial fluid [16]. In the past, the study about the effect of isothermal oxidation time on cp-Ti with its corrosion resistance in the bovine serum was still limited. This research aims to optimize the treatment time of isothermal oxidation at 700°C on the surface properties and corrosion resistance of cp-Ti in bovine serum.

2 Experimentals

2.1 Material

A commercially pure-Titanium (with 99.78% Ti) cast plates having a dimension of 55 x 18 mm x 3 mm were chosen. All the samples were annealed at 900°C for 2 hours in an argon and cooled slowly in the furnace to obtain a uniform initial microstructure condition. For the corrosion test, the annealed samples were cut into Ø 14 mm x 3 mm by laser cutting machine. The adult bovine serum was collected from adult cows in the local slaughterhouse. The serum was separated from the cow blood by spinning process in centrifuge apparatus.

2.2 Isothermal oxidation

Prior to isothermal oxidizing, the samples were ground with abrasive paper # 600, 1200, 5000, and polished with diamond paste to obtain average surface roughness (Ra=0.1 μm). The polished samples were cleaned with distilled water for 15 minutes in ultrasonic cleaner chamber then degreased with alcohol and dried in hot stream air. The isothermal oxidation was performed at 700°C for 0 to 36 hours using the electrical laboratory furnace (Thermo Scientific, USA) in the air. The samples were heated from room temperature to 700°C with the ramp rate was set as default of the furnace (approx. 22°C/minute). The holding time was set for 2, 4, 6, 8, 12, and 36 hours (ramps excluded). The parameters of the oxidation treatment were chosen based on the results of our previous study [17]. After the holding time had been reached, the specimens were cooled naturally in the furnace.

2.3 Surface characterization

To observe the effect of oxidation holding time on surface roughness of the sample, a contact stylus profilometer (Surfcom 120A, Advanced Metrology System, UK) was used. Hardness test of the sample surface was performed using a Vickers microhardness tester (Buehler, USA). The tests were done with an indentation load of 25 to 200 grf for 15 second holding time. The surface morphology of the samples were observed by a scanning electron microscope (JSM-6510 LA, JEOL, Ltd., Japan) with EDS equipment.

To identify the oxide layer phases, an X-ray diffraction (XRD) analyzer (Shimadzu Type XRD 6000, Japan) was used. XRD analysis was undertaken using monochromatic X-ray radiation from a copper tube with a wavelength of Kα1 = 1.5406 Å, voltage 40 kV, and current 30 mA. The diffraction angle (2θ) range was set between 20º and 90º with a step increment of 0.02º and a count time of 0.30 second. The wettability of the surface was assessed with sessile drop method. The contact angles between the drop bovine serum solution (75% distilled water and 25% bovine serum) and the surface samples were measured.

2.4 Corrosion test

The polarization potentiodynamic corrosion tests were performed using Princeton Applied Research Potentiostat PARSTAT 4A. The test samples were set as working electrodes whereas

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SCE Saturated Calomel (sat'd KCL) and two of pure graphite rods were used as a reference and auxiliary electrodes, respectively. 400 mL of bovine serum solution (75% distilled water and 25% bovine serum) was used as the immersion medium. The temperature of immersion medium was kept at 27°C ± 2. The electrochemical test parameter was set to an initial potential of -0.25 V and final potential of +3 V. The scan rate was set at 1.7 mV/s. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined from the Tafel diagram.

3 Results and Discussions

The microstructure of as-cast cp-Titanium is shown in **Fig. 1a**. The microstructure composed of small equiaxed prior β grains with Widmanstaten α in the inner of grain. In contrast, the microstructure of annealed cp-Ti shows equiaxed α grain structure (**Fig. 1b**). The average grains size according to image J software calculation is 28.67μm. The microstructure of titanium can be very different depending on the step of processing due to titanium is allotropy [18]. The annealing was done at temperatures at 900°C, it is above the β transus temperature of the commercially pure-titanium (882°C). The temperature, holding time and cooling rate of the annealing treatment are sufficient to yields equilibrium microstructure with equiaxed grains.

