

Short Communication

Evaluation of the Corrosion Erosion by Cavitation of Multilayer Coatings Type Binary, Ternary and Quaternary Deposited on Steel AISI 4140

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This article presents the evaluation of the corrosion erosion resistance erosion caused by cavitation generated on the binary type coatings [TiN / CrN]₂₀₀, ternary [TiN / AlTiN]₂₀₀ and quaternary [TiCN / TiNbCN]₂₀₀ obtained by physical vapour deposition magnetron sputtering technique multi-target and deposited on 4140 steel substrates by comparing the uncoated substrate. The coatings were exposed to erosive, corrosive conditions and synergy compared to AISI 4140 steel. The electrochemical characterization are employed electrochemical impedance spectroscopy techniques and Tafel polarization curves. With respect to the characterization of degraded surfaces scanning electron microscope was used. The evaluation of the phenomenon of mechanical wear due to cavitation is performed using a high frequency generator. The protective effect in each of the evaluated systems was determined, generating improvements in the mechanical and corrosion properties.

Keywords: cavitation, erosion, corrosion, multilayer, wear.

1. INTRODUCTION

Monolayers type thin films have been used as hard coatings due to their increased hardness and toughness and a low coefficient of friction compared to high speed steels and cemented carbides [1]. Moreover, based on borides, carbides and nitrides, materials have been generally designed to be used in the transition metals [2]. Because these coatings exhibit high temperature resistance, high hardness and resistance to aggressive environments when required [3]. A current line of investigation is the deposition of these materials as a multilayer or superlattice, in the first case involves the use of several

layers, where the former provides a good adhesion to the substrate and the following are selected to promote the aforementioned properties [4]. In the second case the superlattice coatings are two or three layers deposited alternately a few nanometers thick to form a new structure with different physical properties are often dependent on the deposition parameters [5]. The multilayer coatings as have two or more layers of different materials are deposited alternately on a substrate and generally periodically. The thickness of the layers can range from 1nm to 200nm.

With the deposition of multiple layers with different mechanical properties between them, can control problems such as surface tensions and crack propagation [6]. In recent years this type of coating have received great interest due to its high hardness and wear resistance with a low thickness of bilayer, also presenting thermal stability with respect to oxidation, making them suitable for applications of protective tools cutting and other mechanical components [7]. The properties of the multilayer coatings depend on the properties of the constituent materials of the bilayer thickness, and the structure of the interface [8]. The properties of the multilayer coatings depend on the properties of the constituent materials of the bilayer thickness, and the structure of the interface [9]. The growth of multilayer structures with dimensions on the nanoscale, has attracted the attention of much of the scientific and industrial community in recent years for its wear resistance in applications where this phenomenon occurs. Some of these coatings of alternating layers called heterostructures exhibit high hardness, and offers potential advantages for drilling, forming and cutting of various materials.

However, the binary combination of a multilayer materials show only part of the increasing need to obtain materials with improved properties and improved mechanical response performance. The TiN for example, has a limited oxidation resistance at temperatures near 600 ° C where a layer of titanium oxide (TiO₂) is formed [10]. Due to the large difference between the molar volumes of TiO₂ and TiN, compressive stresses are generated on the oxide layer, resulting in delamination and unoxidized nitride exposure to the start of a new oxidation process. Many recent research points to the study of ternary and quaternary materials due to their higher tribological and mechanical properties [11]. The best example for the improvement of the properties by the inclusion of a third component is aluminum titanium nitride (AlTiN) [12]. The inclusion of aluminum atoms within the crystalline structure of TiN, not only increases the oxidation resistance by forming a stable and compact layer of aluminum oxide (Al₂O₃) on the surface, also contributes to a significant increase in hardness, compared with the simple binary nitride, AlTiN being used successfully in high speed machining of metals [13]. To date, few reports in the literature have made significant studies on quaternary coatings such as titanium niobium carbonitride (TiNbCN) which opens the possibility for future work in order to improve the mechanical, tribological and electrochemical properties multicomponent systems [14].

