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Evaluation of the Corrosion Erosion by Cavitation in [TiN/ZrN] Multilayers Coatings

W. Aperador[*], *E. Delgado, J. Duque*

Departamento de Ingeniería, Universidad Militar Nueva Granada, Carrera 11 No. 101-80, Fax:+57(1) 6343200, Bogotá, Colombia.
[*]E-mail: g.ing.materiales@gmail.com

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In this work is presented the mitigation of the damages caused by the corrosion erosion phenomenon through application of $[TiN/ZrN]_{200}$ coatings obtained by the multi-target magnetron sputtering PVD technique and deposited on 4140 steel substrates. The test was performed in a cavitation chamber which is adapted to a potentiostat galvanostat to determinate the corrosion susceptibility. The multilayers were evaluated against the corrosion erosion synergy in a solution composed of 3% NaCl, analyzing the effect of the multilayers period increase. The electrochemical characterization was made by the electrochemical impedance spectroscopy and Tafel polarization curves. By scanning electron microscopy was determined the morphology after the degradation test. Making performance analysis was found that the deposition of the [TiN/ZrN]n multilayers, influences the degradation resistance by the cavitation phenomenon, prolonging the corrosive phenomenon which controls the material deterioration further no mechanical wear.

Keywords: cavitation, corrosion, erosion, multilayers

1. INTRODUCTION

Phenomena as the wear and the corrosion are problems which frequently facing the devices of industrial machines, in special the related with the fluid transport as parts of pumps [1-3]. The corrosion erosion by cavitation is generated subsequently of an accelerated process by the implosion of bubbles on the metal surface, after of boiling or gas generation due to pressure changes, generating the depassivation and accelerating corrosive processes [4-5]. To reduce the corrosive effect has been implemented hard coatings, which are applied on the surface of used devices in different industries such as metalworking, aeronautics, fluid transport, mining and oil. By the hard coatings application is possible increase the wear and the fatigue, achieving an improvement in the useful life of the devices [6-7].

Among the techniques most used for obtaining hard coatings is the physical vapor deposition (PVD), in where the material that will be the coating is evaporated, subsequently it is condensed in a layer form on the substrate [8]. Between the materials that are manufactured by the PVD processes, there are the binary materials as: TiN, CrN, ZrN; the ternary as: TiCN, TiAlN, AlTiN; and the quaternary as: TiAlCrN, TiAlVN, as well as multilayer combinations of those to improve its mechanical properties such as hardness and toughness [9-11].

In the vibrational cavitation the forces that cause the formation and the colapse of the cavities are determined by series of pressure pulsations of high frequency in the liquid interior. These pressure pulsations are generated by a submergible surface which vibrates thus generating pressure waves in the liquid [12]. The generated cavitation in the fluids subjected to special conditions of flow affects the efficiency of hydraulic systems and produces undesirable problems as the increase of noise, vibrations and the erosion [13-14]. The study of the erosion by cavitation becomes difficult because it involves additional phenomena related with the flow and the material behavior that is in contact with the liquid. Some of the factors that influence in the erosion rate produced by a fluid are related with the load that the solid surface is subjected, the geometry of the fluid, the pressures distribution in the system and the specific properties of the fluid. The erosion formation by cavitation depends on the material properties as its hardness, grain size, resistance to corrosion and mechanical stress. One way to increase the protection of the material against the effects that generates the cavitation is to manufacture high strength coatings [15-16].

In this work is proposed mitigate these types of damages by the application of $[TiN/ZrN]_{200}$ coatings obtained using the multi-target magnetron sputtering PVD technique and deposited on 4140 steel substrate. For the development of the test was taken into account the specifications established by the ASTM G32-98 standard, to evaluate the generated degradation simultaneously with the corrosion erosion was adapted a potentiostat galvanostat in the cavitation chamber.

