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Corrosion

Corrosion protection of wrought magnesium alloy (AZ31) via ultrasound-driven growth of a self-healing oxide layer

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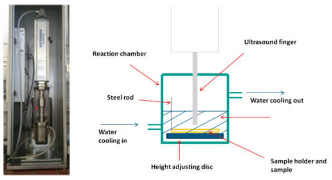
Background and Motivation

- Magnesium is the lightest construction metal
- Its alloys are not corrosion resistant
- Application is limited to mild service environments
- Standard anticorrosion coatings are working with *the damage prevention principle* and are often harmful for health and environment
- Next generation of coatings should be environment-friendly and work with *the damage management principle*

Experimental

Magnesium has not the intrinsic property to build a passivating oxide layer on its surface (P-B ratio <1), which protects the metal against corrosion. For the ultrasound-driven growth of a smart oxide layer an aqueous $Ce(NO_3)_3$ solution with dispersed Halloysite nanotubes was used, because cerium is well-known as a corrosion inhibitor for magnesium. To prevent agglomeration of the Halloysite nanotubes in presence of Ce^{3+} a small amount of NaOH is added to stabilize the dispersion over a couple of hours. By introducing ultrasound in an aqueous solution H_2O_2 is formed in situ, which causes the precipitation of mixed Mg/Ce-oxides on the surface of the substrate. Furthermore Halloysite nanotubes were added to the aqueous solution to prevent micro crack formation in the artificially produced oxide layer due to their unique physical properties. Through introduction of Halloysite in the mixed oxide layer as grown under ultrasound it is possible to prepare a homogeneous crack-reduced coating, which protects the metal against corrosion. The oxide layer has a cellular morphology and a thickness of ~ 1 µm. This is important because thicker or more solid oxide layers tend to develop cracks which results in poor corrosion protection.



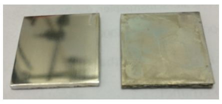


Fig. 2: Hielscher ultrasonic processor UIP2000hd and schematic sketch of the experimental setup. Image of a pretreated coupon with a mirror-like finish (left) and a ultrasound coated coupon (right).

Results

AZ31	Mg	Al	Zn	Mn	Si	Ca	Fe	Ni	Cu	Other
Standard	93.9-96.5	2.5-3.5	0.6-1.4	0.2-1.0	0.10	0.04	0.005	0.005	0.05	0.30
As received	96.27	2.59	0.757	0.332	0.017	0.0018	<0.0012	<0.0010	<0.0005	0.0295

Tab. 1: Chemical composition (in wt%) of AZ31 magnesium alloy measured with OES.

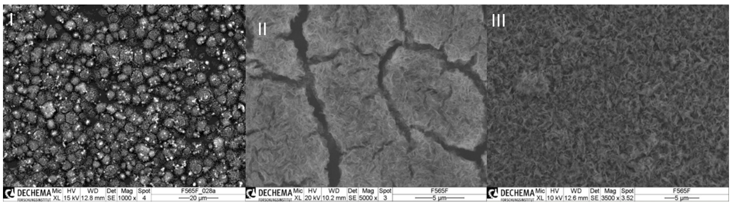


Fig.3: SEM images of coated samples: Without ultrasound, small hills form on the alloy and the surface is uneven and unconnected (I). By application of ultrasound a more homogeneous oxide layer is formed on the substrate, but huge cracks are still present (II). Addition of Halloysite nanotubes reduces the cracking of the oxide layer by enhancing the mechanical stability of the coating (III).

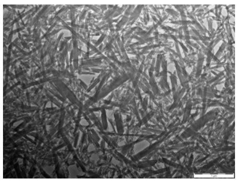


Fig. 4: TEM image of naturally occurring Halloysite nanotubes, without further purification.

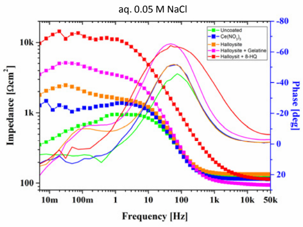


Fig.5: EIS measurements of different treated samples.