In this paper the evaluation of the dynamic corrosion resistance, erosion caused by cavitation and corrosion-erosion coatings [TiN / CrN]₂₀₀ was performed, [TiN / AlTiN]₂₀₀, and [TiCN / TiNbCN]₂₀₀ obtained by PVD magnetron sputtering technique multi-target deposited on 4140 steel substrates with the aim of formulating alternative solutions in industrial applications where such phenomena converge.

2. EXPERIMENTAL

All coatings were deposited on AISI 4140 steel, which were degreased by ultrasonic cleaning in a sequence by 15 minutes of ethanol and acetone. The coatings were obtained by the technique of multi-target rf magnetron sputtering (13.56 MHz). Thin films were deposited as binary coatings, TiN / CrN with Ar (purity 99.9%) as a working gas, the targets are three inches in diameter is comprised Cr (99.9%) and Ti (99.9%). In the process of deposition potential bias (bias) was used 0V dc. The chamber was evacuated by a turbomolecular pump to a base pressure of 10^{-4} mbar prior to the deposition. The pressure during the working process was 6×10^{-3} mbar, with a rf power 100 W on the targets. For multilayers [TiN / AlTiN] 200, 4-inch diameter targets of Ti and Al were used with a purity of 99.9%. The base pressure of the inside of the vacuum chamber was 7.0×10^{-6} mbar. Before starting the deposition the substrates were subjected to a plasma cleaning for 20 minutes under Ar to a bias of -400V on rf. During growth, the working gas was a mixture of Ar (93%) and N₂ (7%) with a total pressure of 6×10^{-3} mbar at a substrate temperature of 300 °C and an bias -70V rf substrate and 350W power.

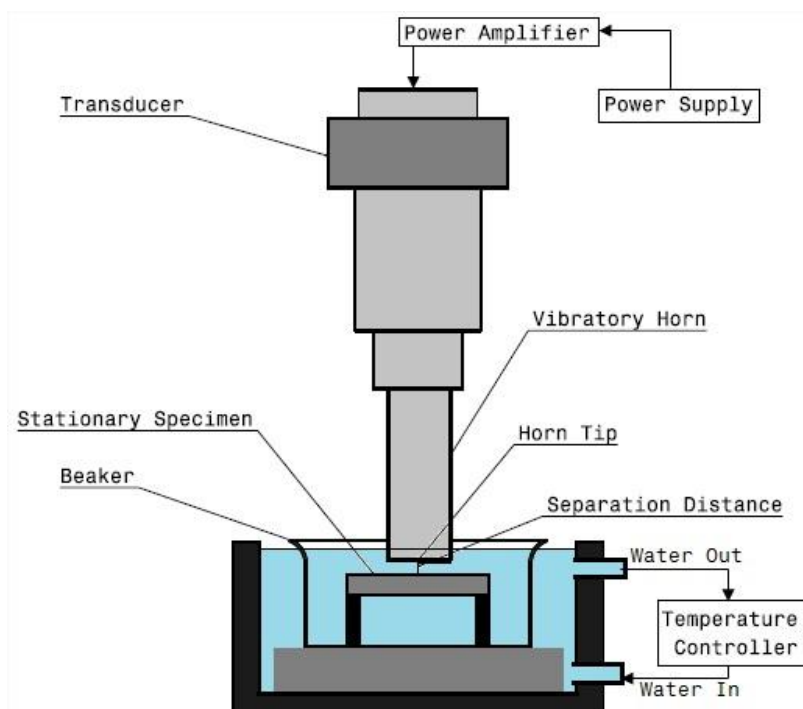


Figure 1. Equipment used for the tests generated by cavitation erosion in an electrolytic médium.

