Corrosion Properties and Bond Strength in Normal Strength Concrete of Al₂O₃ Plasma-Sprayed Plain Bars with ZrCC/Organofunctional Silane Coating

Petr Pokorný 1,*, Nikola Prodanovic 1, Karel Hurtig 1, Veronika Steinerová 1, Jaroslav Fojt 2, Marek Janata 3 and Vlastimil Brožek 3

1 Department of Building Materials, Klokner Institute, Czech Technical University in Prague, 16608 Prague, Czech Republic; nikola.prodanovic@cvut.cz (N.P.); karel.hurtig@cvut.cz (K.H.); veronika.steinerova@cvut.cz (V.S.)
2 Department of Metals and Corrosion Engineering, University of Chemistry and Technology, 16628 Prague, Czech Republic; jaroslav.fojt@vscht.cz
3 The Czech Academy of Sciences, Institute of Plasma Physics, 18200 Prague, Czech Republic; janata@ipp.cas.cz (M.J.); brozek@ipp.cas.cz (V.B.)

* Correspondence: petr.pokorny@cvut.cz

Abstract: In this study, the corrosion properties of plasma-sprayed Al₂O₃ coating (APSS) with a top-coat of zirconium-based conversion coating (ZrCC) and organofunctional silane coating (3-glycidoxypropyltrimethoxysilane; GPTMS) on carbon steel are investigated in detail. Additionally, the bond strength of plain steel bars coated with this system in normal strength concrete are newly tested. The APSS coating exhibits significant porosity, with unfavourable open pores limiting the barrier protection effect. In contrast, the surface roughness (Rₐ) significantly increases, improving the bond strength between steel bars and concrete. Such increase in carbon steel roughness improves bond strength in concrete. The synergic application of ZrCC and GPTMS topcoats significantly enhances the corrosion resistance of the base coat (inhibition effect). The character of the GPTMS coating increases the wettability of the APSS coating, which further positively contributes to bond strength between plain bars and concrete. It is demonstrated that when the ZrCC topcoat is applied without GPTMS, the corrosion resistance increases insignificantly and the surface wettability decreases, negatively affecting bond strength in comparison with carbon steel coated using an APSS base coat only.

Keywords: corrosion of steel in concrete; plasma spray; aluminium oxide; zirconium conversion coating; organofunctional silane coating; bond strength in concrete

1. Introduction

At present, the corrosion of concrete reinforcement is the most important issue limiting the service life of reinforced concrete structures [1,2]. Although the surface of conventional carbon steel reinforcement is protected by the natural alkalinity of the concrete pore solution, significant corrosion may develop mainly due to the carbonation of the concrete cover layer (the reduction of the pore solution pH by CO₂ and NOₓ from the ambient atmosphere) and/or the ingress of chloride anions (the application of de-icing salts and seawater) [3–7]. The resulting voluminous corrosion products cause cracks in the cover layer, increasing the ingress of corrosion stimulants and significantly reducing the reinforcement bond strength in concrete [8,9]—see Figure 1.

The durability of reinforced concrete structures can be improved by increasing the density of the concrete cover layer (through a low w/c of the mix, the use of admixtures
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with pozzolanic effect, increasing a concrete class, etc.) [9,10], by the use of additives increasing the binding of chloride ions (nano-\(\text{Al}_2\text{O}_3\) and carbon-based nanomaterials) [11], or through measures directly related to the corrosion protection of the reinforcement, e.g., the application of cathodic protection [12], corrosion inhibitors [13,14], or protective coatings [12]. Driven by economic reasons and based on long-term experience, epoxy and hot-dip galvanized coatings are preferred in the current construction practice. Non-porous epoxy coatings can significantly extend the service life of reinforced concrete structures (especially against chloride anions) [12,15,16]. However, it has been experimentally verified that the coating is not UV stable and reduces the bond strength of the reinforcement in concrete [17–19]. Also, the hot-dip galvanized coating can provide an extension of the service life of reinforced concrete structures [20–22]. However, in fresh concrete, the coating corrodes under hydrogen evolution, which reduces bond strength [23,24]. According to some studies, corrosion products based on CHZ (calcium hydroxyzincate dihydrate—\(\text{Ca}[\text{Zn(OH)}_3]_2\cdot2\text{H}_2\text{O}\)) may also adversely affect the bond strength of the reinforcement in concrete (pushing off the cement paste) [25]—see Figure 2. However, other studies suggested that these corrosion products significantly increased surface roughness and thus, in turn, could increase bond strength [26].

![Figure 1. Graphic model of surface corrosion of conventional concrete steel reinforcement with the formation of voluminous corrosion products and cracks in the concrete cover (reprinted from [2]).](image)

The bond strength of reinforcement in concrete is an essential factor ensuring the load-bearing capacity of reinforced concrete structures [27–29]. The use of \(\text{Al}_2\text{O}_3\)-based coatings is associated with an increase in the hardness of the steel surface, its mechanical strength (resistance to abrasive wear), and also an increase in surface roughness. The use of plasma-sprayed \(\text{Al}_2\text{O}_3\) coatings on the surface of conventional steel reinforcement may significantly improve the bond strength of reinforcement in concrete. However, the resulting coatings contain naturally open pores [30,31], and the sealing of these pores is crucial for corrosion protection. Organofunctional silanes may ensure perfect sealing and, at the same time, increase the bond strength of reinforced steel in concrete. This coating is used in the industry as an adhesive bridge between concrete and coating systems—usually epoxy-based [32,33]. The advantage for the application of organofunctional silanes to the \(\text{Al}_2\text{O}_3\) (alumina) surface is primarily the more significant reactivity compared to the steel substrate, as is demonstrated in Figure 3 [34,35].
Figure 2. Scheme of changes in ITZ due to the corrosion of the hot-dip galvanized coating in concrete (generation of hydrogen bubbles and precipitation of CHZ corrosion products—the figure takes into account the conclusions of article [25]).

