Nanostructured material performance in corrosive environments
(Corrosion x nanostructured materials)

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Outline

• Brief concept of corrosion.

• The four traditional forms of corrosion protection.

• Corrosion protection through nanostructured materials (parallelism with traditional concepts)

• Final remarks
Transformation of a metal in a metallic ion through its interaction with the species in the exposed environment.
Corrosion process continuity...

- No interaction
  - No corrosion
  - Immunity
  - Very rare

- Active metal
  - Metal or alloy cannot be used in the considered environment

- Metal with corrosion product layer
  - Good performance or localized corrosion
The four practices of corrosion protection

- select another metal or alloy or modify the composition or the microstructure of the metal or alloy: materials science
- interpose a barrier between the metal and the environment: metallic and organic (paint) coatings;
- condition the environment: by adding corrosion inhibitors or oxygen scavengers or by deairing;
- cathodic or anodic protection: by modifying the potential differences across the metal and the environment.
Nanocrystalline (nc) x microcrystalline (mc)

- The use of nc materials is being developed for different purposes, especially due to the physical and mechanical properties such as wear resistance, smoothness and brightness.
- nc materials present a higher density of “microstructural flaws”: the intercrystalline (intergranular) “paths” increase up to almost 50 % when the grain size decreases from 1 µm to 5 nm.
- The classical principle states that the intergranular paths present a higher energy than the bulk grain due to the presence of voids, impurities, segregations. Thus, chemical reactions and diffusing processes are enhanced within grain boundaries.

Let’s see some examples...
Nanocrystalline nickel

ultrapure Ni is produced by electrodeposition.

This material is preferred when better physical and mechanical properties are required:

<table>
<thead>
<tr>
<th>Property</th>
<th>nc</th>
<th>mc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>5 times harder</td>
<td>1</td>
</tr>
<tr>
<td>Wear resistance</td>
<td>170 times more wear resistant</td>
<td>1</td>
</tr>
<tr>
<td>Friction</td>
<td>1/2 of friction coefficient value</td>
<td>1</td>
</tr>
</tbody>
</table>

How about the corrosion resistance?

Studies in H$_2$SO$_4$

- Nanocrystalline (nc) electrodeposited - 32 nm;
- Microcrystalline (mc) 90% cold rolled and full annealed - 100 µm

After electrochemical tests

In classical theory, the performance of Ni in diluted H\textsubscript{2}SO\textsubscript{4} depends on the characteristics of the passive film. The film breakdown occurs within intergranular paths. Thus, the increase of intergranular paths of the \textit{nc} Ni increases the corrosion susceptibility of \textit{nc} Ni in comparison to the \textit{mc} Ni.

\textit{nc} presents better physical and mechanical properties, but is more prone to corrosion.
Fe8Al nanocrystalline alloy

- Thin films (350 nm) of nanocrystalline Fe alloyed with 8 \% of Al were applied on inert substrates (quartz, graphite and gold). The grain size of the alloy was 40 nm.

- The corrosion behavior of nC alloy was compared to a mC alloy with the same composition. The grain size of the mC alloy was in the range between 200 \( \mu m \) and 300 \( \mu m \).

- The corrosion tests in 0,1 mol/L Na\(_2\)SO\(_4\) solution, with:
  - pH = 1. At this pH, a passive film does not form on the alloy which presents an active dissolution, as the formed ferrous ions remain dissolved in the acid. The corrosion reactions are:
    \[
    \text{Me} \rightarrow \text{Me}^{n+} + z\text{e}^{-} \\
    2\text{H}^{+} + 2\text{e} \rightarrow \text{H}_2
    \]
    
  - pH = 6. At this pH, a passive film, constituted by aluminum oxide, is formed on the alloy surface. Thus, the performance of this alloy will depend on the maintenance of the integrity of the passive film. The alloy may suffer localized corrosion (pits). The corrosion reactions, when occur, will be:
    \[
    \text{Me} \rightarrow \text{Me}^{n+} + z\text{e}^{-} \\
    2\text{H}_2\text{O} + \text{O}_2 + 4\text{e} \rightarrow 2\text{OH}^{-}
    \]

Results:

• **pH = 1**: greater corrosion of the nc alloy was observed. Classical behavior was observed: the corrosion was more intense in nc alloy due to its higher intergranular paths.

• **pH = 6**: less corrosion of the nc alloy was observed. Once again the classical behavior was observed: at this pH, a passive film of aluminum oxide was formed. The film formed on nc alloy was more effective than the film formed on mc alloy.

**This later behavior can be explained as follows...**
At the earlier stage of the formation of Al$_2$O$_3$

This region becomes impoverished in Al

Diffusion of Al occurs due to a gradient in the Al content between the region beneath the Al-oxide and the bulk alloy. These diffusion preferentially through the grain boundaries. The diffusion is enhanced in nc alloy due to its higher density of intergranular paths.

As in nc alloy, the protective Al-oxide is formed rapidly, the uniformity and the compactness of passive film is enhanced. This film constitutes an effective barrier and protects the alloy against corrosion.

It is possible to apply Fe8Al alloy films on carbon steel surface as a protective measure.
High temperature oxidation (> 650 °C)  
nc alloy coating – nc thin films

• High temperature resistant alloys normally contain Ni, Cr and Al. The oxidation resistance of these alloys depends mainly on the formation and preservation of an oxide layer constituted mainly by Cr$_2$O$_3$ and/or Al$_2$O$_3$. Large amount of Cr and Al are required. Al impairs the mechanical properties of these alloys.

• The formation and preservation of the oxide film is diffusion dependent (as previously mentioned).