2. EXPERIMENTAL DEVELOPMENT

The evaluation of the erosion-corrosion cavitation resistance was performed using a equipment that has an ultrasonic oscillator mainly composed of an ultrasonic transducer which oscillates at 20 kHz with an amplitude of 100μm, and a sonotrode as is shown in the figure 1. The equipment configuration was made according to the guidelines that indicate the ASTM G32-03 standard. The test method was indirectly, which contemplates the location of the test sample at 0.5 mm from the oscillator tip. The oscillator equipment has adapted the reference electrode – RE (Ag/AgCl), the auxiliary electrode –AE (Platinum wire) and the sample holder(working electrode) WE with a exposed area of 1 cm^2, the electrodes are immersed in a solution composed of 3% NaCl and connected to a potentiostat – galvanostat Gamry PCI-4 model using the Tafel polarization curves technique and electrochemical impedance spectroscopy.

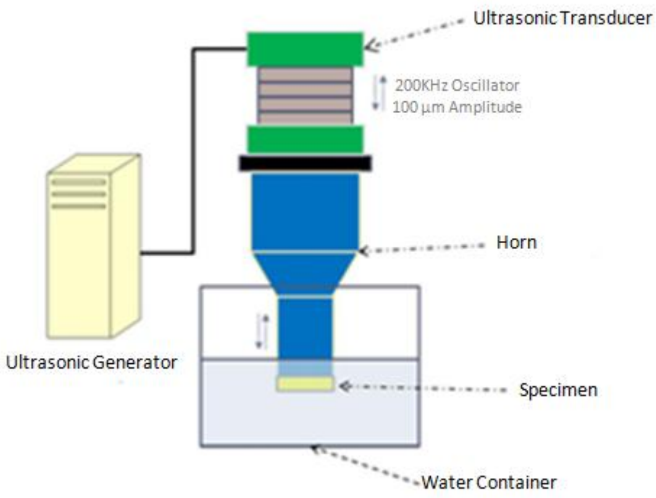


Figure 1. Schematic of cavitation erosion test.

The $[TiN/ZrN]_{200}$ multilayers were deposited on 4140 AISI (diameter 2 cm; thickness 4 mm) and Si (100 orientation, 1.7 cm across; 280 microns thick), which were cleaned by ultrasonic in a sequence of 15 minutes in a bath of ethanol and acetone. The coatings were obtained using the technique of multi-target mangnetron sputtering in r.f (13.56 MHz). For the deposition of the coatings were used targets of 4 inches in diameter of Ti and Zr with a purity of 99.9%. The base pressure at the interior of the vacuum chamber was $4.0x10^{-6}$ mbar. Before initiating the deposition, the substrates were subjected to a cleaning by plasma during 20 minutes in Ar atmosphere at a bias of -400 V in r.f. During the growth, the working gasses were Ar (93%) and N_2 (7%) with a total working pressure of $4.0x10^{-2}$ mbar at a substrate temperature of 250 °C and a substrate bias r.f of -100V with a 350W of power. For the deposition of the multilayers the titanium targets as well as the zirconium were covered periodically by the obturator alternatingly, while the substrate was maintained under circular rotation in front of targets to facilitate the formation of the coatings.

With the purpose of study the influence of the corrosion and cavitation synergy in coatings of multilayers type, systems of $[TiN/ZrN]_n$ were deposited controlling the opening and closing time of the obturator. The thinckness of the coatings was obtained using a DEKTAK 8000 perfilometer with a tip diameter of 12±0.04 µm at a scanning length between 1000 µm – 1200 µm. For the specimens with 200 bilayers, the thickness was 3.00 ± 0.04 µm, given that the coatings were obtained under the same parameters of growth and total deposition time (3 hours), is possible to state that the multilayers systems have a thickness around this value.

The specimens were subjected to wear by cavitation erosion-corrosion during a total exposition time of 480 minutes at 25 °C of temperature in a solution of NaCl 0.5 M. Three evaluations were performed at 30, 180 and 480 minutes. To determine the weight loss due to the erosion, the specimens were removed from the solution at intervals of 30 minutes; cleaned with a jet of water, dried with hot air and weighed on a precision balance (0.1 mg). The phenomena of degradation and superficial characteristics were observed with a scanning electron microscope (SEM) JEOL NeoScope JCM-5000, equipped with an electronic scope with a magnification range of 50-40,000X.

