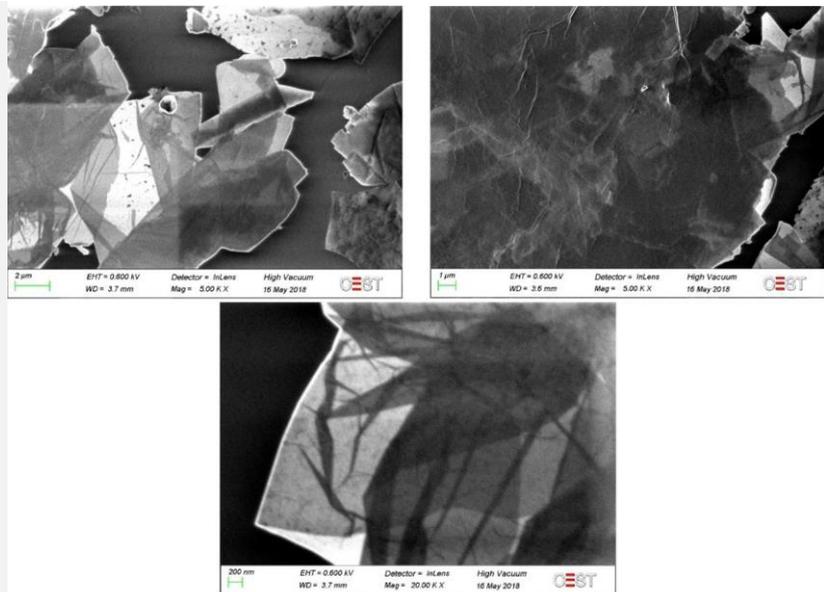


CEST
Centre of Excellence in Electro-chemical Surface Technology and Materials

Programme: COMET – Competence Centers for Excellent Technologies

Programme line: COMET-Centre K1

Type of project: NOVEL COATINGS, multi-firm project, 01/2016-12/2018



GRAPHENE BASED MATERIALS FOR THE APPLICATION ON METALLIC SURFACES

In the scope of the project innovative graphene-based corrosion protective organic coatings were developed for galvanized steel and aluminium surfaces.

Corrosion causes considerable economic damage, which can amount to billions of euros annually. Corrosion is part of everyday life - for example in industrial plants, power plants, in the oil production industry, on bridges or in construction, but also in the aeronautical and the automotive industry. Due to a massive growth of industrial production new innovative ways have to be found in order to meet today's increased requirements for corrosion protection of materials. In addition, the ecological requirements for corrosion protection products, such as the inclusion of Cr(VI) compounds essential for chromating in Annex XIV of the EU Regulation Reach (Registration, Evaluation, Authorization of Chemicals) and the expected entry into force in also in the aeronautical industry in 2024. Furthermore, by finding novel environmentally friendly materials and methods a more effective corrosion resistance might be achieved in a

more low-cost way. For instance, if a specific additive could be found, that, introduced to a paint system, massively can enhance the resistance to corrosion, the thickness of the paint layer could be reduced what of course would be a significant economic aspect. In all of these respects, the profitability and thus the competitiveness of Austrian companies are to be preserved or improved. In this project, nanoadditives, based on the material of the 21st century graphene were synthesized, characterized, modified, applied and tested in corrosion protective organic coatings on steel and aluminium surfaces.

The first important part of the project was to be able to synthesize graphene-based material with appropriate quality by using a possibly low-cost method with a potential for up-scaling. Here, an innovative electro-

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chemical method was modified and further developed. Graphite was exfoliated under anodic conditions in appropriate electrolyte solutions, where at the same time the oxidation of carbon atoms happens. This results in graphene oxide, a nanomaterial composing of carbon atoms and with varying oxidation degree and number of organic functional groups. These functional groups enable for a wide functionalization possibility of the material, due to which a good integrability into the dedicated organic paint systems can be achieved. This was all carried out in the scope of the project, specifically for the steel and aluminium surfaces and for the paint systems provided by the project partners.

