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Short Communication

Diagnostic of the Erosion Corrosion Evolution by Cavitation of $[TiN\text{-}TiAlN]_{200}$ Thin Coatings

W. Aperador[*], *E. Ruiz, A. Delgado*

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 results of the corrosion erosion resistance evaluation by cavitation of the thin films in multilayers form of TiN/TiAlN deposited with 200 bilayers period onto AISI 4140 steel substrates, by means of magnetron sputtering system with reactive r.f. from high purity targets of Ti and Al (99.99%) in an atmosphere composed by Ar/N. The test was performed with a high frequency generator and the sample immersed in a liquid containing sodium chloride. The electrochemical characterization was performed using the techniques of electrochemical impedance spectroscopy and Tafel polarization curves. The microstructural characterization was obtained by scanning electron microscopy. It was state that the coatings subjected only to the phenomena of erosion produced by cavitation generate low damages, due to the material loss is minimum. However, when the coatings are subjected to simultaneous corrosion and erosion damage by cavitation the deterioration is high, owing to the synergy of the two evaluated mechanisms.

Keywords: erosion, corrosion, coatings, cavitation, TiN-TiAlN.

1. INTRODUCTION

The cavitation that is suffered by the materials, is a phenomenon generated by the vapour bubbles due to pressure drop, associated with a high fluid velocity or vibration. One of the consequences of the cavitation is erosion that is observed on the surface [1-3]. The deteriorated metallic pieces apart from the presence by erosion damages also presents wear by corrosion which can be confused with damage caused by the occurrence of vibrations. In the oscillating cavitation test is generated energy that causes the formation of the holes, formed by steps of pressure pulses at high frequencies in the fluid [4]. These pressure pulses are formed by a submergible surface; which vibrates generating pressure waves in the liquid [5]. The generated cavitation in the fluid subjected to special conditions of flow, affects the hydraulic systems efficiency and produces undesirable problems such as increased noise, vibration and erosion [6].

The erosion by cavitation is a consequence of the damages due to fatigue processes that are formed onto the material surface [4]. The cavitation effect can cause the accelerated elimination of the thin film that exists on the metallic material [7]. If this mechanism is generated, the resulted type of material loss is denominated erosion-corrosion cavitation. The superficial properties of the material performance an important role in the nature of the interaction with the protective layer; the most important are the surface passivity of the metal, the corrosion product adherence, the metallurgical condition of the metal, the diffusion of dissolved oxygen, the presence of aggressive ions and the intensity of cavitation[8-9]. These factors determine the corrosion mode and the loss rate of erosion-corrosion.

The hard coatings as nitrides based on transition metals deposited by techniques such as physical vapour deposition and onto different steel substrates, are turned in the solution for many engineering problems among them the corrosion, due to its chemical inertness. Among the above nitrides is the titanium nitride (TiN) that deposited as monolayer keeps a dominant position in the field of hard coatings to enhance the wear resistance. It has improved the properties of this coating including a third component that is known as aluminum titanium nitride (TiAlN), the incorporation of aluminum atoms (Al) in the crystalline structure of the titanium nitride (TiN) not just increases the oxidation resistance by means of the formation of a stable and compact layer in the surface but also contributes to a significant increase in the hardness in comparison with the binary simple nitride[10]. In the last years, it has been made considerable efforts to develop multicomponent coatings as multilayer heterostructures with the purpose of enhance the wear resistance and the oxidation of the coated components[11-12]. The improvements are present on the alternating deposition of two (or more) chemical layers and/or mechanically different, in such a way the stress concentration and the conditions for the nano-cracks propagation can be controlled. Therefore, the multilayers structure can act as nano-cracks inhibitor, moreover of increase the resistance to the fracture [13].

The present article aims to evaluate the relation between erosion, corrosion and the synergism among the erosion generated by cavitation and corrosion in a NaCl solution 3,5 % at 23 ° C, in the $[TiN\text{-}TiAlN]_{200}$ coatings obtained by the technique of multi-target magnetron sputtering PVD and deposited on 4140 steel substrates.

