

THE EFFECT OF A Cr-FREE FINGERPRINT-RESISTANT PASSIVATION FILM ON THE PERFORMANCE OF HOT-DIP 55 % Al-Zn COATED STEEL

VPLIV PROTI PRSTNIM ODTISOM ODPORNEGA PASIVACIJSKEGA FILMA BREZ Cr NA LASTNOSTI OPLAŠČENEGA JEKLA PREVLEČENEGA S PREVLEKO IZ 55 % Al-Zn IZDELANO S POSTOPKOM VROČEGA POTAPLJANJA

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Cr-free fingerprint-resistant hot-dip 55 w/% Al-Zn coated steel (CFAZCS) is a upmarket steel plate product that is widely used in consumer goods with high added value, such as LCD back panels for monitors, as well as various electrical and electronic products. Passivation is a crucial process in the production of CFAZCS, greatly affecting the overall performance of the CFAZCS product. A comprehensive evaluation of passivation films from different manufacturers on the performance of CFAZCS can assist production enterprises in optimizing and controlling the product quality according to the requirements of target customers. This article comprehensively tests and evaluates the performance of corrosion resistance, acid/alkali resistance, anti-yellowing/blackening, paint adhesion, abrasion resistance, fingerprint resistance, and the conductivity of mainstream, commercially available, Cr-free, fingerprint-resistant, passivation solutions, providing guidance for the selection of passivation solutions in production processes.

Keywords: Cr-free fingerprint-resistant passivation film, hot dip 55 w/% Al-Zn coated steel, performance evaluation

Avtorji v članku opisujejo potapljanje jeklene plošče v talini s 55 w/% Al in 45 w/% Zn za njeno zaščito proti prstnim odtisom (CFAZCS; angl.: Cr-free fingerprint-resistant hot-dip Al-Zn coated steel). Izbrano jeklo z visoko dodano vrednostjo se na trgu zelo uporablja za hrbitišča LCD panelov za monitorje, kakor tudi za različne druge električne in elektronske proizvode. Pasivacija je najbolj pomemben postopek pri proizvodnji CFAZCS, ki močno vpliva na lastnosti panelov in seveda posledično na njihovo končno vrednost oz. ceno. Avtorji so izvedli obsežno ovrednotenje pasivacijskih filmov na CFAZCS izdelkih različnih proizvajalcev, ki je pomagala pri optimizaciji in kontroli kakovosti te vrste izdelkov v skladu z zahtevami ciljanega kupca. V tem članku avtorji opisujejo obsežno testiranje in ovrednotenje proti-korozijskih lastnosti, odpornost proti kislinam in lugom, odpornost proti porumenitvi in črnenju, adhezijo barve (odpornost proti luščenju), odpornost proti prstnim odtisom in prevodnost vseh glavnih proizvajalcev ustreznih in komercialno dosegljivih jeklenih izdelkov oplaščenih s tanko plastjo (filmom) brez kroma in odporno proti prstnim odtisom. Rezultati analiz in ovrednotenje le-teh so služili avtorjem tega članka kot vodilo za izbiro optimalnih rešitev postopka pasivacije in tudi celotnega proizvodnega procesa.

Ključne besede: proti prstnim odtisom odporen pasivacijski film brez kroma, vroče potapljanje oziroma oplaščenje jeklene plošče v talini s 55 w/% Al in 45 w/% Zn, ovrednotenje lastnosti

1 INTRODUCTION

Hot-dip 55 w/% Al-Zn coated steel (HDAZCS) is widely used in industries such as household appliances, the auto industry, power-transmission equipment, and the construction industry due to its excellent corrosion resistance and weather resistance. According to a study by Global Info Research, the global market size of HDAZCS was valued at \$620 billion in 2023 and it is projected to reach around \$746 billion by 2030 with a compound annual growth of 2.7 %. The coating layer of HDAZCS consists of 55 % Al, 43.4 % Zn, and 1.6 % Si,

which is known for its corrosion resistance under high temperature, smooth surface, and excellent appearance.^{1,2} However, the chemical properties of metallic zinc are active. If the hot-dipped coating layer does not undergo a passivation treatment, it will quickly darken while generating white corrosion products, such as $(\text{Zn}(\text{OH})_2)_3 \cdot \text{ZnSO}_4 \cdot n\text{H}_2\text{O}$, $\text{NaZn}_4(\text{SO}_4)(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$, and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.^{3,4} The passivation process is a critical step in the production of HDAZCS, affecting the overall performance of the HDAZCS product.⁵ There are primarily two types of passivation processes for the surface of HDAZCS: Cr-containing and Cr-free passivation processes. Due to the environmental toxicity associated with Cr, the Cr-containing passivation process has gradually been phased out, and currently, most manufacturing

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enterprises primarily employ Cr-free passivation processes.^{6,7} With the intensification of competition, downstream manufacturing enterprises increasingly require a Cr-free passive film with superior performance. In addition to excellent corrosion resistance, HDAZCS with a Cr-free passive film are also required to have good performance in anti-yellowing/blackening, acid/base resistance, paint adhesion, abrasion resistance, fingerprint resistance, and conductivity.

Cr-free fingerprint-resistant hot-dip 55 w/% aluminum-zinc steels (CFAZCS) are generally used in industries such as LCD back panels for monitors, as well as various electrical and electronic products, etc., and are classified as upmarket hot-dip aluminum-zinc steel products.⁸ Currently, the core producers of CFAZCS in the world include ArcelorMittal, Shougang, Nippon Steel, POSCO, Baosteel, Pangang Group, JISCO, FE Steel, BlueScope, Doowo Steel, et al. As a core material for the production of CFAZCS, the Cr-free fingerprint-resistant passivation solution is currently dominated by Henkel. In order to break the single source of Cr-free fingerprint-resistant passivation solution, some enterprises including Desytek and Xinyu-Ecosil have actively developed Cr-free fingerprint-resistant passivation solutions to provide alternatives for CFAZCS production enterprises. However, due to the lack of actual usage data and comprehensive performance evaluations, these substitutes for the Cr-free, fingerprint-resistant, passivation solution produced by Henkel have not yet been widely applied to CFAZCS products in mainstream steel enterprises. Therefore, it is particularly important to comprehen-

sively evaluate and compare the performance of the chromium-free fingerprint-resistant passivation solutions produced by different manufacturers. This will provide guidance for CFAZCS producers to select Cr-free, fingerprint-resistant, passivation solutions based on customer demands.

