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Kinetic Characteristics of Different Materials used for Bolting Applications

Report
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Overview

One of the most common problems when dealing with bolted joints in the oil and gas industry is corrosion; corrosion damage can affect the stability of the clamping force and it accelerates mechanical failures such as thread stripping and fatigue. Coatings are the most popular solution to protect bolts from corrosion, and electroplating has been used as a corrosion protection practice for applying a coating to the base metal. Cadmium and zinc have been the two most popular selections for electroplating due to their high corrosion protection properties however, the environmental risk associated to cadmium and the high risk of hydrogen embrittlement induced by sacrificial coatings, cause to look for alternatives for subsea applications. Nickel-cobalt electroplating is used as a treatment for reducing the corrosion on carbon and high-strength steels fasteners; it is smooth, hard, dense, good heat diffuser, abrasion resistant, and it has a very low friction coefficient with a constant nut factor.

Perhaps the main characteristics making Ni-Co alloys highly resistant to corrosion are the high potential in the EFM series and the low current delivered by this material in seawater conditions, however, these same characteristics may bring about some questions regarding its performance as a coating in contact with mild steel, specifically the high potential conditions. The driving force of sacrificial alloys for protecting bare steel is obtained by the potential difference between the two metals, sacrificial coatings have a more negative potential than carbon steel which, creates a galvanic couple where the steel is the cathode and the sacrificial metal is the anode, oxidation occurs on the coating; the case for Ni-Co seems to be the opposite. Ni-Co has a more positive potential than bare steel, the thermodynamics indicates that the galvanic couple between Ni-Co and steel will force the former to become the cathode and the latter to become the anode which, would lead to corrosion of steel. Despite the inevitable mandate of the laws of thermodynamics, galvanic coupling between steel and Ni-Co is barely observed and the reason for this is the low current delivered by Ni-Co in environmental conditions; even though there is a thermodynamic galvanic couple, the low current delivered by the system maintains the steel with corrosion rates if the order of micrometers per year.

One of the ways to investigate the electrochemical performance of Ni-Co and compare it to the performance of stainless steel is by applying electrochemical AC/DC techniques. Electrochemical methods have become one of the most important test in corrosion laboratories; these methods allow electrochemical processes to be performed rapidly over a range of environmental conditions and a range of experimental parameters.

In this report, the Materials Research Laboratory (**MRL**) at **doxsteelfasteners** performed potentiodynamic polarization technique (PPT) and electrochemical impedance spectroscopy (EIS) to test the corrosion properties of four different materials and compare their electrochemical response with the one obtained for bare steel, this will help to elucidate the protective properties of coating and to relate these responses with the galvanic coupling effect between coating and steel substrate.

Experimental Procedure

EIS and PPT tests were performed on bare steel AISI 4140, stainless steel 316, and bare steel with three different coatings: Nickel-Cobalt (Ni-Co), Zinc (Zn), and Zinc-Nickel (Zn-Ni); the Ni-Co electroplating was performed at Doxsteel Fasteners and the Zn and Zn-Ni were commercial coatings. A three-electrode arrangement was used for the electrochemical tests with the different coatings and the stainless steel as working electrodes, a Ag/AgCl electrode as potential reference, and a titanium mesh as the counter-electrode. The electrolyte was a 3.5wt.% NaCl analytical grade in static conditions at 25^0 C and atmospheric pressure. For each test, open circuit potential (ocp) was measured for 1 h, then, EIS was performed followed by PPT. The frequency window for EIS was from 10kHz to 10mHz with a signal amplitude of ±10mV, the potential window for PPT was from -350mV to 200 mV around the ocp with a sweep rate of 10mV/min, this potential window was selected in order to guarantee that all the systems remained in the activation zone. All the tests were carried out on as-received commercial samples with no posterior treatment. For detailed information regarding the electrochemical techniques and the technical parameters, ASTM G3, and ASTM G59, and ASTM G102 were followed [1-3].

