Electrochemical testing of thermal spray coatings using gel electrolytes

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Abstract. The use of electrochemical methods allows fast and inexpensive corrosion measurements of bulk materials with high significance. In the case of thermal spray coatings, electrolyte penetration into open pores up to the substrate material can cause undesired mixed potentials. Furthermore, the implementation of complex geometries or rough surfaces remains a problem. Preconditioning of the surface or the use of the electrochemical cell is required to eliminate leakage. Therefore, reliably measuring corrosion is still a challenging task. This undermines fast monitoring of corrosion performance as a part of the production process. Gelling agents are investigated to increase the viscosity of many electrolytes. A procedure has been developed to determine the concentration level and the mixing conditions. Passivation and pitting-corrosion testing are performed on thermal spray AISI 316L coatings. The electrochemical potential curves as well as the corroded surface layers were studied in comparison to a liquid electrolyte. The suitability of the test on rough surfaces in the sprayed condition was investigated. The results prove the novel approach as an alternative to established electrochemical test methods with extended application range.

1. Introduction
Thermal spray coatings are commonly used to protect surfaces under harsh environmental conditions. The most important applications are providing protection against corrosion and tribological loads. The most challenging requirement for high quality coatings is the corrosion resistance. Complex and cost-intensive preliminary studies are often conducted by standardized test conditions, which are usually developed for bulk material, e.g. salt-spray test, Corrodkote, or potentiodynamic polarization measurement. The open porosity of the coating structure inhibits a selective assessment of the coating properties. In general, the corrosive media penetrate the microporous coating structure and reach the substrate material. This leads to the fact, that the area of the corrosion attack is unknown. Hence, mixed potentials and superimposed corrosion processes are the result of the interaction between coating and substrate.

A quick localized validation test for the quality of coating during production processes is not available so far. Therefore, screening tools for monitoring the quality of coatings during the production process would be beneficial. The most common influencing factors include deviation in quality of feedstock material or fluctuations of process parameters. Electrochemical methods can provide quantifiable results to classify material-specific properties. By electrochemical testing, the relationship of the current density in regards to the potential can be identified. However, the high complexity of the measuring arrangement...
and the low viscosity of the testing agent have thus far prevented widespread use of this process. To overcome these issues, different adaptions are required. Representative and limited potential areas are sufficient to gather reliable information. Therefore, the duration time of validation tests can be reduced significantly. Increasing the viscosity can successfully prevent penetration by the corrosive media. Therefore, gels can be a reliable alternative. One established test is the KorroPad indication test, which focuses on the visualization of corrosion processes with indicator-doped gel pads [1–4]. KorroPad is designed for passivating steels to detect their pitting-corrosion behavior [3]. Few studies have been conducted in recent years which focus on high viscosity gels as agents for corrosion monitoring with electrochemical-instrumented experiments [5–10]. The intended applications are the validation of corrosion properties of sculptures and monuments with non-destructive tests [5,9] and the rebuilding of specific atmospheric conditions like moisturizing films on zinc coatings [7] or artificial mud [8]. Most of the studies use agar-gelled NaCl electrolytes [1–10], with little investigation into the properties of these gels [11,12]. Because of their interaction, the combination of thickeners and electrolytes is still a big challenge. In the case of thermal spray coatings, the gel electrolytes show beneficial properties due to the transfer of the corrosion attack to the surface of the coating.

In a first study, the feasibility of gel electrolytes in potentiodynamic polarization measurements of thermal spray stainless-steel coatings on low carbon-steel substrates are determined. The focus is on gel preparation of NaCl and H$_2$SO$_4$ electrolytes to prevent infiltration into the specific microstructural coating features and to determine the level of corrosion attack compared to low viscous liquid electrolytes.