In this paper, the performance of Cr-free, fingerprint-resistant, passivation solutions produced by Henkel, Desytek and Xinyu-Ecosil was investigated comprehensively. The performance of corrosion resistance, acid/alkali resistance, anti-yellowing/blackening, paint adhesion, abrasion resistance, fingerprint resistance, and conductivity of the passivation films was evaluated and compared based on the relevant China National Standard (GB). This work will provide guidance for relevant manufacturing enterprises in the selection of passivation solutions and the adjustment of product performance, helping them to improve product quality while reducing production costs, thereby gaining a greater advantage in an intense market competition.

2 EXPERIMENTAL PART

2.1 Materials

The DC53D+AZ-type, hot-dip, aluminum-zinc-coated carbon steel produced by JISCO was used as the experimental substrate (thickness 1.0 mm, with Al and Zn content in the surface coating at 55 % and 43.6 % respectively). As required, the substrate metal was laser-cut into specimens with a size of (150 × 100 × 1) mm

Table 1: Composition and content of elements in passivation films

Elements (mol %)	Fe	C	O	N	Si	P	S	Al	Zn	Na
HG	0.749	46.901	16.869	29.398	0.656	0.222	0.458	0.294	4.36	0.094
DS	1.462	44.801	22.716	6.531	21.822	1.584	0.181	0.254	0.774	0.038
XSR	0.909	46.786	17.895	28.107	0.741	0.317	0.382	0.337	4.447	0.098

Table 2: Methods for performance testing and evaluation standards

Performance	Testing method	Evaluation methodology	Criterion of acceptability
Corrosion resistance	Neutral Salt Spray Test, referring to GB/T 10125-2012, using salt spray chamber model LYW-015	Corrosion Area/Rating	Corrosion area less than 5 % after 72 h (GB/T 6461-2002)
Acid resistance	Referring to GB/T 13448-2006, immersion in HCl solution with pH=4 at room temperature for 2 minutes	ΔE^* measurement	$\Delta E^* \leq 3$
Alkali resistance	Referring to GB/T 13448-2006, immersion in NaOH solution with pH=12 at room temperature for 2 minutes	ΔE^* measurement	$\Delta E^* \leq 3$
Anti- yellowing	Referring to GB/T 1740-2007, constant temperature and humidity test chamber model HW-50L	ΔE^* measurement	$\Delta E^* \leq 3$
Anti-blackening	Referring to GB/T 1740-2007, constant temperature and humidity test chamber model HW-50L	ΔE^* measurement	$\Delta E^* \leq 3$
Paint adhesion	Scratch method, referring to GB/T 13448-2006 and GB/T 9286-1998	Visual observation	No peeling
Fingerprint resistance	Coating with Vaseline at room temperature for 30 minutes	ΔE^* measurement	$\Delta E^* \leq 3$
Abrasion resistance	Referring to GB/T 1768-2006, 500 cycles of friction	Abrasion marks observation	—
Conductivity	—	Surface resistivity	$\leq 0.8 \text{ m}\Omega$

or (100 × 70 × 1) mm. The specimens were then deburred using a trimming machine to remove edge burrs, activated by soaking in acetone, rinsed thoroughly with distilled water, and wipe dried with lint-free cotton for subsequent use. The Cr-free fingerprint-resistant passivation solutions were provided by Henkel (Granocoat 621, HG), Desytek (DS981LX, DS), and Xinyu-Ecosil (X220, XSR). The element composition and contents in the passivation solution are listed in **Table 1**. All other reagents used in the tests were of analytical grade.

2.2 Experimental Methods

The passivation solutions were uniformly coated to the substrate surface using a coating bar (OSP-04, Japan), with the coating thickness (dry film) controlled at 0.8–1.2 g/m², resulting in a physical film thickness of approximately 1.0 μm. The drying temperature was set at 130 °C, and the drying time was 10 minutes. Performance testing and evaluation methods were described in **Table 2**. The color difference (ΔE^*) was calculated using the formula $\Delta E^* = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$, where L , a , and b are the tristimulus color coordinates.

2.3 Characterization Methods

The surface morphology and 3D profile of the specimens after the performance testing were observed using

a metallographic microscope (Leica DM2700 M), scanning electron microscope (SEM, Hitachi SU8600), and white-light interferometer (WLI, Mahr MarSurf WM 1003D). The thickness of the passivation film were analyzed using a glow-discharge optical emission spectrometer (GD-OES, HORIBA GD-Profilr2). The elements C, O, and N were determined using an Organic Element Analyzer (OEA, EA1112, Thermo FlashSmart, America), while other elements were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, ELEMENT2, Thermo Scientific, America). The ΔE^* was measured using a colorimeter (KONICA CR-10 Plus).

3 RESULTS AND DISCUSSION

3.1 Morphological characterization of the passivation film

Figures 1a to 1h show the metallographic images of the surfaces of HDAZCS with and without the Cr-free, fingerprint-resistant passivation film (CrFPF) coating. The surface of the HDAZCS without passivation-film coating exhibits obvious zinc-flower structures with dendritic stripes. The zinc flowers are formed by the natural solidification process of the zinc layer during the pulling-out process of the hot-dip, aluminum-zinc coating in the zinc pot (**Figures 1a** and **1b**).⁹ After coating with CrFPF, the zinc-flower structures on the surface of