2. EXPERIMENTAL

The estimation of the damage caused by the cavitation effect in a corrosive fluid was perfomed by equipment which has an ultrasonic oscillator composed by ultrasonic transducer that oscillates at 20 kHz with 100 μm of amplitude, and a sonotrode as is shown in the figure 1. The equipment configuration was performed taking into account the guidelines that are indicated at the ASTM G32-03 standard. The test method was indirectly; which contemplates the specimen location at 0.5 mm of the oscillator tip. The oscillator equipment has adapted the reference electrode – RE (Ag/AgCl), the auxiliary electrode – AE (Platinum wire) and the sample holder the working electrode – WE with an exposure area of 1 cm^2, the electrodes are immersed in a solution composed of 3.5% NaCl and connected to a potentiostat – galvanostat Gamry PCI-4 model using the electrochemical impedance spectroscopy and Tafel polarization curves techniques.

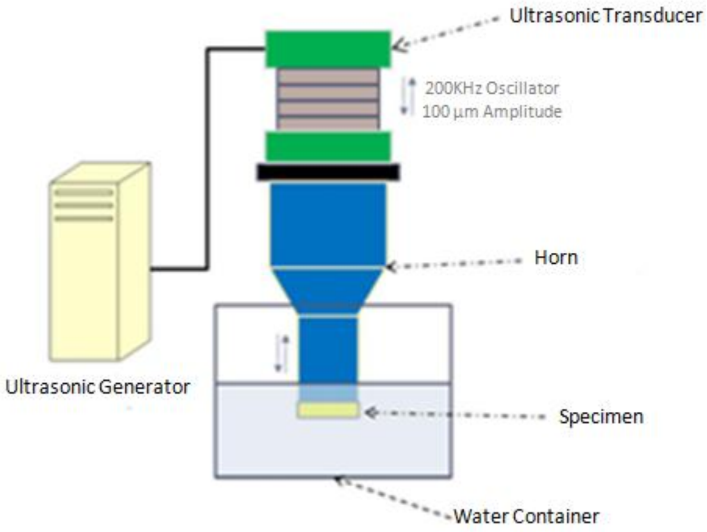

Figure 1. Device used for conducting the tests of cavitation - erosion, assisted for corrosion.

The $[TiN/TiAlN]_{200}$ multilayers were deposited on AISI 4140 steel substrates and Si (100), which were degreased by ultrasonic in a 15 minutes sequences of ethanol and acetone. The coatings were obtained by the multi-target magnetron sputtering in r.f (13.56 MHz). For the coatings deposition were used targets with 4 inches of diameter of Ti and Al having a purity of 99.9%. The base pressure inside the vacuum chamber was $7.0x10^{-6}$ mbar.

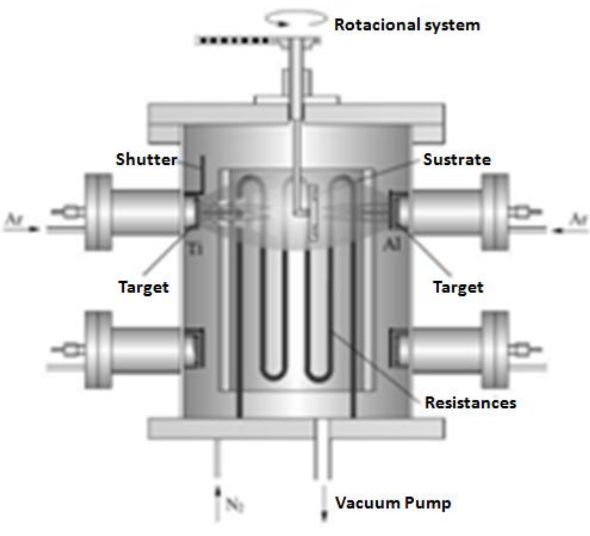

Figure 2. Schematic diagram of the multi-target magnetron sputtering system

Before the deposition star, the substrates were subjected to plasma cleaning during 20 minutes in Ar atmosphere at a bias of -400 V in r.f. During the growth, the working gases were a mixture of Ar (93%) and N2 (7%) with a total working pressure of $6x10^{-3}$ mbar at 300 °C of substrate temperature and a r.f bias of -70 V of the substrate. For the deposition of the multilayers the aluminum target was periodically covered by the shutter, while the substrate was kept under circular rotation in front the targets to facilitate the coatings formations. A scheme of the multi-target magnetron sputtering system used in this work is shown in the figure 2.

