Properties and performance of spin-on-glass coatings for the corrosion protection of stainless steels in chloride media

Lampert, Felix; Jensen, Annemette H.; Din, Rameez U.; Gonzalez-Garcia, Yaiza; Møller, Per

Published in:
Materials and Corrosion

Link to article, DOI:
[10.1002/maco.201710016](https://doi.org/10.1002/maco.201710016)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Lampert, F., Jensen, A. H., Din, R. U., Gonzalez-Garcia, Y., & Møller, P. (2018). Properties and performance of spin-on-glass coatings for the corrosion protection of stainless steels in chloride media. *Materials and Corrosion*, 69(9), 1279-1291. <https://doi.org/10.1002/maco.201710016>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Properties and performance of spin-on-glass coatings for the corrosion protection of stainless steels in chloride media

Lampert, Felix; Jensen, A.H.; Din, Rameez U.; Gonzalez Garcia, Yaiza; Møller, Per

DOI

[10.1002/maco.201710016](https://doi.org/10.1002/maco.201710016)

Publication date

2018

Document Version

Accepted author manuscript

Published in

Materials and Corrosion

Citation (APA)

Lampert, F., Jensen, A. H., Din, R. U., Gonzalez-Garcia, Y., & Møller, P. (2018). Properties and performance of spin-on-glass coatings for the corrosion protection of stainless steels in chloride media. *Materials and Corrosion*, 69(9), 1279-1291. <https://doi.org/10.1002/maco.201710016>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

Properties and performance of spin-on-glass coatings for the corrosion protection of stainless steels in chloride media

Felix Lampert ^a, Annemette Hindhede Jensen ^b, Rameez Ud Din ^c, Yaiza Gonzalez-Garcia ^d, Per Møller ^e

^a Technical University of Denmark (DTU), Department of Mechanical Engineering,
Produktionstorvet, Building 425, 2800 Kgs. Lyngby, Denmark, e-mail: felamp@mek.dtu.dk

^b SiOx ApS, Bybjergvej 7, 3060 Espergærde, Denmark, e-mail: annemette@siox.dk

^c Technical University of Denmark (DTU), Department of Mechanical Engineering,
Produktionstorvet, Building 425, 2800 Kgs. Lyngby, Denmark, e-mail: rudin@mek.dtu.dk

^d Delft University of Technology, Department of Materials Science and Engineering, 2628CD
Delft, The Netherlands, e-mail: y.gonzalezgarcia@tudelft.nl

^e Technical University of Denmark (DTU), Department of Mechanical Engineering,
Produktionstorvet, Building 425, 2800 Kgs. Lyngby, Denmark, e-mail: pm@mek.dtu.dk

Corresponding author: Felix Lampert, e-mail: felamp@mek.dtu.dk

Abstract

Spin-on-glass deposition was investigated as viable alternative to increase the durability and performance of 316L steel in chloride environment. The buildup of a detrimental interface oxide was prevented by non-oxidative thermal curing of the coatings, which leads to a transformation to an inorganic, SiO₂-like material. The degree of polymerization was found dependent on the curing temperature; however, curing at the maximum investigated curing temperature of 800 °C led to an incomplete transformation, showing less SiO₂-like character with respect to thermally grown oxide or fused silica. Electrochemical analysis by electrochemical impedance spectroscopy and anodic cyclic polarization indicated that the coatings behave as imperfect barrier coatings, which may enhance the passive properties of the substrates. The coatings showed, in association with substrate defects, unevenly distributed coating flaws, which may act as initiation points of pitting corrosion and decrease the corrosion resistance of coated substrates in Cl⁻ containing media. The films showed instability in aqueous environment due to imperfect polymerization.

Keywords

Coatings, Corrosion Resistance, Film, Passivity, Pitting, Stainless Steel

1 Introduction

Gasketed plate heat exchangers are widely applied in e.g. generic heating or cooling systems in marine applications. Since the corrosion resistance of many alloys is strongly compromised in hot sea water, the application necessitates the use of highly corrosion resistant plate materials such as Ti-alloys, which exhibit outstanding performance in aggressive Cl^- containing media. Due to the high material cost, novel corrosion protection concepts are under investigation to enable the use of new and more cost efficient materials. In the present work, surface modified AISI 316L steel is investigated as potential candidate for the next generation heat exchanger plates. In our previous work¹, we have demonstrated the deposition of thin SiO_2 -like coatings from a spin-on-glass (SOG) precursor as viable process to modify the surface of stainless steel components. The process of SOG deposition originates from the deposition of highly insulating interlayer dielectric films in microelectronics applications^{2,3} and has recently emerged into the surface finishing industry due to its good applicability to metallic substrates and its high potential to modify the surface characteristics of the substrate⁴⁻⁶. Similar surface modifications by the incumbent processes (sol-gel, vapor or liquid phase deposition) have shown to improve the corrosion resistance⁷⁻¹⁰, wear properties^{11,12}, surface roughness^{13,14} and resistance towards biofouling^{13,15} or biocompatibility^{16,17} in the past. In analogy, SOG deposition is under investigation as viable surface modification to improve the corrosion resistance of the substrate¹⁸, whilst significantly decreasing the surface roughness⁴⁻⁶ and decreasing the susceptibility towards biofouling and scaling in heat exchanger applications.

The process generally relies on the deposition of a liquid hydrogen silsesquioxane (HSQ) containing precursor solution, followed by a thermal polymerization, forming a fully inorganic, SiO_2 -like surface film^{2,3,19,20}, which offers potential advantages in processing cost, ease of

application, reduction of hazardous reaction products or film quality with respect to the incumbent deposition processes¹. Further, due to the gradual transformation from the resinous precursor to an inorganic ceramic, the process offers a wide range of possible coating properties, ranging from loosely bonded, hydrogenated films to highly polymerized and virtually hydrogen-free coatings^{19,20}.

Our recent studies of SOG curing in air^{21,22} showed an extensive degradation of the substrate surface due to thermal oxidation at the coating/substrate interface. The buildup of a thick thermal oxide at the interface impaired the corrosion performance and coating adhesion of samples cured above 400 °C and restricted the curing temperature and achievable degree of coating polymerization. Further, the coatings, suffered from inadequate chemical stability due to their loose cross-linking, and hence curing in air was found to be inappropriate for the polymerization of HSQ-based corrosion barrier coatings on stainless steel substrates. Our previous results¹ have shown that the formation of a thick interfacial reaction zone between the coating and substrate can be efficiently suppressed by lowering of the oxygen partial pressure in the curing atmosphere, enabling the deposition of HSQ-based coatings without the unfavorable oxidation of the coating/substrate interface. Thus, curing in non-oxidative atmosphere revokes the restrictions in curing temperature and enables higher degrees of coating polymerization, i.e. potentially higher chemical coating stability.