Figure 3. Showing the difference in reactivity with organofunctional silane between steel and aluminium oxide (alumina—Al₂O₃)—reprinted from [35].

The application of a single layer of mono-silanes increases the corrosion resistance of the underlying metal [36,37]. However, higher resistances have been achieved when using multiple layers [38]. In this context, bis-silanes characterized by two alkoxy-silane groups (at both ends of the molecule) have been successfully and most widely applied. Bis-silanes form a more homogeneous coating with higher thickness. Coatings are mainly based on:

- amino-silane (bis-[3-(triethoxysilyl)propyl]amine), increasing the hydrophilicity of the surface;
- tetrasulfide-silane (bis-[3-(triethoxysilyl)propyl]tetrasulfide), acting hydrophobically [39,40].

See a representation of the molecules of both silanes in Figure 4.
Figure 4. Representation of the two most commonly tested bis-silanes in metal surface treatment: (A) bis-aminosilane and (B) bis-tetrasulfidesilane; reprinted from [40].

The application of organofunctional silanes in the form of coatings is based on the hydrolysis of alkoxy groups in order to form the corresponding silanols, and the subsequent adsorption to the surface via hydrogen bridges with free OH groups on the surface. Usually, the application of organofunctional silanes on the surface is associated with the final step of drying at elevated temperatures. During this step, a crosslinking reaction of individual molecules occurs—this is called condensation and polymerization of the organofunctional silane coating [36,41–43]. The general mechanism of organofunctional coating formation is shown in Figure 5.

Figure 5. Illustration of the mechanism of adsorption of organofunctional silane molecules onto a metal surface to form hydrogen bridges (A), and subsequent condensation with polymerization (B) to form a continuous coating—reprinted from [36].
The first goal of this study is to assess the effectiveness of the application of monosilane (organofunctional silane) 3-glycidyloxypropyltrimethoxysilane (GPTMS—see Figure 6) in sealing open pores in plasma-sprayed Al₂O₃ coating on steel reinforcement surfaces. Although organofunctional silanes have been marginally tested before in sealing pores in ceramic coatings, the commercially available organofunctional silane GPTMS has never been tested. The application advantage for the coatings industry in using this organofunctional silane is based on the availability of the formulation in a pre-hydrolysed and oligomerized form. This formulation is also significantly more affordable than more expansive bis-silanes. However, the effect of organofunctional silanes on reinforcement bond strength has not been investigated either. Considering that the theoretical basis suggests (see Figure 3—higher reactivity with silica phase) a favourable effect of organofunctional silanes on bond strength, the second goal of this study is to verify this hypothesis by means of an experimental campaign.

Figure 6. Structural formula of applied organofunctional silane (GPTMS) in oligomerized form and pre-hydrolysed for direct application to the steel surface with a plasma-sprayed coating of Al₂O₃—reprinted from [35].

2. Materials and Methods

The plasma-sprayed Al₂O₃ (APSS) coating was applied to each steel sample before the application of further coatings, such as the zirconium-based conversion coating (ZrCC) and the organofunctional silane coating (GPTMS). Flat carbon steel samples (100 mm × 20 mm × 2 mm) were used to identify the corrosion properties of individual coatings. The carbon steel sample composition is detailed in Table 1. Plain carbon steel bars (l = 1000 mm, d = 10 mm) were used to quantify the bond strength of coated steel in concrete. The sample composition of the plain steel bars is detailed in Table 2.

Table 1. Composition of flat steel samples (GD-OES).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content</td>
<td>0.10</td>
<td>0.03</td>
<td>0.22</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.43</td>
<td>0.14</td>
<td>0.07</td>
<td>balance</td>
</tr>
</tbody>
</table>

Table 2. Composition of plain bar steel 10216 (GD-OES).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe</th>
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<tbody>
<tr>
<td>Content</td>
<td>0.11</td>
<td>0.05</td>
<td>0.19</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.33</td>
<td>0.11</td>
<td>0.04</td>
<td>balance</td>
</tr>
</tbody>
</table>
For bond strength tests, a test cube ($a = 150$ mm) was made, with plain bars positioned into the centre of concrete samples using an internal wooden rhomboid at the bottom of the mould and an external clamp (made from polyacrylate using 3D printing—Prusa 3D printer i3MK3S+ (Prusa Research, Prague, Czech Republic)) at the top of the form—see Figure 7. In total, 28 cube moulds were prepared including 4 duplicates of 7 plain steel bar samples. Further, 5 cube moulds were prepared without plain steel bars for the concrete strength test (Figure 8). Portland cement CEM I 42.5 R (Českomoravský cement, a.s., Mokrá—Horákov, Czech Republic) was used to produce the cube moulds, and its composition is shown in Table 3. The normal-strength concrete (NSC) was prepared according to the protocol in Table 4. The concrete batch was homogenized for 10 min with the concrete mixer GIFOS MB80 at a speed rotation of 30 rotations per minute. The cube mould filling was performed step-wise in 3 layers, with each layer being compacted for 5 min with a hand-vibrating device (Eibenstock EBR 125.1, Elektrowerkzeuge GmbH Eibenstock, Eibentock, Germany). All samples were cured in medium humidity (65% RH, $21 \pm 1$ °C) for 24 h. After the curing period, they were fully submerged in distilled water ($20.5 \pm 1$ °C) for 27 days.

Figure 7. Images of plain steel bars centred at the centre of cube forms. The red annotation shows the bottom wooden insert. The blue annotation shows the top 3D-printed polyacrylate clamps.

