Improving the corrosion resistance of thermally sprayed zinc- and zinc-aluminum coatings by anodizing

A. Mertke, R. Feser, D. Proba, University of Applied Sciences South Westphalia, Iserlohn, Germany

Abstract

The importance of thermally sprayed coatings on steel structures for corrosion protection has recently increased. Thermally sprayed zinc and zinc-aluminum coatings are usually used in highly corrosive marine environments. The interesting thing about such sprayed coatings is that with ongoing corrosive load the layer porosity decreases by an internal oxidation and the corrosion resistance of these coatings increases simultaneously.

The aim of this work was to improve the corrosion resistance of zinc and zinc-aluminum spray coatings by additional anodizing. For this purpose anodizing of zinc spray coatings was firstly investigated in three different electrolytes. In the second step, zinc anodizing in electrolyte with the most promising behavior was optimized by changing the anodizing parameters. Then in the last step, thermally sprayed zinc-aluminum coatings were anodized in the electrolyte with optimized oxidation parameters. The effects of anodic oxidation were investigated by means of electrochemical measurements, scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX) and visual observations. Anodizing process has improved polarization resistances of both coatings considerably.
Results of long-term investigations will be presented in the future.

1 Introduction

The economic interest in thermal spraying, a process developed by M. U. Schoop [1] over 100 years ago, has recently increased in different industrial sectors. Because of advantages such as the single-sided coating and the possibility to coat large-sized, but also high-strength steel constructions, thermal spraying plays an important role in corrosion protection. Based on good corrosion resistance, ZnAl15 spray coatings are preferably used in aggressive environments, such as for the protection of bridges [2] and for the protection of offshore wind energy devices (OWEA) [3]. Supporting constructions of offshore wind energy devices are usually protected by duplex systems. These systems consist of a ZnAl15 spray metallization, which is usually post-treated by an organic sealer, and one or more organic topcoats [3]. Post-treatment of such coatings is an important element for improving corrosion protection. But not in all desirable applications spray coatings can be treated with organic sealers, as shown by results of spray galvanizing of high strength screw connections, which are currently under development [4, 5]. Because of that zinc anodizing for post-treating thermally sprayed coatings was examined in this work.

Anodizing of zinc and anodizing of aluminum are completely different in formation mechanism, chemistry and structure of the oxide layers. In contrast to aluminum, zinc is usually anodized by using alternative current (AC) and exhibits oxide layers, which are formed by complex structure consisting of zinc ions, oxides and different anions from the electrolyte, such as phosphates, chromates and tungstates [6, 7]. Benefits, for example formation of uniform oxide layers over the entire surface, high resistance against temperature, abrasion, and corrosion, but also the excellent paint adhesion, which are mentioned in literature [6, 7], make this post-treatment very attractive for a variety of applications without or with an additional topcoat. It is known that oxide layers produced in electrolytes based on hexavalent chromium, exhibit particularly high corrosion resistance, but due to its toxicity, electrolytes without chromium were used in this work.

The aim of this work was to test the feasibility of a post-treatment based on anodizing process for thermally sprayed Zn and ZnAl15 coatings. That was investigated by means of electrochemical measurements, scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX) and visual observations.

2 Experimental

Samples consisting of ac-sprayed [8] zinc and zinc-15% aluminum on mild steel were produced by Grillo Werke AG. Before metalizing, the steel surface was blast cleaned with corundum. Table 1 shows a summary of the spraying parameters.

Table 1: Overview of spraying parameters

	Wire feed rate [m/min]	Working current [A]	Working voltage [V]	Pressurized Air [bar]	Spraying distance [mm]	Spraying position	Coating-thickness [µm]
Zn-coating	36	80	18,5	4	150	horizontal	70
ZnAl15-coating	36	70	19	4	150	horizontal	70

This work is divided into three steps, which are presented in figure 1.

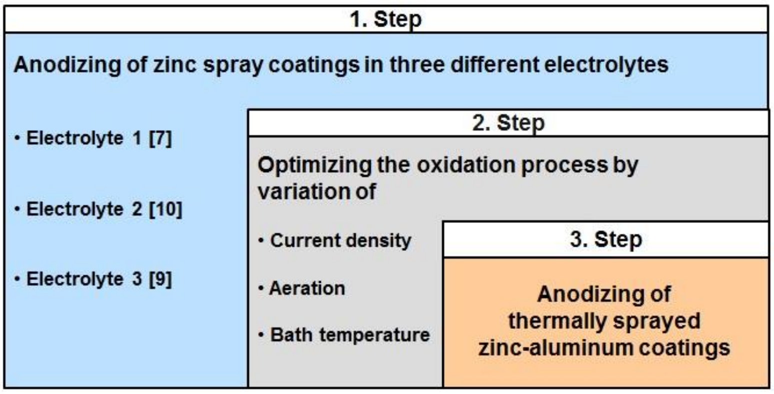

Figure 1: Research methodology

In the first step only thermally sprayed zinc coatings were anodized in three different electrolytes. Table 2 shows the compositions of these electrolytes. Only chromium-free electrolytes were used.