For the deposition of the multilayer the aluminum target was periodically covered by the shutter, while the substrate was kept under circular rotation in front of the blank to facilitate the formation of the coatings. [TiCN/TiNbCN]_n multilayers were deposited two stoichiometric TiC and Nb targets with purity at 99.9% for both targets. The deposition parameters for obtaining high-quality coatings were sputtering power of 400 W for TiC and 350 W for the Nb target; substrate temperature of 300 °C; under circular rotation substrate with 60 RPM, to facilitate the formation of the

stoichiometric quaternary film. The sputtering gas was a mixture of Ar 76% (50 sccm) and N₂ 24% (16 sccm) with a total working pressure of $6 \cdot 10^{-3}$ mbar. An unbalanced r.f. bias voltage, which generates a constant voltage offset of -50V was applied. Moreover our magnetron sputtering device has a substrate positioning substrate system in relationship to target spot, this parameter permits obtain the bilayer number ranging from 200.

The estimation of the damage that can occur due to the cavitation in a corrosive fluid was performed using equipment comprising an ultrasonic oscillator consisting mainly of an ultrasonic transducer which oscillates at 20 kHz with an amplitude of 100 μm , and a sonotrode, and is shown in Fig. 1. The computer configuration was performed taking into account the guidelines indicating the ASTM G32 -03 standard. The test method was indirectly, which provides the location of the sample to 0.5 mm from the tip of the oscillator. Oscillator team has adapted the reference electrode - ER (Ag / AgCl), the counter -EA (Platinum wire) and the specimen -ET with a display area of the sample of 1 cm², the electrodes are immersed in a solution composed of 3.5 % NaCl and connected to a potentiostat - Gamry galvanostat model PCI -4 using the techniques of electrochemical impedance spectroscopy and Tafel polarization curves.

For the evaluation of cavitation erosion – corrosion a potentiostat galvanostat model Gamry PCI-4 was used using the technique of electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. Immersing the specimens were placed in a 0.5 M NaCl solution prepared with distilled water. The cell comprising a counter electrode (platinum wire), a reference electrode of Ag / AgCl electrode working as AISI 4140 steel was used coated with the multilayers. Nyquist diagrams were obtained with frequency sweeps between 100 kHz and 0.001 Hz using a sinusoidal signal amplitude of 10 mV and exposed area of 1 cm²; Tafel diagrams were obtained at a scan rate of 0.5 mV / s in a range of voltages from -0.25 V to 1V, the standards used in the measurement criteria and calculations correspond to ASTM G5, G 52 and G59.

To determine the weight loss due to erosion by cavitation, the samples were subjected to wear due to cavitation erosion corrosion - for a total exposure time of 480 minutes at 23 ° C in a solution of 3.5% NaCl, the samples were removed from the solution at time intervals of 30 minutes, cleaned with a jet of water, dried with hot air, and weighed on a precision scale (0.1 mg). Degradation phenomena were observed with an electron microscope (SEM), the surface characteristics were determined with JEOL SEM NeoScope JCM-5000 equipped with an electron optics with magnification range from 50 to 40.000 X

3. RESULTS AND DISCUSSION

3.1 Electrochemical tests

In Figure 2, are observed diagrams Tafel polarization curves where we initially compare the corrosion potential values obtained for the coatings, generally corrosive erosive incidence medium was clearly observed in the change of the potential rest, since for these test conditions thin films tends to behave more actively for the systems evaluated at 480 minutes while in a time of 30 minutes

evaluating the trend is towards noble potential. As can be determined that the presence of chloride ion and the erosive effect generates mass loss by corrosion erosion synergistic effect [15]. When comparing coatings, it is seen that the best performance is generated by the thin film type binary, followed by quaternary coatings and by more active behavior was the ternary, this is because compounds based on chromium are those with greater resistance to corrosion, aluminum ternary element containing coatings that generally resists corrosion, however when the Cl ion passivation disappears and is highly reactive.