A total of 21 plain steel bars and 12 flat steel samples were plasma-sprayed with $\text{Al}_2\text{O}_3$ coatings (APSS), as shown in Figure 9. Medium-purity (95.5 wt.%) alumina oxide powder AH 240 was applied (due to the relatively low price of the powder) using a hybrid water-stabilized plasma torch WSP-H 500 (The Czech Academy of Sciences—Institute of Plasma Physics). Before the alumina oxide application, the steel sample surface was sandblasted with corundum abrasive. The final surface roughness was $5.5 \mu$m ($R_s$). The plasma torch output was 150 kW, generated by a direct current of 500 A. The resulting electric arch between the tungsten cathode and the inner cooled rotational anode had an outlet temperature of 25 000 K, and the flow speed was 7000 m·s$^{-1}$. The plasma enthalpy was approximately 300 MJ·kg$^{-1}$. The $\text{Al}_2\text{O}_3$ powder was fed to the plasma jet at a feeding distance of 75 mm, and the spray distance was 450 mm. The chosen distances promote the formation of a harsh coating with higher porosity, reducing the required amount of $\text{Al}_2\text{O}_3$. The coating application was performed in two layers, resulting in a total thickness of 220 $\mu$m. Between layer depositions, the steel surface was cooled with pressurized air to reach a temperature of 110 °C.
Figure 8. Image (A) shows 28 cube forms with plain steel bars for the bond strength test. Image (B) shows 5 samples without plain steel bars for the concrete compressive cubic strength test.

Table 3. Cement composition guaranteed by the producer (CEM I 42.5 R).

<table>
<thead>
<tr>
<th>Compound content (wt.%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
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<tr>
<td>content</td>
<td>64.2</td>
<td>19.5</td>
<td>4.7</td>
<td>3.2</td>
<td>1.3</td>
<td>3.2</td>
<td>0.78</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 4. Content by m³ of concrete for cubic samples used for pull-out test.

<table>
<thead>
<tr>
<th>Admixture</th>
<th>Content</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement (CEM I 42.5 R)</td>
<td>365</td>
<td>pure Portland cement without admixtures</td>
</tr>
<tr>
<td>aggregate</td>
<td>900</td>
<td>fraction 0/4-fine sand</td>
</tr>
<tr>
<td></td>
<td>585</td>
<td>fraction 4/8</td>
</tr>
<tr>
<td></td>
<td>285</td>
<td>fraction 8/16</td>
</tr>
<tr>
<td>mixture (w/c)</td>
<td>0.55</td>
<td>distilled water was used</td>
</tr>
</tbody>
</table>

Furthermore, some samples were coated with a zirconium-based conversion coating (ZrCC) as a topcoat. In total, 7 plain steel bars and 4 flat steel samples were coated with ZrCC only, and the other 7 plain steel bars and 4 flat steel samples were coated with a combination of ZrCC and organofunctional silane coatings (3-glycidyloxypropyltrimethoxysilane, GPTMS). The coating was deposited by dipping the samples in commercially available reagents. The ZrCC bath contained (NH₄)₂ZrF₆ and (NH₄)₃PO₄ diluted in distilled water, while the GPTMS bath was based on a pre-hydrolysed and oligomerized form of 3-glycidyloxypropyltrimethoxysilane diluted in distilled water. The ZrCC-coated samples were extensively washed. The ZrCC- and GPTMS-coated samples were cured under the conditions described in Table 5. The key abbreviations are explained in Table 6.
Figure 9. Application of plasma-sprayed Al₂O₃ coating on the surface of a plain steel bar with a WSP-H 500 torch.

Table 5. Coating conditions of different treatments.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Composition of Solution</th>
<th>Exposure Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>APSS</td>
<td>powder application in plasma stream, Al₂O₃ (95.5% of purity — content of SiO₂, TiO₂, Fe₂O₃, MgO, CaO)</td>
<td>used torch WSP-H 500, 150 kW/500 A, plasma: 25,000 K, 7000 m/s, 300 MJ/kg</td>
</tr>
<tr>
<td>ZrCC</td>
<td>3% wt. commercial solution of ((NH₄)₂ZrF₆, NaF, (NH₄)H₂PO₄, NH₄OH) in distilled water</td>
<td>dipping application at temperature (21.0 ± 1 °C), 10 min exposure time, stirring, drying at 35 °C for 2 h</td>
</tr>
<tr>
<td>GPTMS</td>
<td>10% wt. commercial solution of oligomerized GPTMS in distilled water</td>
<td>dipping application at temperature (21.0 ± 1 °C), 15 min exposure time, stirring, drying at 95 °C for 20 min</td>
</tr>
</tbody>
</table>

Table 6. Abbreviation table.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Type of System</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>uncoated steel</td>
<td>steel surface without coatings</td>
</tr>
<tr>
<td>APSS</td>
<td>coating on a steel surface</td>
<td>Plasma-sprayed Al₂O₃ coating</td>
</tr>
<tr>
<td>ZrCC</td>
<td>coating on a steel surface</td>
<td>plasma-sprayed Al₂O₃ coating with zirconium-based conversion coatings</td>
</tr>
<tr>
<td>GPTMS</td>
<td>coating on a steel surface</td>
<td>plasma-sprayed Al₂O₃ coating with zirconium-based conversion coatings and 3-glycidoxypropyltrimethoxysilane as topcoat</td>
</tr>
<tr>
<td>SCPS</td>
<td>exposure solution for coated steel surface (electrolyte)</td>
<td>simulated concrete pore solution (pH = 13.0) with 3.5 wt.% NaCl</td>
</tr>
</tbody>
</table>

The steel samples with Al₂O₃ coating were cut transversally and polished with an automatic polishing machine (Struers LaboPol 5, Struers GmbH, Willich, Germany), polishing paper with a grit size of P60—P2400, and diamond polishing paste. Sample cooling and washing were performed with ethanol (98 wt.%). The plasma-sprayed Al₂O₃-coated steel transversally cut samples were imaged with an electron microscope JEOL JSM IT-200 (JEOL Ltd., Tokyo, Japan).
The composition of flat steel APSS sample coating was analyzed using X-ray diffraction (Malvern Panalytical, Malvern Panalytical V. B., Almelo, The Netherlands) with CuKα radiation over the angular range of 5–90°. The porosity of samples was analyzed using a mercury porosimeter AutoPore IV—Micromeritics. In total, 5 samples were measured, and the total measured area was 0.5 cm².