With the purpose of study the influence of the synergy among the dynamic corrosion, erosion and corrosion erosion in multilayers coatings, [TiN/TiAlN] systems were deposited with a period of 200 bilayers controlling the opening and closing times of the shutter. The thinness of the coatings was obtained by a profilometer DEKTAK 8000 with a tip diameter of 12±0.04 μm at a scanning rate between 1000 – 1200 μm.

For the evaluation of erosion by cavitation-corrosion a potentiostat – galvanostat PCI-4 model was used, using the techniques of electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. The specimens were located under immersion in a NaCl 0.5 M solution prepared with distilled water. The cell composed by a counter-electrode (Platinum wire), a reference electrode of Ag/AgCl and as working electrode was used AISI 4140 steel coated with [TiN/TiAlN] multilayers. The Nyquist diagrams was obtained with frequency sweeps between 100 kHz and 0.001 Hz using an amplitude of the sinusoidal signal of 10 mV and an exposed area of 1 cm^2; the Tafel diagrams was obtained at a scanning velocity of 0.5 mV/s in a range of voltages from -0.25 V to 1 V using an exposed of 1 cm^2, the used standards in the measurement conditions and calculations corresponding to the ASTM G5, G 52 and G59 [14-16].

To determinate the weight loss due to the erosion by cavitation, the specimens were subjected to wear by cavitation erosion-corrosion during a total exposition time of 480 minutes at 23 °C in a solution of 3.5% NaCl, the specimens were removed of the solution at intervals of 30 minutes, they were cleaned with a water jet, dried with hot air and weighed in a precision balance (0.1 mg). The degradation phenomena were observed with a scanning electron microscope (SEM), the superficial characteristic were determined with a SEM JEOL NeoScope JCM-5000 equipped with an electronic scope with a magnification range of 50 to 40.000 X.

3. RESULTS AND DISCUSSION

In the figure 3 is shown the Nyquist diagrams of the [TiN/TiAlN] coatings and the 4140 steel subjected to erosion by cavitation and corrosion simultaneously, the test of the substrate as well as the coatings were evaluated to 8 hours of wear. It can be observed that the coatings have a different electrochemical response for each of the test times, for the diagrams analysis was started from the real part (Z´) and the imaginary part (Z´´); from 0 to Z´ and Z´´ 90 kΩ cm^2 associated to the intercept of the curve with the x-axis. In these results were observed a strong of the semi-domes dependence that describes the electrochemical behaviour in relation with the time test. The solution resistance value in the analysed systems is similar for all the analysed specimens and in average has a value of 42 Ω cm^2.

The steel without coating shows a unique semi-dome and it is associated to the Randles cell type behaviour, in where the impedance value indicates a electrochemical interaction of the solution and the substrate caused by the oxide layer that forms on steel with the contact of the aggressive solution which is subjected, indicating a low value and a poor performance against wear phenomena in combination, the multilayer coating of $[TiN/TiAlN]_{200}$, show two time elements; the first is a semicircle in the high frequencies, this correspond to the passive layer and/or the dielectric properties of the coating, the second semicircle is associated to the interface among the multilayers and the substrate, this corrosive process is found for low frequencies [17].