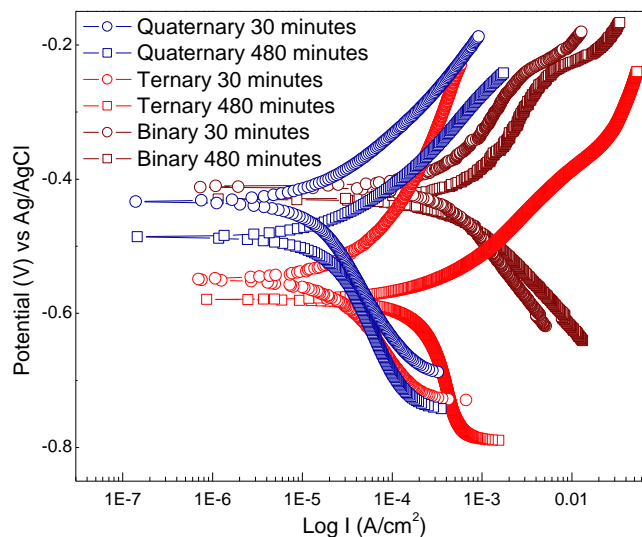


Figure 2. Tafel polarization curves of coatings binary, ternary and quaternary subjected to erosion corrosion tests.

Multilayer coatings into bilayer, shows the active solution, while thin films [TiN / AlTiN]₂₀₀, and [TiCN / TiNbCN]₂₀₀ generate current densities less compared to systems [TiN / CrN]₂₀₀, (table 1). This is an indication that the coatings protect the metal surface from corrosion [16]. Corrosion of the thin films starts when the protective layer has chemical solution on the surface due to contact with electrolyte solution and the effect of erosion.

Table 1. Electrochemical parameters of the binary, ternary and quaternary coating, to determine the rate of deterioration.

	Ternary	Quaternary	Binary
Corrosion current, i_{corr} (A/cm ²)	$2.15 \cdot 10^{-4}$	$1.43 \cdot 10^{-5}$	$5.61 \cdot 10^{-4}$
Open circuit potential (mV) vs Ag/AgCl	- 582	- 485	- 427

Corrosion of the thin films on NaCl solution is uniform corrosion shape. During the dissolution process, the cathodic reduction produces oxygen reduction, furthermore the multilayers generate

mechanical protection, contributing to protection against erosive wear phenomena of cavitation, so you can show that the lower corrosion current generated less weight loss in all tested mechanisms. The mass loss is also associated with the absorption by the coating, causing the metal ions surrounding which leads to a decrease.

The combined effect erosive and degradation between electrochemical wear suggests that the aggressiveness of adsorption generated chloride ions and their reaction with the coated surface, which leads to the formation of surface degradation. The combined effect generated by cavitation and saline generate increased anodic dissolution of the metal. As can be seen in the dissolution of metal, which is produced in the anode region. The corrosion current values indicate that the mode of inhibition is anodic process.

According to the polarization curves Tafel allowed observing the effect of variations in the form of protection on AISI 4140 steel in the electrochemical system of the behavior of the material with respect to different areas of the polarization curve. First, it is possible to differentiate the action of the corrosive medium from predominant polarization is presented in each case, as it provides an approximation of the type of surface acting mechanism in each case, for example, for the binary system observed at 480 minutes is observed from evaluation cathodic polarization branch type of charge transfer, therefore, once crossed the potential barrier will start the corrosion process of general type, while for the coatings ternary and quaternary shows that the predominant polarization is of diffusive type, therefore, once crossed the potential barrier reactions will be governed by the diffusion of ions and oxygen through the barrier of electrolyte and the consequent generation of corrosion products stable means to protecting the base material.

3.2 Electrochemical Impedance

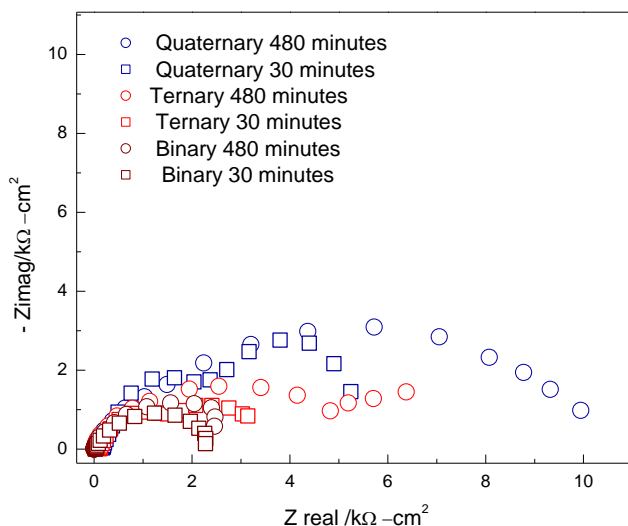


Figure 3. Nyquist diagram of the multilayer coatings evaluated by the effect cavitation erosion and corrosion.