Table 2: Composition of electrolytes

	Electrolyte 1 [7]	**Electrolyte 2 [10]**	**Electrolyte 3 [9]**
Zinc coating	41g/L WO_3*H_2O 98ml/L 28% NH_4OH 66ml/L 85% H_3PO_4 18,5g/L NH_4F	28 g/L NaOH 10 g/L $NaClO_2$	17 g/L NaOH 12 g/L $NaNO_2$

In the second step, anodizing in electrolyte with the highest potential was optimized by changing the current density, bath temperature and bath aeration. Then in the last step, thermally sprayed zinc-aluminum coatings were anodized in the electrolyte with optimized oxidation parameters.

All these systems were investigated by linear polarization in 0,1M NaCl solution. Layer composition for and after anodizing were examined by means of optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray microanalysis (EDX) and visual observations.

3 Results

3.1 Anodizing of zinc spray coatings

3.1.1 Measurement of driving voltage during anodizing

During the anodizing of thermally sprayed zinc coatings, driving voltages were measured (figure 2). Two different behaviors were recognized. The driving voltage during anodizing process increased in electrolyte 1 and decreased in other electrolytes. Because of the Ohm's law, the driving voltages already give a first indication about the protection behavior of produced oxide layers.

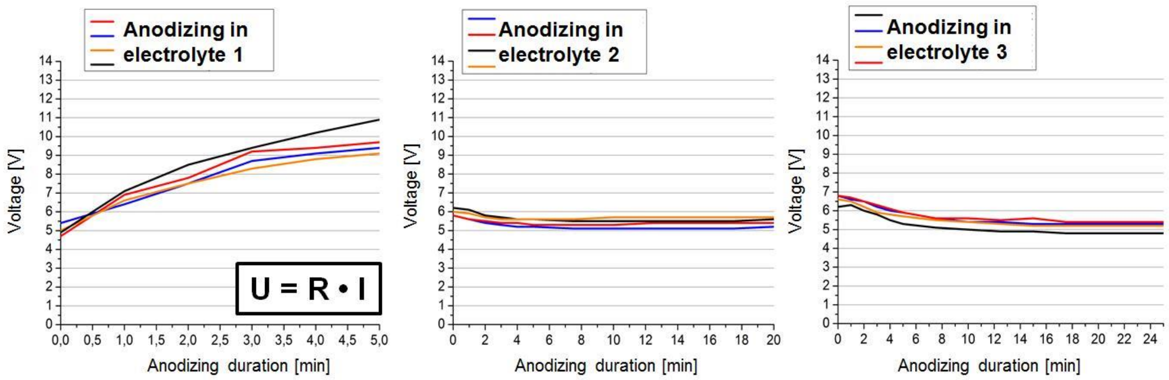

Figure 2: Development of the drive voltage during anodizing of zinc spray coatings

3.1.2 Visual observation

The oxidized surfaces appear black, as already mentioned in literature. Figure 3 shows the coating systems which were examined in the first step. Only oxide layer produced in electrolyte 1 appears especially homogeneous.

