Phosphonate primers as new Cr-free nanotech coating

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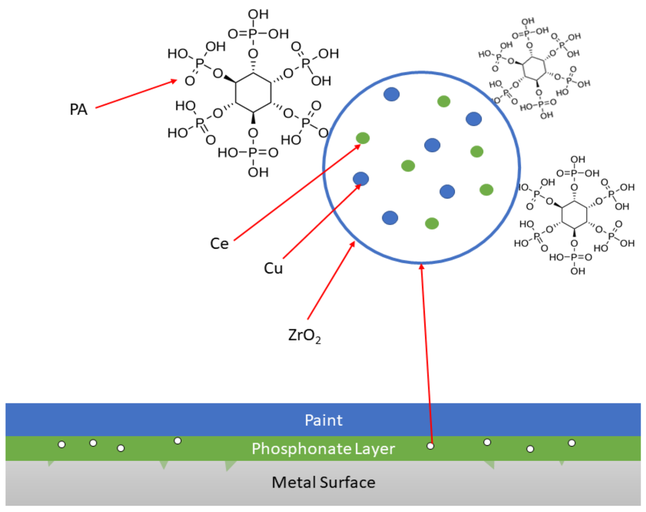
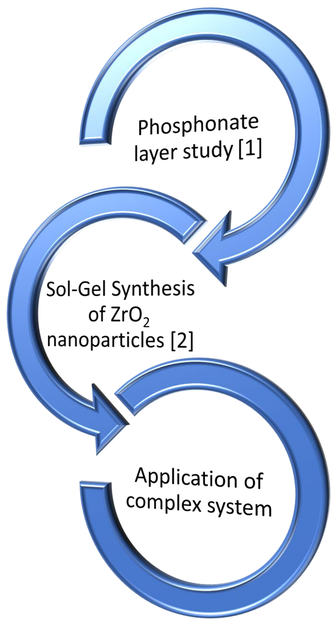
ABSTRACT

Deterioration of metallic materials is a crucial problem in today's industry. Development of formulas that counter corrosion and improve protection by paints is therefore essential. Until few years ago, this sector was covered by chromium treatments, very effective on all substrates, but very toxic. The consequent regulations are driving requests towards the development of Cr-free primers, greener treatments, less and less toxic materials. In this context, zirconium-based formulations with the addition of rare earths (e.g. cerium), known for their great redox and self-healing properties, are having great success and considered natural substitutes for Cr coatings.

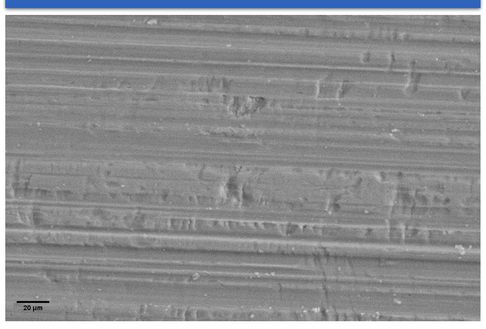
Anticorrosive coatings based on phosphonate primers were here investigated. Thin films of organic phosphonate were prepared and deposited by dipping on three different metal substrates (aluminum, galvanized steel, steel), with the goal of increasing the adhesion of paint and obtaining the passivation of the surface. Usually, in industries, amorphous or crystalline phosphating treatment are performed with Zn, Mo and Ni salts, on the contrary, with this treatment only organic phosphorous is used. To increase the anticorrosion properties nanotechnologies are very promising, also thanks to the possibility of introducing hybrid organic-inorganic materials, so zirconia nanoparticles (ZrO_2 NPs) doped with anticorrosive agent, such as phytic acid (PA), Cu and Ce, were added as nanofillers to the phosphonate, obtaining a Cr-free nanotech primer.