## 2. Experimental and materials
Corrosion-resistant AISI 316L stainless-steel coatings were prepared by atmospheric plasma spraying (APS) and wire arc spraying using either air or nitrogen for atomization. As powder material, the gas-atomized 80.46.1 powder (GTV Verschleißschutz GmbH, Luckenbach, Germany) with a particle size distribution of -53+22 µm was selected and processed with the GTV APS F6 gun. Arc sprayed AISI 316L coatings were deposited by using the wire arc spray unit VISU ARC 350 (Oerlikon Metco, Wohlen, Switzerland) with the Ø 1.6 mm thick 85T wire (TAFA Inc. A Praxair Surface Technologies Company, Concord, NH, USA). The composition of the spray materials and the process parameters are listed in table 1 and table 2.

| Table 1. Nominal composition of the AISI 316L feedstock materials. |
|---------------------------------|---------|---------|---------|---------|---------|--------|--------|--------|--------|
| AISI 316L                       | Cr  | Ni   | Mo    | Mn    | Si     | C      | P      | S      | Fe     |
| Powder                          | 17  | 12.5 | 2.5   | -     | -      | 0.02   | -      | -      | 1      |
| Wire                            | 17  | 12   | 2.5   | 2     | 1      | 0.08   | 0.045  | 0.03   | bal.   |

A low carbon steel EN S235 with the dimension of Ø 40 mm x 10 mm was used as the substrate material. Grit blasting was conducted before the single-side coating process using corundum EK F 24 (~800 +600 µm), air pressure of 2.5 bar, a nozzle-surface distance of 250 mm, and an angle of 70°. Afterward, the substrates were cleaned in an ethanol ultrasonic bath. Prior to the electrochemical corrosion test, the coatings were ground and polished up to a diamond paste of 9 µm.
Table 2. APS and wire arc spray parameters.

| Process                  | Ar (slpm) | H₂ (slpm) | Current (A) | Voltage (V) | Atomizing gas pressure (bar) | Powder flow (g/min) | Spraying distance (mm) | Offset (mm) | Surface velocity (m/s) |
|--------------------------|-----------|-----------|-------------|-------------|-----------------------------|---------------------|------------------------|-------------|------------------------|
| APS                      | 50        | 10        | 600         | -           | -                           | 2 x 38              | 140                    | 5           | 1                      |
| Wire arc spraying        | -         | -         | 180         | 27          | 4                           | -                   | 130                    | 6           | 1.2                    |
| - Air                    |           |           |             |             |                             |                     |                        |             |                        |
| Wire arc spraying        | -         | -         | 140         | 42          | 7                           | -                   | 100                    | 5           | 1                      |
| - N₂                     |           |           |             |             |                             |                     |                        |             |                        |

Two types of electrolytes were considered for the electrochemical corrosion tests choosing 0.5 M NaCl to investigate the pitting corrosion behavior and 0.05 M H₂SO₄ to determine the passivation properties of the AISI 316L coatings. The electrolytes were prepared by gelling the liquid electrolyte with polyacrylic acid (Carbopol 71G NF Polymer, Lubrizol, Advanced Materials Europe, Brussels, Belgium). The electrolyte concentration was not adjusted due to the small additions of Carbopol. The amount of Carbopol was adjusted to increase the viscosity up to 450–500 mPa·s suitable to prevent penetration of the open porosity of the thermal spray coatings. Therefore, a mass fraction of 2.5 % Carbopol was added into the NaCl electrolyte and a mass fraction of 6.5 % into the H₂SO₄ electrolyte.

The viscosity was measured by tuning fork vibration method using the viscometer (Vibro Viscometer SV-10, A&D Company, Limited, Tokyo, Japan) at temperatures of 25 °C. The NaCl electrolyte was neutralized using NaOH to reach a pH value of 7. The pH value of H₂SO₄ electrolyte was 1.2. Using a motorized stirrer for the gel electrolyte preparation turned out to be the best method to prepare homogeneous gels. Furthermore, the practicality of the gel electrolytes was assessed by determining the temperature-viscosity dependence of the applied electrolyte compositions.