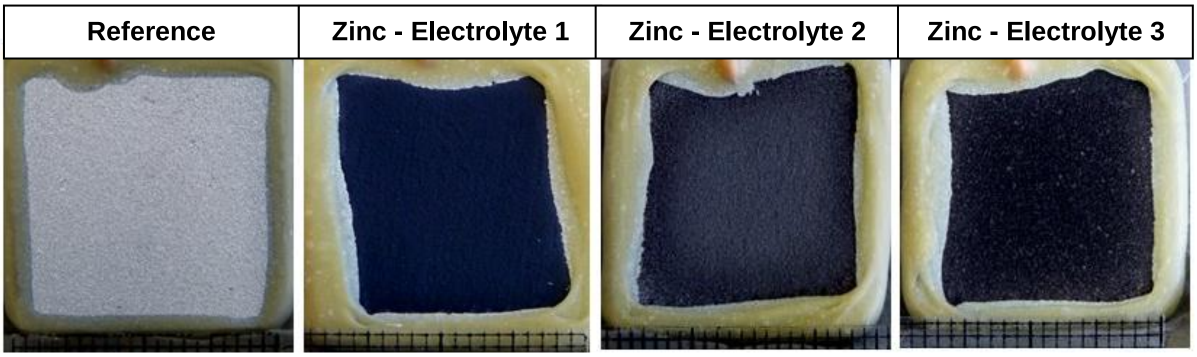

Figure 3: Zinc spray coatings anodized in three different electrolytes

3.1.3 Linear polarization

Linear polarization was carried out in air saturated 0,1M NaCl solution to study the influence of oxide layers to electrochemical behavior. In these investigations a three electrode system was used with the saturated Ag/AgCl electrode as reference electrode, platinum counter electrode and samples as working electrode.

Table 3 shows the experimental parameters of linear polarization. After 15 minutes of air flushing, anodic and cathodic curves were recorded separately starting from open circuit potential (OCP).

Table 3: Experimental parameters of linear polarization

Solution	Scanning range	Scanning velocity	Scan step	Temperature
0,1M NaCl	±300 mV	360 mV/h	0,5 mV	RT

Figure 4 shows the results of linear polarization. The measured current density was plotted against the standard hydrogen potential. It is clearly evident that only zinc spray coating anodized in electrolyte 1, shows a considerable increase in polarization resistance. The other two samples exhibit results which are comparable to results from reference sample.

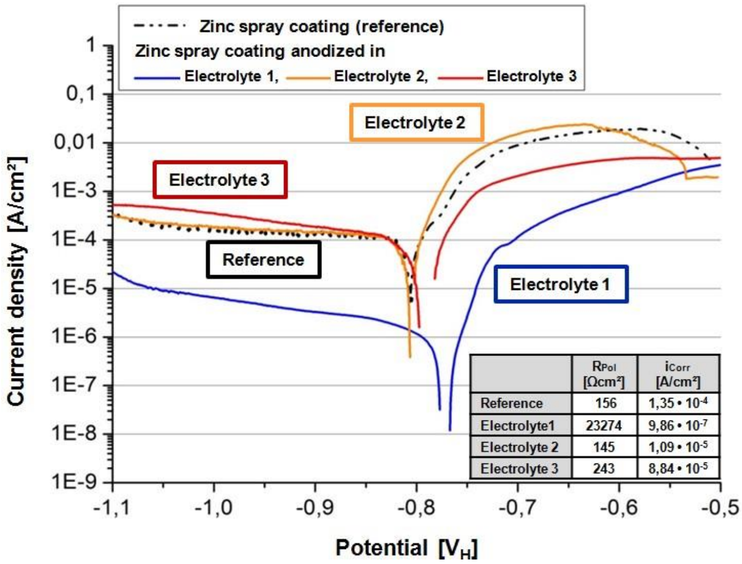

Figure 4: Polarization curves of anodized zinc spray coatings, measured in 0,1M NaCl solution

3.1.4 Morphological Analyses

Changes in layer composition were examined by means of optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX) before and after Zinc anodizing.

Figure 5 shows a metallographic cross section of a zinc spray coating after anodizing in electrolyte 1. Only this sample exhibits measurable thickness of oxide layer.

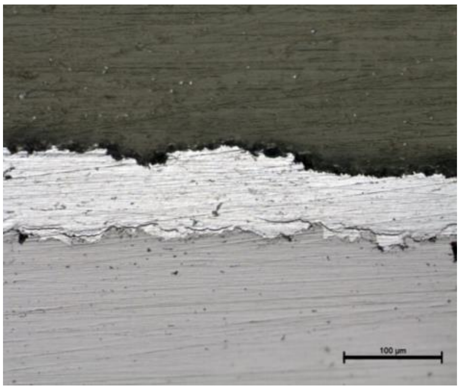

Figure 5: Cross section of zinc spray coating anodized in electrolyte 1

Investigations with scanning electron microscope (SEM) and energy dispersive X-ray microanalysis (EDX) clearly show an oxide layer, which extends partially into the inner coating and consists of zinc, oxygen and tungsten. This oxide layer exhibits some pores, as mentioned in literature before.