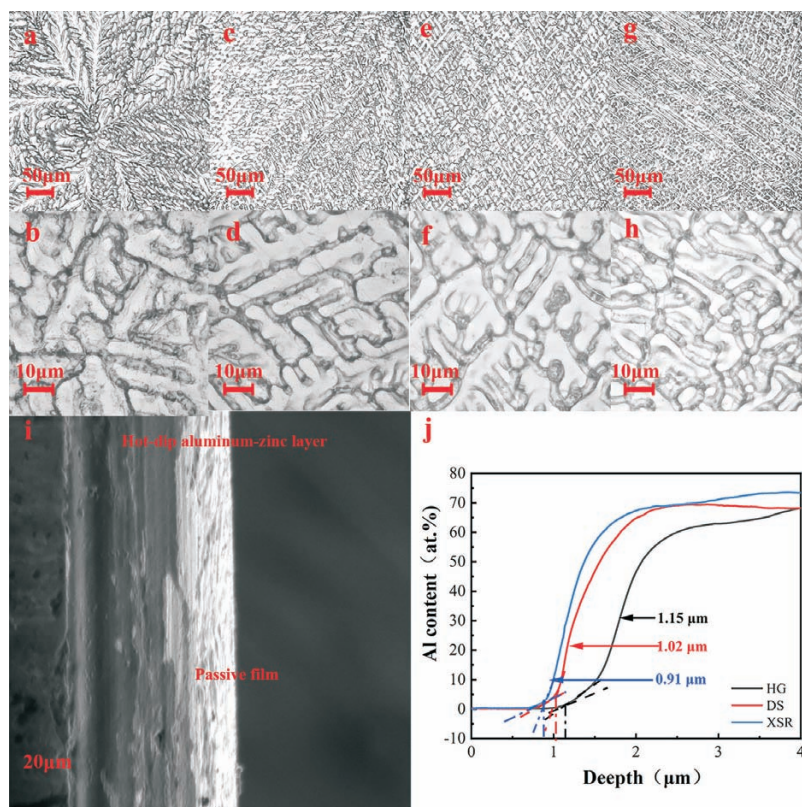


Figure 1: Metallographic images of the surface of HDAZCS without passivation film coating (a, b) and with CrFPF coating (HG: c, d; DS: e, f; XSR: g, h); SEM image of a typical DS passivation film (i); Depth distribution curve of Al element content (j)

HDAZCS become less prominent, and the dendritic stripes widen and form a 3D interconnected network structure. The stripes of the HG and DS passivation films exhibit rectangular microstructures that are interconnected. The rectangular microstructure formed by the HG passivation film is more regular than that formed by the DS passivation film, but the spacing between the stripes is larger in the HG passivation film than in the DS passivation film (**Figures 1c–1f**). The stripes of the XSR passivation film exhibit an irregular network structure, with a higher density compared to the HG and DS passivation films (**Figures 1g and 1h**). **Figure 1i** shows an SEM image of the DS passivation film. It can be observed that the thickness of the hot-dip aluminum-zinc coating is approximately 20–40 μm , with the passivation film covering its surface being around 1.0 μm thick. Analysis of the longitudinal distribution of the Al content along the specimen surface was performed using GD-OES. Since all three passivation solutions do not contain Al elements, a sharp increase in the Al element content indicates that the argon-ion beam has penetrated the passivation film and reached the surface of the hot-dip, aluminum-zinc coating. Therefore, the depth corresponding to the initial sharp increase in Al element content corresponds to the thickness of the respective passivation film.¹⁰ As shown in **Figure 1j**, when the loading mass is 1.2 g/m², the thickness of the HG, DS, and XSR passivation films is 1.15 μm , 1.02 μm , and 0.91 μm , respectively.

3.2 Evaluation of corrosion resistance of passivation films

Referring to the GB/T 10125-2012 (Artificial atmosphere corrosion test – Salt spray test), specimens with and without a passivation film coating were subjected to a 72-h neutral salt-spray test. Simultaneously, the performance of the specimens was evaluated using the method specified in GB/T 6461-2002 (Rating of the specimens and specimens corroded on metal substrates and metal and other inorganic coatings). Based on the corrosion area and appearance of the specimens after the test, the protection rating (R_p) and appearance rating (RA) were determined. After the 72-h neutral salt-spray test, the surface of the specimens coated with the HG passivation film exhibited a moderate color change due to the corrosion of the aluminum-zinc layer.¹¹ More than 1.6 % of the total surface area of the specimen suffered from corrosion due to the breakage of the passivation films, while over 37 % of the total surface area exhibited a severe color change due to the damage of the passivation films.¹² The corresponding corrosion resistance rating of the HG passivation film was 6/1 m A. The corrosion area was less than 5 % after a 72-h test, indicating acceptable corrosion-resistance performance for the HG passivation film (**Figure 2a**). The specimen coated with the DS passivation film showed only a small amount of pitting corrosion on the surface after the salt spray test, with the

corroded area of the base Al-Zn coating for only 0.03 % of the total area. There was no significant darkening area caused by extensive damage to the passivation film. The performance rating is 9/10 vs B, indicating good corrosion resistance (**Figure 2b**). The specimen coated with the XSR passivation film displayed more pronounced pitting corrosion and surface darkening compared to specimens coated with HG and DS passivation films. The corrosion area of the base Al-Zn coating exceeded 1.6 % of the total surface area, with the remaining surface showing a severe color change due to extensive damage to the passivation film, which covered over 25 % of the total area. The performance rating was 5/1 x A. Despite the corrosion area being less than 5 % after a 72-h test, the passivation film showed discoloration and a deeper color, indicating a less-than-ideal corrosion resistance performance. However, overall, the specimen still met the requirements for corrosion resistance (**Figure 2c**).

The corrosion morphology caused by the neutral salt-spray corrosion on the surface of passivation films can be observed through metallographic images. The diameters of the pitting corrosion pits on the surfaces of the specimens coated with HG, DS, and XSR passivation films were approximately 18–29 μm , 33 μm , and 15–23 μm , respectively. The specimen coated with the DS passivation film has the largest diameter of pitting corrosion, but the quantity was relatively small. On the other hand, the specimen coated with the DS passivation film exhibited the densest distribution of pitting corrosion, with individual pit diameters being the smallest (**Figures 2d–2f**). The blackened areas on the specimen surfaces were observed by SEM. It was evident that the passivation-film network on the surface of the specimen coated with HG passivation film remained relatively intact. However, it was noticeable that the underlying Al-Zn coating was visible beneath the passivation film, indicating that the neutral salt spray had caused thinning of the passivation film, resulting in partial loss of protection in some areas (**Figure 2g**). The passivation film network structure in the blackened areas of specimen coated with DS passivation film had undergone slight damage, but the protection remained intact (**Figure 2h**). Meanwhile, the passivation film in the blackened areas of the specimen coated with XSR passivation film still exhibited a network structure, but with reduced network density. In some areas, the network structure has disappeared, exposing the underlying Al-Zn coating and weakening the protection of the substrate (**Figure 2i**). These results indicated that DS passivation film exhibits the best corrosion-resistance performance, while the XSR passivation film shows the poorest corrosion-resistance performance, although still meeting the national standard requirements.