The feasibility of gel electrolytes for corrosion testing of thermal spray coatings was determined by measuring potentiodynamic polarization curves in a 3-electrode cell arrangement. The cell consisted of a silver chloride reference electrode (Ag/AgCl saturated KCl electrode), a Pt plate as a counter electrode, and the sample acted as a working electrode with a testing area of Ø 1 cm. The measurement was controlled with a potentiostat PS6 (Sensortechnik Meinsberger GmbH, Waldheim, Germany). For all tests, the volume of the electrolytes was around 200 ml. After measuring the open circuit potential for 15 minutes, the potential scan was conducted over a range of 950 mV, starting at -250 mV relative to the open circuit potential, and a scan rate of 0.1 mV/s. The result of the polarization measurements were used to derive the corrosion potentials E_{corr} and corrosion current densities i_{corr} using the Tafel slopes. A comparison between a liquid and gel electrolyte using the same electrochemical cell and identical parameters was made and the corrosion attack was assessed.

Metallographic investigations were conducted to investigate the corrosion attack. The optical microscope GX51 (Olympus, Shinjuku, Japan) equipped with a SC 50 camera (Olympus, Shinjuku, Japan) was used for analysis of the cross-sections.

3. Results and discussion

3.1. Coating characterization

Figure 1 shows the AISI 316L coatings in the sprayed condition, revealing the altered structural properties with the different thermal spray processes. The APS coating contains lamellar and oxidized splats, non-molten particles, and pores (figure 1a). The porosity content of (6.7 ± 1.6) % and a coating thickness of (287 ± 14) μm were measured. Figure 1b and figure 1c show the typical lamellar micro-structure of wire arc sprayed coatings. Using compressed air as the atomizing gas causes significant
oxidation of the spray particles, while nitrogen reduces this effect. With a porosity of (3.1 ± 0.6) % and (1.9 ± 0.3) %, the arc sprayed coatings are denser than the APS coating. The coating thickness is (470 ± 40) µm and (540 ± 21) µm, respectively.

![Figure 1. AISI 316L coatings’ microstructure in polished condition. (a) APS, (b) wire arc spraying using air and (c) nitrogen as atomizing gas.](image)

3.2. Gel electrolyte characterization

To prepare gel electrolytes, which prevent the penetration in the micropores of thermal spray coatings, the gelling of the 0.5 M NaCl and 0.05 M H₂SO₄ electrolyte was examined as it related to the addition of the thickener Carbopol. The thickening results in the ability of the polyacrylic acid to form a networked microgel structure in aqueous solutions [13]. Figure 2a represents an exponential increase of the viscosity with the amount of Carbopol addition and shows different gelling behavior, which depends on the electrolyte. In general, electrolytes tend to reduce the viscosity of Carbopol gels and additionally show a pH dependency of the gelling properties. Maximum viscosity is achieved by neutralization [14,15]. Hence, a neutralization with NaOH to a pH value of 7 during the preparation of NaCl electrolyte was necessary to increase the viscosity. The viscosity was defined between 450–500 mPa·s for the present study. Repetitions of the viscosity measurements after several days revealed that the gel electrolytes continue to be stable at room temperature, which is beneficial for ease of storage.

Another experiment focused on the temperature stability of the gel electrolytes (figure 2b). The NaCl gel electrolyte with a mass fraction of 2.5 % Carbopol addition shows a steady viscosity level up to 65 °C. In contrast, a steep decline can be observed for H₂SO₄ gel electrolyte with a mass fraction of 6.5 % Carbopol. Figure 2c and figure 2d show images of both gel electrolytes. Due to the gelling agent, the electrolytes become opaque. During mixing, mechanical entrapment and chemical generation caused the formation of bubbles in the H₂SO₄ electrolyte, which could not be prevented in spite of trying several different preparation methods. Kim et al. investigated the microstructure properties of the Carbopol gel network in detail and faced similar problems [16].
3.3. Electrochemical-instrumented corrosion tests using gel electrolytes

