Thin film growth of Ti/TiO2 and Cr/CrN on moving stainless steel wires by cathode magnetron sputtering and the study of localized corrosion resistance of the coated wires

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Abstract: The objective of this work is to study the growth of Ti, TiO2, Cr, and CrN thin films on 316L stainless steel wires, in order to functionalize these wires. An original technology has been developed to coat these moving wires with the development of a cleaning chamber, followed by a deposition chamber constituted by an inverted cylindrical magnetron, to ensure the uniformity of coatings on a substrate of circular geometry. Thin films of TiO2 have been deposited to obtain interference colors from these wires, used in architecture. CrNx coatings have been developed to replace electrolytic chrome plating. Studies of XPS, XRD, SEM and TEM-ASTAR highlight the morphological, chemical and structural complexity of the coatings.

The structures are correlated with the process parameters such as the temperature and the magnetic field. For a cathode with a heterogeneous magnetic field, partial poisoning of the target is then observed during the increase in the oxygen flow, allowing the development of multilayers (Ti/TiO2) during a single pass through the cathode. TiOx-based coatings exhibit chemical and structural gradients in cross section, due to plasma heterogeneities within the cylindrical cathode. The development of a second cathode with a more homogeneous magnetic field has enabled the possibility to obtain a more homogeneous in thickness metallic layer of chromium, from a chemical and structural point of view. Reactive sputtering deposition has been validated with deposits of CrNx, also remaining homogeneous throughout their thickness as the nitrogen flow increases.

The influence of deposition temperature on the microstructure of Ti, TiO2, Cr and CrN was studied. TEM-ASTAR phase and orientation mappings, combined with DRX and EDS studies, have enabled the identification of atypical phases during the development of deposits at temperatures around 550 °C. Thus, these Ti films exhibit Laves phases; while those of Cr present quasi-amorphous Cr, sometimes stable FeCr (DRX), sometimes metastable (MET). The study of TiO2 deposits produced at temperatures > 500 °C reveals oxidation of the steel surface.

Finally, the use properties such as coloring, mechanical properties or durability are presented. The outstanding result of this thesis is to show experimentally that the resistance to localized corrosion of these coated wires is controlled in the first order by the substrate, in a chlorinated medium. The

coatings, although more noble than the substrate, do not constitute an effective barrier, because they have defects such as porosities or even lack of coverage. Changes in the passive film of 316L stainless steel have also been shown by sputtering these wires to simulate changes in the steel surface as coatings are grown. These modifications degrade the pitting corrosion resistance of the wires as the temperature increases and the atmosphere is reactive. For temperatures > 500 °C and in an atmosphere of argon and oxygen, the surface of the steel consists of an oxide layer of several tens of nm, while it consists of a layer of iron oxide in an atmosphere of argon and nitrogen. Electrochemical studies show a degradation in the corrosion resistance of these stainless steel wires, this degradation even becomes catastrophic when these wires are sputtered in reactive atmospheres and at high temperatures. The resistance to localized corrosion of the coated substrates shows the same evolution, thus validating the importance of the modifications of the passive films as a function of the temperature and of the atmospheres during the development of the coatings and during the sputtering of the wires.