Electrochemical tests included corrosion potential measurement ($E_{corr}$) and polarization resistance ($R_p$) measurements for 162 h. The tests were carried out on 4 samples and measured every hour. A silver/silver chloride electrode (SSCE) served as the reference electrode. The test was performed in a simulated concrete pore solution (SCPS see Table 6) with the addition of chloride anions (3.5 wt. % NaCl). The SCPS was prepared by mixing CaO (p.a.) and NaCl (p.a.) in distilled water for 3 h (21.0 ± 1 °C) until a saturated solution was achieved. The final pH was buffered to 13.0 with KOH (p.a.). After the assembly of the setup and the filling of cells with simulated concrete pore solution, the start of measurement was delayed for 15 min before starting the sequential measurement of $E_{corr}$ and $R_p$ (the so-called $R_p/E_{corr}$ trend). The total exposed area of the samples was 4.5 cm². The polarization resistance value was evaluated as the linear coefficient of current density and potential in the vicinity of $E_{corr}$ (polarization range: −20 to +20 mV; scan rate: 0.1 mV·s⁻¹).

The electrochemical impedance spectra were measured in the frequency range from 10 kHz to 10 mHz, with 10 mV/$E_{corr}$ AC amplitude within a 14 h period. The measurement was performed in a three-electrode setup in a PTFE press-on cell of cylindrical shape (the total area of the sample was always 4.5 cm²). Glassy carbon rods were used as counter electrodes placed on the axis of the capillary outlet. Electrochemical measurements were performed using the Electrochemical Multiplexer ECM 8 (which allows the measurement of 4 parallel samples), with the Reference 600 potentiostat (Gamry Instruments, Warminster, PA, USA).

The roughness of plain uncoated steel (US) bars, APSS, and GPTMS samples was measured before the bond strength test. Each of the 5 randomly selected samples was measured in 3 lengthwise tracks with the Mitutoyo SJ-400 device (Mitutoyo, Kawasaki, Japan). The wettability of flat-coated steel samples (APSS, ZrCC, and GPTMS) was measured with the SEE System (ADVEX Instruments, Brno, Czech Republic) goniometer, using the sessile drop technique with distilled water. The measurements were carried out on a total of 4 parallel samples (each sample was measured at 3 different locations).

The pull-out test, as described by RILEM RC6 [44] and ASTM C234-91a [45], was performed to assess bond strength. The bond strength of coated steel bars with concrete compared to uncoated plain steel bars was assessed by means of a bond stress slip. The slip was measured using an LVDT sensor (Micro-Epsilon Messtechnik GmbH, Ortenburg, Germany) located at the opposite end of the loaded steel bar sample. The anchorage length was given by the concrete cube sample and plastic tube separation, as shown in Figure 10. The pull-out test was performed using the 100 kN TIRA test machine (Figure 11). The displacement of the unloaded end of the plain bar controlled the test. A constant loading rate of 0.005 mm·s⁻¹ was applied. The test was terminated after reaching a slip of 2.0 mm.

![Figure 10. Experimental setup of pull-out bond strength test between a plain bar and normal strength concrete—anchorage length is in red.](image-url)
3. Results and Discussion

For easier orientation in the text of this paper, the Results and Discussion section is divided into three subsections.

In Section 3.1, the APSS coating is described (without ZrCC and GPTMS coatings) for the average thickness on the surfaces of steel and plain bar samples, and the porosity is visually evaluated by means of SEM and also mercury porosimetry. This subsection discusses the results of the roughness of the APSS coating on the surface of the plain bars, and the phase composition of the coating using XRD is discussed. In Section 3.2, the corrosion resistance of flat steel specimens with the APSS coating and with the ZrCC and GPTMS topcoats is evaluated. Corrosion resistance testing was performed on flat steel samples in simulated concrete pore solution (SCPS) via the $E_{corr}/R_p$ trend and EIS characteristics. Finally, in Section 3.3, the bond strength of plain bars with and without APSS coating (and also the effect of coating ZrCC and GPTMS) in normal-strength concrete was evaluated using the pull-out test. In this subsection, the surface contact angle of flat steel specimens with APSS coatings is also evaluated, as is the influence of the presence of ZrCC and GPTMS.

3.1. Analysis of the APSS Coating

Figure 12 shows the SEM image of the outer surface of the plasma-sprayed Al$_2$O$_3$ coating (APSS) on the surface of a flat steel sample. The APSS coating has a typical splat structure with spherical grains with a most common diameter of 30–50 µm [46,47]. Cracks and smaller pores are visible between the outer splats. However, more significant pores are seen at the splat boundaries between the individual spherical splats. The cross-section
of the APSS coating (Figure 13) reveals the presence of typical semi-molten and unmolten particles with a typical porosity of 2–5 µm. However, this figure also shows continuous porosity greater than 5 µm with cavern formation in the coating [48,49]. Through capillary phenomena, the filling of these caverns with outer electrolyte can occur. However, Figure 13 also shows the typical presence of semi-molten and over-molten particles of oxide impurities in the used AH 240 powder [49,50]. Considering the expected presence mainly of α-Al2O3 in the APSS coating on steel, an open porosity of approximately 4.4% can be expected [51]. However, porosity measurements using mercury porosimetry (see Figure 14) on flat samples showed the very frequent presence of pores of 5 µm pore diameter, but also pores with a diameter significantly larger than 10 µm. The total porosity of the flat samples was determined to be around 0.15% on average.

Figure 12. Surface splat structure of plasma-sprayed Al2O3 coating on flat steel samples—detail vision.

Coating thickness measurements were performed using cross-sectional SEM images (30 measurements from each sample type, i.e., flat steel samples and plain bars). On the flat samples, the average coating thickness was 217 ± 14 µm. On the circular surface of the plain bars (probably due to the more complex surface geometry), a lower coating thickness of 208 ± 11 µm was found.

