

# Supplementary Materials: Electrochemical Corrosion of Nano-Structured Magnetron-Sputtered Coatings

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**Table S1.** Electrochemical corrosion studies of magnetron sputtered films.

Coating	Test	Electrolyte	Main Remark/Reference
<b>Stainless Steel 316 (L)</b>			
a-C:H	OCP, EIS, PTD	0.9% NaCl	The hydrogenated coatings performed best when compared with the non-hydrogenated coatings, which may be attributed to the lower density of superficial defects, more compact morphology, and lower amount of graphitic bonds, which gave rise to a decrease in coatings' conductivity [47].
a-C	OCP, EIS, PTD	3.5% NaCl	The potentiodynamic curves showed an improve corrosion protection of the films, by reducing the density current; in addition, the corrosion potential shifted to higher potential compared to both SS316l and pure a-C coatings. However, when silver rose to 8.4 at.%, the corrosion resistance decreased with respect to that for a middle content of silver [51].
Ti/a-C	OCP, EIS, PTD	0.89% NaCl	The corrosion resistance of SS 316L was enhanced. Corrosion resistance of coatings is dependent on the porosity level of the coatings [11].
Cr-C	OCP, PTD	1 mM H <sub>2</sub> SO <sub>4</sub>	Higher Cr content (74 at.%) shows higher corrosion resistance; however, it is less noble. It is evidenced that carbon is also oxidizing, as demonstrated by XPS [50].
a-C:Ti and a-C:Cr	OCP, EIS, PTD	SBF	Both coatings reveal an improved corrosion performance due to the Ti and Cr oxides on the surface. Yet, Cr-doping increases the corrosion resistance of a-C coatings through a decrease of the $sp^2/sp^3$ ratio [12].
TiN, AlN and Ti <sub>1-x</sub> Al <sub>x</sub> N	OCP, EIS, PTD	SBF and 3.5% NaCl	Ti <sub>1-x</sub> Al <sub>x</sub> N films have an improve corrosion performance due to the addition of Al into the TiN coating, which causes microstructure densification and subsequently a decrease in the grain size and reduced surface roughness [92].
TiN, TiAlN and TiN/TiAlN	OCP, EIS, PTD	3.5% NaCl	Both TiAlN and TiN/TiAlN have better corrosion resistance than the single TiN layer and bare substrate. For the TiAlN, the incorporation of Al passivates the surface and blocks the pores, increasing the resistance to corrosion [27].
TiN, TiAlN, CrN	OCP, PTD	9% NaCl, 3.4% HCl	In TiN <sub>x</sub> film, the conversion from a rich Ti film to a pure TiN film increases the dissolution rate of the system, which is accompanied by a clear modification of the films morphology, from compact to more porous films [28].

