

Improved ceramic oxide layers on magnesium alloys through a combination of pulsed plasma-electrolytic oxidation and chemical nanotechnology

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Background and Aims

The use of magnesium as a construction material can be very beneficial especially in application fields where weight reduction plays an important role, as in automobile or aviation industries. Due to its very low weight, a broader use of magnesium could help to significantly reduce fuel consumption and the associated costs and pollution. However, the widespread application of magnesium alloys is still considerably hindered by their high susceptibility to corrosion. A second issue is its low resistance to abrasion. One possible approach to enhance both corrosion and wear resistance of magnesium alloys is their pretreatment by anodic oxidation. Specifically, plasma-electrolytic oxidation (PEO) is a promising technique since it allows the generation of ceramic type oxidic coatings with very good adhesion to the substrate and excellent protective properties.

The aim of this work is the development of a modified PEO process which improves on the corrosion protective properties as well as on the energy consumption associated with conventional PEO treatments.

In particular, this new process will involve the implementation of nanoparticles into the generated anodic oxide layers. These could act as fillers for the pores of the oxide layer and thus enhance their barrier properties. Furthermore, nanoparticles could carry corrosion inhibitive substances like lanthanide cations in order to introduce self-healing properties to the coatings. The composition of the anodizing bath is to be optimized with respect to the protective properties of the resulting coatings and the energy consumption during anodizing.

Results

Immobilizing corrosion inhibitors on microporous nanoparticles

- Mesoporous SiO₂ nanoparticles as carriers for corrosion inhibiting lanthanide cations
 - High surface area and loading capacity
 - Tailoring of loading and release behaviour via functionalization of particle surface
- Loading of carrier particles with lanthanide cations
 - Grafting of particle surface with amino functionality
 - Increased affinity and loading capacity for lanthanide cations (fig. 1).

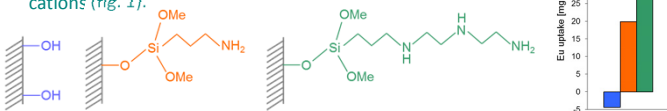


Fig. 1: Enhanced lanthanide cation loading capacity of functionalized particles.

- pH-dependant release of lanthanide cations
 - Inhibitor release at acidic pH by protonation of amine function (fig. 3 and 4)

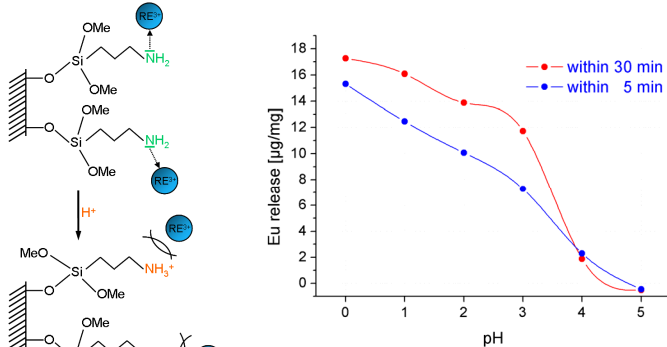


Fig. 2: Lanthanide cation release through protonation of amine functionality.

Fig. 3: pH-dependant Eu³⁺ release after 5 min and 30 min.

→ Selective release of lanthanide cations at low pH, starting between pH 5 and 4 (fig. 3).

Immobilizing corrosion inhibitors on zeolite nanoparticles

- Zeolite nanoparticles as carriers for corrosion inhibiting lanthanide cations
 - Materials: Zeolite X and Zeolite Y
 - Loading by immersion of particles in Ln(NO₃)₃ solution (fig. 4)
- Loading capacity of different zeolite types (same framework, different Al content)

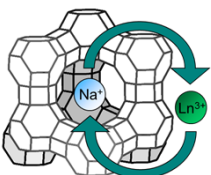


Fig. 4: Loading of zeolites with lanthanide cations by ion exchange.

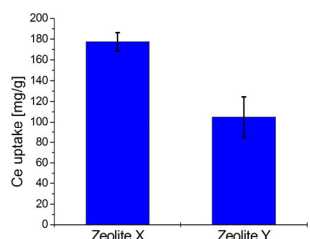


Fig. 5: Loading capacities of Zeolite X and Zeolite Y.

→ Superior lanthanide uptake by aluminum rich Zeolite X (fig. 5).

- Release of lanthanide cations from zeolites by corrosion induced presence of Mg²⁺

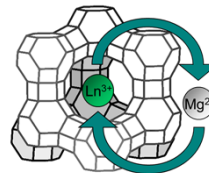


Fig. 6: Release of lanthanide cations from zeolites by ion exchange.

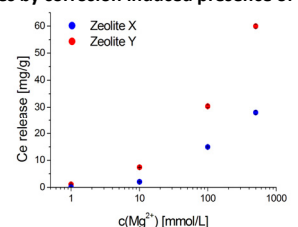


Fig. 7: Release of lanthanide cations depending on Mg²⁺ concentration.

→ Superior lanthanide release by aluminum poor Zeolite Y (fig. 7).

PEO and simultaneous nanoparticle incorporation

- Optimization of anodizing bath composition
 - Pulsed galvanostatic anodizing of Mg AZ31 (20 mA/cm²)
 - Anodizing bath with 10 g/L Na₂SiO₃ and varying KOH content:

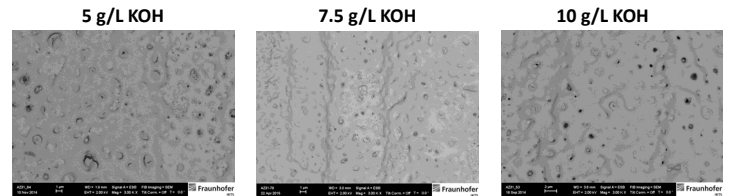


Fig. 8: Surface morphology after anodizing in anodizing bath with varying KOH content.

→ Reduction of KOH content renders closed pores (fig. 8).

- Incorporation of nanoparticles into PEO coating
 - Pulsed anodizing of Mg AZ31 (20 mA/cm²)
 - Incorporation of compact nanoparticles via addition to anodizing bath (fig. 7)
 - Incorporation of lanthanide cation filled zeolite particles via addition to anodizing bath (fig. 8)

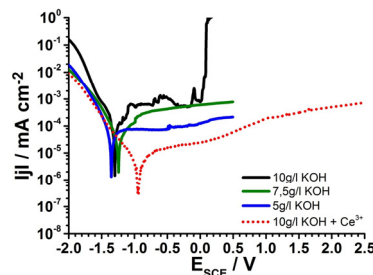


Fig. 9: Potentiodynamic polarization curves of AZ31 anodized without (solid lines) and with zeolite particles (dashed lines).

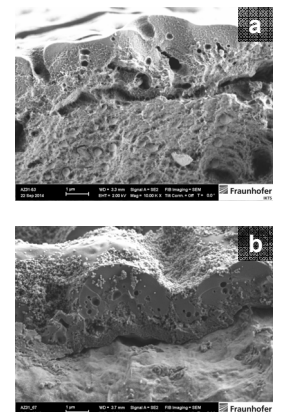


Fig. 10: Cross sections of Mg AZ31 anodized without (a) and with (b) nanoparticle incorporation.

→ Compact nanoparticles fill up cavities in the coating (fig. 10).
→ Corrosion inhibitor filled zeolite particles enhance corrosion properties (fig. 9).

Project partners

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