

UNDERSTANDING THE CORROSION MECHANISM IN CHROME COATINGS

BIOVIA MATERIALS STUDIO CASE STUDY



Cars are driven in harsh environments where metal parts are exposed to water, dirt, road salts and metal particles worn off from other parts. Most cars are still built of iron since it is a great construction material, but iron corrosion is a significant disadvantage. Modeling corrosion processes can help scientists better understand corrosion mechanisms with a view to making chrome coatings more durable.

Challenge:

Atotech is one of the world's leading suppliers of specialty chemicals, equipment, service and solutions for printed circuit board, advanced packaging and semiconductor manufacturing, as well as decorative and functional surface finishing. Researchers at Atotech wanted to understand the corrosion process in chrome coatings and how the environment influences the process.

Solution:

Combining electrochemical experiments with Scanning Electron microscopy observations and ab initio molecular dynamics using the CASTEP module in BIOVIA Materials Studio modeling and simulation software revealed that metal ions that might be present in the dust covering the coating can accelerate corrosion.

Benefits:

Modeling corrosion processes can be used to develop more resistant chrome coatings in the future.

There is a long history of trying to prevent corrosion by painting the metal parts of cars or using sacrificial anodes in marine environments. However, paint tends to wear off, so it is desirable to have more wear-resistant coatings for parts in heavy use. Nickel was used in the early days of automotive development but was soon superseded by chromium plating. Many people today can probably remember the large, shiny, chrome-coated grilles and bumpers of American cars in the 1950s and 60s.

Chrome coatings - a highly complex, multilayer technology - are used everywhere today to make metallic and plastic parts more esthetic and durable. They may incorporate up to three layers of nickel beneath the top chromium layer. The purpose of the multilayer design layers is to keep the chromium layer as intact as possible by directing the corrosion attack towards the nickel layers, so the non-noble nickel in the middle of the nickel layer stack acts as a sacrificial layer.

Ions in road salts have been identified as the culprit in many corrosion processes. It has been experimentally demonstrated that nickel corrosion is the result of chlorine ions penetrating through cracks in the chromium layer. The chlorine ions infiltrate the nickel layers by attaching at defects such as edges or vacancies on the nickel surface. The chlorine ions form a Cl-Ni complex on the surface which can dissolve in water. In addition, there are further indications that metal ions, which are deposited on the surface of the coating from dust, may further enhance the rate of corrosion on the nickel layer, but there is no clear mechanism available.

The purpose of the investigation undertaken by researchers at Atotech was (1) to verify the current theories about the role of chlorine in the corrosion process and (2) to extend the theories to also include the role of metal ions [1].

Method:

The researchers at Atotech combined electrochemical experiments with Scanning Electron Microscope (SEM) observation of the coatings after different stages of corrosion. The research team also used extensive ab initio molecular dynamics (MD) simulations using the CASTEP module in BIOVIA Materials Studio to get detailed atomistic insights into the mechanism. The ab initio molecular dynamics method combines quantum mechanical energy and force calculations using Density Functional Theory along with classical mechanics to describe the dynamics of atom movements in the system.

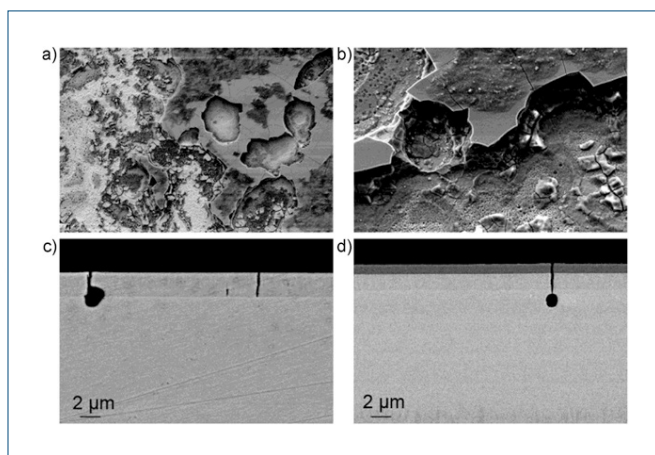


Figure 1. SEM images of the corroded chrome coatings. The top views in a) and b) show that the top chromium layer is intact where it is not undercut. The bottom views in c) and d) show how the cracks penetrate down through the chromium and bright nickel layer and expand to form a large void in the semi-bright nickel layer. Reprinted with permission from ref. [1]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Results:

The SEM investigation of the chrome coatings revealed that the top layer of the intact sections of the coatings was indeed chromium, while the pitting corrosion extended deep down into the nickel layers as shown in Fig. 1. This indicates that the corrosion takes place in the sacrificial nickel layers, and the top chromium layer is not corroded. The open pits resulting from the extensive corrosion of the nickel layers may instead lead to such large voids underneath the chromium layer that the chromium breaks up and delaminates, even though it is not directly corroded.