Our recent investigations on air-cured SOG systems^{21,22} emphasized that severe corrosive failure of inadequately coated stainless steels may be expected in Cl⁻ containing media. Since our previous investigation of non-oxidatively cured coatings was solely focused on curing at 500 °C and electrochemical testing in Cl⁻-free, buffered neutral solution¹, the successful application of the technology as coating for marine heat exchanger plates necessitates a comprehensive

investigation of the corrosion performance as well as the coating properties over a broad curing temperature range and in Cl^- containing media. Further, the previously indicated poor chemical stability of loosely polymerized coatings was only studied on inhomogeneous and rough substrate, demanding for further systematic research to conclude on the chemical coating stability and the chemical coating breakdown of HSQ-based films in aqueous environment.

In this work, HSQ-based coatings were deposited on AISI 316L substrates and thermally polymerized in protective atmosphere at temperatures between 400 and 800 °C to form highly cross-linked, sub-micrometer thick surface coatings. The coating morphology and microstructure was studied by atomic force microscopy and scanning/transmission electron microscopy. Further, The coating chemistry was characterized by infrared spectroscopy and X-ray photoelectron spectroscopy and the coating properties were investigated by water contact angle and nanoindentation measurements. Moreover, the barrier efficiency of the coatings was studied electrochemical impedance spectroscopy and the effect of coating on the substrate passivity was characterized by potentiodynamic cyclic polarization and spot-testing in aqueous NaCl solution. Lastly, the long term coating stability was investigated by ageing in a salt spray chamber.

2 Experimental

2.1 Thin film deposition

SOG films were deposited on AISI 316 L substrates with no. 2B surface finish (dimensions: 100 x 50 mm² area and 1 mm thickness; chemical composition shown in Table 1) and Si-wafer (thickness 675 µm, front side polished, backside etched) substrates. The deposition was carried out by the process previously described by Lampert et al.¹, i.e. the deposition of a flowable oxide

film (Dow Corning FOx 25) by dip-coating, followed by solvent evaporation (soft-bake) at 160 °C for 0.5 h in an open furnace and thermal polymerization in a retort furnace under constant flow of 0.45 l/min Ar with addition of 0.05 l/min H₂ gas at atmospheric pressure. The annealing temperature of the polymerization treatment was varied between 400 and 800 °C and the coated metallic substrates are designated with “sample *curing temperature*” in the following. The metallic substrates were prepared by immersion degreasing, followed by anodic degreasing and acid picking²² and the Si substrates were cleaned by flushing in organic solvent. All substrates were allowed to dry in air before further processing. Generally, the substrates were dip-coated with 1 mm/s withdrawal rate; however, due to the particular needs for valid nanoindentation measurements, the withdrawal rate was increased to 5-10 mm/s for the samples used for nanoindentation. A SiO₂ reference was grown by wet oxidation of a Si wafer (thickness 500 µm, front side polished, backside etched) substrate under flow of 3 l/min H₂ together with 2 l/min O₂ at 1050 °C, yielding an oxide thickness of 464 nm (measured by spectral reflectance).

2.2 Characterization

2.2.1 Coating microstructure and properties

Atomic force microscopy (AFM). Measurements were performed using a Bruker-Dimension Edge instrument (BRUKER AXS SAS, France) operating in tapping mode. The microscope was fitted with a Bruker model RTESP probe with a Sb doped Si cantilever with ~ 300 kHz resonance frequency.

Nanoindentation. Nanoindentation was performed on a CSM-Instruments system on thin films deposited on Si wafer. To avoid substrate-induced artefacts^{23,24}, an indentation depth/film thickness ratio of max. 1:10 was maintained for all films by varying the film thickness (thickness

values of the measured films are shown in Table 2). An increase in film thickness beyond the values reported in Table 2 was impractical due to film fracture during curing. The system was operated with a Berkovich indenter at 0.5 mN maximum load and 1 mN/min linear loading/unloading rate. The indentation modulus was calculated as described by ISO 14577-1²⁵ based on the indenter area function derived by the method described by Oliver et al.²⁶. The indenter area function was calibrated on fused silica reference slide with a plane strain modulus of 75.2 ± 0.4 GPa (indentation modulus of 73.3 ± 0.4 GPa).

Electron microscopy. Scanning electron microscopy (SEM) was performed on a Helios Nanolab 600 dual beam microscope fitted with a field emission gun, Pt gas insertion system and a Ga⁺-ion source. SEM images were acquired under 5 kV accelerating voltage and the beam currents indicated in the respective figure captions. Coating cross sections were prepared by Focused Ion Beam (FIB)-milling at 30 keV accelerating voltage. Prior to SEM analysis, the samples were sputter-coated with a conductive Au-film and the investigated areas were protected by a Pt deposition before ion beam milling. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai T20 TEM fitted with a LaB₆ filament electron source operated at 200 kV. TEM lamellae were prepared by the method described by Lampert et al.²².

Fourier transformed infrared spectroscopy (FT-IR). FT-IR was performed on a Thermo Scientific Nicolet iN10 MX in transmission mode on films deposited on Si-wafer (deposited by dip-coating at 1 mm/s withdrawal speed). The IR-background was acquired on an uncoated reference wafer.

X-ray photoelectron spectroscopy (XPS). XP-spectra were acquired on a Thermo Scientific L-Alpha⁺ instrument fitted with a monochromated Al K-Alpha X-ray source at a photon energy of 1486.7 eV. The spectra were recorded under ultrahigh vacuum on a circular area with a diameter

of 400 μm and with the use of a flood gun to compensate for surface charging. The peak fitting was performed using the commercial software Thermo Advantage 5.949.

Water contact angle. The water contact angle was measured on coated AISI 316L substrates on an Attension Theta contact angle meter by the sessile drop method, using a droplet volume of 10 μl at room temperature. The values reported herein are the standard deviated averages of five individual measurements.

2.2.2 Electrochemical/chemical properties

Spot testing. For spot testing, 5 g $\text{K}_3\text{Fe}(\text{CN})_6$ was dissolved in 1 l of in 3.5 wt.% NaCl aqueous solution. The solution was deposited on the surface with a pipette and allowed to soak for 5 min. Afterwards the liquid was carefully removed with a pipette and the surface was allowed to fully dry in air prior to further investigation.