• nc high temperature resistant alloys: the amount of Al required is lower in nc alloy because the rate of Al diffusion is enhanced due to high density of grain boundaries. This behavior permits a formation of more uniform, adherent and compact oxide layer. For example: in Ni-Cr mc alloys, 8 % of Al is required whereas in Ni-Cr nc, only 2 % of Al guarantees a good performance.

![Image of Ni-20Cr-2Al after exposure at 1000 °C for 100 h]

GAO, WEI; LI, ZHENGWEI. Nano-structured alloy and composite coatings for high temperature applications. Materials research. 7(1):175-182, 2006
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Organic coating

The painting of metallic materials is a widely adopted practice. The performance depend on:

- **nature of the resin**: alkyd, epoxy, phenolic, etc...
- **nature of the pigment**: for example, to improve anticorrosive properties
- **surface treatment**: to improve the coating adhesion
Ceramic nanoparticles

Nanoparticles of TiO₂, SiC, Al₂O₃ (pigments) are incorporated into organic coatings in order to enhance the barrier properties and, thus, to improve the corrosion resistance.

Let’s see na examples...
Ceramic nanoparticles

- The use of nanoparticles as pigments in paints

There is a significant improvement of the paint performance: better corrosion resistance, gloss retention, better resistance to mechanical damages (the nanoparticles are hard)!
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- Fosfatization with Cr (steel)
- Alodine- fosfocromatization (Al)
- Adhesion promoter prime coatings
Corrosion inhibitors

“Smart” coatings: chromate coated galvanized steel - when requested (moisture condenses on the surface), the system responds to protect the substrate.

NaCl          NaCl + chromate

Chromate is good but toxic
Smart coatings

Thin films containing TiO$_2$ nanoparticles applied on Al and Al alloys – there are many attempts to apply this type of films on Al and Al alloys aiming to replace the “smart” chromate conversion coatings. But the obtained performance is not good:

- Even with a great effort attempting to avoid the formation of pores and cracks, the corrosion protection performance is low because the film acts only as a barrier;

- The solution for this problem was the development of new technology: to store an inhibitor in the nanoparticles which is released when requested. Ceasing the stimulus, ceases release.

It took some time to imitate chromate conversion coating behavior which has been in use for a long time....
Smart coatings

Thin films with TiO$_2$ nanoparticles applied on Al - do not present a good performance:
Smart coatings

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]
\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 2\text{OH}^- \]

The alkalinization release inhibitor...
Smart coatings

The alkalization release inhibitor.

\[
\begin{align*}
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Cathodic protection

A natural potential is established across the metal environment interface which is known as CORROSION POTENTIAL or OPEN CIRCUIT POTENTIAL.

In general, corrosion potential is higher than the equilibrium potential.

\[
\text{Me}^{n+} + \text{ne}^- \rightleftharpoons \text{Me} \tag{corrosion}
\]

Cathodic protection is a protection technique in which the metal/environment potential is lowered by:

- using an electric current;
- connecting it to another less noble metal.
Anodic protection (applied only to metals which undergo passivation): is a protection technique in which the metal/environment potential is increased in order to enhance the protective characteristics of the passive film.
Ceramic nanoparticles incorporation in sol-gel films

Thin films with ceramic-TiO$_2$ nanoparticles applied on AISI 316 stainless steel - the protection mechanism is different in dark and light conditions:

- **In the absence of light**: the TiO$_2$ coating acts as an effective barrier. Experiences show that, in a dark condition, 40-nm of TiO$_2$ nanoparticles, incorporated in a 400-nm sol-gel film, are able to reduce the corrosion current in three order of magnitude in chloride-containing solutions;

- **In the presence of light**: photogenerated electrons are generated in the conduction bands of the TiO$_2$ nanoparticles. These electrons are transferred to the stainless steel substrate and cause a decrease of the open circuit potential. **In this situation, the stainless steel is subjected to cathodic protection.**

Conductive coatings

- Conductive polymers (polyaniline, polythiophene and polypyrrole) have been used as protective coating of carbon steel due to their special electrochemical characteristics and their electronic and ionic conductive capacity.

- These polymers are able to increase the open circuit potential up to more positive levels, in the range of passivation. This behavior protects the substrate through anodic protection mechanism: a compact and adhered oxide layer is formed between the interface metal/polymer which acts as an effective corrosion protection barrier.

It is possible to incorporate in the conductive coatings organic or inorganic nanoparticles, with oxidizing properties, such as $\text{MnO}_2$, $\text{V}_2\text{O}_5$, $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$.

This practice guarantees the oxidizing capacity (to shift open circuit potential to more positive values) and thus, improve the corrosion resistance capacity of the conductive coatings.
Conductive coatings

- Tests were conducted:
  - Conductive films obtained with polypyrrole (electrodeposition using a rotating electrode):
  - Polypyrrole + Fe₃O₄ (particle size from 200 nm to 300 nm, clusters ~1 µm),

- Immersion tests in NaCl solution showed that the oxidizing capacity of the conductive polymer increases in the presence of oxides, and this increase was greater for Fe₃O₄. This ensures a more effective surface passivation of the steel substrate, improving the efficiency of anodic protection.
Final remarks

• The classical corrosion and corrosion protection principles seem to be valid for nanostructured materials.

• The use of nanostructured material is already a reality and it should be widespread soon.

• **Attention:** in all consultant literature, the corrosion studies were conducted through electrochemical tests (polarization curves, linear polarization and electrochemical impedance spectroscopy) and accelerated corrosion tests (such as salt spray).

• In the eighties of the past century, coatings, known as new generation coatings, were launched into the automotive industry as presenting excellent corrosion resistant properties. The corrosion resistance of these coatings were evaluated through laboratory tests similar to those of nanostructured coatings. Huge amounts of money were lost...

• The characterization techniques of nanostructured materials are at a very advanced stage but the corrosion resistance behavior of evaluation tests must be improved.
Thank you for your kind attention