Figure 15 shows the results of the measurement of APSS coating phase composition using X-ray diffraction (the thickness of the coating prevents the detection of the underlying steel). From the results, it is clear that the coating is formed only through the modification of Al2O3. The impurity content of the powder used is only influenced by the presence of the different Al2O3 modifications. The α-Al2O3 phase is only represented by approximately 22 wt.%, the γ/δ-phase is the most represented (approximately 70 wt.%), and the δ-phase is the least represented (approximately 8 wt.%). A similar APSS coating composition on carbon steel was previously achieved using torch WSP-H 500 [52]. The obscurative of these phases and the relatively higher impurity content condition the observed porosity of the APSS coating.
Figure 13. Detailed demonstration of the natural open porosity of the plasma-sprayed Al₂O₃ coating on flat steel samples.

Figure 14. Pore size distribution of plasma-sprayed Al₂O₃ (APSS) coating on flat steel samples (overview; curves—mean values).
A comparison of the roughness of plain steel bar samples without coating (US), with APSS coating only, and finally APSS with GPTMS (topcoat) is shown in Figure 16. It is evident that the application of plasma-sprayed Al₂O₃ coatings increases the surface roughness (Rₐ) of the plain steel bars by approximately a factor of 10, and it is also evident that the thickness of the GPTMS coating does not significantly reduce the natural porosity of the APSS coating.

Figure 16. Bar chart of coating roughness results for plain steel bars.

3.2. Corrosion Properties of Coated Flat Steel Samples in SCPS

The hydrolysis of organofunctional silanes in aqueous solutions (or in aqueous solutions with base alcohols) leads to the formation of the corresponding silanols (the hydrolysis is shown by the system of subsequent equilibrium reactions in Equation (1)). Through
free OH groups, these silanols can adsorb to the metal surface, and by means of subsequent condensation and polymerization (usually at elevated temperatures), they can form a network (cross-linking) of Si-O-Si bonds (see Equations (2) and (3)) and create a continuous coating [41,53–55].

\[
\begin{align*}
R - Si(OR)_3 & \leftrightarrow R - Si(OR)_2 OH \\
R - Si(OH)_3 & \leftrightarrow R - Si(OH)(OH)_2 \\
(-Si - OH) + (OH - Si -) & \leftrightarrow -Si - O - Si - + H_2O \\
(-Si - OH) + (RO - Si -) & \leftrightarrow -Si - O - Si - + ROH
\end{align*}
\]

However, adsorption on the carbon steel surface is quite difficult for silanols, and the number of free OH groups on the metal surface plays an important role (see Figure 5). Neither the clean metal surface nor the conventional steel corrosion products (polymorphs of FeO(OH)) are suitable surfaces for the application of organofunctional silanes [56,57]. For this reason, it is very often recommended to expose the steel to an alkaline environment (pH ideally close to the isoelectric point, i.e., 9.5) [57] or to pickle the surface in sulfuric acid [58,59]. Sufficient amounts of OH groups for good adhesion to organofunctional silane can provide conversion coatings; in this respect, Ce\(^{III}\)-based coatings [60–62], phosphate coatings [63], and zirconium-based coatings [64,65], among others, have been successfully tested. The additions of Zr(NO\(_3\))\(_4\) directly to silane baths enhance the barrier protective effects of the resulting coating [66]. In engineering practice, zirconium (ZrCC)- and titanium (TiCC)-based conversion coatings are very often used in painted steel technology (often in combination) as a modern phosphate-free and chromate-free (Cr\(^{VI}\)) process [67]. Based on these facts, the application of ZrCC was preferred over other conversion coatings in this work. It is assumed that during the coating of APSS with ZrCC, the precipitation of ZrO\(_2\)-2H\(_2\)O and Zr(HPO\(_4\))\(_2\) (the phosphate formed is ultimately minor) occurs according to reactions (4)-(6) in the open pores of APSS on the steel surface. The conversion coating thus formed on the steel surface significantly improves the adhesion properties of organofunctional silane (GPTMS). It is further established that GPTMS adsorbs very readily to the APSS surface (even to the inner surface of open pores in the APSS coating) to form a continuous coating. These assumptions are shown in Figure 17.

ZrF\(^{5-}\)(aq) + 4OH\(^-\)(aq) → ZrO\(_2\)·2H\(_2\)O(s) + 6F\(^-\)(aq)  
H\(_2\)PO\(_4\)\(^-\) → HPO\(_4\)\(^2-\) + H\(^+\)  
Zr\(^{4+}\) + 2HPO\(_4\)\(^2-\) → Zr(HPO\(_4\))\(_2\)  