The morphological characteristics of the corroded areas were further determined using WLI. As shown in **Figure 2j**, after 72 h of neutral salt-spray corrosion, the

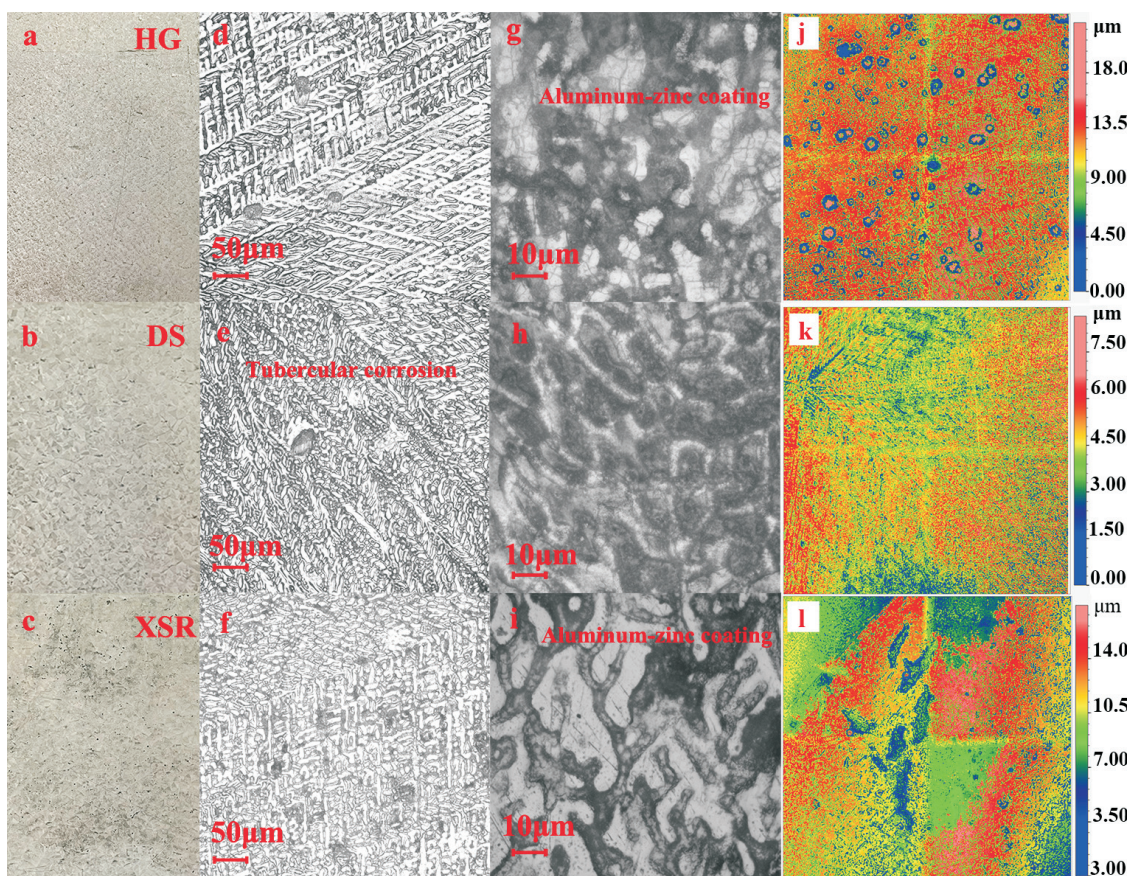


Figure 2: Optical (a-c), metallographic (d-f), and WLI (j-l) images of the specimens coated with different passivation films after 72 hours of salt-spray corrosion

specimen coated with the HG passivation film exhibited regular pitting corrosion (blue area) on the surface. The depth of the pitting corrosion pits reached up to approximately 12 μm, covering 1.0 % of the observed area. The depth of the pits exceeded the thickness of the passivation film, indicating substantial damage to the passivation film in the pitting-corrosion area. Additionally, the underlying Al-Zn coating began to corrode, although the corrosion did not reach the surface of the steel. The height variation of the passivation film outside the pitting corrosion area was minimal, indicating effective protection provided by the passivation film. On the other hand, the blackened area on the surface of the specimen coated with the DSR passivation film exhibited a corrosion morphology characterized by a mixture of strip corrosion and pitting corrosion, with the maximum depth of the corrosion pits reaching approximately 12 μm, covering 2.27 % of the observed area (**Figure 2l**). In contrast, the specimen coated with the DS passivation film showed only a small amount of strip corrosion and pitting corrosion, with the depth of the corrosion pits around 5 μm and the corrosion area occupying only 0.44 % of the observed area (**Figure 2k**). These results indicated that the DS passivation film provided superior protection to the base Al-Zn coating. Tafel curves further demonstrate that the DS passivation film exhibited supe-

rior corrosion resistance compared to both the HG and XSR passivation films. As shown in **Figure 3**, the corrosion potentials of the specimens coated with HG, DS, and XSR passivation films are -0.64, 0.18, and -0.64 V, while the corrosion current density for the specimens coated with HG, DS, and XSR passivation films were 1.031×10^{-4} , 6.346×10^{-7} and 8.611×10^{-5} A cm⁻², respec-

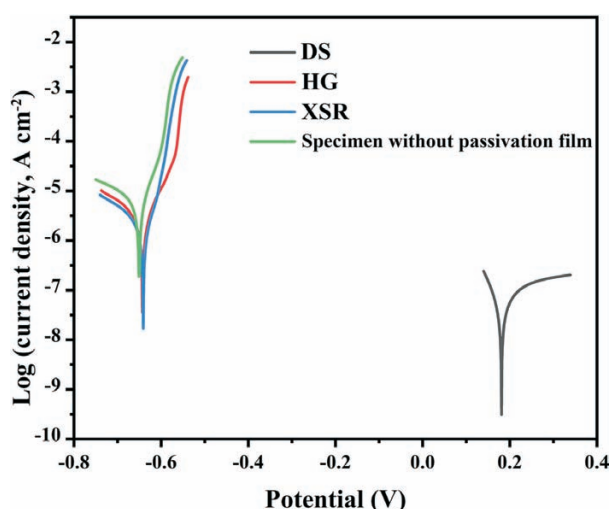


Figure 3: Tafel curves of specimens coated with different passivation films

tively (**Figure 3**). A higher corrosion potential and low corrosion-current density indicate a stronger obstruction against Cl^- ions in the solution for coatings deposited on specimens. This is advantageous for suppressing the occurrence of electrochemical corrosion because the increased charge transfer resistance reduces the electron transfer rate between the anode and the cathode, thereby slowing down the corrosion reaction.^{6,13} The corrosion potentials of the specimens coated with passivation films were generally higher than these of the specimen without a passivation film, indicating that passivation films of HG, DS, and XSR all contribute to enhancing the corrosion resistance of the zinc-aluminum coatings. Among them, the corrosion resistance of the DS passivation film was the best.