Anodic cyclic potentiodynamic polarization (anodic CP). Anodic CP was performed with an ACM Instruments GillAC potentiostat in a flat corrosion cell which suppresses localized corrosion at the crevice between the rubber gasket and substrate²⁷. The measurements were conducted in 400 ml of 3.5 wt.% NaCl aqueous solution on an area of 1 cm^2 . The system was excited with a Pt counter electrode and the potential was measured with a KCl saturated Ag-AgCl electrode. The measurements were performed after a settling time of 3600 s with a scan rate of 1 mV/s. The experiments were repeated at least three times for consistency.

Electrochemical impedance spectroscopy (EIS). EIS data acquisition was performed on a Gamry Ref600 potentiostat in a flat cell with 2.1 cm^2 sample area and in 15 ml of 3.5 wt.% NaCl aqueous solution. The potential was measured with a saturated calomel electrode (SCE) and perturbed by a Pt counter electrode with an amplitude of 10 mV around the open circuit potential

after a cell settling time of 3600 s. The data analysis was carried out by the electrical equivalent circuit approach with the commercial software Gamry Echem Analyst V 6.31. Data validation was carried out by an automatic Kramers-Kronig test and conversion between constant phase elements and equivalent capacitance was carried out by the approach presented by Hsu et al.²⁸. The individual measurements were repeated five times for consistency.

Accelerated corrosion testing. Coatings on stainless steel substrates and films on Si-wafer (HSQ-based films were deposited by dip-coating at 1 mm/s withdrawal speed) were artificially aged by neutral salt spray testing according to ISO 9227²⁹. The coatings on stainless steel were investigated after ageing for 1000 h and the films deposited on Si wafers were periodically investigated in two-week intervals with a maximal ageing time of six weeks.

3 Results and Discussion

Coating topography. The surface morphology of a coated substrate (sample 600) has been studied by AFM and compared to an uncoated reference substrate, as presented in Figure 1(a). The reference exhibits roughness average of $R_a = 38.9$ nm with flat plateaus on the hills, which are separated by the characteristic valleys along the grain boundaries from the descaling step during sheet metal production³⁰ (Figure 1(a)). However, this absolute roughness is, to a large extent, constituted by the grain narrow and deep boundary valleys which partially undercut the grains¹ and limits the roughness profile determination by the applied method. As previously shown on coating cross sections¹, the coating deposition from a liquid allows for flow of the precursor into substrate defects, yielding an overall decrease in R_a surface roughness by 60.4 % to $R_a = 15.4$ nm (calculated from Figure 1(b)). Despite the excellent leveling capability, the grain boundary structure from the substrate protrudes through the coating and constitutes the major

contribution to the overall surface roughness (Figure 1(b)). To determine the physical roughness of the spin-on-glass coating, the coating topography was acquired on a near-planar coating region and the residual waviness imposed from the substrate was levelled and filtered by 2D Fast Fourier Transform Filtering. Without influence from the substrate, the coating shows nanometer-scale topography with a R_a roughness of 0.19 nm (Figure 1(c)).

Overall, the coating morphology deviates from the morphologies that can be achieved by competitive processes such as chemical vapor deposition¹³, which does not significantly level substrate roughness, or liquid phase deposition³¹, which yields inherently rough films. Due to the similarities in process characteristics, SOG-deposition shows similarities in surface morphology to sol-gel silica¹³, which has previously shown excellent substrate levelling and a decrease in R_a roughness of 45 % with respect to untreated 2B finished stainless steel. These results have a strong impact on the prospective application of the technology on heat exchanger plates, since the surface roughness is expected to strongly affect the adherence of contaminations such as inorganic deposits or biological films and the cleanability of the components. Further detailed investigations are necessary to verify this hypothesis.

Film and interface chemistry. The coating microstructure with focus on the interface between coating and substrate has been investigated by TEM and a bright field micrograph of a coating cross-section is shown in Figure 2. The coating/substrate transition is rendered sharp in the micrograph, indicating that the curing process has successfully suppressed the buildup of a unfavorable, thick interfacial oxide, like it was previously reported for air-cured HSQ-based enamels^{21,22}.

Further, the coating chemistry was characterized by FT-IR and the FT-IR absorbance spectra of all curing conditions, together with an absorbance plot of a thermally grown SiO_2 are shown in

Figure 3(a). The spectral features were identified based on the data reviewed by Lampert et al.²¹. In agreement with other groups^{2,32}, the thermal treatment leads to a distinct shift from HSQ-cage- to ladder-structure (i.e. polymerization of the oligomeric precursor), together with a distinct decrease in intensity of the Si-H stretching vibration and the various bending vibrations below 950 cm⁻¹ wavenumber. Similar to previous reports^{2,3,21}, the degree of polymerization is assessed based on the normalized integrated Si-H stretching absorption, as shown in Figure 3(b). The residual Si-H absorption decreases to 72% for curing at 400 °C and to 0 % for curing at 700 °C, indicating a significantly increased thermal budget of the process with respect to curing in air ambient²¹ and the formation of virtually hydrogenation-free oxides for curing above 700 °C. Furthermore, hydroxylation, based on a broad absorption band between 3200 and 3660 cm⁻¹ wavenumber^{33,34}, is evident for films cured at 600-700 °C. As visualized in Figure 3(b), the film cured at 600 °C shows a significantly increased integrated area of the hydroxyl absorption feature with respect to the film cured at 700 °C, indicating an increased silanol content³⁵. The presence of hydroxyl in non-oxidatively cured HSQ-based films has been previously observed by other groups²⁰, who have hypothesized that the hydroxylation originates from rapid water uptake of the incompletely polymerized films after curing. In comparison to the thermal oxide, the film cured at 800 °C retained a vibrational feature at 878 cm⁻¹ wavenumber (circled feature in Figure 3), which has previously been assigned to the Si-H bending vibrations^{32,36} in a Si-rich oxide. Further, the feature indicates that, despite the complete loss of the Si-H stretching feature, even films cured at 800 °C contain a minor degree of hydrogenation and are, thus, incompletely transformed to SiO_x.

The film stoichiometry after the maximum expected conversion (800 °C) has been investigated by XPS and compared to the thermally grown oxide. The emissions were fit on a Shirley-type

background and routinely deconvoluted into the Si $2p_{1/2, 3/2}$ spin-orbit components (Figure 4) with a peak-to-peak offset of 0.63 eV. Surface charging was referenced to the adventitious C1s, C-C, peak at 284.8 eV. The thermally grown oxide is fit to a single set of partner lines with a Si $2p_{3/2}$ peak position of 103.3 eV, indicating the presence of stoichiometric SiO₂ (Figure 4 (a))^{37,38}. Similarly, the Si $2p_{3/2}$ peak position for the HSQ-based oxide (Figure 4(b)), indicates the presence of SiO₂; however, the peak shoulder on the low binding energy side of the dominating emission reveals a divergence from the thermal oxide. In analogy to previous investigations^{39,40}, the shoulder is interpreted as Si emission due to the formation of Si nano-domains in the film and fit to a set of partner lines with a Si $2p_{3/2}$ peak position of 99.5 eV⁴¹⁻⁴³. Apart from S⁴⁺ and Si⁰ - emissions, the deconvolution of the Si 2p emission reveals a further spin-orbit couple with a Si $2p_{3/2}$ peak position of 101.5 eV. In agreement with previous investigations^{42,44}, we correlate the 101.5 eV peak to Si²⁺, indicating the presence of Si-sub-oxides, such as SiO.