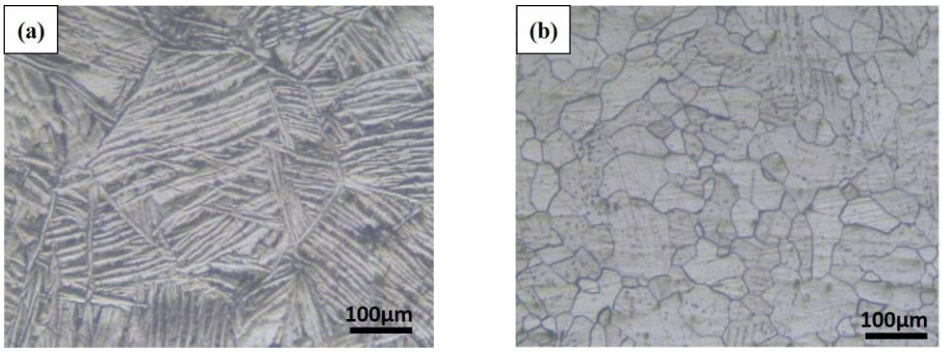

Fig. 1 Microstructure of as-cast cp-Titanium (a), annealed at 900°C for 2 h (b)

3.1 Surface morphology

Fig. 2 shows the change of surface morphology of the untreated and treated titanium surface sample at 700°C for 4, 8, 12, and 36 hours by SEM. The surface of untreated sample exhibit the smooth surface with scratches still appears due to the polishing process (**Fig. 2(a)**). While on the surface that treated thermal oxidation for 4 hours was showed the growth island of the oxide layer (**Fig. 2(b)**). For the sample that treated for 8, 12 and 36 hours showed the existence of a relatively similar in size of oxide layer which covered the surfaces (**Figs. 2 (c-e)**). The growth of oxide layer was formed gradually, a longer holding time of treatment caused the entire surface evenly covered by a layer of oxide. The oxide layer for the 12 hours treated samples show the fine spherical grains. Meanwhile, the treatment at 36 hours exhibit the coarse rod structure with sharp edges. The increase of treatment time influence the size of particle the grains. The EDS results show the composition of the surface reveal the oxygen increase due to the prolonged holding time. The increase of the oxygen level indicates the surface of treated cp-Ti covered by TiO_2 phase oxide layer.

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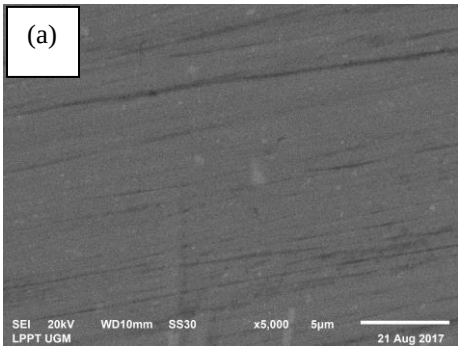
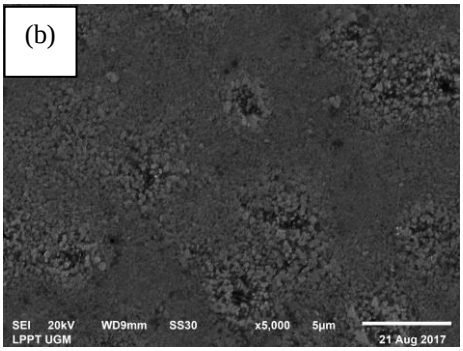
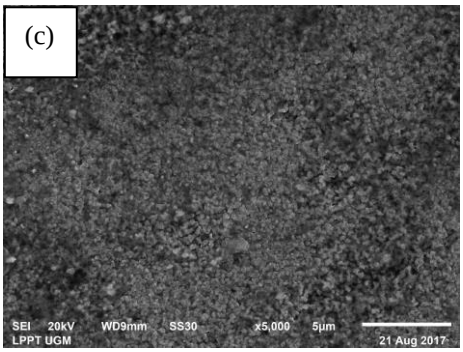