Results

EIS was performed in order to investigate the corrosion properties of the different materials, Figure 1 shows the EIS spectra for the three different coatings compared to the behavior of bare steel in the same environmental conditions. In this figure it can be observed the differences in magnitude and shape of EIS signal for all the materials, the magnitude is related to the electrochemical response to the environment, in this case, the corrosion resistance; the shape of the signal is caused by other factors such as layering, electrochemical processes or simply by electrodic geometry. Regarding corrosion rate, the higher the impedance magnitude signal, the higher the corrosion resistance. From the experimental data in Figure 1, Ni-Co coating offers the highest resistance to corrosion, its magnitude is 20 times higher than stainless steel and a couple of hundred times higher than the sacrificial coatings. This means that Ni-Co can be considered as an effective protection against corrosion in aggressive environments, such as seawater. The shape of the EIS signal is a matter of discussion too, the signal for Zn showed two-time constants with adsorption at low frequencies; meaning that this sacrificial coating produced chemical species that adsorbed on the surface, such as hydrogen; on the contrary, the signal from stainless steel and Ni-Co did not show the adsorption signal, indicating that hydrogen was not adsorbed on the electrodic surface. The three-time constants found in the Ni-Co EIS signal are associated with the interfacial impedance of steel, the impedance belonging to the coating, and the protective finishing layer in doxsteel fasteners products. It is evident the corrosion protection offered by Ni-Co coating on 4140 steel compared to the other tested coatings in this report.