Figure 3a shows the polarization curves of the APS and wire arc sprayed AISI 316L coatings as well as the low carbon steel substrate using 0.5 M NaCl gel electrolyte in comparison with the corresponding liquid electrolyte. As expected from the galvanic series and the Cr content, the low carbon steel substrate shows the lowest corrosion potential. The wire arc sprayed coating with nitrogen atomizing gas possesses the highest corrosion potential $E_{\text{Corr}}$. With the increase in oxide content, the corrosion potential decreases for APS and air-atomized wire arc sprayed coatings. Figure 3b summarizes the behavior of the gel electrolyte during the potential scan. When the corrosion begins, the gel electrolyte starts to gel further and the corrosion products remain at the surface causing a smoother ascent on the anodic slope (figure 3a). In table 3, the corrosion potentials $E_{\text{Corr}}$ and corrosion current densities $i_{\text{Corr}}$ were derived from the polarization curves using the Tafel slope. As a result, comparable values could be determined independently of the use of liquid or gel electrolytes. This ensures a direct comparability of the results. However, no significant influence on the characteristics of the current density-potential curve can be observed from the formation of mixed potentials by substrate contact when using liquid electrolytes.
Figure 3. (a) Polarization curves of AISI 316L coatings tested in 0.5 M NaCl electrolyte and gel electrolyte. (b) Gel electrolyte behavior during polarization scan.

Table 3. Summary of the results of the potentiodynamic polarization tests.

| 0.5 M NaCl electrolyte | Substrate | APS | Wire arc spraying - Air | Wire arc spraying - N₂ |
|------------------------|-----------|-----|------------------------|----------------------|
| **E<sub>Corr</sub>** (mV) | liquid   | -515 | -168                   | -237                 | -99            |
|                        | gel      | -502 | -183                   | -221                 | -86            |
| **i<sub>Corr</sub>** (mA/cm²) | liquid | 0.009 | 0.028                   | 0.023                 | 0.005          |
|                        | gel     | 0.007 | 0.023                   | 0.034                 | 0.007          |

Figures 4 and 5 compare the corrosion phenomena related to the used electrolyte. In contrast to liquid electrolytes, gels cause a homogeneous corrosion attack. In addition, crevice corrosion at the edge of the test area can be prevented. Due to the open porosity, the liquid electrolyte corrodes the steel substrate and several isolated rust spots appear at the coating’s surface. This is in accordance with [5,6,9] who studied agar-based NaCl electrolytes.

Figure 4. Comparison of the corrosion attack at the AISI 316L coating surface using 0.5 M NaCl electrolyte (upper row) and gel electrolyte (lower row).

Figure 5 shows the cross-sections of the different coatings for NaCl electrolyte in both liquid and gel state. The duration of the experiments at high current densities caused a severe corrosion attack of the
coatings. However, the gel electrolyte prevented the penetration of the coatings up to the substrate (figure 5b, d, and f in comparison with figure 5a, c and e).

Figure 5. AISI 316L coatings’ microstructure after electrochemical corrosion tests in 0.5 M NaCl electrolyte and gel electrolyte, respectively, APS (a & b), wire arc spraying (c & d), and wire arc spraying using nitrogen as atomizing gas (e & f).

Figure 6 shows the first results of the experiments with H₂SO₄ electrolytes. In a direct comparison between liquid and gel electrolytes, similar corrosion potentials can be detected. However, the active and passive sections of the curves deviate. The main issue is the bubble containing gel electrolyte (figure 2d), which leads to insufficient coverage of the corrosion area (figure 6, small image). In addition, the contact area of the sample and the electrolyte varies, particularly because of the infiltration of the coating by the liquid electrolyte, leading to different current densities.
Figure 6. Polarization curves of AISI 316L wire arc sprayed coatings tested in 0.05 M H$_2$SO$_4$ electrolyte and gel electrolyte.