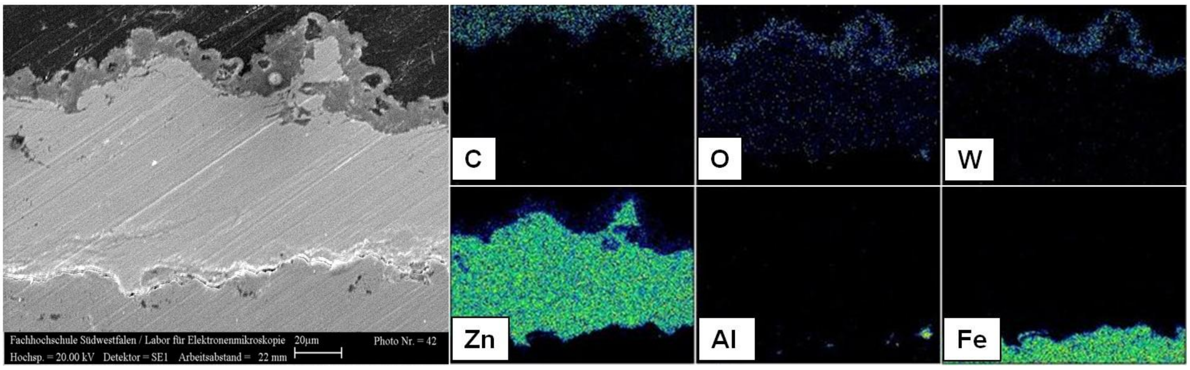

Figure 6: SEM and EDX on zinc spray coating anodized in electrolyte 1

3.2 Optimizing the anodizing process

Anodizing of zinc spray coating in electrolyte 1 converses clearly zinc into Zinc/Tungsten-Oxide layers and increases considerably the polarization resistance. For this reason electrolyte 1 was chosen to optimize layer properties. Table 4 summarizes five recipes of different anodizing parameters.

Table 4: Recipes for anodizing thermally sprayed zinc coatings

Recipe	Current density [A/cm²]	Bath temperature [°C]	Aeration
R1	0,6	60	no
R2	0,6	60	yes
R3	0,6	23 (RT)	no
R4	0,4	60	no
R5	0,2	60	no

3.2.1 Visual observation

Figure 7 shows visual observation after anodizing. It is clearly evident, that an increase of current density darkens the visual appearance. An aeration shows no effect, but a decrease of the temperature further darkens the visual appearance.

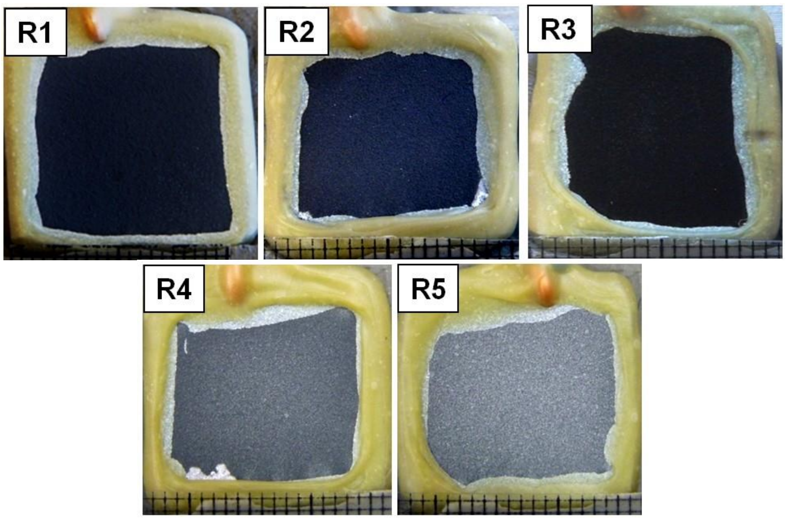

Figure 7: Zinc spray coatings anodized in electrolyte 1 acc. to recipe 1 to 5

3.2.2 Linear polarization

Figures 8 and 9 show the results of linear polarization. It is striking that all samples show a considerable increase in polarization resistance, whereby samples anodized according to recipes 1 and 2 exhibit the highest values.