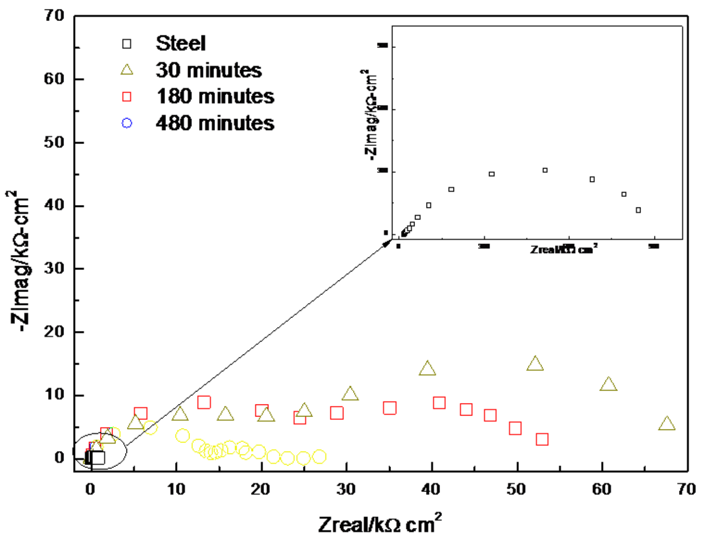

Figure 3. Nyquist diagrams for the substrate and the $[TiN/TiAlN]_{200}$ multilayers evaluated at different times.

The figure 4 shows the equivalent circuit used in the simulation of the impedance data for the multilayers. Of the circuit can be extract the values of the polarization resistance (*Rp*). The results indicate that the polarization resistance decreases in function of the test time increase. For the multilayers were obtained that the equivalent circuit have two elements of phase constant distributed inside the circuit (*CPE1 y CPE2*) which allow to consider the two constants of relaxation time. Therefore if the *CPE1-R1* couple predominates at high frequencies can be origin by the passive layer and/or the dielectric properties of the multilayer, while the *CPE2-R2* predominant couple at low frequencies is a characteristic of the corrosive process among the steel/multilayers which is associated to surface defects, whereby the solution can interface with the steel substrate. The *CPEs* distributions are widely used in the experimental data settings, because allow analysing properly the semicircles low presence of depressed. Therefore, the depressed semicircle is due to dispersion in the constant time generally, caused by irregularities in the steel surface, surface roughness, and in general to certain processes associated with an irregular distribution of the applied potential (10 mV) to obtain the EIS data. The admittance representation of a *CPE* (*YCPE*) shows a fractional potential that depends on the angular frequency (ω): *YCPE = YP(j*ω*)α* where *Yp* is a real adjustable constant used in the non-lineal adjust by least-squares.

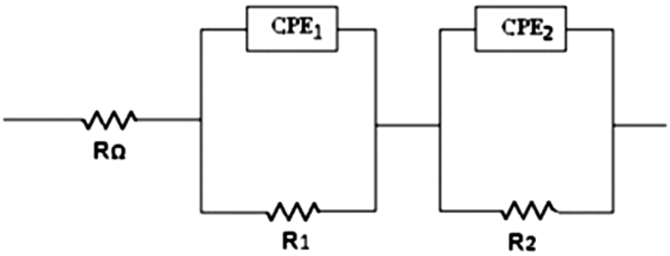

Figure 4. Equivalent circuit generated in the evaluation of the erosion by cavitation electrochemically assisted $[TiN/TiAlN]_{200}$.

The Tafel polarization curves that were obtained in the figure 5, allow to observe that the corrosion potentials obtained in the multilayers compare with the substrate, acquire values with a tendency to the cathodic areas (protection), moreover as the evaluation time is increased, the potential decays, moving towards anodic areas, with respect to the corrosion current density (Icorr), the values of this property decreases in comparison to the substrate, at the compare the values of Icorr, it is obtained that the [TiN/TiAlN] coating evaluated at 30 minutes shows the best performance and subsequently increases the degradation value due to the rugosity change that has been provoked by the synergistic effect, since the surface irregularities are caused by the effect of the cavitation and metallic dissolution owing to the electrochemical effects generated after 30 minutes.

