

Nanoparticle modified anodizing-layers with increased alkali resistance

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Background and Motivation

- Aluminium alloys are important materials in lightweight construction
 - Requirements for the application of aluminium alloys especially in aerospace and automotive industries: corrosion and alkali resistance
 - Sulfuric acid anodizing (SAA) is a frequently used surface treatment for corrosion protection of aluminium alloys in automotive applications
 - For sufficient corrosion resistance sealing is necessary, but common sealing methods (e.g. hot water sealing) are not protecting against strong bases
 - Aluminium oxide is stable till a pH of 8.5 is reached, but chemical cleaners are often far more basic
 - Alkali resistance can be achieved by impregnation of the surface and pores with suitable nanoparticles, e.g. from ZrO_2
- ➔ **Development of new environmentally compliant process as surface treatment for aluminium alloys which offers a high corrosion and alkali resistance up to a pH of 13.5**

Approach

Alloy Series	Principal Alloying Element
1xxx	99.000% Minimum Aluminum
2xxx	Copper
3xxx	Manganese
4xxx	Silicon
5xxx	Magnesium
6xxx	Magnesium and Silicon
7xxx	Zinc
8xxx	Other Elements

Aluminium alloys used for anodizing:

- 1xxx series (1050)
- 5xxx series (AlMg1)
- 6xxx series (AlMg0.5Si)

Preparation of the oxide-layer and impregnation:

Step 1: Sulfuric acid anodizing (SAA) process ➔ open pores (20-40 nm):



Step 2: ZrO_2 nanoparticle based impregnation: inorganic protective coatings at relatively low sintering temperatures due to the high surface activity of nanoparticles ➔ suitable impregnation with sealed pores

Impregnation



➔ **Surface protection method based on established SAA and easy to handle impregnation procedure**

Aim:

- Optimal pore design by process optimization
- Impregnation based on chemical nanotechnology
- No hot or cold water steam sealing
- Perfect penetration and anchoring of the impregnation on the oxide-layer
- Use of dispersed inorganic alkali resistant nanoparticles
- Improvement of the mechanical stability of the oxide layer
- Enhancement of the barrier properties

Impregnation:

- Dip-coating
- Electrophoretic deposition
- "Wet in Wet"-chemistry

Investigations:

- Electrochemistry (LSV, EIS, etc.)
- Exposure tests (salt spray test, etc.)
- Tests at project associated companies

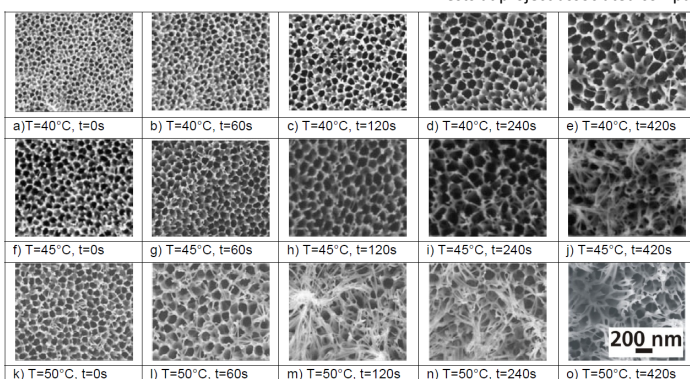


Fig.2: Experiences in pore design of PAA-layers in former project. Correlation of pore morphology, time and treatment temperature.

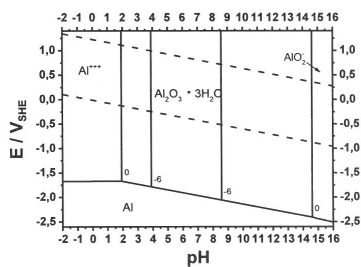


Fig.1: Pourbaix diagram of Aluminium, passive region between pH 3.9-8.6.

Fig.3: Schematic sketch of impregnation.

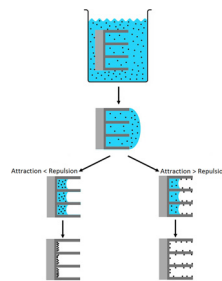


Fig.4: Sample holder for anodizing.



Nanoparticle dispersions

- Long-time stability of dispersions (few days)
- Particle size 6-8 nm
- Inhibition of agglomeration
- Functionalisation of nanoparticles for zeta potential adjustment

Experiences from former project: Dip coating of PAA layers in different SiO_2 impregnation media

➔ **Most promising:** Commercial SiO_2 -dispersion LEVASIL® 300/30%, average particle size: 9nm, solids content: 30, pH:10

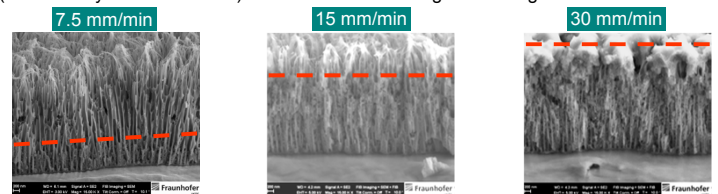
➔ **Systematic investigation of parameters influencing the impregnation**

Aging: tests with different aged samples ➔ often inhomogeneous impregnation ➔ aging difficult to control, **best results:** wet-on-wet method

Temperature: no significant influence of moderate temperature differences (15 °C and 40 °C) and therefore viscosity changes between 5.6 mPas and 3.0 mPas of the dispersion

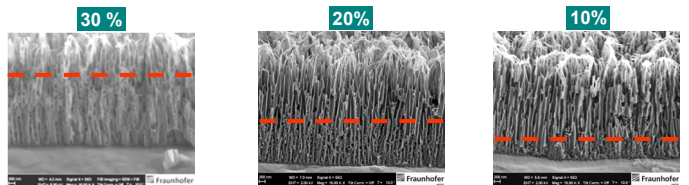
Coating time: no significant difference in the impregnation between 60s and 600 s

Withdrawing rates: increasing the withdrawing velocity ➔ increasing filling height (indicated by the dashed line) ➔ allows to control degree of filling:



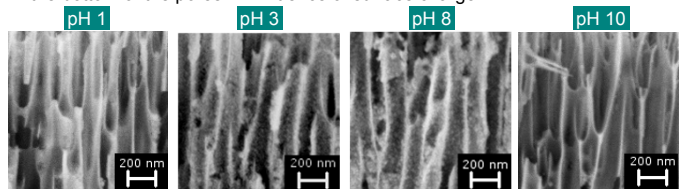
Solids content

Decreasing the solids content ➔ decreasing filling height (indicated by the dashed lines) ➔ allows to control degree of filling



pH

Doesn't alter filling height significantly but for pH 3 and pH 8 particles are also deposited at the pore walls near the surface of the anodising layer and not only in the bottom of the pores ➔ influence of surface charge



Project Partner

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