Film hydrophobicity. A plot of water contact angle vs. curing temperature is shown in Figure 5. Samples 400-500 show a decreasing water contact angle with increasing curing temperature, however, hydrophobic behavior (contact angle > 90 °). For sample 600, the average contact angle steeply decreases to 57 °, followed by a local minimum for sample for sample 700 (average 44.5 °). Further, an increase in the curing temperature leads to a recovery in average contact angle to 57 ° for sample 800. In agreement with earlier observations^{3,21}, the hydrophobicity of HSQ-based coatings primarily depends on the competition between water repellency from non-polar Si-H bonds and water attraction from polar silanol. While samples 400 and 500 appear hydrophobic due to their high Si-H ratios, the samples cured at higher temperatures retain less hydrophobic character, due to their high degree of Si-H dissociation in combination with the formation of

silanol. Hereby, the local minimum in contact angle of sample 700 likely arises from hydrophilicity due to the presence of polar silanol under absence of retained Si-H.

Mechanical properties. The mechanical properties, i.e. the film hardness and the elastic modulus, have been determined on films deposited on Si wafer by depth-sensing nanoindentation. Representative load vs. displacement curves for all curing conditions and a fused silica reference slide are shown in Figure 6(a). Clearly, all curves show hysteretic behavior without sudden compliance changes and non-linear unloading, indicating the typical elastic/plastic behavior expected for amorphous SiO_2 ²⁶. In agreement with the spectroscopic analysis, increasing the curing temperature increases the SiO_2 -like character of the films; however, the curve-shape does not fully converge towards the shape determined for the thermally grown oxide. The load vs. displacement curves shown in Figure 6(a) were analyzed with the routine outlined by Oliver et al.²⁶, requiring the assumption of a Poisson's ratio for the calculation of the indentation modulus. Liou et al.¹⁹ assumed a Poisson's ratio of 0.33 for HSQ-based films irrespective of the degree of polymerization, which conflicts with the observation that high temperature-cured HSQ-based films behave strongly SiO_2 -like (the Poisson's ratio of amorphous silica is 0.17^{26,45}). Consequently, we propose that the Poisson's ratio assumed by Liou et al.¹⁹ is an overestimate for the SiO_x -like films investigated in this study and we suggest, in analogy to the value determined by other groups for generic SOG films^{45,46}, a Poisson's ratio of 0.25 for further analysis.

The indentation moduli for the investigated films are, together with the indentation hardness, plotted in Figure 6(b). Both, the indentation modulus and the indentation hardness obtained for the fused silica slide are within the previously reported range for SiO_2 ^{23,24,26,47}, validating the accuracy of the applied method. Further, in agreement with previous results¹⁹, both the

indentation modulus and hardness increase with curing temperature. However, the quantification conflicts with the data presented by Liou et al.¹⁹ and we report significantly more compliant and softer properties for the films cured at high temperature. The observed deviation may originate from differences in curing conditions and applied indentation loads or, since the group used a simplified model for the indenter-area function, differences in analysis procedure.

Overall, the distinctly more compliant behavior together with the decreased indentation hardness of the film cured at 800 °C with respect to the fused silica reference indicates, in agreement with the spectroscopic analysis, weaker polymerization or incomplete densification²⁴, even at the highest investigated curing temperature.

Electrochemical barrier properties. The coating barrier properties were evaluated by EIS and a representative EIS Bode plots for determined on sample 400, 600, 800 and an uncoated reference is shown in Figure 7. Samples 500 and 700 showed equivalent results and were excluded from the plot. In accordance with previous investigations^{1,21}, the experimental data of the coated samples were fit as a porous coating with the electrical equivalent circuit $R_s-(Q_{coat}(R_p-(Q_{dl}(R_{ct}-W))))$ and the reference with a Randles equivalent circuit⁴⁸. The results of the equivalent circuit fit are indicated by the solid lines in Figure 7. Further, the standard deviated average fitting results (based on five measurements) are plotted vs. the curing temperature in Figure 8. As visible from Figure 8(a), the charge transfer resistance stays constant over curing temperature within the given certainty limit. Similarly, the average pore resistance stays constant, with exception of sample 700, where the pore resistance is decreased with respect to the other curing temperatures. In analogy to our previous investigation²¹, the coating capacitance increases with curing temperature (Figure 8(b)), which is presumably due to an increase in coating density^{3,49,50}, hydroxylation³ and water uptake⁵¹⁻⁵³. The double layer capacitance (Figure 8(c)) remains, with

exception of sample 700, constant throughout the curing temperature range, indicating good and virtually constant substrate coverage, while the strayed value obtained for sample 700 is in agreement with the decreased pore resistance. Considering both the coating density and hydrophobicity as governing factors for the barrier efficiency, the strayed value may originate from an unfavorable combination of hydrophilic behavior (Figure 5) together with incomplete polymerization.

Overall, the resistive coating behavior appears increased with respect to the previously reported air-cured films²¹ (with exception of sample 700). This increase in coating performance may originate from an increased hydrophobicity for the temperature regime from 400-600 °C and an increased coating density at high curing temperatures. Since the data allow a clear distinction between coating and charge transfer resistance, the coating acts as an imperfect barrier and clearly possesses defects which allow electrolyte transfer to the substrate. Thus, the coating quality clearly deviates from e.g. CVD based SiO_x coatings on mirror polished substrates, which have previously shown perfect barrier performance with a single capacitive plateau over the entire frequency domain⁷. The nature of the given defects cannot be determined solely based on EIS analysis, however, the significant experimental error observed from Figure 8 indicates that the coating defects are unevenly spread over the surface, i.e. originate from inhomogeneous coating imperfections such as cracks, pinholes or delamination.