3. RESULTS

In the figure 2 is observed that the solution resistance (Rr+s) at different evaluation levels is very similar; which indicates that the coating resistance on the surface has a tendency to kept constant. The value of the coupling composed of the R1 resistance and the CPE1 capacitance, is related to the reactions formed on the external layer, these parameters are reduced as far that the evaluation time increases. The same behavior is noticed for the denominated R2 resistance, where is observed that at higher evaluation time the value of those parameters are lower. The value of CPE2 capacitance decreases due to the passivating layer of the coating that starts to be vulnerable owing to the effect of corrosion erosion synergy.

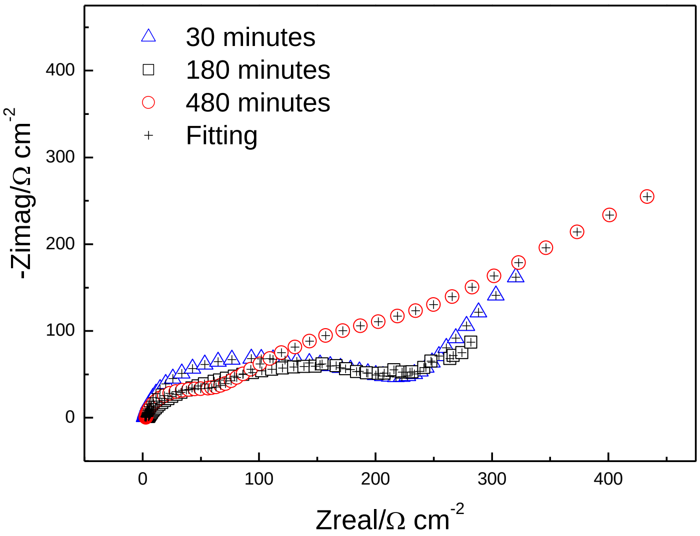


Figure 2. Nyquist diagram for multilayer evaluated versus time.

The impedance spectroscopy technique that was applied to the $[TiN/ZrN]_{200}$ coatings gives a physical model, for the three evaluation states. In the figure 3 is obtained a time constant, which is observed in the impedance spectra at low frequencies that allows finding a time constant related to the contact layer with the corrosive fluid. The response at high frequencies allows the determination of the coating resistance. The presence of dislocated semicircles suggests a behavior of non ideal of the capacitor, leading to the introduction of the constant phase element (CPE), which allows increasing the precision on the determination of the polarization resistance [17].

The figure 2 shows the coatings behavior subjected to cavitation erosion and subsequently the electrochemical evaluation at 30, 180 and 480 minutes. The circuit of the figure 3 shows a first resistance (Rr+s) associated to the first reaction that has the coatings in contact with the solution, it is found at high frequencies 100kHz; then we found a CPE and a resistance associated to the first elements that are on the coating in its external part, these elements can be due to generated reactions or superficial absorption of some species with the chloride ion penetration; at low frequencies can find other elements such as a CPE and a resistance, these elements are associated to a zone of interface transition coating-steel; at low frequencies domain normally is found the load transfer process in combination with the mass transfer process.

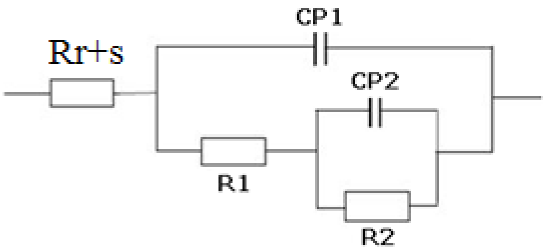


Figure 3. Equivalent circuit used to fit multilayer impedance data.

In the figure 4 is observed the obtained polarization curves, which allow finding the values of the anodic and cathodic slopes in each case that, are shown in the table 1 along with the values of current density and corrosion rate for each one of the studied cases. The found parameters with the polarization curves let to use the Stern – Geary equation to find the densities of corrosion current. It was determined that the higher corrosion rate was for the multilayers exposed to 8 hours of test, with a period of 200 bilayers, finding a 5.45 mpy value. In the case of the 3 hours test the used deposition conditions generate a significant change in the behavior against the corrosion deposits, obtaining intermediate values of 1.21 mpy. With the 30 minutes evaluation was noticed a marked influence of the evaluation time in the lower grade of deterioration of the deposit, finding corrosion rate values much reduced (0.095 mpy) in comparison with the other evaluation time.

Table 1. Found electrochemical parameters with the Tafel polarization curves.