Figure 18 shows the E\(_{corr}\) and R\(_p\) (E\(_{corr}/R_p\)) trend for the samples of the plasma-sprayed Al\(_2\)O\(_3\) coating without additional surface treatment (APSS), then the APSS coating with the zirconium conversion coating (ZrCC), and finally with the application of hydrolysed GPTMS solution. From the measurement results, it is clear that APSS does not provide significant protection to the underlying steel due to its open porosity (the existence of pores larger than 10 µm in diameter; see Figure 14). The usual passive layer on the steel surface (the effect of the alkaline environment) does not form because of the presence of Cl\(^-\) in SCPS. Since the Rp value for the APSS samples is around 1.0 Ω·m\(^2\) throughout the exposure time, SCPS reaches the underlying steel through open porosity very quickly. The resulting corrosion products of the steel would subsequently very easily break down the integrity of the APSS coating if applied to the surface of the reinforcement in concrete. From this point of view, this coating cannot be considered suitable for application to the surface of concrete reinforcement. The results of the E\(_{corr}/R_p\) trend measurements further show that the protective effect of only the ZrCC conversion coating surface treatment (precipitation on the steel surface in open pores; see Figure 17) is quite negligible (the usual thickness of this surface treatment is only about 300 nm [68,69]). In this case, the measured R\(_p\) values do not differ throughout the exposure time from those measured for the APSS samples. It is possible to consider that chloride anions very quickly disrupt the continuity of the conversion coating, or with the ZrCC bath coating process. The coating fails to form on the steel surface in the open pores (for this type of samples, a short exposure time may be involved). A significant difference in the time dependence of E\(_{corr}\) and R\(_p\) was measured
for the APSS samples with the ZrCC and the GPTMS coating. It is evident, that in contrast to the application of ZrCC alone, organofunctional silane significantly affects the corrosion behaviour of APSS samples. Although the barrier protective effect of the coating is insignificant (low $R_p$ values at the beginning of the exposure, only two times higher than in samples without GPTMS), the $R_p$ values already increase sharply after about 15 h. This trend is steady, and apparently (although significantly slower than at the beginning of exposure) would exceed the period of the test. In this case, the $R_p$ values at the end of the exposure are approximately six times higher than those for the APSS and ZrCC samples. It can be expected that the dissolution of the organofunctional silane coating and the sealing of the pores in the plasma-sprayed $\text{Al}_2\text{O}_3$ coatings occur in SCPS during exposure. It can also be expected that the precipitation of insoluble silicon compounds occurs directly on the steel surface (exposed steel surface in open pores).

![Figure 17. Schematic of the surface occupation of steel sample with plasma-sprayed $\text{Al}_2\text{O}_3$ coating by ZrCC and GPTMS (displaying also the expected surface occupation of open pores in APSS).](image)

The measured impedance spectra (Bode plot: log $Z_{mod}$ vs. log frequency and phase angle vs. log frequency) with equivalent circuits used for its fitting are shown in Figure 19 (APSS coating only), Figure 20 (APSS coating with ZrCC), and finally Figure 21 (APSS coating with ZrCC and GPTMS). In the equivalent circuits (ECs), $R_{rel}$ is solution resistance, and $R_1$ and CPE1 represent pore solution resistance and $\text{Al}_2\text{O}_3$ layer capacity, respectively. $R_2$ and CPE2 represent phase boundary steel-pore solution. $R_3$ and CPE3 are associated with the high-frequency region and represent the influence of GPTMS. The used ECs are in the good agreement with the proposed ZrCC and GPTMS mechanism stated in Figure 17. The results of the specific resistances ($R_1$ to $R_3$) after 12 h, 72 h, and finally 168 h of exposure are plotted in Figure 22. The charge transfer resistance ($R_2$) for all three types of samples is the key to the evaluation of the corrosion process. There was a gradual increase during the exposure for the APSS samples, indicating a slight stabilization of the passive layer due to the alkaline environment (the protective effect of $\text{OH}^-$ anions in SCPS is more significant than the stimulating effect of Cl$^-$). In the case of samples with ZrCC addition, the situation was similar; there was only a slight increase in the charge transfer resistance ($R_2$), probably caused by the inhibition effect. There was a significant increase in $R_2$ in the case of GPTMS samples. This again indicates the inhibition of corrosion damage to steel by molecules released from the organofunctional silane coating (adsorption inhibition mechanism). The resistance $R_1$ (pore resistance) in the case of APSS decreased slightly during the exposure; this could be due to the increasing concentration of ions in the pores. In the case of the ZrCC samples, there was a slight increase in $R_1$ compared to APSS, indicating lower conductivity. For the GPTMS samples, an equivalent circuit with one extra
R-C element (R3, CPE3) was used. This element represents the top layer of the organosilane, which can form molecules large enough to partially block open pores up to 10 µm in size. Both R1 and R3 increased slightly during exposure, which may indicate the formation of larger molecules that subsequently increased surface and pore blockage.

Figure 18. Time dependency of $E_{\text{corr}}$ and $R_p$ for four parallel samples in simulated concrete pore solutions (overview; curves—mean values).

Figure 19. Time-dependent impedance spectra for APSS only coating (Bode plot: log $Z_{\text{mod}}$ vs. log frequency and phase angle vs. log frequency).
Figure 20. Time-dependent impedance spectra for APSS and ZrCC coating (Bode plot: log $Z_{\text{mod}}$ vs. log frequency and phase angle vs. log frequency).

Figure 21. Time-dependent impedance spectra for APSS + ZrCC and GPTMS coating (Bode plot: log $Z_{\text{mod}}$ vs. log frequency and phase angle vs. log frequency).

Figure 22. Point evaluation of R1–R3 (t) EIS spectra for all coated samples in SCPS.
Based on the above, a model of the predicted protective effect of GPTMS against the corrosion of the underlying steel coated with plasma-sprayed Al₂O₃ coating can be proposed; see Figure 23. It is clear from the literature that in the case of exposure to the silane coating in a strongly alkaline environment, the dissolution of the silanes occurs to form finely dispersed SiO₂ particles (and the formation of H₂O or the corresponding simple alcohols) [36,37,70–72]. The SiO₂ particles can converge to SiO₃²⁻ due to the strongly alkaline environment, as seen in reaction (7). This anion can diffuse and/or migrate (due to the presence of Fe²⁺/Fe³⁺ formed by the anodic corrosion process at the steel surface) to the steel surface in open pores and block the charge exchange reaction during the corrosion process (formation of a continuous layer of CaSiO₃ and/or FeSiO₃).

\[
\text{SiO}_2 + 20\text{H}^- \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O} \quad (7)
\]

Already amorphous SiO₂ particles may be able to effectively block the access of the electrolyte to the steel substrate in pores with smaller pore diameters. Regarding the inhibition of the corrosion process, it is necessary to discuss the mobility of Cl⁻ versus SiO₃²⁻ anions. Although there are very few relevant data on the mobility of SiO₃²⁻ ions (low stability and high reactivity), it can be concluded that the mobility of chloride anions will be higher (higher diffusion coefficient and lower ion radius) than that of SiO₃²⁻ anions [73–75]. However, the higher concentration of SiO₃²⁻ ions in the Al₂O₃ coating pores in the early stages of exposure may play an essential role in rapidly inhibiting the corrosion process. From this point of view, the degree of occupation of the steel surface in the open pores by the applied organofunctional silane may also be substantial.