Passivity breakdown. It was shown by EIS that the coated substrates have access to the electrolyte. Hence, an electrochemical response of the substrate at externally imposed polarization is expected and the coated substrates were, together with an uncoated reference substrate, investigated by anodic CP. As reference, a representative polarization curve of an uncoated substrate is indicated in all potential vs. current diagrams in Figure 9. Similar to our

previous investigation, the reference material shows a clear hysteresis loop with a distinct breakdown and re-passivation at the corrosion potential together with current transients from metastable pit formation⁵⁴ below the breakdown potential (Figure 9(a-c)). The reference measurements showed excellent repeatability with an average breakdown potential of 529 mV vs. Ag-AgCl at a standard deviation of 24 mV (at a population of six measurements). Generally, the coated samples show a significant decrease in corrosion potential. In analogy to a previous study⁷, we suggest that the decrease in corrosion potential originates from a locally changed electrolyte composition in microscopic coating defects; however, due to the significant changes in both passive layer composition and morphology⁵⁵, we cannot exclude that the potential shift originates from an alteration of the electrochemical characteristics of the substrate. In contrast to the uncoated reference, the coated samples show a significant spread in breakdown potential. Representative CP plots of samples 400, 600 and 800 are shown in Figure 9(a-c). Since samples 500 and 700 showed qualitatively similar behavior, representative curves for these samples are omitted from the plots.

In agreement with other groups^{7,56-58}, the application of the coating reduces the passive current density, indicating a reduction of the exposed substrate surface. Analysis of sample 400 (Figure 9(a)) shows a general increase in breakdown potential with respect to the reference together with depression of metastable pitting during the positive sweep, indicating excellent barrier efficiency of the coated system. Similarly, an increase in breakdown potential is observed for sample 600, as shown by curve A in Figure 9(b). The increase in breakdown potential is inconsistent and, as shown by curve B, the surface treatment may decrease the breakdown potential and initiate pronounced current transients below the breakdown potential. A further increase in curing temperature, as in the case of sample 800 (Figure 9(c)), yields similar behavior, i.e. a possible

anodic shift in breakdown potential (curve A), together with a possible cathodic shift in breakdown potential (curve B). The increased performance obtained over the entire curing temperature range demonstrates that well-functioning coatings may efficiently suppress the initiation of pitting corrosion. Similar observations have been previously reported for a variety of silica coatings on stainless steels^{7,9,12}, together with the herein observed fluctuations in breakdown potential⁷. The fluctuations were previously presumed to be due to a large disparity of the dielectric coating rigidity, which may induce local coating breakdown at varying potentials. However, negative-shifts in breakdown potential or pronounced current transients on the forward sweep were not reported⁷. Hence, the herein observed deterioration in passive properties cannot be explained solely by the previously outlaid dielectric film breakdown theory⁷. Other authors⁵⁹ reported substrate sensitization due to carbide precipitation as failure mechanism of sol-gel coated stainless steels after high temperature sintering. The effect can, however, be neglected due to the low carbon content of the herein used substrates (Table 1), which is expected to prevent carbide sensitization within the applied temperature range and the short applied curing times⁶⁰. Consequently, we suggest, in analogy to the breakdown theory previously outlaid for air-cured HSQ-based coatings²¹, that the coating may act as micro-crevice or stable pit cover at microscopic coating defects.

To conclude on the nature of the preliminary breakdown and potential coating defects, sample 600 has been investigated by spot testing in 3.5 wt.% NaCl aqueous solution with addition of $K_3Fe(CN)_6$. The sample shows a clear response to the indicator solution after 5 min of immersion in form of irregularly distributed precipitation of blue pigment (Figure 10(a)), indicating the local release of Fe^{2+} through the coating due to the initiation of localized corrosion. The localized pigmentation was analyzed by ion beam cross-sectioning (Figure 10(b)). Although not shown

here, the analysis was repeated on several spots and the following observations were found to be reproducible. Void formation between the coating and the substrate in interrelation with coating delamination is visible in the immediate vicinity of the pigment, supporting the hypothesis of micro-crevice corrosion at microscopic coating defects. Further, the defect is observed directly at a grain boundary, i.e. at a particularly large coating cross-section induced by substrate roughness. The exact origin for the coating delamination was not investigated in this study; however, we suggest that the observed coating failure roots from inappropriate pretreatment, leading to residual surface contamination in narrow surface voids, mismatch in thermal expansion coefficient between the resinous HSQ and the substrate, or stress due to volumetric shrinkage of the coating.

Based on the observation of pronounced metastable pitting during anodic polarization and the localized release of Fe^{2+} at microscopic coating delamination, we propose the failure mechanism schematically illustrated in Figure 11: The coating delaminates at a substrate defect such as a grain boundary valley. The so created micro-crevice fills up with electrolyte through a coating defect such as a micro-fissure or general coating porosity and is subsequently acidified in analogy to conventional crevice corrosion theory (i)⁶¹. As the occluded anodic site evolves in size, the coating may rupture, leading to dissolution of the aggressive crevice electrolyte and, consequently, re-passivation (ii). Alternatively, the coating is sustained during the growth of the anodic site, yielding a large subsurface pit, which may eventually grow to a sufficient size to sustain stable growth after rupture of the covering coating (iii).

Overall, the results emphasize the importance of the substrate finish and pretreatment on the performance of (sub-) micron barrier coatings, showing that e.g. excessive substrate roughness may lead to preliminary coating failure. Further, the results indicate that HSQ-based coatings

pose a viable solution to increase the corrosion performance of stainless steels in the absence of coating defects. Since the defects were associated with the substrate roughness, we propose that the preliminary failure may be eliminated by the use of a higher-grade substrate finish, yielding more reliable coating systems.

Chemical coating stability. In our previous study²¹ it was suggested that HSQ-based coatings are, dependent on the degree of polymerization, chemically unstable during ageing under salt spray testing conditions. To analyze the coating dissolution rate, a thermal oxide and HSQ-based films cured between 400 and 800 °C were aged by neutral salt spray testing and periodically analyzed by (FIB-)SEM. The ion beam milled cross sections of the oxides at the initial state (reference) and terminal state (full dissolution or end of the experiment) are shown in Figure 12. The respective reduction in film thickness vs. ageing time is plotted in Figure 13(a). All HSQ-based films show a significant decrease in thickness, leading to full dissolution of the films cured at 400 °C (after 2 weeks of ageing) and 500 °C (after 4 weeks of ageing) together with a partial dissolution of the films cured above 500 °C. Moreover, the remaining films show a homogeneous coverage, indicating that the material dissolution occurs from the film surface, leading to successive material removal and thinning on the films. In agreement with our previous observations²¹, the dissolution rate (indicated in Figure 13(b)) correlates with the curing temperatures, whereby higher curing temperatures yield higher coating stabilities. The dissolution of the thermal oxide is insignificant.