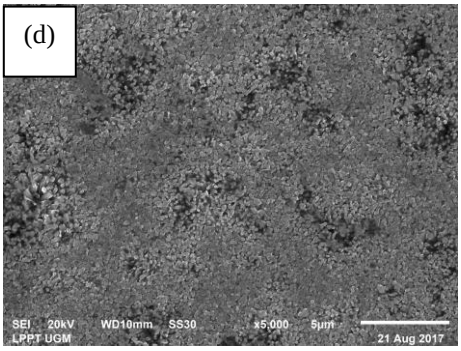
Element	Mass%
Ti	93.85
Others	balance



Element	Mass%
Ti	59.93
O	40.07



Element	Mass%
Ti	50.48
O	44.14
Others	balance



Element	Mass%
Ti	51.56
O	48.44

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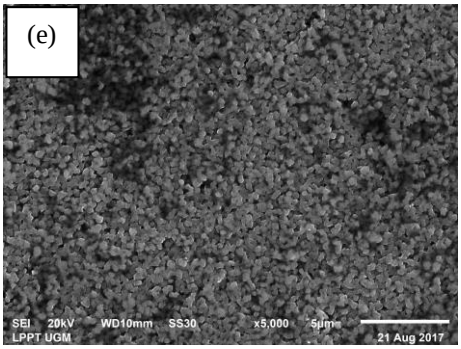

Element	Mass%
Ti	51.56
O	48.44

Fig. 2 Morphology of cp-Titanium surface untreated and after isothermal oxidation at 700ºC : untreated (a), 4h (b), 8 h (c), 12 h (d), and 36 h (e)

3.2 Composition of oxide layer phase

Fig. 3 exhibits the XRD spectrum of the untreated and treated sample. The composition of untreated surface primarily consisted of α-Ti peaks (Ti). There are no peak appears at *2θ* between 20º to 30º. This indicates rutile phase is not formed on the untreated sample surface. The peaks of T_iO_2 rutile and Ti_3O phase appeared in the XRD pattern after the oxidation. The treated samples were mainly composed of rutile T_iO_2 and Ti_3O. According to the papers [19][20], the peaks *2θ* at 27.54º, 36.06º, 41.32º and 54.28º are stated as rutile structure T_iO_2. The titanium oxide (Ti_3O) phase was also found nether similar oxidation conditions in papers [10]. Oxidation holding time increased to 12 and 36 hours the rutile T_iO_2 became the predominant peak while Ti_3O was relatively reduce in peak intensity. Shankar et al [21] reported the oxide layer that obtains by oxidation treatment on cp-Titanium are a protective rutile TiO2 layer which responsible for the enhancement of corrosion resistance. Its also increases the surface hardness and resistance to wear [22].

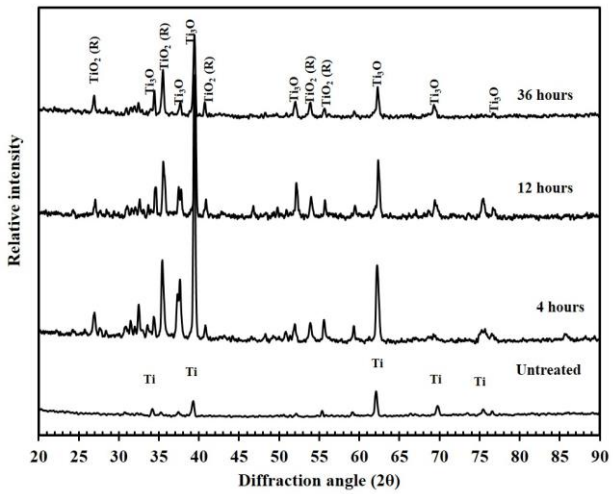

Fig. 3 XRD spectra of the surface sample of untreated and isothermal oxidation treated for 4 h, 12 h, 36 h.

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3.3 Surface microhardness

Fig. 4 shows the microhardness measurements of the sample surface with different of indentation loads. Hardness of the surface layers acquired at the temperature of 700ºC for 4-36 hours ranged from 5.31 ± 0.58 to 8.69 ± 0.85 GPa at the indentation load of 0.245 N. In the higher indentation load, the hardness of the surface layer dropped to ranged from 3.36 ± 0.29 to 6.85 ± 0.49 GPa at the indentation load of 1.89 N. It has been measured that the surface microhardness of the treated sample decreased as the indentation load increased. The 4 hours treated sample reveal a decreased hardness significantly when indentation load increases while the hardness of sample with 12 and 36 hours of treatment reveals the moderate decrease of the hardness. This phenomenon has been caused by the longer of holding time the thicker of an oxide layer was obtained. Increased hardness also influenced by the oxygen diffusion zone that formed underneath the oxide layer [23].