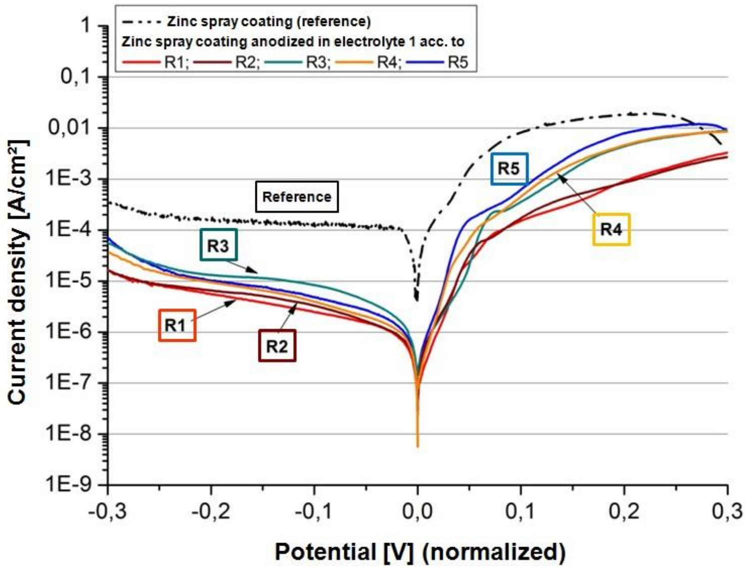

Figure 8: Polarization curves of zinc spray coatings anodized in electrolyte 1 acc. to R1-R5, measured in 0,1M NaCl solution

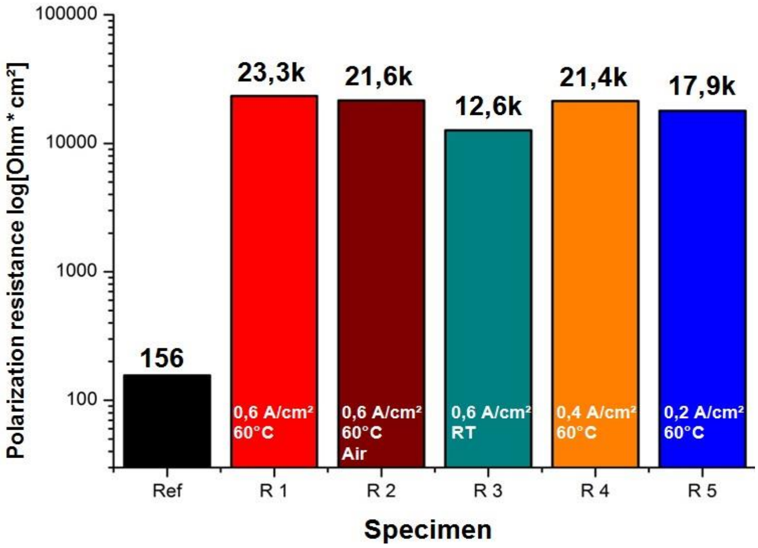

Figure 9: Polarization resistances of samples anodized in electrolyte 1

3.2 Anodizing of thermally sprayed zinc-aluminum coatings

Zinc spray coatings anodized in electrolyte 1, according to recipe 1, exhibit the highest values of polarization resistance. For this reason, in the last step of this work thermally sprayed ZnAl15 coatings were anodized in the same manner.

3.2.1 Morphological Analyses

Oxide layers produced on thermally sprayed zinc and zinc-aluminum coatings exhibit comparable structure (figure 10, left). Figure 10 (right) shows that the oxide layer mostly consists of zinc, oxygen and tungsten.

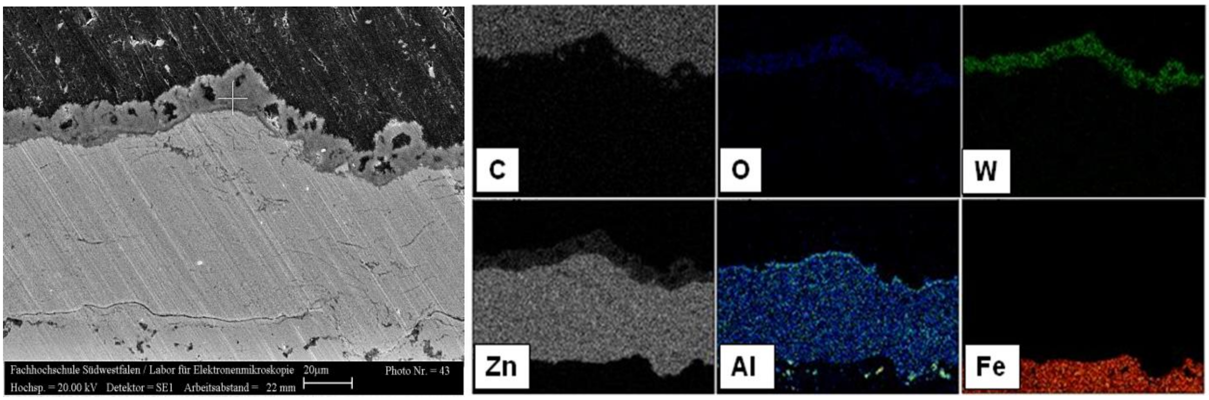

Figure 10: SEM and EDX on ZnAl15 spray coating anodized in electrolyte 1 acc. to recipe 1