Amorphous SiO₂ is thermodynamically unstable in aqueous solution at 35 °C and may dissolve into silicic acid under the given test conditions (Figure 14). This is in agreement with results from Deltomee et al.⁶², who stated that silica dissolves into various forms of silicic acid in neutral aqueous solution, whereby the solubility is significantly increased for the amorphous

silica polymorphs with respect to the crystalline ones. Moreover, previous groups^{63,64} have shown that the dissolution kinetics of SiO₂ films in near neutral solution may be significantly increased for SiO_x films of poor quality. As revealed by IR-spectroscopy, film curing up to 700 °C leads to films defects, such as significant hydrogenation or film hydroxylation. Even for the films cured at 800 °C, the spectroscopy analysis indicated a minor degree of hydrogenation together with the presence of Si-sub-oxides while the nanoindentation analysis revealed inferior mechanical properties with respect to fused silica and, thus, indicated weaker cross linking or a decreased film density²⁴. Overall, the coating analysis indicated an imperfect transformation of the resin to SiO₂ or an incomplete densification for HSQ-based films for curing temperatures ≤ 800 °C, which may greatly account for the advanced dissolution speed of the HSQ-based films with respect to the thermally grown oxide.

In analogy to our previous work²¹, the coated stainless steel substrates have been subjected to 1000 h of salt spray testing and investigated by FIB-SEM to conclude about the film chemistry in the application. Cross-sectional micrographs of sample 400, 600 and 800 after salt spray testing, together with a cross section of sample 600 before salt spray testing, are shown in Figure 15. In agreement with the dissolution rates described in Figure 13(b), difference in residual coating thickness and coverage is evident for the coatings cured at different temperatures. While the reference exhibited a thickness of ~ 0.17-1.27 μm (indicated in Figure 15(a)), the coating of sample 400 is fully removed (Figure 15(b)) and only coating remnants remain at the previously large coating cross-sections of sample 600 (Figure 15(c)). Analysis of sample 800 (Figure 15(d)) shows that the coating thickness is significantly reduced; however, a thin coating film with high coverage remains on the surface. These results indicate that further work on the optimum curing parameters is necessary to enable long-term performance of the coatings in applications such as

heat exchanges. Results from Liou et al.¹⁹ indicated that SOG films may be fully transformed to SiO₂ by highly oxidative curing, which is, however, not feasible on stainless steel substrates due to the previously described deterioration of substrate properties^{21,22}. As shown by Bremmer et al.³, SOG films are susceptible to very low concentrations of O₂ and we propose that e.g. a precise dosing of O₂ into an inert atmosphere may increase the curing performance without deterioration of the substrate properties, and thus increase the SiO₂-like character of the material significantly.

4 Conclusions

The deposition of thin films from HSQ precursor was demonstrated as a viable process to deposit (sub)-μm thick coatings on stainless steel substrates. The coating precursor could flow freely on the surface during deposition and the coating was capable of leveling the pickled surface of a no. 2B finished stainless steel substrate to a R_a roughness of 15 nm. The degree of film polymerization was dependent on the curing temperature, yielding virtually hydrogenation free oxides for curing above 700 °C. However, curing at 800 °C in Ar/H₂ atmosphere did not lead to complete transformation to SiO₂ and a significant amount of lower valent Si was detected in the films. Further, the elastic modulus and film hardness showed an increasing trend with increasing curing temperature, however, remained below the values observed for fused silica. The coating hydrophobicity correlated with the residual hydrogenation and hydroxylation, showing hydrophobic behavior for films cured below 600 °C and hydrophilic behavior for films cured above 500 °C. All films showed high barrier properties in NaCl electrolyte, however, generally acted as imperfect barrier coatings which allowed electrolyte to penetrate to the substrate. Polarization measurements indicated a potential increase in breakdown potential for coated films.

This increase was inconsistent due to the presence of inhomogeneously spread coating defects. Defects originating from substrate roughness were found to trigger microscopic coating delamination, which further triggers the initiation of micro-crevice corrosion between the coating and the substrate. All coatings cured with the herein applied curing conditions were unstable in aqueous environment and showed significant dissolution rates during neutral salt spray testing. Further, a trend between dissolution rate and degree of polymerization was evident, with increasing polymerization leading to higher coating stability.

Acknowledgements

We thank SiOx Aps, Esbjerg, DK, for the deposition of coatings and acknowledge the work done by all other project partners. Further, Innovation Fund Denmark is acknowledged for funding this work under grant number 50-2014-1.

References

1. Lampert, F., A.H. Jensen, R.U. Din, and P. Møller, *Surf. Coatings Technol.* 307 (2016): pp. 879–885.
2. Siew, Y.K., G. Sarkar, X. Hu, J. Hui, A. See, and C.T. Chua, *J. Electrochem. Soc.* 147 (2000): p. 335.
3. Bremmer, J.N., Y. Liu, K.G. Gruszynski, and F.C. Dall, *Mater. Res. Soc. Symp. Proc.* 476 (1997): pp. 37–44.
4. Mohaghegh, K., H.N. Hansen, H. Pranov, and G. Kofod, “A Study on the Surface Roughness of a Thin HSQ Coating on a Fine Milled Surface,” in 14th Euspen Int. Conf. -

- Dubrovink (2014).
5. Mohaghegh, K., H.N. Hansen, H. Pranov, and G. Kofod, “Verification of Thickness and Surface Roughness of a Thin Film Transparent Coating,” in Proc. 13th Euspen Int. Conf. (Berlin, 2013).
 6. Hobæk, T.C., M. Matschuk, J. Kafka, H.J. Pranov, and N.B. Larsen, *J. Micromechanics Microengineering* 25 (2015): p. 035018 (9pp).
 7. Pech, D., P. Steyer, and J.-P. Millet, *Corros. Sci.* 50 (2008): pp. 1492–1497.
 8. Meth, S., N. Savchenko, F.A. Viva, D. Starosvetsky, A. Groysman, and C.N. Sukenik, *J. Appl. Electrochem.* 41 (2011): pp. 885–890.
 9. Vasconcelos, D.C.L., J.A.N. Carvalho, M. Mantel, and W.L. Vasconcelos, *J. Non. Cryst. Solids* 273 (2000): pp. 135–139.
 10. Atik, M., P. de Lima Neto, L.A. Avaca, M.A. Aegerter, and J. Zarzycki, *J. Mater. Sci. Lett.* 13 (1994): pp. 1081–1085.
 11. Garzino-Demo, G.A., and F.L. Lama, *Surf. Coatings Technol.* 68/69 (1994): pp. 507–511.
 12. Gallardo, J., A. Duran, I. Garcia, J.P. Celis, M.A. Arenas, and A. Conde, *J. Sol-Gel Sci. Technol.* 27 (2003): pp. 175–183.
 13. Santos, O., T. Nylander, R. Rosmaninho, G. Rizzo, S. Yiantsios, N. Andritsos, A. Karabelas, H. Müller-Steinhagen, L. Melo, L. Boulangé-Petermann, C. Gabet, A. Braem, C. Trägårdh, and M. Paulsson, *J. Food Eng.* 64 (2004): pp. 63–79.
 14. Baba, K., R. Hatada, S. Nagata, H. Fujiyama, G.K. Wolf, and W. Einsinger, *Surf. Coatings Technol.* 75 (1995): pp. 292–296.