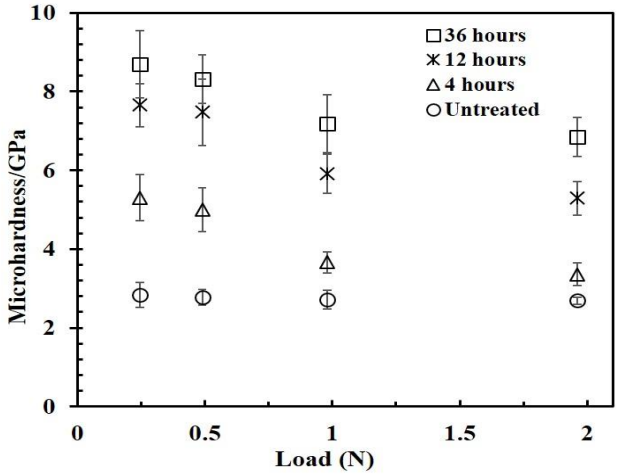

Fig. 4 The effect of indentation load on the surface microhardness of untreated and treated sample

3.4 Surface roughness and wettability

The effect of holding time on the surface roughness and wettability of cp-Titanium are shown in **Fig. 5**. It is clear the surface roughness (Ra) value increased with the increasing holding time. The similar result has been found by others researchers that surface roughness increases when titanium subjected to thermal oxidation treatment at 600-800ºC [24], [25]. In this study, the surface roughness yield to the value of 0.13µm, 0.26µm, and 0.31µm for 4, 12, and 36 hours holding times, respectively. According to Aniolek [23], the growth of the oxide layer on the surface was considered as the factor that influences of the surface morphology change.

Results of drop contact angles measurements before and after thermal oxidation are presented in **Fig. 5**. The measurements showed that thermal oxidation led to a decrease of drop contact angles. It can be seen that the drop contact angle of untreated, 4, 12, and 36 hours is approximately 67º, 66º, 55º, and 47º, respectively. The obtained contact angles values are similar result for Ti64 after oxidation at 700 ºC for 4 h presented in paper [15].

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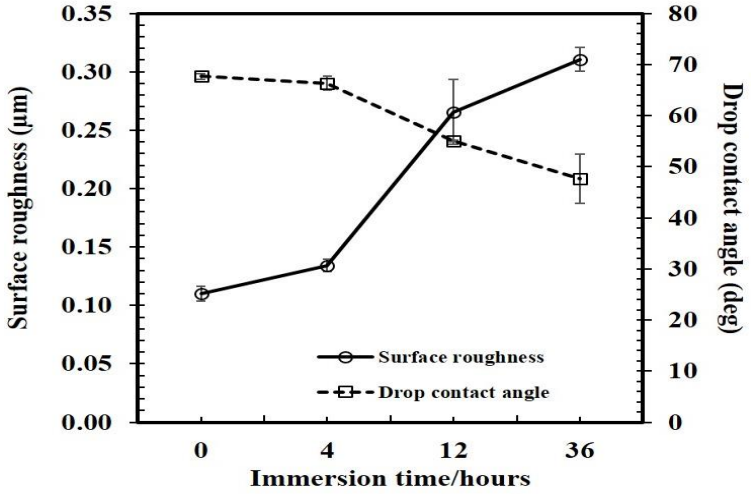
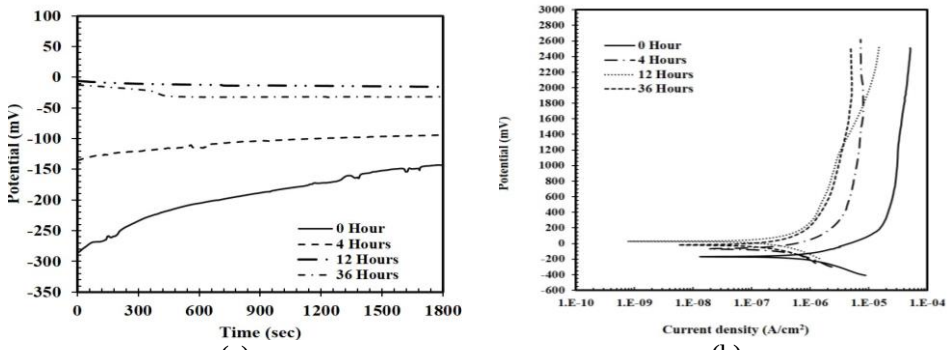


Fig. 5 Effect of holding time on the roughness and wettability

The wettability is very crucial parameters for the implants because as a point of the growth of tissues on the surface [26], enhances of wear resistance and improves the corrosion resistance [15]. Drop liquid solution contains protein. The treated samples for 12 and 36 hours have a large amount of rutile TiO_2, so its easier to absorb proteins than untreated and 4 hours treated samples. According to Elias et al. [27], the surface properties of the titanium affect the protein behavior on the surface, especially for adsorption and adhesion. In the other hand, an increase in surface roughness caused reduced in drop contact angle [28].