4. Conclusions
In this study, the influence of electrolyte viscosity in terms of potentiodynamic polarization measurements of thermal spray coatings was investigated. AISI 316L coatings were produced using APS and wire arc spraying processes with different atomizing gases. The corrosion behavior of the coatings and the substrate material were determined by potentiodynamic polarization tests in 0.5 M NaCl and 0.05 M H$_2$SO$_4$ electrolytes. With polyacrylic acid (Carbopol), the viscosity of the electrolytes was successfully increased to 450–500 mPa·s. The used polyacrylic acid, which gels at room temperature, shows disadvantages regarding the production of homogeneous gel electrolytes. However, the suitability of gel electrolytes was proven by comparative measurements with liquid electrolytes. Independent of the coating structure, a comparable trend of the measurement curves could be seen. This proves that mixed potentials exert only a minor influence on the measurement. Cross-section images in the area of corrosion measurement show that infiltration of the coating structure can be prevented by using gel electrolytes. The electrochemical-instrumented tests are capable of revealing variations in the microstructure of coatings such as oxide content, alloying elements, and porosity. Using gel electrolytes in combination with electrochemical-instrumented methods can be beneficial for quality control in the production of thermal spray coatings. Construction of a modified electrochemical test cell would support the transfer of electrochemical testing from theory into practice as well as permits the usage of manifold electrolyte composition. Nevertheless, more experimental test data is necessary to classify the test method for thermal spray coatings.

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References
[1] Burkert A, Klapper H S and Lehmann J 2012 Novel strategies for assessing the pitting corrosion resistance of stainless steel surfaces Materials and Corrosion 64 8 675-682
[2] Rosemann P, Müller Th, Babutzka M and Heyn A 2015 Influence of microstructure and surface treatment on the corrosion resistance of martensitic stainless steels 1.4116, 1.4034 and 1.4021 Materials and Corrosion 66 1 45-53
[3] Kauss N, Heyn A, Halle T and Rosemann P 2019 Detection of sensitisation on aged lean duplex stainless steel with different electrochemical methods *Electrochimica Acta* **317** 17-24
[4] Rosemann P and Kauss N 2018 Visualisierung werkstoffbedingter Lochkorrosionsanfälligkeit durch die KorroPad-Prüfung *WOMAG* **7-8** doi: 10.7395/2018/Rosemann1
[5] Ramírez Barat B and Cano E 2019 Agar versus agarose gelled electrolyte for in situ corrosions studies on metallic cultural heritage *ChemElectroChem* **6** 2553–2559
[6] Monrrabal G, Ramírez Barat B and Cano E 2018 Non-destructive electrochemical testing for stainless-steel components with complex geometry using innovative gel electrolytes *Metals* **8** doi: 10.3390/met8070500
[7] Babutzka M and Heyn A 2017 Dynamic tafel factor adaption for the evaluation of instantaneous corrosion rates on zinc by using gel-type electrolytes *IOP Conf. Ser.: Mater. Sci. Eng.* **181** 012021
[8] Spark A J, Cole I, Law D, Marney D and Ward L 2016 Investigation of agar as soil analogue for corrosion studies *Materials and Corrosion* **67** 1 7-12
[9] Monrrabal G, Guzmán S, Hamilton I E, Bautista A and Velasco F 2016 Design of electrolytes for electrochemical studies on metal surfaces with complex geometry *Electrochimica Acta* **220** 20–28
[10] Subbiah K, Velu A, Kwon S J, Lee H S, Rethinam N and Park DJ 2018 A novel in-situ corrosion monitoring electrode for reinforced concrete structures. *Electrochimica Acta* **259** 1129-1144
[11] Umoren S A, Li Y and Wang F H 2010 Synergistic effect of iodide ion and polyacrylic acid on corrosion inhibition of iron in H$_2$SO$_4$ investigated by electrochemical techniques *Corrosion Science* **52** 2422-2429
[12] Lee W K, Lim Y Y, Leow A T C, et al. 2017 Factors affecting yield and gelling properties of agar *J Appl Phycol* **29** 1527–1540
[13] Carnalo J O and Naser M S 1992 The use of dilute viscometry to characterize the network properties of carbopol microgels *Collois Polym Sci* **279** 183-193
[14] Technical Data Sheet TDS-730 2010 Viscosity of Carbopol® polymers in aqueous systems Lubrizol Advanced Materials Inc., Edition August 13, 2010
[15] Giuseppe E di, Corbi F, Funicello F, Massmeyer A, et al 2015 Characterization of Carbopol® hydrogel rheology for experimental tectonics and geodynamics *Tectonophysis* **642** 29-45
[16] Kim J Y, Song J Y, Lee E J and Park S K 2003 Rheological properties and microstructures of Carbopol gel network system *Colloid Polym Sci* **281** 614-623