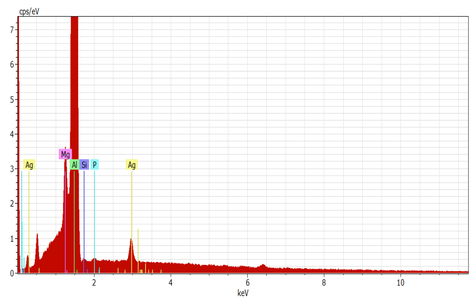
Morphological and elemental analysis were carried out for the three different metal substrates coated by the phosphonate primer without and with ZrO_2 NPs filler, whose morphology and composition were investigated by SEM, EDS and XRF, confirming the presence of Ce, Cu, P, Zr. Polarization measurements and neutral salt spray (NSS) chamber corrosion tests confirmed the increment in corrosion resistance, as the NSS resistance increased from 50 to 800 h for coated steel.



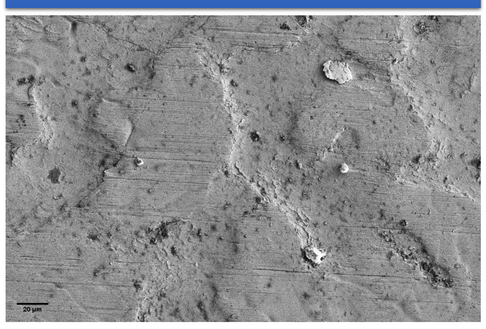


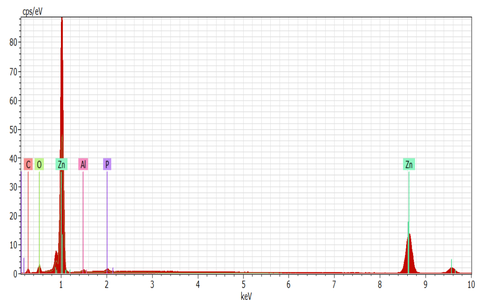
Aluminum B-209 Alloy
Sample with phosphonate layer without NPs



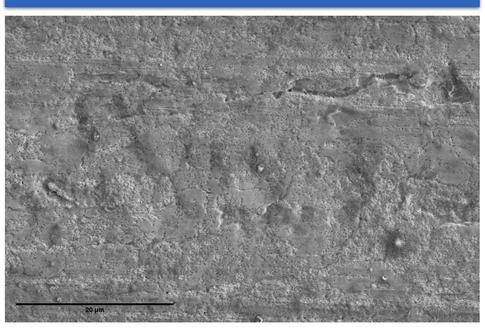


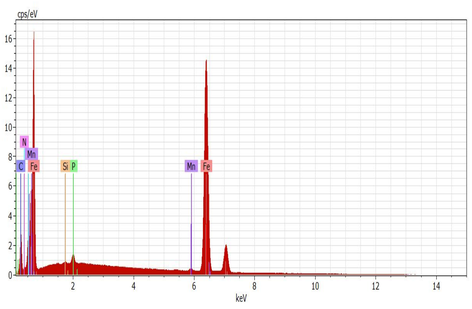
HDG Steel
Sample with phosphonate layer without NPs