15. Rosmaninho, R., O. Santos, T. Nylander, M. Paulsson, M. Beuf, T. Benezech, S. Yiantsios, N. Andritsos, A. Karabelas, G. Rizzo, H. Müller-Steinhagen, and L.F. Melo, *J. Food Eng.* 80 (2007): pp. 1176–1187.
16. Walke, W., Z. Paszenda, T. Pustelny, Z. Opilski, S. Drewniak, M. Ko, and M. Basiaga, *Mater. Sci. Eng. C* 63 (2016): pp. 155–163.
17. Walke, W., Z. Paszenda, M. Basiaga, P. Karasinski, and M. Kaczmarek, “EIS Study of SiO₂ Oxide Film on 316L Stainless Steel for Cardiac Implants,” in *Inf. Technol. Biomed.* Vol 4., eds. E. Piętka, J. Kawa, and W. Wieclawek (Cham: Springer International Publishing, 2014), pp. 403–410.
18. Pranov, H., “Reactive Silicon Oxide Precursor Facilitated Anti-Corrosion Treatment, US 2014/0154441 A1” (USA, 2014).
19. Liou, H., and J. Pretzer, *Thin Solid Films* 335 (1998): pp. 186–191.
20. Többen, D., P. Weigand, M.J. Shapiro, and S.A. Cohen, *Mater. Res. Soc. Somposium Proc.* 443 (1997): pp. 195–200.
21. Lampert, F., A.B. Christiansen, R.U. Din, Y. Gonzalez-Garcia, and P. Møller, *Corros. Sci.* (In Press. August 24th 2017) (2017).
22. Lampert, F., S. Kadkhodazadeh, A.H. Jensen, R.U. Din, and P. Møller, *J. Electrochem. Soc.* 164 (2017): pp. C231–C239.
23. Li, H., and J.J. Vlassak, *J. Mater. Res.* 24 (2009): pp. 1114–1126.
24. Kallingal, C.G., M. Tomozawa, and S.P. Murarka, *J. Electrochem. Soc.* 145 (1998): pp. 1790–1794.

25. Standardization, E.C. for, “ISO 14577-1:2002 E Metallic Materials - Instrumented Indentation Test for Hardness and Materials Parameters - Part 1: Test Method” (2003).
26. Oliver, W.C., and G.M. Pharr, *J. Mater. Res.* 7 (1992): pp. 1564–1583.
27. Qvarfort, R., *Corros. Sci.* 28 (1988).
28. Hsu, C.H., and F. Mansfeld, *Corrosion* 57 (2001): pp. 747–748.
29. “EN ISO 9227:2012 Corrosion Tests in Artificial Atmospheres - Salt Spray Tests” (2012).
30. “Designation: A959-16 Standard Guide for Specifying Harmonized Standard Grade Compositions for Wrought Stainless Steels,” ASTM International (2016).
31. Wang, L., S. Yu, and J. Cho, *J. Am. Ceram. Soc.* 92 (2009): pp. 2388–2391.
32. Albrecht, M.G., and C. Blanchette, *J. Electrochem. Soc.* 145 (1998): pp. 4019–4025.
33. Brinker, C.J., and G.W. Scherer, “2.4.3. IR-Raman Investigations of Gel Dehydroxylation,” in *Sol Gel Sci. Phys. Chem. Sol-Gel Process.* (1990), pp. 582–588.
34. Innocenzi, P., *J. Non. Cryst. Solids* 316 (2003): pp. 309–319.
35. Pliskin, W.A., *J. Vac. Sci. Technol.* 14 (1977): p. 1064.
36. Lucovsky, G., J. Yang, S.S. Chao, J.E. Tyler, and W. Czubatyj, *Phys. Rev. B* 28 (1983): pp. 3225–3233.
37. Donley, M.S., D.R. Baer, and T.G. Stoebe, *Surf. Interface Anal.* 11 (1988): pp. 335–340.
38. Nefedov, V.I., Y. V. Salyn, G. Leonhardt, and R. Scheibe, *J. Electron Spectros. Relat. Phenomena* 10 (1977): pp. 121–124.
39. Hessel, C.M., E.J. Henderson, and J.G.C. Veinot, *Chem. Mater.* 18 (2006): pp. 6139–

- 6146.
40. Hessel, C.M., E.J. Henderson, and J.G.C. Veinot, *J. Phys. Chem. C* 111 (2007): pp. 6956–6961.
 41. Weijs, P.J.W., J.F. van Acker, J.C. Fuggle, P.A.M. van der Heide, H. Haak, and K. Horn, *Surf. Sci.* 260 (1992): pp. 102–112.
 42. Nguyen, T.P., and S. Lefrant, *J. Phys. Condens. Matter* 1 (1999): pp. 5197–5204.
 43. Wittmer, M., P. Oelhafen, and K.N. Tu, *Phys. Rev. B* 33 (1986): pp. 5391–5400.
 44. Alfonsetti, R., L. Lozzi, M. Passacantando, P. Picozzi, and S. Santucci, *Appl. Surf. Sci.* 70–71 (1993): pp. 222–225.
 45. Doucet, L., and G. Carlotti, *Mater. Res. Soc. Somposium Proc.* 356 (1994): pp. 215–220.
 46. Carlotti, G., G. Socino, and L. Doucet, *Appl. Phys. Lett.* 66 (1995): pp. 2682–2684.
 47. Cao, Z., and X. Zhang, *Scr. Mater.* 56 (2007): pp. 249–252.
 48. Mansfeld, F., H. Shih, H. Greene, and C.H. Tsai, “Analysis of EIS Data for Common Corrosion Processes,” in *Electrochem. Impedance Anal. Interpret.* (1993), pp. 37–53.
 49. Toivola, Y., J. Thurn, and R.F. Cook, *J. Electrochem. Soc.* 149 (2002): pp. F9–F17.
 50. Liu, W.-C., C.-C. Yang, W.-C. Chen, B.-T. Dai, and M.-S. Tsai, *J. Non. Cryst. Solids* 311 (2002): pp. 233–240.
 51. Brasher, D.M., and A.H. Kingsbury, *J. Appl. Chem.* 4 (1954): pp. 62–72.
 52. Castela, A.S., and A.M. Simões, *Corros. Sci.* 45 (2003): pp. 1631–1646.
 53. Lindqvist S.A., *Corros. - NACE* 41 (1985): pp. 69–75.