![Figure 23. Proposed mechanism of protection of the steel surface in the case of the application of organofunctional silane coating (GPTMS) on the surface of plasma-sprayed Al₂O₃ coating (APSS).](image)

### 3.3. Bond Strength of Coated Plain Bar Steel Samples in Concrete

In the case of coated concrete reinforcement, it is necessary to verify the effect of the coating (its mechanical properties, surface roughness, surface contact angle, and possible corrosion in the concrete) on bond strength in concrete [24,25,76]. The bond strength of the reinforcement in concrete fundamentally influences the load-bearing capacity of the structure; a gradual decrease in the bond strength of the reinforcement in the concrete due to the corrosion damage of the steel surface can lead to collapse [28,29,77].

The roughness of the APSS coating is significantly higher than that of uncoated plain bars (see Section 3.1 and Figure 16) and is not significantly affected by the GPTMS coating. Thus, it is very likely that the increased roughness of APSS specimens will provide a significant increase in the bond strength of plain bars in concrete [25,76]. The surface contact angle is also important for the bond strength of the coated reinforcement in concrete. A good surface wettability of the coated concrete reinforcement ensures the perfect coverage.
of the surface with cement paste (the occupation of the surface by portlandite—Ca(OH)$_2$ crystals), which results in a higher bond strength [25,78,79]. The low surface wettability (high surface contact angle) of epoxy coatings results in a lower bond strength of the coated reinforcement in concrete [17,80,81]. For these reasons, the effect of the different surface treatments (APSS without topcoat, ZrCC, and GPTMS) on the steel surface contact angle was verified, and the results are shown in Figure 24 and subsequently in the bar chart in Figure 25. From the results, it is clear that the contact angle for the APSS sample surface (without topcoat) is approximately 36°, and the subsequent surface treatment via ZrCC increases the wetting angle (increases the surface hydrophobicity) to a wetting angle value of approximately 61° (the reason for this may be the formation of specific ZrF$_6$-rich Al-rich jagged structures, giving the surface a lotus flower effect [82]). If the topcoat is composed of ZrCC and GPTMS, the surface hydrophilicity increases very significantly (the wetting angle is 0°). It is evident that GPTMS can significantly cover the surface of the plasma-sprayed Al$_2$O$_3$ coating and avoid the influence of ZrCC on the intrinsic wettability of the surface. A prior application of ZrCC is not strictly necessary to apply GPTMS to the APSS effectively. The reason for the increase in the wettability of the Al$_2$O$_3$ surface is the presence of OH groups from the open oxirane ring of 3-glycidyloxypropyltrimethoxysilane [83,84]. The surface Al$_2$O$_3$ plays a significant role in the hydrophilic properties of GPTMS—hence the considerable level of compatibility of the two solids.

Figure 24. The surface contact angle for each type of coating.

Figures 26 and 27 show the results of the bond strength tests of plain steel bars in concrete of the C30/37 strength class (the average cube strength of the concrete was 47.7 ± 2.2 MPa). Figure 26 shows the curves (mean values) of bond stress versus slip, and Figure
Figure 25 shows a bar chart reflecting the statistically evaluated ultimate bond strength and slip results for each coated plain bar specimen.

Figure 25. Bar chart showing the surface contact angle measurements for all coatings (see Figure 24).

Figure 26. Results of pull-out tests (overview; curves—mean values).
If the bond strength is tested on plain bars, then the overall bond force \( T_{c,i} \) (see Equation (8)) cannot be influenced by the force of the mechanical resistance of the specific concrete cover layer \( f_{\sigma} \). These facts are described by Equations (9) and (10), and the individual variables of these equations are summarized in Table 7. The contact area of the test plain bars with the concrete is determined only by the total area of the bar body \( (A_b) \) and is not affected by the total area of the bar ribs \( (A_r) \) [24,25,76,85,86].

\[
T_{c,i} \approx i_{fad}^{A,b} + i_{f}^{A} + i_{f_{\sigma}}^{A}
\]  
\[
i_{fad}^{A} \gg i_{fad}^{A,b} + i_{f}^{A} + i_{f_{\sigma}}^{A}
\]  
\[
A_r = 0 \rightarrow T_{c,i} \approx i_{fad}^{A,b} + i_{f}^{A,b}
\]

Table 7. Description of individual variables from Equation (8).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{c,i} )</td>
<td>bond force</td>
<td>N</td>
</tr>
<tr>
<td>( i )</td>
<td>contribution of force</td>
<td>N</td>
</tr>
<tr>
<td>( f_{\text{fad}} )</td>
<td>complete adhesion of cement paste force</td>
<td>N</td>
</tr>
<tr>
<td>( f_{f} )</td>
<td>friction force</td>
<td>N</td>
</tr>
<tr>
<td>( f_{\sigma} )</td>
<td>force of mechanical resistance of specific concrete cover layer</td>
<td>N</td>
</tr>
<tr>
<td>( A_b )</td>
<td>total area of bar body</td>
<td>m(^2)</td>
</tr>
<tr>
<td>( A_r )</td>
<td>total area of bar ribs</td>
<td>m(^2)</td>
</tr>
</tbody>
</table>

Although plain bar steel is rarely used as a concrete reinforcement (rather, for prefabricated parts, mostly ribbed steel reinforcement is used—for example, B500B), bond strength testing (pull-out test or beam test) using plain bars can very sensitively take into account the influence of the coating used on bond strength in concrete (the test factors are the complete adhesion of cement paste force \( f_{\text{fad}} \) and friction force \( f_{f} \)). If the bond strength of the B500B reinforcement with concrete is tested, then the results of \( T_{c,i} \) are influenced by the mechanical properties of the concrete at the reinforcement/concrete phase interface.