3.2.2 Linear polarization

Figure 11 shows polarization curves of anodized Zn- and ZnAl15- spray coatings in comparison to their references. Thermally sprayed ZnAl15 reference coating exhibits inhibited oxygen reduction, as mentioned in literature [11]. Polarization curves of anodized samples clearly show a beneficial contribution of aluminum.

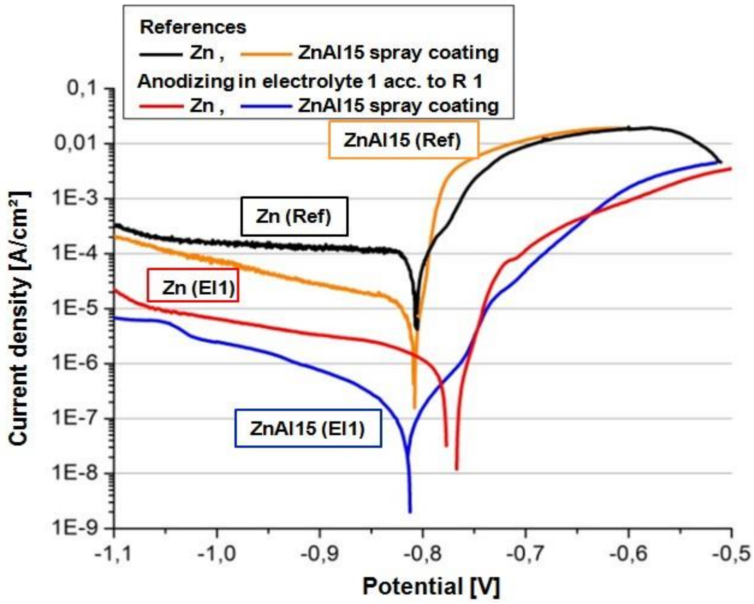

Figure 11: Polarization curves of Zn and ZnAl15 spray coatings anodized in electrolyte 1 acc. to recipe 1, measured in 0,1M NaCl solution

Due to aluminum content inside the anodized spray coatings polarization resistances were increased considerably (figure 12).

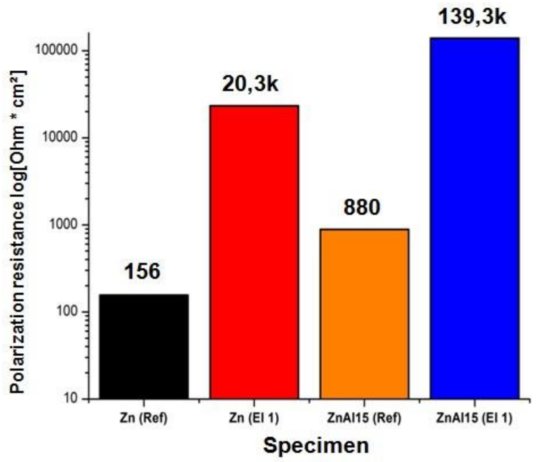

Figure 12: Polarization resistances of anodized Zn and ZnAl15 spray coatings

4 Conclusions

The aim of this work was to test the feasibility of a post-treatment based on anodizing process for thermally sprayed Zn and ZnAl15 coatings. For this purpose chromium-free electrolytes were investigated firstly on zinc spray coatings and only the electrolyte with highest potential was used for anodizing zinc-aluminum spray coatings.

This work clearly demonstrates that a controlled anodizing of small components coated by Zn and ZnAl15 spray coatings can be easily realized.

Anodizing in electrolyte based on tungsten trioxide, exhibits most promising results. The oxide layers produced on thermally sprayed coatings are homogeneous and have a dark appearance. Polarization resistances of both spray coatings were increased considerably, whereas spray coatings with aluminum content exhibit higher values by factor six. This protective oxide layers extend partially into the inner coating and consist of a combination of zinc, oxygen and tungsten.

Characteristics such as high abrasion resistance and good ability to coat, which are known from literature, are of great importance for screw connections.

Long-term behavior with and without organic coatings is now being examined and the results will be presented in the future.

5 References

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