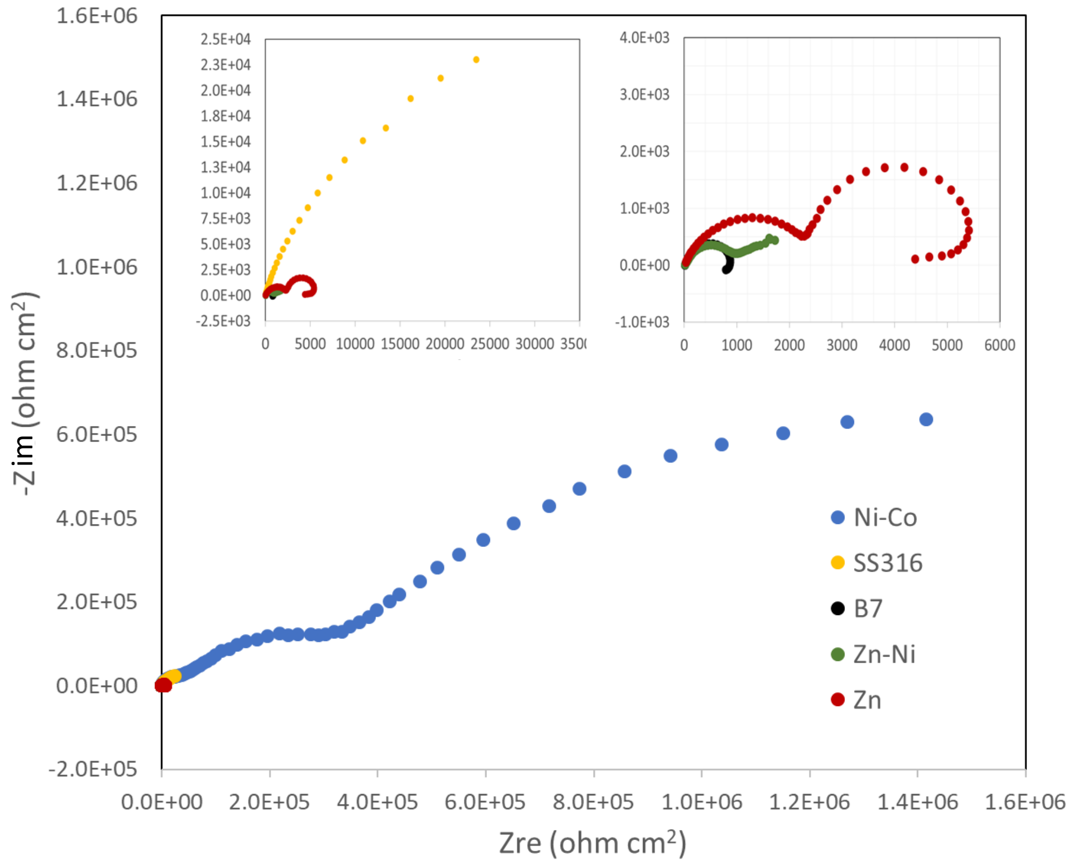

Figure 1. EIS data for Ni-Co, SS316, AISI 4140 (B7), Zn-Ni, and Zn in 3.5wt% NaCl.

Potentiodynamic plots were performed in order to evaluate the kinetic parameters of the different materials and to compare the performance of the barrier coating, Ni-Co, with stainless steel; the main idea is to compare the electrochemical signal for stainless steel and Ni-Co and to elucidate the galvanic effect that these metals can form with carbon steel, such galvanic couple would be detrimental for the latter. Figure 2 is a comparison showing the PPT tests for all the materials tested in this report, the values for corrosion potentials (E_{corr}), corrosion current density (i_{corr}) and corrosion rate (V_{corr}) are given in Table 1.

Table 1. Kinetic parameters obtained from PPT for different materials in 3.5 wt% NaCl.

Material	E_{corr} (mV vs Ag/AgCl)	i_{corr} /10^{-6} (A/cm^2)	V_{corr} (mmpy)
Ni-Co	-176	0.022	2.43e-4
SS316	-197	0.496	5.55e-3
B7	-625	8.225	0.092
Zn-Ni	-909	11.20	0.140
Zn	-960	4.599	0.059