3.3 Evaluation of the acid/base resistance performance of passivation films

Following the GB/T 13448-2006 (Test methods for color-coated steel sheets and steel strips), the acid/base resistance of the passivation films was tested. Additionally, according to the GB/T 11186.3-1989 (Measurement method for coating color – Part 3: calculation of color difference), the color difference (ΔE^*) of the specimens before and after testing was measured and calculated. A ΔE^* value of ≤ 3 % is considered acceptable. After the acid-resistance test, optical photographs showed a slight darkening of the surfaces of specimens coated with HG, DS, and XSR passivation films. The

ΔE^* before and after testing respectively reached 0.78 %, 1.06 %, and 0.56 % for the HG, DS, and XSR passivation films, all below the acceptable standard of less than 3 % (**Figure 4a–4c**). Metallographic photographs revealed no significant changes on the surfaces of specimens coated with the HG, DS, and XSR passivation films after the acid-resistance test. The network structure formed by the passivation film remained intact and clear. In the DS passivation film, there were a few black spots appearing, and the color of the protruding part of the passivation film darkened slightly. Although the network structure of the HG passivation film remained clear, the color of the protruding parts also darkened slightly. Meanwhile, the XSR passivation film showed a minimal change after the acid-resistance test (**Figure 4d–4f**). It was evident that the XSR passivation film exhibited the best acid resistance performance.

After the alkali resistance test, the optical photographs of specimens coated with HG, DS, and XSR passivation films showed no significant changes compared to before the test. The corresponding ΔE^* were 1.22 %, 0.32 %, and 0.76 %, respectively, all below the acceptable standard of less than 3 % (**Figure 4g–4i**). Metallographic photographs revealed that the HG, DS, and XSR passivation films all exhibited a large number of uniformly distributed black spots after the alkali-resistance test. This may be due to the reaction between some metal oxides in the passivation solution and the alkaline solution.⁶ The black spots in the HG passivation film

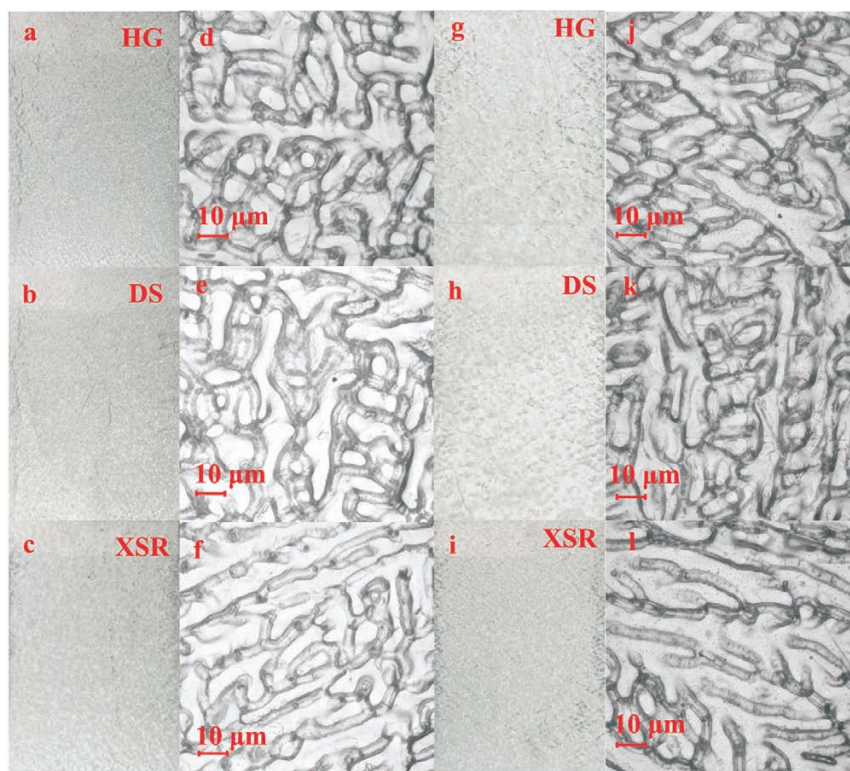


Figure 4: Optical (a–c) and metallographic (d–f) images of specimens coated with different passivation films after acid-resistance testing; Optical (g–i) and metallographic (j–l) images of specimens coated with different passivation films after alkali resistance testing

were the most densely distributed but have smaller diameters, whereas those in the XSR passivation film were sparser but have larger diameters. The test results indicated that the alkali-resistance performance of the DS passivation film was superior to that of the XSR and HG passivation films.

3.4 Evaluation of the anti-yellowing/blackening performance of passivation films

Referencing GB/T 1740-2007 (Test method for resistance to humidity and heat of coating films), the anti-yellowing/blackening performance of the passivation films was determined. Additionally, according to GB/T 11186.3-1989, the ΔE^* was measured and calculated. A ΔE^* value of ≤ 3 % is considered acceptable. From **Figure 5a–5c** it can be observed that after 80 minutes of standard anti-yellowing testing, the surfaces of the specimens coated with HG, DS, and XSR passivation films all exhibited varying degrees of yellowing. Among them, the XSR passivation film showed the most pronounced yellowing, with large areas of yellowing spots, which were deeper in color. The DS passivation film showed lighter and more uniform yellowing, while the HG passivation film exhibited slight yellowing, but with localized areas of deeper yellowing spots (**Figure 5a–5c**). The ΔE^* before and after testing for the HG, DS, and XSR passivation films reached 5.29 %, 2.51 %, and 5.25 %, respectively. Only the ΔE^* value of the DS passivation film was below the acceptable standard of

less than 3 %. The color differences of the HG and XSR passivation films did not meet the acceptable standard. From the metallographic photographs (**Figure 5d–5f**), it can be observed that although the network structure of the HG and XSR passivation films remained intact after the yellowing resistance test, a large number of black spots appeared within the passivation film. Compared to the HG and XSR passivation films, the density of black spots in the DS passivation film was lower, demonstrating superior yellowing resistance performance.

Figure 5g–5i presents the optical photographs of specimens coated with HG, DS, and XSR passivation films after the anti-blackening test. It can be observed that the color of all the samples darkened, and numerous darker black spots appeared after the blackening test. The ΔE^* before and after testing for the HG, DS, and XSR passivation films reached 1.24 %, 1.94 %, and 4.44 %, respectively. The ΔE^* values of the HG and DS passivation films were both below the acceptable standard of less than 3 %, while the ΔE^* value of the XSR passivation film did not meet the acceptable standard of less than 3 %. The metallographic photographs showed that after the anti-blackening test, the black spots in the XSR passivation film were the most pronounced and dense, but the passivation film remained intact and still provides protection to the substrate.