The technique of electrochemical impedance spectroscopy, which is used to estimate the capacity of protection of the coatings on the metal immersed in 3.5% NaCl and subjected to cavitation (Fig. 3). All impedance data were modeled using the appropriate equivalent circuit as shown in Figure 4. Two time constants are obtained, the first constant phase element connected together with the parallel resistance is associated to the protective effect of thin films, whereas the second resistive capacitive coupling (R2-CPE2), is due to the transfer charge located between the coating and the substrate [17]. The solution resistance is similar to the systems evaluated at 30 and 480 minutes in all systems evaluated.

According to Nyquist, depending on the time of evaluation is obtained at the test time 480 minutes deposition conditions used generate a significant change in the behavior of corrosion deposits, yielding the lowest values of impedance on all systems evaluated. For the evaluation to 30 minutes a marked influence of the evaluation was noted in the lower degree of deterioration of the shell, being the highest impedance values compared to higher evaluation time. Additionally, the values of the impedance module at low frequency for all samples coated with ternary and quaternary systems are higher than that of the coated sample in binary form. Coating resistance as well as the charge transfer resistance of the thin film gradually increases with respect to the number of elements. This indicates that the quaternary systems generate more stable to protect the metal from corrosion in NaCl medium and subjected to cavitation erosion.

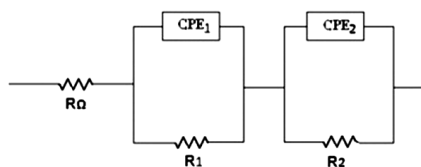


Figure 4. Equivalent circuit model used for the electrochemical response of multilayer coatings tested at 30 and 480 minutes

3.3 Wear

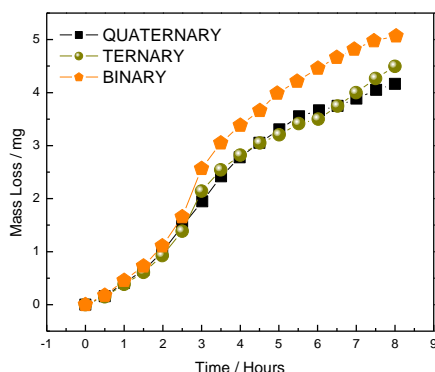


Figure 5. Curves wear coatings subjected to cavitation erosion in saline electrolyte.

Figure 5 shows the mass loss curve versus time. The process is divided into three stages in the systems evaluated. There is an initial phase that rises up to 120 minutes, characterized by the gradual increase of the mass loss (an incubation phase), then accelerated back volume loss at 120 minutes to 360 minutes growth observed (maximum speed). The surface layer is highly deformed after total evaluation due to cavitation erosion produced by fatigue fracture. Such mechanical damage is associated with damage sequence starting with the accumulation of plastic strain, and then the crack initiation occurs, then the growth of the crack propagation and ending with the removal of particles.

According to the criterion of ASTM G32-03 standard, the coatings obtained in binary form, ternary and quaternary generate damage by cavitation effect, as seen in the curve of the mass loss rate of wear is observed adhesive type, since the effect of the multilayer generates a minimal loss of mass, this result indicates that wear micromechanisms are those responsible for the presence and progress of degradation phenomena, which favor increased removal of the outer layers of the material.