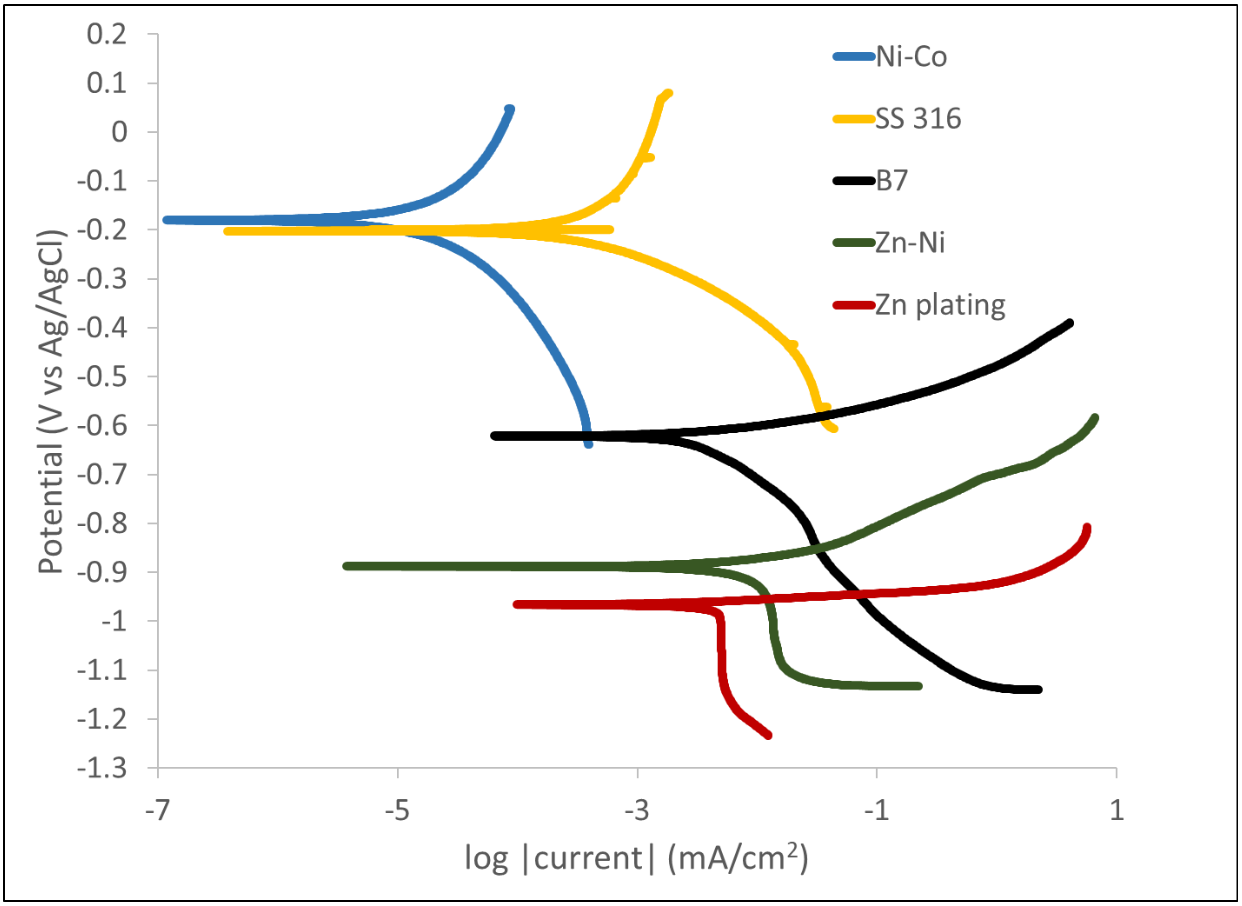

Figure 2. Potentiodynamic plots for Ni-Co, SS316, AISI 4140 (B7), Zn-Ni, and Zn exposed to 3.5wt% NaCl.

As it can be observed in Figure 2, both, stainless steel and Ni-Co, have a more positive potential than carbon steel, which is an indication of the formation of a galvanic couple compromising the integrity of the latter; Zn and Zn-Ni have a more negative potential and they are shown here as a mere reference as sacrificial galvanic couples with carbon steel. Although Ni-Co and SS have similar potential values, the current that each system delivers is quite different; according to Tafel analysis, the corrosion current density delivered by SS is 20 times higher than the one for Ni-Co. This difference in current is even higher if we consider the "crossing points" with the carbon steel curve, is at these points where a galvanic couple is formed; the galvanic current for SS is 100 time higher than that one for Ni-Co, this means that stainless steel will increase the corrosion rate of carbon steel 100 times over Ni-Co. Although the kinetic analysis shows the likely formation of a galvanic couple between Ni-Co and carbon steel, this has been rarely seen in service conditions and in the environmental tests performed on this material at laboratory level; Ni-Co plating does not induce the corrosion of the substrate.

Conclusions

Electrochemical impedance spectroscopy (EIS) and potentiodynamic tests (PPT) were performed on different materials used for bolting applications. The tests revealed the electrochemical nature of these materials exposed to a 3.5wt% NaCl electrolyte. According to EIS, Ni-Co plating showed the highest corrosion resistance amongst all the tested coatings, and PPT tests showed that Ni-Co delivers the lowest corrosion current density amongst all the tested materials; the current associated to galvanic coupling between Ni-Co and carbon steel is 100 time lower than stainless steel with carbon steel.

- EIS showed that Ni-Co offers the highest corrosion resistance in 3.5wt% NaCl compared to stainless steel, Zn, and Zn-Ni.
- The EIS signal shows the presence of adsorbed species on sacrificial coatings, these species may be related to hydrogen adsorption and likely to hydrogen embrittlement.
- PPT tests show that Ni-Co does not form a galvanic couple that compromises the carbon steel integrity, stainless steel does induce corrosion of carbon steel.
- The high current delivered by sacrificial coatings promotes hydrogen production and may promote hydrogen embrittlement in the base-material.

References

[1] ASTM G3-14, "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing". (West Conshohocken, PA: ASTM, 2015).
[2] ASTM G59-97 (2014), "Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements" (West Conshohocken, PA: ASTM, 2015).
[3] ASTM G102-89 (2015) e1, "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements" (West Conshohocken, PA: ASTM, 2015).