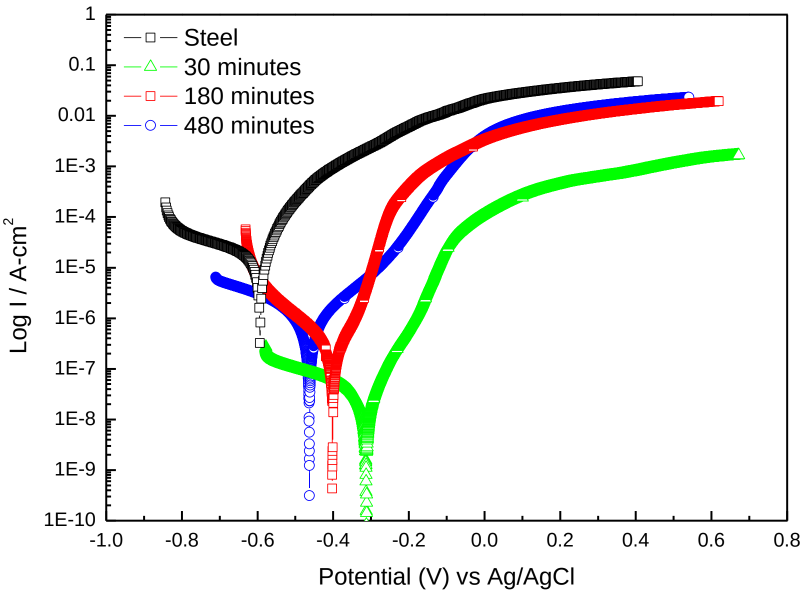

Figure 5. Tafel polarization curves of the substrate and coatings subjected to tests generated by cavitation erosion and assisted for corrosion.

Corrosion rates were obtained from the equation of Stern - Geary :

$$i_{corr} = \frac{\beta_a \beta_c}{2.303\, R_p\, (\beta_a + \beta_c)} \quad (1)$$

Where : Rp corresponds to a polarization resistance, bc is the cathodic Tafel slope and where ba is the anodic Tafel slope .

These slopes are the Tafel polarization curves which are found in Figure 5, indicates a first approximation of the behavior in this corrosive solution also corroborated the information obtained in the Nyquist diagrams due to unlike polarization resistance in each of the materials tested, therefore the polarization resistance is a parameter that varies, values of corrosion rate with the values are current corrosion since directly proportional, therefore can be said that the values of polarization resistance are inversely proportional to the values of the corrosion rate , this is derived from the equation of Stern - Geary .

The polarization curves obtained allow to find the values of the cathodic and anodic rates in the three time of evaluations, which are shown in Table 1 together with the values of current density and corrosion rates for each of the cases studied. The parameters found using the polarization curves allow to use the equation of Stern - Geary to find the current density (icorr).

In the table 1 can be determine the values of wear taking into account the values of the Tafel polarization curves, of such curves can be appreciated that the mass loss is presented after 30 minutes in the coated specimens. The coated material produced from the polished substrate presented a period of initial mass loss inferior of the substrate. Therefore, the wear rate of the coated specimens under different times generates an increase in the degradation value in function to the increment of evaluated time. Comparing the value with the polarization resistance in function of the evaluated time, can be seen that the lower resistance value to the corrosive erosive effect is presented in the substrate, thus generating the highest value of corrosion rate, as the test time increases is generated a diminution in the polarization resistance which indicates a significant increase in the corrosion rate, reaching values of 2.83 mpy at the 480 minutes.

Table 1. Parameters of rate, current and corrosion potential of the substrate and the coatings subjected to the combined effect of cavitation erosion and corrosion.