To investigate the thermal weight-loss behavior of the different passivation films, the passivation solutions were vacuum-dried at 80 °C for 12 h to remove the solvent.

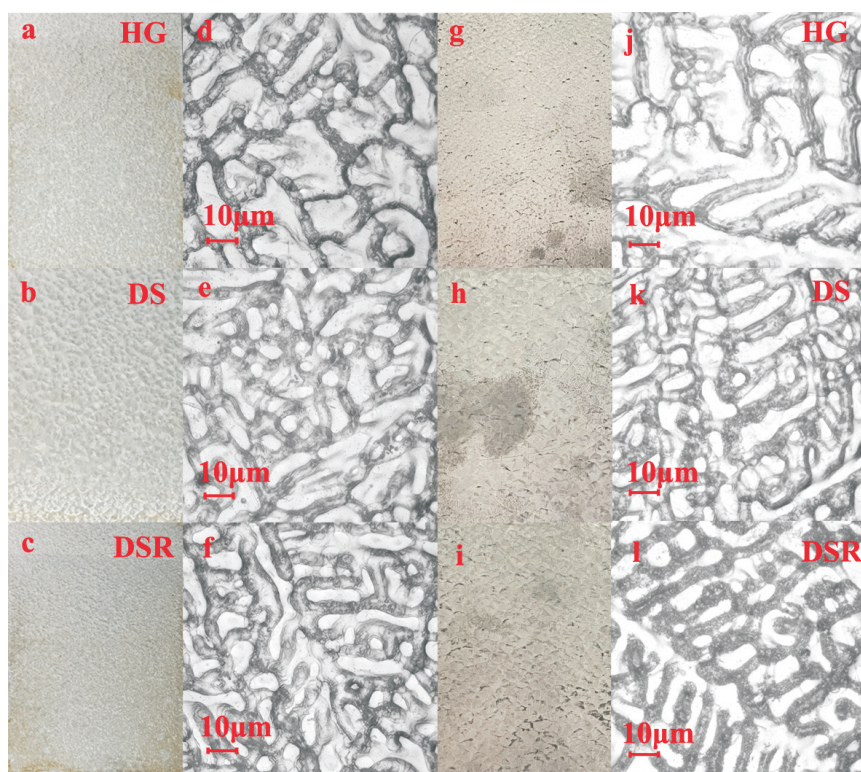


Figure 5: Optical (a–c) and metallographic (d–f) images of specimens coated with different passivation films after the yellowing-resistance test; Optical (g–i) and metallographic (j–l) images of specimens coated with different passivation films after the blackening-resistance test

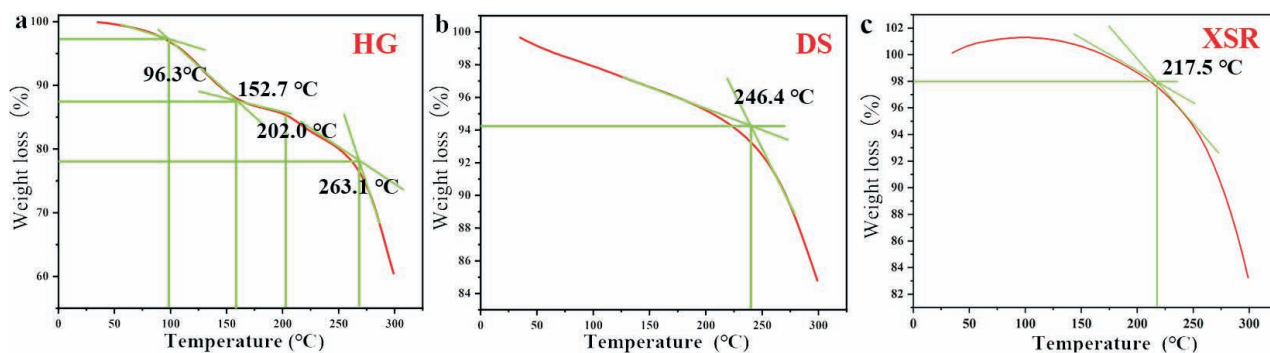


Figure 6: Thermal weight-loss curves of different passivation films

The obtained solids were ground into powder and subjected to thermal weight-loss testing. As shown in **Figure 6**, when the temperature rose to 300 °C at a rate of 5 °C/min in an inert atmosphere, the powder obtained from drying the HG passivation solution exhibited a slow weight loss of 2.84 % below 96.3 °C. In the temperature range of 96.3 to 152.7 °C, the first rapid weight-loss zone was observed, reaching 9.39 % weight loss. Subsequently, in the range of 152.7 to 202 °C, the second slow weight-loss zone was observed, with a weight loss of 3.37 %. The second rapid weight-loss zone occurred between 202 °C and 263 °C, with a weight loss of 7.82 %. This was followed by intensified weight loss due to the thermal decomposition and carbonization of the organic passivation film, reaching a total weight loss of 39.52 % at 300 °C¹⁴. The first rapid weight loss zone corresponds to the dehydration of the film-forming agent, while the second rapid weight loss zone is likely due to the decomposition of the organic polymer film, which is the main cause of yellowing in the HG passivation film. For the

powder obtained from drying the DS passivation solution, a continuous and slow weight loss of 7.2 % was observed as the temperature remains below 246.4 °C, after which a sharp weight loss occurs. The slow weight loss below 246.4 °C is attributed to the increasing polymerization degree of the main film-forming component, the silane coupling agent.¹⁵ The sharp weight loss observed above 246.4 °C is due to the thermal decomposition and carbonization of the organic components. The powder obtained from drying the XSR passivation solution exhibited a slow weight loss rate below 217.5 °C, but a sharp weight loss occurred when the temperature exceeded 217.5 °C. This indicated that the thermal stability temperature of the XSR passivation film was lower than the test temperature of the yellowing resistance (240 °C), and the rapid yellowing of the passivation film caused by its thermal decomposition resulted in its poor yellowing-resistance performance.