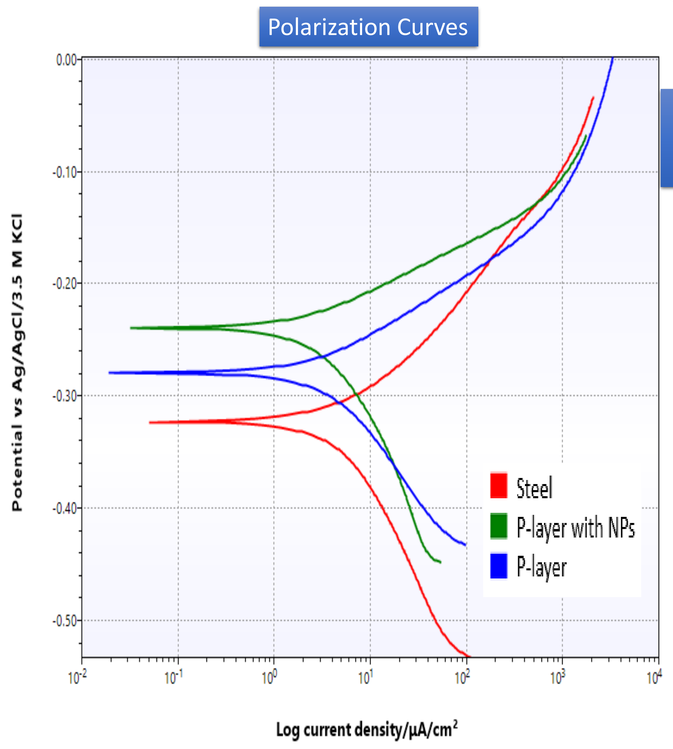


Steel A1008
Sample with phosphonate layer without NPs





Polarization Curves



NSS

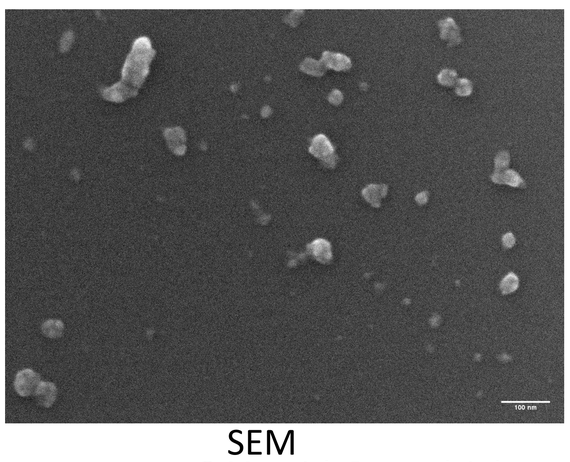
Steel A1008
Sample with phosphonate layer without NPs
After 800 h of NSS

Nanoparticles Synthesis

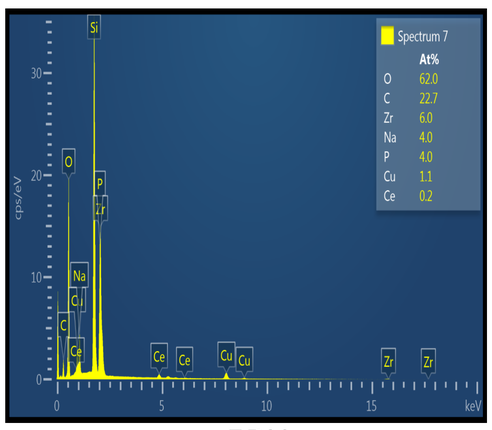
Modified sol-gel method [2]

Doped with metals

Modification with organic anti-corrosion molecules [3]



SEM



EDX

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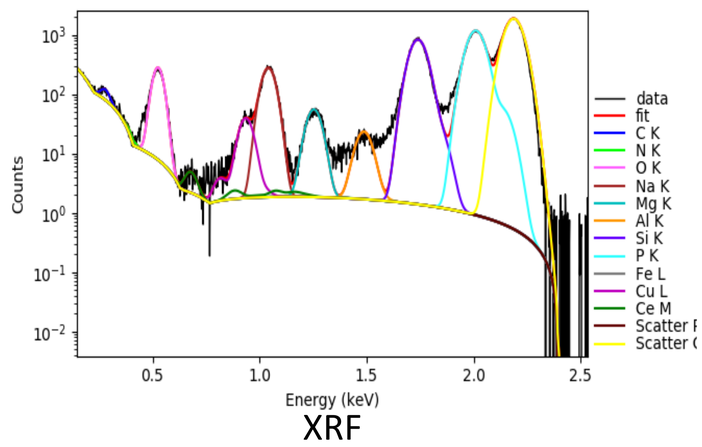
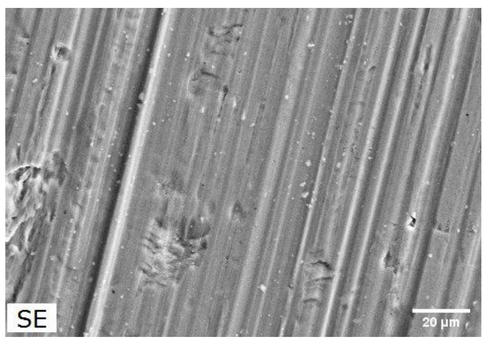
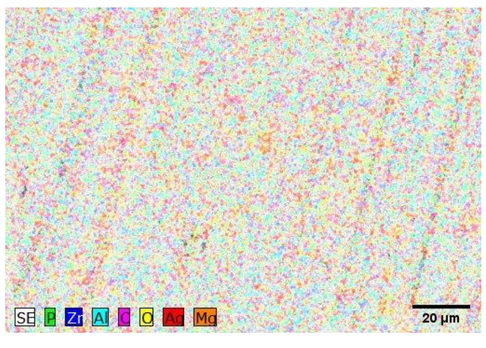