ZrN-Ag	PTD	3.5% NaCl	The results showed that better corrosion resistance was obtained for higher bias potentials, associated with the change of the film structure due to bias-induced ion bombardment [32].
ZrCN and ZrCN:Ag	OCP, EIS, PTD	0.89% NaCl	Low Ag content in ZrCN coatings improves the electrochemical properties, controlled by the coating's microstructure. Higher levels of Ag reduce polarization resistance, suggesting an active electrochemical behavior due to silver presence [37, 87].
<b>Ti or Ti6Al4V Alloy</b>			
DLC	EIS, PTD	3% NaCl	The corrosion protection is improved using graphite-methane in comparison to graphite-hydrogen. Modeling the EIS results demonstrate that the resistance simulating the pores is higher for DLC compared to a-C:H [49].
a-C:Ti	OCP, PTD	Hank's solution	a-C films with lower than 3.1 at.% Ti are stably passive. However, when Ti content increases to 15.2 at.%, the a-C film exhibits dynamic passivation, being susceptible to crevice pitting corrosion [52].
a-CN <sub>x</sub> and a-CN <sub>x</sub> :Ti	OCP, PTD	Tyrode's Simulated Body Fluid (SBF)	a-CN <sub>x</sub> :Ti coatings with low amount of Ti, inhibit graphitization, revealing lower current density and higher corrosion potential as compared with Ti6Al4V, improving their corrosion behavior [53].
ZrN:Si	OCP, EIS	0.9% NaCl	Si addition in low amounts increases the corrosion resistance of films. For a Si content around 8 at.%, the film achieves the best corrosion resistance [38].
ZrCN and ZrCN:Hf	OCP, PTD	Ringer Solution	Although both coatings reveal superior anticorrosive properties related to the substrate, corrosion behavior was improved by adding Hf to the basic ZrCN coating, being enhanced by the increase of the non-metal/metal ratio [10].
TiAlN and WC:C	OCP	Artificial saliva	Both coatings improve the electrochemical properties of $\beta$ -Ti. However, TiAlN showed a superior corrosion protection without visible surface dissolution, when compared with WC:C coatings [101].
ZrN	OCP, PTD	Artificial saliva	ZrN coating improves corrosion behavior of Ti substrate. Its corrosion properties are strongly dependent on the deposition conditions [19].
<b>NiTi Alloy</b>			
Si/SiC/DLC	OCP, PTD	Tyrode's SBF	Si/SiC-graded interlayers play an important role in improving the adhesion and subsequently the corrosion resistance of DLC coating and match the substrate performance [127].
Ti/TiC	OCP, EIS	SBF	Ti/TiC films provide significantly better corrosion resistance and stability compared to the uncoated NiTi substrate, reducing corrosion rates [106].
ZrN	OCP, PTD	Artificial saliva	ZrN coating has better performance toward corrosion than uncoated-NiTi [102].
DLC	OCP, EIS	PBS	DLC coatings match NiTi corrosion performance. Polarization and pore resistance increase as the film thickness increases [94].
<b>Al Alloys</b>			
Si-DLC	PTD	0.3% NaCl	The incorporation of Si into DLC improves the corrosion resistance due to the reduction of the internal stress [54].

TiN	PTD	3% NaCl	The columnar growth of TiN films is avoided by applying a bias potential that creates defects and generates new nucleation sites [7].
AlN	PTD	3.5% NaCl	It is demonstrated that the main corrosion source of PVD coatings is represented by pores and pinholes. Substrates with smoother surfaces can produce coatings with less and smaller defects [10].
<b>Stainless Steel 304</b>			
TiN	PTD	3.5% NaCl	Larger structural pores in the form of the detachment of the particles are a path for the corrosion products, resulting in increased local stress [70].
Ti/TiN	OCP, PTD	3% NaCl	Ti/TiN multilayers improve the corrosion performance of SS 304 better than TiN monolayers, since Ti/TiN multilayers enhance the impermeability of the columnar film [71].
CrN	Scanning electrochemical microscopy	3.5% NaCl	The main cathodic reaction of the pitting region is the reduction of dissolved oxygen, producing hydroxyl ions and resulting in increased pH [17].
CrN	EIS, PTD	3.5% NaCl	The films deposited at lower pressures showed lower density currents but an active behavior in the PTD test. The Rp tends to decrease for coatings deposited at lower pressures, due to the reduction of porosity [62].
<b>Glass</b>			
TiNx	OCP, EIS, PTD	0.9% NaCl	The PDT test demonstrated that, as nitrogen is increased, the area in contact with the electrolyte increases by creating a more porous structure [21].
TiN-Ag	OCP, EIS, PTD	Synthetic sweat	The Rp is reduced as silver increases, down to values close to the one of Ag, related to the oxidation of Ag and formation of AgCl [33].
<b>Silicon</b>			
DLC, DLC:N and DLC:PtRu	OCP, PTD	Hank's solution	N incorporation into a DLC matrix does not change significantly the corrosion behavior of DLC control. Yet, Pt and Ru increase the anodic potential resistance and subsequently inhibit pitting corrosion [57].
NiTi and NiTi/TiN	OCP, EIS, PTD	PBS	TiN film shows better corrosion performance than NiTi film, due to the increase of surface area [81,105].
<b>AISI M2 or High Speed Steel</b>			
TiNx	OCP, EIS, PTD	Artificial sweat	Stoichiometric composition (50 at.% N) shows the lower thermodynamic tendency to corrode. Best corrosion resistance is found for films containing low percentages of N, due to a denser structure [24,25].
WTiN	OCP, EIS, PTD	0.1 M KCl	Coated steel always presents better corrosion resistance than uncoated steel. The OCP of the coated samples shows a tendency to decrease as a function of time, tending to the values of the steel [34].
NbN	PTD	4.7% NaCl	Niobium passivates by an oxide layer of Nb <sub>2</sub> O <sub>5</sub> , which protects the system against corrosion. Sudden delamination of the coatings material is observed, which may be due to the pitting corrosion or the generation of corrosion products within the pores [20].
CrN/NbN	PTD	4.7% NaCl	Etching is used to improve the films electrochemical performance showing opposite consequence on CrN and NbN coatings, improving and deteriorating the resistance, respectively [128].