	Ecorr / mV	βa (mV/ decade)	βc (mV/ decade)	Icorr / μA	Corrosion rate / mpy
Steel 4140	-593	25.7	24	63.80	29.15
[TiN/TiAlN] 30 minutes	-494	274e-3	277 e-3	0.173	784.9e-3
[TiN/TiAlN] 180 minutes	-312	276e-3	239 e-3	0.271	1.23
[TiN/TiAlN] 480 minutes	-463	306e-3	312e-3	0.624	2.83

In the figure 6 is observed the deterioration of the superficial layers of the coatings. After cavitation in a fluid with NaCl content. In the figure 6a, the erosive effect is observed for 30 minutes obtaining the cracks formation due to the hardening process that that has been generated on the coating by bubbles that move between the waveguide and the coated surface, the energy generates a superficial damage in form of grooves. The 6b image shows a higher energy concentration since is obtained detachment of the external layer and cracking of itself, additionally the diameter of the superficial damage increase with an approximate diameter of 50 microns; it is owing to the first groove formation that is concentrated in cracks generated by surface fatigue. Finally is observed the figure 6c, where the synergistic effect of the corrosion erosion by cavitation shows a greater damage due to the combined action of the static corrosion and erosion, as well as the increase of the test time and the suspended particles by the loosening of hard-coated [18].