Parameter	480 minutes	180 minutes	30 minutes
β_a (mV/decade)	145.3	16.4	1.23
β_c (mV/decade)	165.3	12.3	6.34
i_{corr} (μA)	10.4	2.23	0.176
Ecorr (mV)	-332	-274	-301
Corrosion rate (mpy)	5.45	1.21	0.095

In the figure 4 relating to test carried out at 30 minutes may be observed a cathodic section and when the potential increases over the corrosion potential is observed the existence of a passive area, in which the current density is relatively independent of the potential.

If the potential increases even more, is reached a critical value of potential denominated potential breakdown or pitting potential, for which is produced a sharp increase of the current density indicating that has been produced the rupture of the passivity and has been started located corrosion on the surfaces. For the performed test at 180 and 480 minutes is observed a strong difference with the coating evaluated at the 30 minutes, due to the current density is more than one order of magnitude higher. This result is indicating that the coating is adequate, however when is evaluated at high times and the synergy erosion corrosion generates intermediate values of wear, owing to the corrosion current has increased, which indicates that the coating has a load transfer reaction produced on the $[TiN/ZrN]_{200}$ surface easily, being the redox reaction that take place on the same controlled by diffusion. Indeed, due to the porosity increases of the coatings the passivility, which is a superficial property that increases by the cavitation effect in the material and the combined corrosion phenomenon [18].

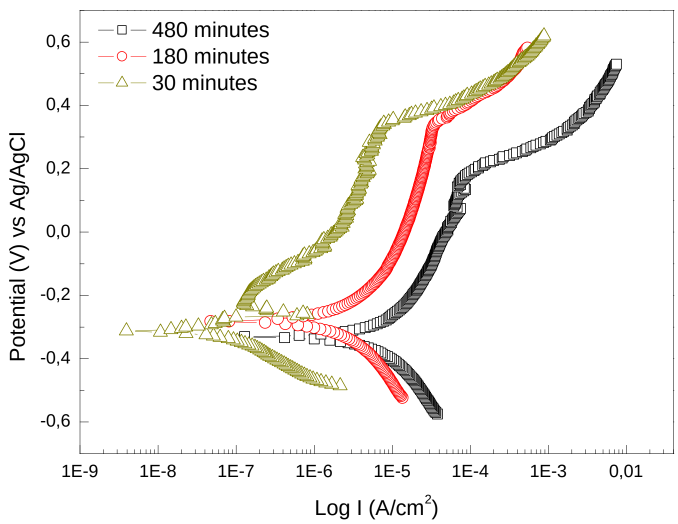


Figure 4. Tafel polarization curves corresponding to the evaluated corrosion erosion in the multilayers.

3.1. Erosion

In the figure 5 is observed the behavior of the erosion rate curve evaluated in function of time, where is noticed that the $[TiN/ZrN]_{200}$ coatings generate several wear phases, initially is the state denominated incubation where the coating subjected to cavitation generates a depreciable erosion due to the loss mass is depreciable until the 180 minutes of evaluation , subsequently is obtained an increase of loss mass owing to the superficial fatigue generated by the wear phenomenon, the tendency is enhance the detachment of the coating, to the end of the test. By using the criteria of the ASTM G32-03 standard, is obtained that this coating type generates a low detachment by the erosive effect due to the mass loss curve before the 180 minutes generates a minimum value [19]. In the second evaluation stage is found that the wear rate increase is due to the adhesive wear, since the multilayer effect generates a minimum mass loss, it indicates that the micro- mechanisms of wear are those responsible of the presence and advance of wear phenomena and favor further removal of the outer layers of the material [20].