The results of the APSS bond strength tests (with and without topcoat) indicate that the increase in the roughness of the plain bar in the case of the application of plasmasprayed Al\(_2\)O\(_3\) coating by a factor of approximately 10 results in an increase of the ultimate
bond strength in concrete by a factor of more than 4 (increase in the effect of the fi factor). However, the influence of wettability on the ultimate bond strength is also evident (surface wettability is influenced by the fa factor). When only ZrCC was applied to the plasma-sprayed Al2O3 coating, the surface hydrophobicity increased and the surface contact angle increased by approximately 70%, resulting in a decrease in ultimate bond strength of approximately 30% compared to APSS (without topcoat). On the contrary, the increase in surface wettability when GPTMS was applied not only eliminated the negative effect of the ZrCC coating, but it also increased the ultimate bond strength of the plasma-sprayed Al2O3 coating by approximately 10%. Through the bond strength tests, it was verified that the applying of any coating (APSS or APSS with topcoats) prolongs the slip of plain bars. The gradual destruction of the top layer of plasma-sprayed Al2O3 coatings occurs in the case of APSS (cohesion breaking in the coating), which has a lower adhesion to the core of the APSS coating (the adhesion of the top layer of plasma-sprayed coating may be lower due to the increasing thermal insulation properties of the surface). The application of ZrCC can disrupt the non-cohesive top layer of Al2O3 through the presence of free F\(^{-}\) anions in the coating (Equation (4)), which can be removed during the formation of the concrete cube samples prior to bond strength testing using the pull-out test. Therefore, the slip for ZrCC specimens may be lower than that for APSS specimens without a topcoat. However, the reduction in bond strength can also be caused by partial displacement between the two layers of the APSS coating. Increasing the wettability of the topcoat through the application of GPTMS increases the ultimate bond strength and the slip value. In this case, the disturbance of the topcoat layer of organofunctional silane due to the formed alkaline concrete pore solution of concrete during the preparation of specimens for bond strength testing can be discussed.

In general, it can be summarized that applying an APSS coating significantly increases the ultimate bond strength (the effect of increase in surface roughness), and the subsequent application of organofunctional silane in the form of GPTMS provides a further increase in ultimate bond strength. The effective necessity of applying ZrCC before applying GPTMS is not evident from the bond strength testing results. The sufficient adhesion and compatibility of organofunctional silane with Al2O3 have been previously demonstrated [34,35,87–89]. However, coating the concrete steel reinforcement of concrete with APSS and subsequently with, e.g., GPTMS increases the slip in the bond strength testing, i.e., even small shear forces can slightly displace the reinforcement and stimulate crack formation in the structure, which may reduce its overall load-bearing capacity. Structures containing such coated reinforcement may exhibit a higher sensitivity to, for example, cyclic loads.

4. Conclusions

This paper describes the effect of the plasma-sprayed Al2O3 coating (APSS—core coating) on the corrosion behaviour and bond strength of plain steel bars in concrete. In order to increase the corrosion resistance of the APSS porous coating, other surface treatments (topcoats) were tested, namely, zirconium-based conversion coatings (ZrCC) and a combination of ZrCC and organofunctional silane (3-glycidyloxypropyltrimethoxysilane)—GPTMS.

The most important findings of this study can be summarized as follows:

- The core coating (APSS) exhibited significant adhesion to the steel surface and increased the surface roughness compared to the uncoated plain bars.
- Mercury porosimetry results confirmed the significant porosity of the core coating with the presence of open pores.
- The results of electrochemical testing in simulated concrete pore solution contaminated with chloride anions confirmed the insufficient protective properties of the core coating. Similarly, the application of only ZrCC coating (topcoat) on the APSS surface increases the corrosion resistance insignificantly.
- A twofold protective effect of the combined organofunctional silane-GPTMS coating on the underlying carbon steel is based on the dissolution of the GPTMS coating (topcoat) in the highly alkaline simulated concrete pore solution environment, forming mainly \( \text{SiO}_2^{2-} \), blocking the pores of the APSS coating (open pores up to 10 \( \mu \text{m} \) in size), and inhibiting the corrosion process of the underlying steel in open pores.

- Increasing the roughness of the plain steel bars by applying a core coating (APSS) together with increasing the wettability of the GPTMS topcoat leads to a substantial increase in bond strength in concrete. However, the APSS coating (with or without a topcoat) exhibited higher slip values. This is why further investigations of the possible higher sensitivity of reinforced concrete structures with this reinforcement to cyclic loading are necessary.

- The application of the ZrCC coating as the only topcoat increases the surface contact angle, which results in the reduced bond strength of plain bars in concrete (compared to APSS-coated steel without topcoat).

Further research in this area should focus on investigating the protective properties of other groups of organofunctional silanes (amino-silane, mercapto-silane, etc.). In particular, the use of thicker coatings (prepared using tensides at higher exposure temperatures) should be verified. The effects of these coatings on bond strength should be also assessed.

In common civil engineering structures, the application of a combined surface treatment (APSS with topcoat) to the surface of conventional carbon steel reinforcement would be challenging. The major drawbacks are significant economic, technological, and time requirements associated with the implementation of a core APSS coating. The subsequent application of organofunctional silane is less demanding. However, this topcoat is insufficiently resistant to abrasion. This is why it needs to be handled with caution during storage and the subsequent execution of the reinforced concrete structure. This complex coating system can be beneficially used locally, particularly in areas with extreme depositions of chloride anions, providing sufficient protection against corrosion and increasing bond strength in concrete.

**Author Contributions:** Methodology, K.H.; Validation, V.S.; Formal analysis, M.J.; Investigation, P.P., N.P. and J.F.; Resources, V.B.; Writing—original draft, P.P. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research has been supported by the Czech Science Foundation under Grant No. 20-24234S.

**Data Availability Statement:** Data are contained within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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