3.5 Evaluation of the corrosion characteristic

The curve of open circuit potential (OCP) versus immersion time of the untreated and treated sample in bovine serum liquid are shown in **Fig. 6 (a)**. The values of the OCP for the untreated



(a) (b)

Fig. 6 (a) Curve of open circuit potential (OCP) vs time, (b) curve of potentiodynamic polarization

and treated not exhibit any significant change. The OCP of untreated sample started at a negative potential and shift to the more positive potential up to -143 mV. The OCP of the treated sample

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(4 hours) began change direction to more positive values until it stabilized and reached an OCP of -94 mV. For the sample that treated for 12 and 36 hours, the OCP show the relatively stable condition from the start to the end of the test and the OCP value reach of – 15 mV and -31 mV for 12 and 36 hours, respectively. A shift of the open potential to the positive state was found in this experiment and in a match with the previous finding [29].

The result of potentiodynamic polarization test of untreated and treated samples are shown in **Fig. 6 (b)**. It is clearly the curve shows that untreated and treated sample exhibit the similar passivity behavior in bovine serum solution of 25% bovine serum and 75% distilled water. The current density of the samples were determined from the Tafel polarization curve as 1.16 μA/cm^2, 0.932 μA/cm^2, 0.275 μA/cm^2, and 0.51 μA/cm^2 for the untreated sample, 4 hours, 12 hours and 36 hours thermal oxidize samples respectively (**Table 1**). The corrosion resistance of cp-Titanium increases due to experienced by thermal oxidation treatment. The shift of the current density in the direction of a lower value and along with a more positive E_{corr}, it describes the treated sample able to provide a more excellent corrosion resistance than the untreated ones. The similar finding has been reported in a paper [15] for Ti64 oxidized in bovine serum solution. On the other hand, the existence of proteins in the bovine serum as electrolytic liquid is capable to protect the titanium surface against oxygen diffusion. The bovine serum is a solution with rich of protein. Khan et al [14] revealed that the presence of the proteins can be as inhibitor or accelerate the corrosion of the metal. The best of corrosion resistance achieve by 12 hours treated sample but there are no significant differences for all treated samples. Thermal oxidation treatment of commercially pure titanium at 700^{o}C for 4-36 enhances the hardness, wettability, and corrosion resistance.

Table 1 Result of corrosion test of untreated and treated cp-Titanium

Sample condition	E_{corr} (mV vs SCE)	I_{corr} (μA/cm^2)	Corr. rate (mmpy)	I_{pass} at +0.2 V (μA/cm^2)	I_{pass} at + 2 V (μA/cm^2)
Untreated	-163	1.160	0.01	15.8	44.39
4 Hours	-87.8	0.932	0.0081	2.38	8.04
12 Hours	38.7	0.275	0.0024	0.78	10.5
36 Hours	-19.8	0.510	0.0044	0.92	5.11

4 Conclusions

1. The thermal oxidation enhances the surface hardness of cp-Titanium. Oxidation at a temperature of 700^{o}C for 4-36 hours leads to the formation of rutile oxide layers TiO_2 and Ti_3O
2. Surface hardness of treated samples yield of 5.31 ± 0.58 to 8.69 ± 0.85 GPa at the indentation load of 0.245 N and dropped to ranged from 3.36 ± 0.29 to 6.85 ± 0.49 GPa at the indentation load increase to 1.89 N. The longer time of thermal oxidation treatment would promote the thickness of the oxide layer.
3. The surface roughness increase significantly compared to the untreated surface. It is clear that there is 2 to 3 times increase in the surface roughness. The evolution of the structure of the oxide layer at the surface as a function of holding time causes the increase in surface roughness.
4. The wettability of cp-Titanium has been improved by isothermal oxidation treatment, the contact angle decreased by approximately 4^o to 20^o.

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5. The presence of the oxide layer formed at 700°C enhance the corrosion resistance of cp-Titanium in bovine serum

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