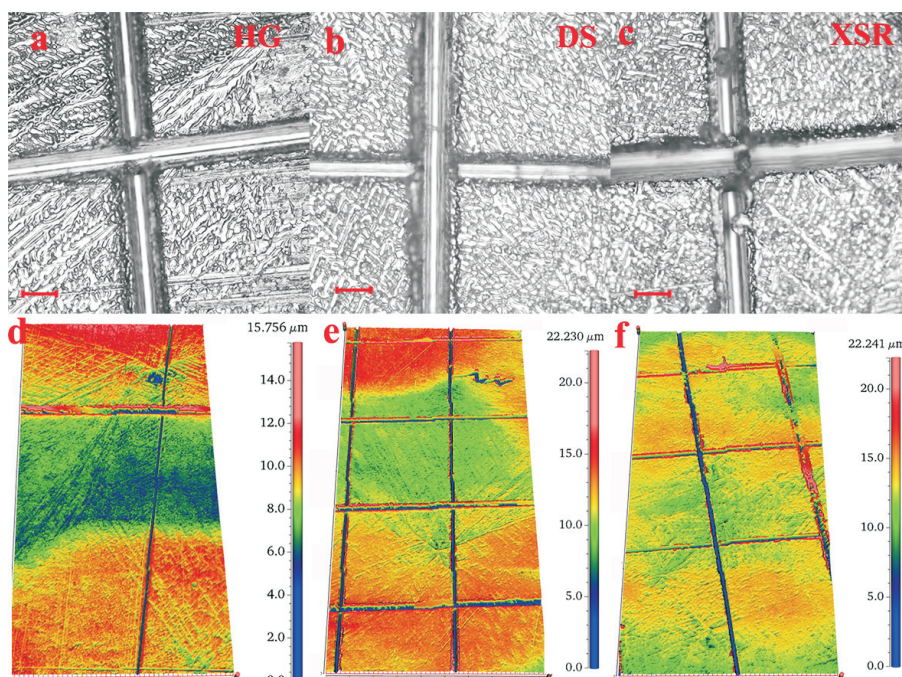


Figure 7: Metallographic (a-c) and WLI (d-f) images of specimens coated with different passivation films

3.5 Evaluation of the paint adhesion of the passivation films

The evaluation of the paint adhesion of the passivation films was conducted in accordance with GB/T 13448-2006 (Test methods for color-coated steel sheets and strips) and GB/T 9286-2021 (Cross-cut test for paints and varnishes). Grid patterns were cut into the specimen surface using a gridded knife, and then adhesive tape was used to peel off the coating in the grid area following the standard method. The area of coating detachment was observed to assess the coating performance of the passivation films. The metallographic images and surface morphology measured by WLI showed clear grid marks in the grid areas of the HG, DS, and XSR passivation films. The passivation films remained intact, and no detachment of the passivation films was observed (**Figure 7**). The results of the paint-adhesion test indicated that the coating performance of the HG, DS, and XSR passivation films all meet the standard for grade 0, which complies with the performance requirement of ≤ 3 .

3.6 Evaluation of the abrasion-resistance performance of the passivation films

Evaluation and comparison of the abrasion-resistance performance of passivation films were conducted following GB/T 1768-2006 (Test method for wear resistance of

paints and varnishes – Part 2: rotating rubber abrasion). The abrasion wheel used was calibrated with an elastic rubber CS-10 wheel, with an abrasion load of 250 g. After 500 cycles of abrasion on the Taber Abraser, the wear amounts of specimens coated with the HG, DS, and XSR passivation films were similar, measuring (3.5, 3.4, and 3.7) mg, respectively. Optical, SEM, and WLI images of all passivation films after 500 cycles of abrasion testing displayed varying degrees of damage with evident traces of abrasion (**Figure 8**). Among them, the damage to the XSR passivation film was the most pronounced, with the passivation film nearly disappearing in the abrasion area. HG and DS passivation films remained relatively intact after the abrasion experiment, with over 80 % of the areas still protected by the passivation film. Metallographic images revealed varying degrees of damage to the passivation films after abrasion testing, but the passivation film network still existed, maintaining its protective function on the Al-Zn coating. 3D-profile images show that the scratches on the HG passivation film were more densely distributed, but generally shallower, while those on the DS passivation film were more sparse but deeper. The results of the abrasion-resistance test indicated that HG, DS, and XSR passivation films all exhibited good abrasion-resistance performance, with the HG and DS passivation films slightly outperforming the XSR passivation film.

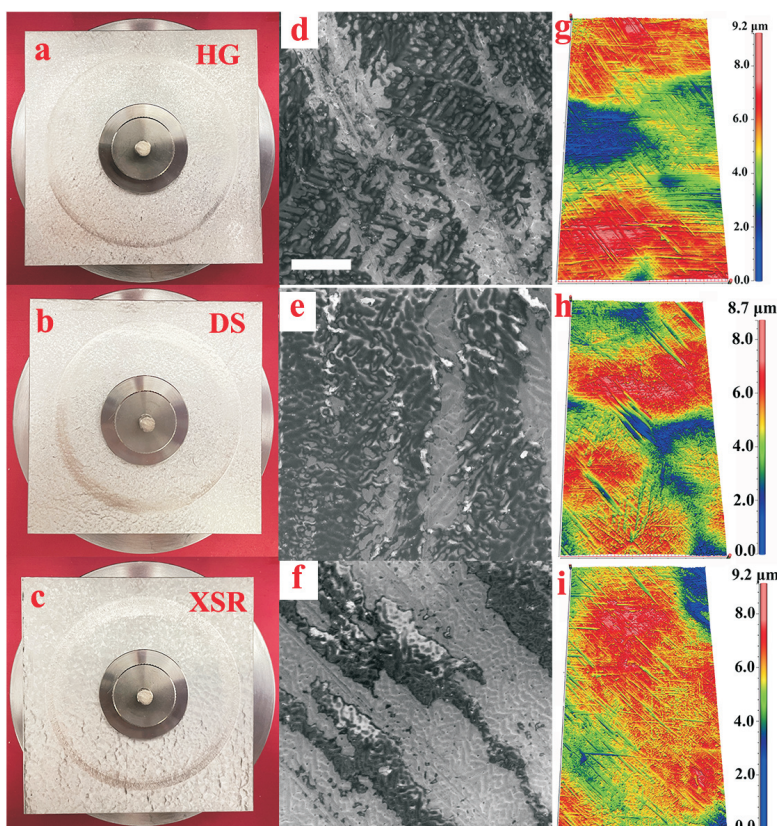


Figure 8: shows Optical (a-c), SEM (d-f), and WLI (g-i) images of specimens coated with different passivation films

3.7 Other performance evaluations

The fingerprint-resistance performance is an important index for evaluating the Cr-free, fingerprint-resistant passivation film. Fingerprint marks are typically caused by the sweat from operators' fingers, so the fingerprint-resistance performance test used white Vaseline as a simulated medium for human sweat. A small amount of Vaseline was evenly applied to approximately half of the sample surface using a clean cotton ball. After 30 minutes, the Vaseline on the surface was wiped off with a clean cotton ball, and the color difference (ΔE^*) of the coated surface was measured, with $\Delta E^* \leq 3.0$ considered as the pass criterion. The color differences of the samples coated with the HG, DS, and XSR passivation films after the fingerprint-resistance test were 0.41, 0.66, and 1.14, respectively, all less than 3.0, meeting the quality requirements. However, the fingerprint-resistance performance of the HG and DS passivation films was significantly better than that of XSR passivation film.

