

## Towards the Mechanism of the Accelerated Nickel Corrosion of Decorative Coatings in the Presence of Metals and Their Salts

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Nowadays, conventional decorative nickel-chromium coatings, consisting of a multilayer of different nickel deposits and a terminal chromium layer are ubiquitous in daily routine. Such systems have to be able to resist destructive environmental conditions, especially when applied on parts of cars. While the influences of chloride and different road salts on the corrosion of nickel and chromium within such multi-layer systems has been extensively investigated, [1] the impacts of metals such as iron and copper and their salts is considerably less elucidated. [2, 3] The role of chloride as pitting corrosion-inducing anion has been pointed out. Numerous proposed mechanisms exist in the literature, of which many are similar. [4] However, most of the existing models are based on limited experimental evidence and a basic understanding on the molecular level is still lacking. By employing microscopic, electrochemical, and theoretical studies, we attempted to combine existing models for pitting corrosion and corrosion in the presence of different ions with recent quantum chemical methods. The corresponding calculations should contribute to a better understanding of the mechanism on the molecular level.

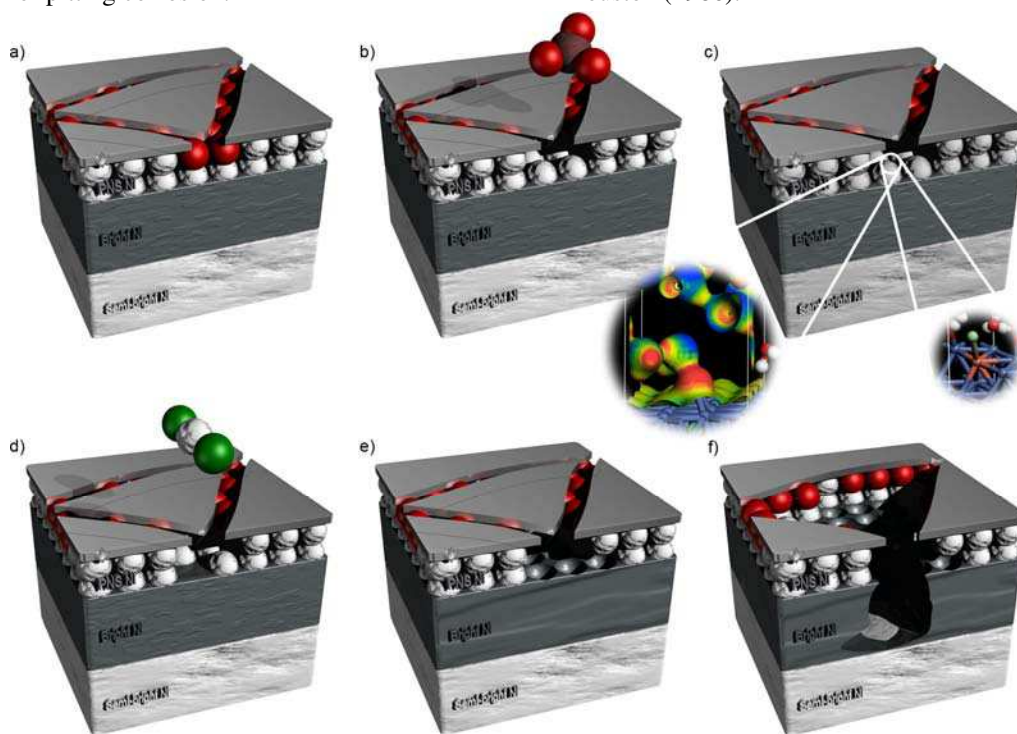
Microscopic studies suggested accelerated nickel corrosion to account for the extensive failure of decorative nickel chromium coatings when exposed to certain metals and their salts. Electrochemical experiments further confirmed the crucial role of chloride, cupric, and ferric ion containing salts, which were found before on the corroded surface. Density functional theory calculations were used in the following to explain experimental observations and to obtain a detailed understanding of the mechanism of the accelerated corrosion on the molecular level. The results of the calculations were discussed taking into account literature known models for pitting corrosion.

The results obtained from experimental and theoretical studies yielded an elaborate mechanistic picture of the processes accounting for acceleration of the corrosion of nickel and the resulting failure of decorative nickel-chromium coatings in the presence of certain salts and metals. Scheme 1 depicts a schematic representation of some of the proposed processes. Metallic iron accelerates nickel dissolution by removal of the protective nickel oxide layer (Scheme 1a, b). Such a chemical destruction of the passive oxide surface film can be found again in the initial stage of pitting corrosion. [4] This pathway adds to existing adsorption as well as penetration and migration theories to explain effects exerted by chloride and physical damage to account for pitting and crevice corrosion. [4] Adsorption of chloride on nickel oxide might additionally lead to the formation of pits while adsorption on bare nickel prevents repassivation. Various metals and their salts further exert a detrimental influence on the corrosion of nickel by lowering the Fermi level and, thereby, increasing the corrosion current and the nickel dissolution rate (Scheme 1c). Additional effects arise from cathodic polarization of cupric and ferric ions. Subsequent strong chloride-induced corrosion of the micro-discontinuous nickel layer and the bright nickel deposit underneath is followed by exfoliation of the chromium layer on top (Scheme 1d–f). Hence, exfoliation is a result of the loss of adhesion owing to accelerated corrosion of the underlayer.

In combination with experimental findings, quantum chemical calculations revealed a comprehensive notion of the mechanism. The results are in very good agreement with existing models and provide further insights into the mechanisms on the molecular level. Based on the results presented here, novel corrosion protection systems for decorative exterior parts with distinctly improved corrosion performance may be developed in the future.

### References

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**Scheme 1.** Schematic representation of some of the processes which are suggested to be responsible for the accelerated corrosion of decorative nickel-chromium coatings. Oxygen is represented by red, chloride by green, and iron by brownish-red spheres.