The first step of the computational study was to investigate the role of chlorine ions in the corrosion process with a focus on the reaction at the nickel surface. The researchers built a supercell model of the nickel (111)-surface using Materials Studio and added ions mixed with water molecules in contact with the surface using the Amorphous cell module. The ab initio MD simulations confirmed the established theory that the chlorine ions drive the corrosion process. The simulations showed how the chlorine ions attached at defect sites on the nickel

surface. The attachment of the chlorine ions, on one hand, prevented the formation of a water complex on the surface. The chlorine ion, on the other hand, formed a complex with under-coordinated nickel atoms on the surface.

This complex destabilizes the attachment of the nickel atoms to the surface, and the complex dissolves into the surrounding water. This process is schematically shown in Fig. 2.

The electrochemical experiments extended the investigation of the corrosion process by including copper and iron ions. The measurements showed an increased corrosion current indicating that the corrosion process is indeed accelerated by the metal ions.

It is well known that adsorbing atoms and ions on a metal surface change the Fermi level in the system and work function. This in turn changes the reactivity of the surface. The researchers at Atotech used this relationship to investigate the effect of adsorbing the metal ions on the nickel surface. The DFT calculations demonstrated that copper and iron atoms, and even more significantly their ions, inflicted a significant decrease of the Fermi level. This indicates that adsorbing the metal ions makes the nickel surface even more susceptible to adsorb the chlorine ions, thereby accelerating the corrosion process.

Additional calculations of the adsorption of metal ions and a nickel oxide surface revealed that the iron ions would also impact the nickel oxide surface, demonstrating that iron is a strong accelerator for the corrosion of the nickel layers.

Conclusions:

The combination of the SEM observations, electrochemical experiments and DFT calculations confirmed that the chlorine ions in road salts are strong drivers of the corrosion process in the nickel layer. The extended investigation revealed that iron ions are also strong accelerators. This microscopic understanding of the corrosion process may be used to redesign multilayer chrome coatings in the future to make the coatings more durable even in harsh environments.

References

[1] R. Schmidt, K.-O. Thiel, F. von Horsten, C. Spickermann, G. Vazhenin, N. Bülke, P. Wachter, P. Hartmann and H.-J. Schreier, *Materials and Corrosion* 65, 959 (2014). © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

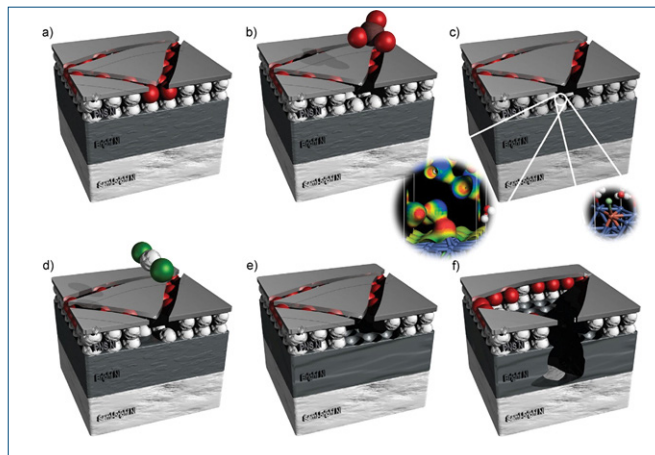


Figure 2. Schematic representation of the corrosion process. b) Water and chlorine ions may diffuse through cracks in the chromium top layer to penetrate the nickel layers. c) The chlorine ions attach to the nickel surface and d) form NiCl₂ complexes that may dissolve. e) This leads to successive extraction of nickel, which create voids under the chromium top layer. This leads eventually to the delamination of the top chromium layer and the formation of large pits. Reprinted with permission from ref. [1]. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

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