54. Pistorius, P.C., and G.T. Burstein, *Philos. Trans. R. Soc. Ser. A* 341 (1992): pp. 531–559.
55. Lampert, F., S. Kadkhodazadeh, T. Kasama, K.V. Dahl, A.B. Christiansen, and P. Møller, *To Be Submitt. 2017* (2017).
56. Hwang, T., H. Lee, H. Kim, and G. Kim, *J. Sol-Gel Sci. Technol.* 55 (2010): pp. 207–212.
57. Pech, D., P. Steyer, A.-S. Loir, J.C. Sánchez-López, and J.-P. Millet, *Surf. Coatings Technol.* 201 (2006): pp. 347–352.
58. Nikrooz, B., M. Zandrahimi, and H. Ebrahimifar, *J. Sol-Gel Sci. Technol.* 63 (2012): pp. 286–293.
59. Trazaskoma-Paulette, P.P., and A. Nazeri, *J. Electrochem. Soc.* 144 (1997): pp. 1307–1310.
60. Kriaa, A., N. Hamdi, and H. Sidhom, *Prot. Met.* 44 (2008): pp. 506–513.
61. Laycock, N.J., J. Stewart, and R.C. Newman, *Corros. Sci.* 39 (1997): pp. 1791–1809.
62. Deltomee, E., N. de Zoubov, and M. Pourbaix, “Silicon,” in *Atlas Electrochem. Equilibria Aqueous Solut.* (Houston, 1996), pp. 458–463.
63. Klause, M., U. Rothhaar, M. Bicker, and W. Ohling, *J. Non. Cryst. Solids* 356 (2010): pp. 141–146.
64. Kang, S.-K., S.-W. Hwang, H. Cheng, S. Yu, B.H. Kim, J.-H. Kim, Y. Huang, and J.A. Rogers, *Adv. Funct. Mater.* 24 (2014): pp. 4427–4434.

Tables

Table 1: Chemical composition of the substrates (by Optical Emission Spectroscopy). In addition, traces (< 0.1 wt.%; > 0.01 wt.%) of P, Nb, V, W were detected.

Element	Cr	Ni	Mo	Mn	Si	Cu	Co	N	C	Fe
Composition (wt.%)	16.8	10.4	2.07	0.92	0.47	0.41	0.21	0.048	0.019	bal.

Table 2: Dip coating withdrawal speed and final film thickness (determined from cross-sectional imaging on fractured wafers) of films used for nanoindentation

Curing temp. (°C)	400	500	600	700	800
Thickness (μm)	1.41	1.16	0.89	0.89	0.82

Figure captions

Figure 1: AFM plots of (a) uncoated reference coupon, map size $20 \times 20 \mu\text{m}^2$; (b) SOG coated substrate, map size $20 \times 20 \mu\text{m}^2$; (c) SOG coated substrate (high magnification), map size $0.5 \times 0.5 \mu\text{m}^2$.

Figure 2: Bright-field TEM image of the coating (cured at 600°C) on AISI 316L substrate in cross-sectional geometry.

Figure 3: (a) FT-IR absorption spectra of HSQ films deposited on Si wafer after curing at various temperatures. The identification of the spectral features was carried out according to the data reviewed by Lampert et al.²¹; (b) Remaining percentage of Si-H based on the Si-H stretching absorption edges at $2260\text{--}2285 \text{ cm}^{-1}$ observed in FT-IR.

Figure 4: Deconvolution of Si 2p emissions: (a) Thermal oxide; (b) HSQ-resin after curing at 800°C .

Figure 5: Water contact angle vs. curing temperature on coated AISI 316L substrates.

Figure 6: (a) Indentation load vs. displacement curves determined on HSQ-based films and fused silica as reference. (b) Indentation modulus for different curing treatments. The error bars indicate the standard deviation over 5 individual measurements.

Figure 7: EIS Bode plots of test coupons in 3.5 wt.% NaCl aqueous solution. The solid lines are on the basis of the fitted model.

Figure 8: Results of EIS fits vs. curing temperature: (a) Normalized pore/charge transfer layer resistance (R_p/R_{ct}); (b) Normalized coating capacitance, C_{coat} ; (c) Normalized double layer

capacitance, C_{dl} . The values represent average values of 5 measurements with the indicated standard deviation.

Figure 9: Anodic CP curves in neutral 3.5 wt.% NaCl aqueous solution: (a) sample 400; (b) sample 600; (c) sample 800. The reference is indicated in all figures.

Figure 10: Spot test on sample 600: (a) Top view optical micrograph of a pigment precipitated within the spot test on sample 600; (b) SEM image of ion beam milled cross section along pigment precipitation. Microscope settings: TLD, beam current 43 pA

Figure 11: Schematic illustration of micro-crevice corrosion at delaminated coating cross-sections.

Figure 12: SEM analysis on ion beam cross sections of HSQ-based films on Si-wafer substrate before (reference) and after ageing by neutral salt spray testing. “ox.” indicates the film layer. All films were protected by a double layered Pt. deposition (“Pt”) during analysis. SEM settings: TLD; beam current 26 pA.

Figure 13: (a) Thickness reduction vs. ageing time based on SEM analysis; (b) Dissolution rate vs. curing temperature. The rates for curing from 400-500 °C were calculated based on 2 weeks of ageing and the rates for curing from 600-800 °C and the thermal oxide were calculated based on 6 weeks of ageing.

Figure 14: Free energy vs. temperature for the dissolution of amorphous silica to silicic acid. Calculated with HSC Chemistry 5.11.

Figure 15: SEM micrographs of ion beam milled cross sections of: (a) sample 600 before salt spray testing (reference); (b) sample 400 after salt spray testing; (b) sample 600 after salt spray testing; (c) sample 800 after salt spray testing.

Figures

Figure 1

1

2 Figure 2

1

2 Figure 3

1

2

3 Figure 4

1

2 Figure 5

1

2

3 Figure 6

1

2 Figure 7

1

2 Figure 8

1

2 Figure 9

1

2 Figure 10

1

2 Figure 11

1

2 Figure 12

1

2 Figure 13

1

2 Figure 14

1

2 Figure 15