A low surface resistance is beneficial for the rapid transfer and diffusion of electrons, reducing electrostatic buildup and lowering safety risks. Typically, the surface resistance of CFAZCS is required to be less than $0.8 \text{ m}\Omega$. The surface resistance of the samples coated with the HG, DS, and XSR passivation films was measured using the Mitsubishi Electric MCP-T370 resistivity meter. The results indicated that the surface resistance of the samples coated with the HG, DS, and XSR passivation films was $0.04 \text{ m}\Omega$, meeting the performance requirements.

4 CONCLUSIONS

The evaluation results of the passivation films demonstrated that the DS passivation film met all the standard requirements for corrosion resistance, acid/base resistance, anti-yellowing/blackening, paint adhesion, abrasion resistance, fingerprint resistance, and surface resistance performances. Except for its poor anti-yellowing performance, the HG passivation film met the standards for all other aspects. However, the anti-yellowing/blackening performances of the XSR passivation film did not meet the standards. The DS passivation film showed optimal performance in corrosion resistance, alkali resistance, and anti-yellowing performances, while the HG passivation film excelled in anti-blackening and abrasion resistance. The XSR passivation film performed best in acid resistance.

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5 REFERENCES

- J. K. Chang, C. S. Lin, W. R. Wang, S. Y. Jian, High temperature deformation behaviors of hot dip 55 wt% Al-Zn coated steel, *Appl. Surf. Sci.*, 511 (2020), 145550, doi:10.1016/j.apsusc.2020.145550
- A. Al-Negheimish, R. R. Hussain, A. Alhozaimey, D. Singh, Corrosion performance of hot-dip galvanized zinc-aluminum coated steel rebars in comparison to the conventional pure zinc coated rebars in concrete environment, *Constr. Build. Mater.*, 274 (2021), 121921, doi:10.1016/j.conbuildmat.2020.121921
- D. Persson, Thierry, O. Karlsson, Corrosion and corrosion products of hot dipped galvanized steel during long term atmospheric exposure at different sites world-wide, *Corros. Sci.*, 126 (2017), 152–165, doi:10.1016/j.corsci.2017.06.025
- Y. Gao, S. Kainuma, M. Yang, S. Ishihara, D. Inoue, Galvanic corrosion behavior of hot-dip Al and 55Al-Zn coatings applied to steel bolted joints in atmospheric environments, *Constr. Build. Mater.*, 401 (2023), 132694, doi:10.1016/j.conbuildmat.2023.132694
- B. Pan, H. Sun, S. Shang, W. Wen, M. Banu, J.C. Simmer, B.E. Carlson, N. Chen, Z. Liu, Z. Zheng, P. Wang, J. Li, Corrosion behavior in aluminum/galvanized steel resistance spot welds and self-piercing riveting joints in salt spray environment, *J. Manuf. Process.*, 70 (2021), 608–620, doi:10.1016/j.jmapro.2021.08.052
- L. Zhaohua, L. Cheng, X. Zhengfeng, J. Rong, X. Yu, Z. Yannan, Electrochemical Corrosion Behavior of Chromium-Free Composite Passivation Film on Galvanized Steel, *Int. J. Electrochem. Sc.*, 13 (2018) 7, 6473–6483, doi:10.20964/2018.07.60
- Z. Yu, J. Hu, H. Meng, A review of recent developments in coating systems for hot-dip galvanized steel, *Front. Mater.*, 7 (2020), 1–19, doi:10.3389/fmats.2020.00074
- J. Pan, X. Tang, Y. Li, Influence of treatment time on performance of Cr(III)-based conversion coatings on hot dip Zn–55Al–1.6Si coated steel sheet, *Coatings*, 9 (2019) 5, 297, doi:10.3390/coatings9050297
- T. Guo, C. Liu, C. Ran, X. Dong, Effects of spangle size on performances of hot-dip 55 %Al-Zn alloy coating, *Int. J. Electrochem. Sc.*, 13 (2018) 10, 9505–9519, doi:10.20964/2018.10.07
- T. Sanchez, S. Zanna, A. Seyeux, M. Vaudecal, P. Marcus, P. Volovitch, J. Świątowska, Conversion coating distribution on rough substrates analyzed by combining surface analytical techniques, *Appl. Surf. Sci.*, 556 (2021), 149734, doi:10.1016/j.apsusc.2021.149734
- I. O. Wallinder, W. He, P. E. Augustsson, C. Leygraf, Characterization of black rust staining of unpassivated 55 % Al-Zn alloy coatings, Effect of temperature, pH and wet storage, *Corros. Sci.*, 41 (1999) 12, 2229–2249, doi:10.1016/S0010-938X(99)00043-8
- G. Wang, H. Li, P. Li, X. Li, Y. Wang, Effect of cerium on the microstructure and anti-corrosion performance of Al-Zn coatings, *Surf. Coat. Tech.*, 473 (2023) 130046, doi:10.1016/j.surfcoat.2023.130046
- J. E. Ramón, I. Martínez, J. M. Gandía-Romero, and J. Soto, Improved Tafel-Based Potentiostatic Approach for Corrosion Rate Monitoring of Reinforcing Steel, *J. Nondestruct. Eval.*, 41 (2022) 4, 70, doi:10.1007/s10921-022-00903-z
- H. Lin, Q. Li, S. Zhang, L. Zhang, G. Hu, X. Hu, Involvement of the organics in aqueous phase of bio-oil in hydrothermal carbonization of lignin, *Bioresour. Technol.*, 351 (2022), 127055, doi:10.1016/j.biortech.2022.127055
- A. K. Balan, S. Mottakkunnu Parambil, S. Vakyath, J. Thulissery Velayudhan, S. Naduparambath, P. Etathil, Coconut shell powder reinforced thermoplastic polyurethane/natural rubber blend-composites: effect of silane coupling agents on the mechanical and thermal properties of the composites, *J. Mater. Sci.*, 52 (2017) 11, 6712–6725, doi:10.1007/s10853-017-0907-y