3.4 Morphology evaluation wear

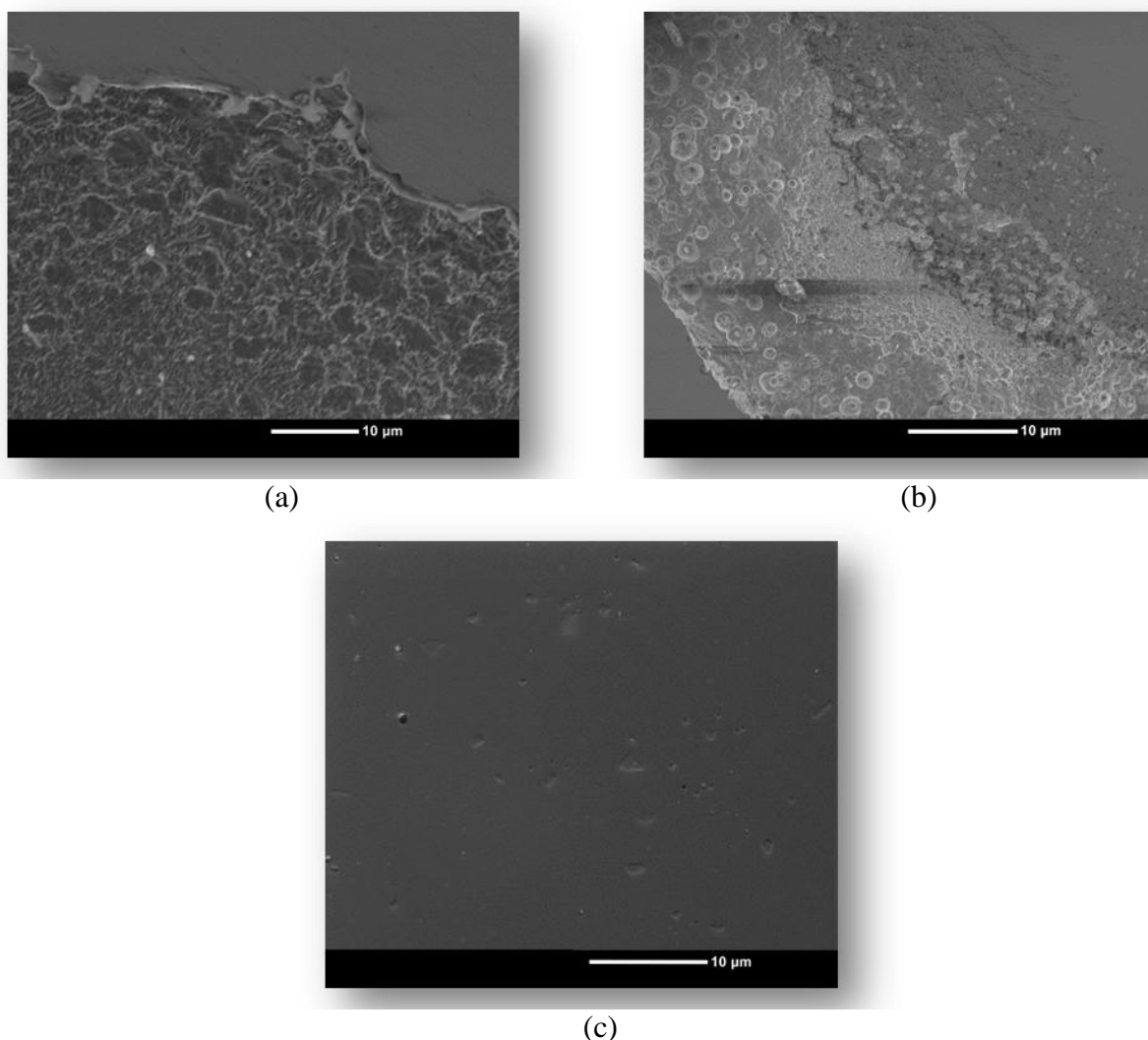


Figure 6. Micrographs of coatings subjected to the combined effects of erosion corrosion. a) coating binary, b) ternary and c) quaternary.