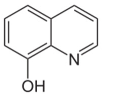


Fig. 6: Lewis-structure of 8-Hydroxyquinoline

Approach

- A sponge-like Mg/Ce-oxide layer can be generated by ultrasound cavitation
- Inorganic corrosion inhibitor for self-healing ability is incorporated into oxide layer
- Halloysite nanotubes are introduced into the oxide layer during preparation to prevent cracking by mechanical strengthening

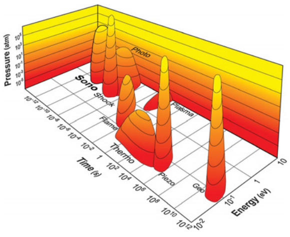


Fig. 1: Domains of chemistry as a function of time, pressure and energy.[1]

Facts of high intensity ultrasound[1]

- Frequency 20 kHz – 15 MHz
- Velocity in typical liquids 1000 – 1500 m/s
- Wavelength 100 µm – 10 cm
- Temperatures up to 5000 K
- Heating and cooling rates of 10^{10} K/s
- Shockwaves up to 60 kbar
- Interparticle collisions with ~100 m/s
- Sonolysis of water
  → Formation of H_2 / H_2O_2 / $H^\bullet$ / $HO^\bullet$ / O_2 / HO_2

Outlook and further work

Corrosion Tests

- Coatings with and without Halloysite addition are already tested
- Enhanced coatings are in the pipeline
- Investigation of corrosion with different methods (e.g. electrochemical impedance spectroscopy (EIS), salt spray test et cetera)

Post-treatment

- Enhancing corrosion properties by post-treatment procedure
- Healing of introduced cracks by hot water steam treatment
- Generation of hierarchical $Mg(OH)_2$ structures to get hydrophobic properties
- Wettability is extreme reduced, but only for short time immersion because $Mg(OH)_2$ is soluble in water
- Apply water-insoluble low energy material to reach even superhydrophobic range and prevent dissolution of the coating

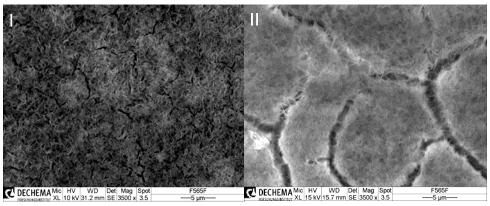
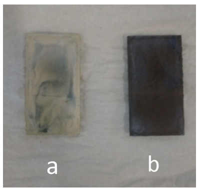


Fig.7: Ultrasound coating with Halloysite enforcement on AZ31 before (I) and after (II) hot water steam treatment.



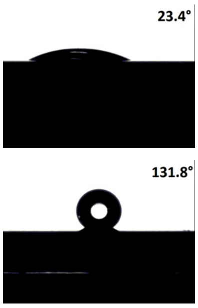


Fig.8 (left)/9 (right): Hydrophilic Mg/Ce-oxide sponge after coating (a). Hydrophobic surface after hot water steam post-treatment (b). Contact angles of Sample a and b.

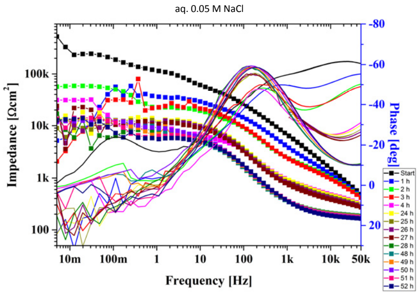


Fig.10: EIS measurement of Halloysite nanotube enforced Mg/Ce-oxide sponge which was treated with hot water steam to get a hydrophobic surface. At the beginning Impedance values over 500 kΩcm² are reached, by dissolution of the $Mg(OH)_2$ layer Impedance decreases quickly.

Project Partner

C.-N. Liu, M. Wiesener, G. Grundmeier (Universität Paderborn, TMC)

References

[1] H. Xu, B. W. Zeiger, K. S. Suslick, *Chem. Soc. Rev.*, **2013**, 42, 2555-2567.