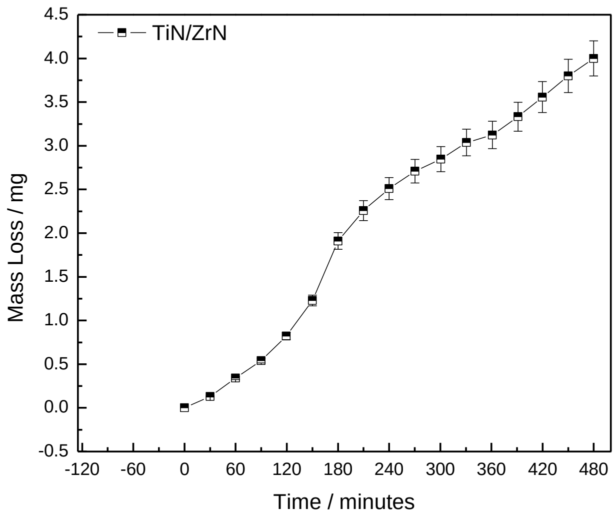
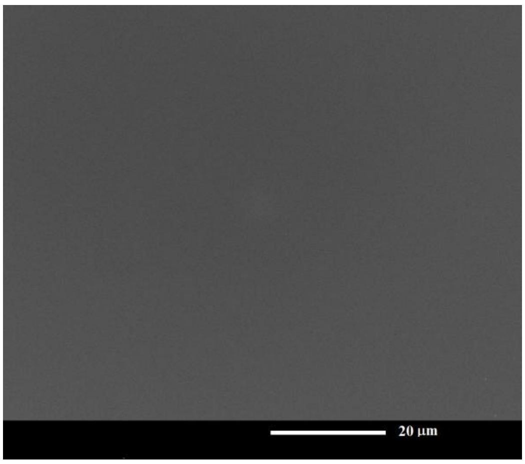


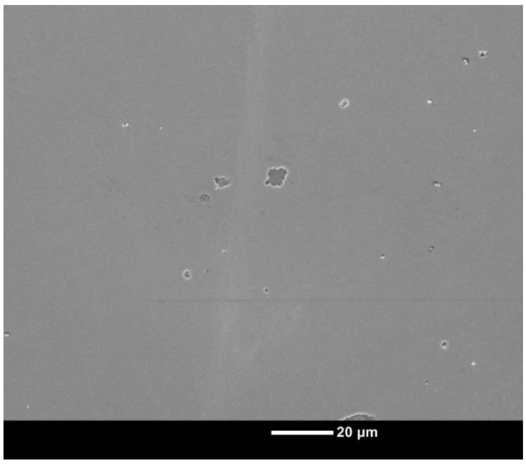
Figure 5. Wear curve generated in the cavitation erosion test.

3.2. SEM

In the figure 6 is observed the micrographs of the evaluated coatings in function of the time (30, 180 and 480 minutes). The interface volume behaves as a compact phase softer in the hard material in layer. The energy dissipation is made in the interface, due to a reduction of the coating fragility. In the micrograph of the figure 6b and 6c were shown the failures that have suffered the multilayers coatings where can be observed the failure that increases owing to the exposition time, given evidence of the deflection of the cracks at the interface, the increase in the superficial wear is low due to the limits between the interfaces inside the layers, this is generated by the perpendicular orientation of the grain with respect to the growth orientation of the layer.



(a)



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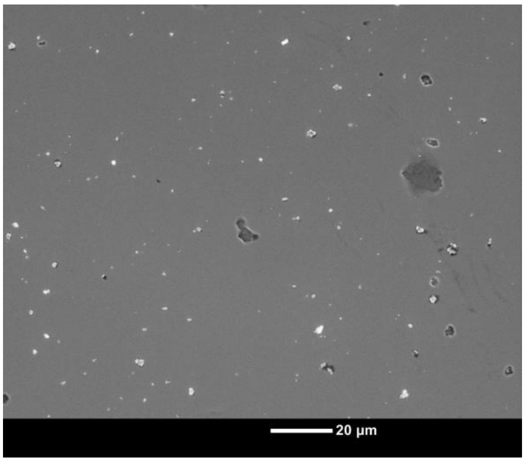
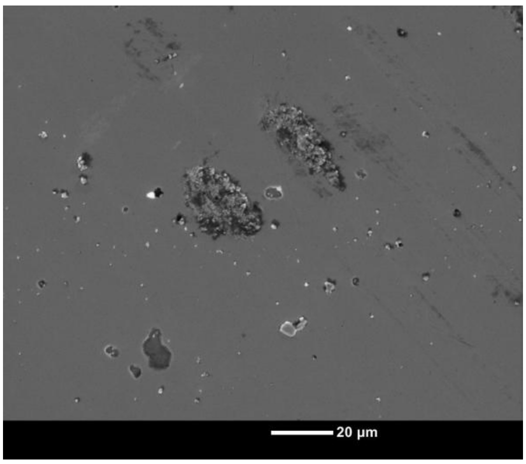