Fig. 6 SEM micrographs of the generated test after 480 minutes test the cavitation in a fluid containing NaCl, in surface figure 6a are shown, the coating surface [TiN / CrN] seen 200, where the degradation of the coating on the bottom of the figure is seen, this wear is due to erosion caused by the effect of bubbles on the film impacted a mechanical damage associated with subsequent dissolution of the coating is observed ternary (see Figure 6b) shows a lower intensity of mechanical damage, in the top right of the surface cracking due to hardening of the surface by continuous erosive effect is obtained, since there is a greater concentration of energy in the area described. For the effect observed in the coating [TiCN / TiNbCN] 200 (see Figure 6c), is obtained that the surface is affected by the erosive effect, no corrosive effect because the coating effect is evidenced passivity.

4. CONCLUSIONS

The binary type coating [TiN / CrN] 200, ternary [TiN / AlTiN] 200 and quaternary [TiCN / TiNbCN] 200, deposited on AISI 4140 alloy steel improves performance against power assisted cavitation corrosion, this increase is due to the density and the number of bilayers in the multilayer existing, generating a dispersion of the surface energy.

Comparing bilayer multilayer coatings shows an active solution, the thin films [TiN / AlTiN] 200 and [TiCN / TiNbCN] 200 and lower current densities generated compared to systems [TiN / CrN] 200; however such coatings quaternary generate more stable to protect the metal from corrosion in NaCl medium.

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Reference

1. P. H. Mayrhofer, C. Mitterer, L. Hultman and H. Clemens, *Prog Mater Sci*, 51 (2006) 1032
2. K.-D. Bouzakis, N. Vidakis, K. David, *Thin Solid Films*, 355–356 (1999) 322
3. D. Kottfer, M. Ferdinandy, L. Kaczmarek, I. Maňková and J. Beňo, *Appl Surf Sci*, 282 (2013) 770
4. M. Lattemann, S. Ulrich, *Surf Coat Tech*, 201 (2007) 5564
5. Y.K. Pan, C.Z. Chen, D.G. Wang and Z.Q. Lin, *Mater Chem Phys*, 141 (2013) 842-849
6. C Rincón, J Romero, J Esteve, E Martínez and A Lousa, *Surf Coat Tech*, 163–164 (2003) 386
7. A. K. Krella, *Surf Coat Tech*, 228 (2013) 115
8. K. Holmberg, A. Laukkanen, A. Ghabchi, M. Rombouts, E. Turunen, R. Waudby, T. Suhonen, K. Valtonen and E. Sarlin, *Tribol Int*, 72 (2014) 13
9. L. Vernhes, M. Azzi and J.E. Klemberg-Sapieha, *Mater Chem Phys*, 140 (2013) 522
10. X. Sun, Q. Zhang, Y. Liu, N. Huang, P. Sun, T. Peng, T. Peng and X.-Zhong Zhao, *Electrochim Acta*, 129 (2014) 276
11. G Tomandl, M Mangler, E Pippel and J Woltersdorf, *Mater Chem Phys*, 63 (2000) 139
12. Y. Birol and D. Ísler, *Mat Sci Eng A-Struct*, 528 (2011) 4703
13. J.K. Chen, C.L. Chang, Y.N. Shieh, K.J. Tsai and B.H. Tsai, *Procedia Engineering*, 36 (2012) 335
14. J.C. Caicedo, C. Amaya, L. Yate, M.E. Gómez, G. Zambrano, J. Alvarado-Rivera, J. Muñoz-Saldaña and P. Prieto *Appl Surf Sci*, 256 (2010) 5898
15. J.C. Caicedo, G. Cabrera, W. Aperador, H.H. Caicedo and A. Mejia. *Vacuum*, 86 (2012) 1886

16. X. Zhang, X. Liu, C. Fan, Y. Wang, Y. Wang and Z. Liang, *Appl Catal B-Environ*, 132–133 (2013) 332
17. M.T. Mathew, E. Ariza, L.A. Rocha, A.C. Fernandes, F. Vaz, *Tribol Int*, 41 (2008) 603

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