XRF

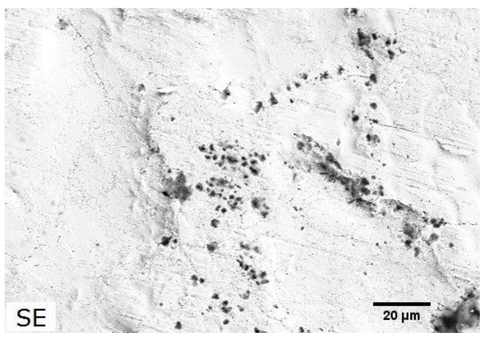
@ TwinMic beamline @ Elettra, A. Gianoncelli

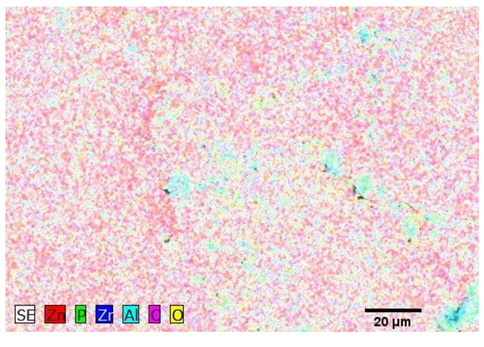
Aluminum B-209 Alloy
Sample with phosphonate layer and NPs



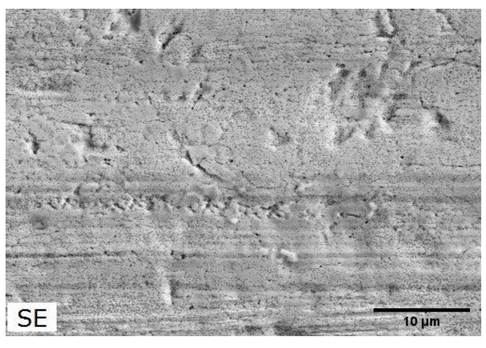


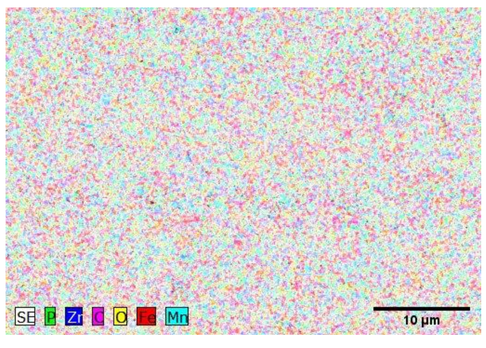
HDG Steel
Sample with phosphonate layer and NPs





Steel A1008
Sample with phosphonate layer and NPs





CONCLUSION

- Development of organic layer based on phosphonate molecules which increases paint adhesion and corrosion resistance, confirmed with polarization curves and NSS tests (from 50 h of bare steel to 800 h of modified surface), without the use of zinc or other metals salts
  - As shown in polarization curves for steel, with protective layers E_{corr} is shifted through more noble potential and i_{corr} through lower values, the same occurs with aluminum alloy and HDG steel
  - Phosphonate protected metals show better corrosion resistance to NSS tests than silane based primers used in industry
- Synthesis of zirconia nanoparticles doped with Ce and Cu, loaded/modified with organic phosphonate to increase dispersibility and anti-corrosion properties
- Formulation of stable organic primer with dispersed nanoparticles
- Deposition of phosphonate layer loaded with nanoparticles under evaluation for corrosion protection
- Preliminary results from polarization measurements shown better anticorrosion properties on the 3 metals tested, NSS tests are ongoing

FUTURE OUTLOOK

- Improvement of nanoparticles: synthesis, doping and functionalizing agents to increase anticorrosion and self-healing properties
- Improvement of formulation: long-lasting stability of the complex material with nanoparticles, formula without precipitation of NPs
- Better characterization of the system obtained
- Plant tests to confirm results and commercialize the designed product

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