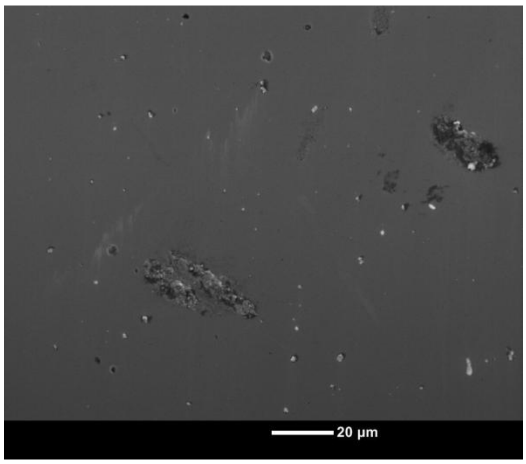
(c)

Figure 6. Erosion phenomenon micrographs generated multilayer coatings evaluated at different time. a) 30, b) 180 and c) 480 minutes.

In the figure 7 is observed the micrograph of the surface exposed to a set phenomena of erosion corrosion by cavitation, this mixed phenomenon is generated after a accelerate process by the implosion of bubbles on the metal surface, later than of the boiling and generation of gases due to the pressure changes, generating the depassivation and accelerating the corrosive processes. The micrographs of the multilayer with 200 bilayers after the process of corrosion erosion by cavitation. In the figure 7a and 7b is observed that part of the coating has been deteriorated due to the corrosive effect, additionally is noticed how the coating has suffered wear mechanisms by cracking. In the figure 7c different zones are distinguished: the center zone of the micrograph shows the noxious effect generated by the action of the corrosion and the coating cracking, leading by generated by the energy dissipated in the 480 minutes of evaluation. Furthermore, it is observed gray zones at the extremes, where the protective effect has generated defense mechanisms and low cracking zones, these areas show a surface without fracture that presents the protection given by the multilayer [21-22].



(a)



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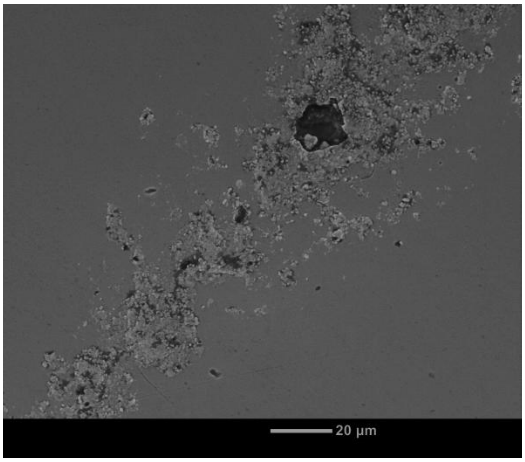

(c)

Figure 7. Micrographs of coatings exposed to erosion corrosion evaluation at different times. a) 30, b) 180 and c) 480 minutes.

4. CONCLUSIONS

The corrosion erosion cavitation test allows to determine the adequate performance of the $[TiN/ZrN]_{200}$ multilayers coatings, due to its low mass loss observed at the erosion cavitation test. The electrochemical test obtained by the Tafel polarization curves in the corrosion erosion test show the good performance that generate the multilayers, due to the shift towards positive potentials at the evaluation time; initially the Tafel polarization curve indicates a protection due to the achieved passivation at short evaluation times, subsequently a general dissolution is determined, this behavior is owing to the aggressive effect generated by the corrosion and the addition of the erosion together. Using the technique of electrochemical impedance spectroscopy was obtained the corrosion resistance value and the physical model that indicates the values of the coating protection.

By means of the technique of scanning electron microscopy, the protector effect of the multilayers was observed; due when the system was evaluated independently it was obtained how the accelerated corrosion affects on the coating which shows a surface degradation by the corrosive effect, subsequently the corrosive erosive effect is observed owing to cavitation , for the coated specimens is noticed wear mechanism caused by the suffered cracking by the erosive effect, and a zone of generalized corrosion due to the corrosion effect.

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