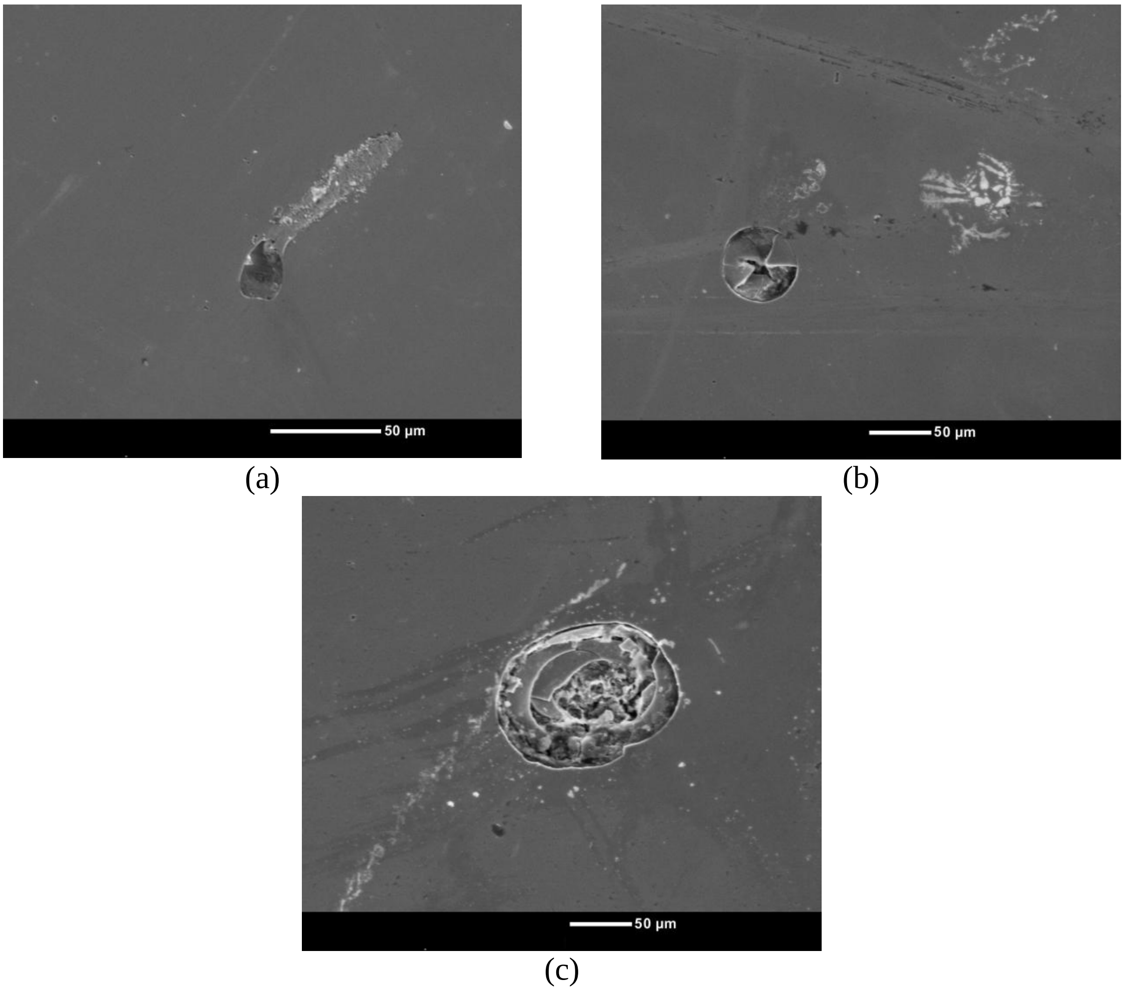

Figure 6. Micrographs of the coatings then of cavitation erosion and corrosion. a) Coatings tested at 30 minutes, b) coatings tested at 180 minutes and c) coatings tested at 480 minutes.

4. CONCLUSIONS

The $[TiN/TiAlN]_{200}$ coatings deposited onto AISI 4140 steels improve performance against the mechanism of cavitation assisted by corrosion, this increase is due to density and the number of bilayers existing in the multilayers, since generates an energy dispersion superficially, the protection was noticed in whole test, and it was determined that the best performance is at Transient evaluation times, owing that the accumulation of the cavitation phenomenon generates an increase in the material damage. By means of scanning electron microscopy was corroborated the damage evolution by cavitation as the evaluation time increases, generating by suspended particles and the distribution of surface energy. The beginning of the mechanical damage is assisted by the electrolyte that content ions which moderately dissolve the protective layer.

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Reference

1. E. Lauer, X.Y. Hu, S. Hickel, N.A. Adams, *Comput Fluids*, 69 (2012) 1.
2. J. LUO, W.l. XU, Z.P. Niu, S. J Luo, Q.-W. Zheng, *J Hydrodyn, Ser. B*, 25 (2013) 895.
3. S. Koch, R. Court, W. Garen, W. Neu, R. Reuter, *Spectrochim Acta B*, 60 (2005) 1230.
4. Y. Xiang Yang, Q. Xi Wang, T.S. Keat, *Ultrason Sonochem*, 20 (2013) 1098.
5. Z.A. Zhou, Z. Xu, J.A. Finch, J.H. Masliyah, R.S. Chow, *Miner Eng*, 22 (2009) 419.
6. N.A. Tsochatzidis, P. Guiraud, A.M. Wilhelm, H. Delmas, *Chem Eng Sci*, 56 (2001) 1831.
7. F. Cheng, S. Jiang, *Appl Surf Sci*, 292 (2014) 16.
8. Y.-C. Wang, Y.-W. Chen, *Exp Therm Fluid Sci*, 32(2007) 403.
9. O. Takakuwa, M. Nishikawa, H. Soyama, *J Mater Process Tech*, 212 (2012) 1716.
10. M. V. Bagal, P. R. Gogate, *Ultrason Sonochem*, 20 (2013) 1226.
11. W. Bu-Qian, H. Herman, *Wear*, 134 (1989) 311.
12. S.-J. Kim, S.-J. Lee, I.-J. Kim, S.-K. Kim, M.-S. Han, S.-K. Jang, *T Nonferr Metal Soc*, 23 (2013) 1002.
13. A. Pawlak, A. Rozanski, A. Galeski, *Mech Mater*, 67 (2013) 104.
14. ASTM G5-09 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, West Conshohocken, PA, American Society for Testing and Materials, 2011.
15. G52 - 00 Standard Practice for Exposing and Evaluating Metals and Alloys in Surface Seawater - See all versions, West Conshohocken, PA, American Society for Testing and Materials, 2011.
16. ASTM G59-04 Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements, West Conshohocken, PA, American Society for Testing and Materials, 2009.
17. A. K. Krella, *Surf Coat Tech*, 228 (2013) 115.
18. W.P. Schiffers, S.J. Shaw, D.C. Emmony, *Ultrasonics*, 36 (1998) 559.