The targeted development of graphene-based material was carried out according to a profound scientific investigation of the material, where a complex analysis of the composition and the structure, using techniques from the simplest chemical analytical ones until the instrumental analytical ones were used. By Raman Spectroscopy the oxidation and exfoliation grade, by Scanning Electron Microscopy, X-Ray Diffraction and Atomic Force Microscopy the structure and by chemical methods the composition were determined. The composition was finely tuned by different chemical synthesis methods. Not only the graphene based material, but also free-standing (not applied on metallic surface yet) paint layers containing graphene based material were studied regarding their permeability for different corrosive species like water and oxygen molecules and for important compounds of targeted technical applications (e.g. for galvanized steel surfaces zinc permeability plays an important role). Here, an innovative, self-developed electrochemical testing was considered and used. According to the findings it was possible to determine the most appropriate graphene-based material composition to be applied in a corrosion protective paint system and a strong improvement of the corrosion properties could be predicted.

After application of the graphene-based material containing paint on steel and aluminium surfaces, a corrosion testing consisting of electrochemical and technical investigations was carried out. The electrochemical impedance testing showed improved resistances of the layer ($>10^8 \Omega$, 2-3 orders of magnitude higher than layers without graphene), one order of magnitude lower water uptake and corrosion currents.

Scanning Kelvin Probe investigations showed that graphene-based material can protect surface where coating has been injured – the potential characteristics shows that the anodic reaction is inhibited (Figure 1).

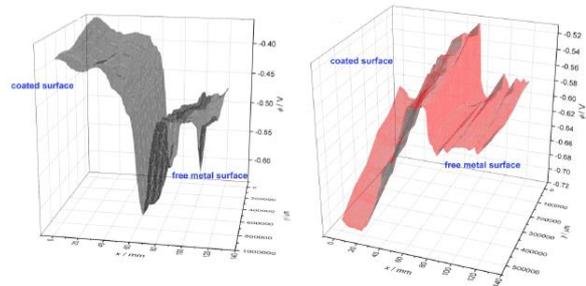


Figure 1: 3D scans of a 100 x 100 mm surface area in the transition region (direction coated – non-coated part)

Neutral (NSS) and Copper Accelerated Acetic Acid Salt Spray Tests (CASS) show at least two times higher lifetime and an inhibited cathodic delamination for steel and aluminium samples coated with the graphene-based paint layers (Figure 2).

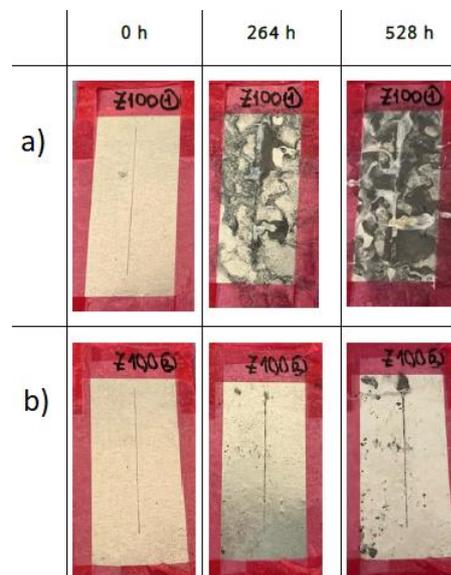


Figure 2 NSS testing of coated galvanized steel coupons (a) without graphene-based material, b) with graphene-based material in the coating)

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Impact and effects

The obtained excellent results present a remarkable economic benefit. By using graphene based material in the organic coating, thinner layers may be applied, or also thinner galvanic zinc layers would be necessary for same organic coating thickness, resulting in considerable energy savings, in the first place for the automotive and the marine industry. BASF Coatings, voestalpine, Welser Profile, TU Vienna and CEST have filled a patent based on the excellent results achieved in the NOVEL COATINGS project (application in progress).

Moreover, the findings can revolutionize different other industry sectors not only due to corrosion aspects, but also other functional properties. Keeping in

mind, that in this project, a simpler graphene materials based composite was developed, it paved the way in direction of aeronautical systems, where the integrated water impermeable, lightning strike and fire protective properties and the de-icing potential due to a high conductivity of graphene based materials are in the centre of interest. Here, based on the success of NOVEL COATINGS, a CEST-proposed project has already been granted for EU funding (\mathcal{N}° 886376 GRAPHICING, project leader Dr. Peter Velicsanyi) and renowned European aeronautical companies started cooperation with the centre, as well.

Project coordination (Story)

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- BASF Coatings GmbH, Germany
- Welser Profile GmbH, Austria
- Vienna University of Technology, Austria

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