TiN	OCP, EIS, PTD	3.5% NaCl	The porosity of the films is altered by using a two-grid attachment magnetron type, due to the increment of the ion bombardment, decreasing the current density of the films [63].
<b>Other Steels</b>			
Ti/C	OCP, EIS, PTD	3% NaCl	The Ti/C gradient layers decrease the corrosion current and consequently the corrosion rate of Rex 734 alloys, as well as increase the polarization resistance [4].
TiN/NbN	OCP, PTD	0.5 M HCl 3% NaCl	The number of interfaces in the TiN/NbN system shows that by increasing the number of layers, the corrosion current is reduced, and less pits are observed on the surface [72].
TiN, TiCN	PTD	3.5% NaCl	TiCN coatings demonstrate better corrosion resistance compared to TiN, due to a smoother surface and more compact morphology [61].
TiN/Si <sub>3</sub> N <sub>4</sub>	EIS, PTD	3.5% NaCl	TiN corrosion resistance improves as an Si <sub>3</sub> N <sub>4</sub> amorphous phase is incorporated in the coatings, which may be explained by the dielectric character of the phase and the denser morphology of this phase [39].
TiCN/NbCN	EIS, PTD	3.5% NaCl	It is demonstrated that by lowering the multilayer period, a lower porosity is attained, improving the corrosion resistance of the coatings [73].
CrN, TiN, TiAlN	EIS, PTD	3.5% NaCl	TiAlN presents better corrosion resistance as compared to TiN and CrN single layers, due to the formation of an Al <sub>2</sub> O <sub>3</sub> layer that passivates the films surface [29].
Cr-CrN	OCP, EIS, PTD	3% NaCl	Cr-CrN multilayer coating improves substrate corrosion resistance, due to the multilayers' interfaces blocking the propagation of cracks and dislocations and avoiding the continuity of pinholes and pores [78,103].
CrN	PTD	H <sub>2</sub> SO <sub>4</sub> NaCl	CrN and Cr <sub>2</sub> N coatings in sulfuric acid show a more protective behavior when compared to pure Cr films. On the contrary, in saline solutions, CrN films do not confer protection [129].
CrAlN	EIS, PTD	3.5% NaCl	When Al content increases in the CrAlN, the polarization resistance decreases, explained by the oxidation of Al [35].
VN	EIS, PTD	3.5% NaCl	The polarization resistance of the coating decreases when the bias voltage is increased, growing also the number of defects on the surface [130].
<b>Others</b>			
TiAlCN/CN <sub>x</sub>	OCP, PTD	SBF	The multilayer coating shows an enhanced general corrosion protection related to the Cr-Co-Mo alloy alone, and pitting corrosion is avoided [107].
TiN	OCP, PTD	0.9% NaCl	TiN coating matches the substrate performance showing a much lower passivation current density [100].
Ti/TiN	OCP, EIS, PTD	Artificial saliva	Slight improvement in the polarization resistance is observed when NdFEB is coated with TiN films, the increment of the number of layers also increases R <sub>p</sub> up to a value that remains constant [8].
BCN	Dissolution rate	1 M HCl 1 M NaCl 1 M NaOH	BCN dissolution rate varies in each electrolyte, with NaOH>NaCl>HCl, showing a correlation between the dissolution and the pH. In addition, the coatings show a lower dissolution rate as carbon increases in the coatings [41].
PT = Potentiodynamic test OCP = Open circuit potential EIS = Electrochemical impedance spectroscopy			



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