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# Prospects of using metallic nanocoatings to improve the operational characteristics of welded joints

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## Abstract

The potential of employing nanostructured metallic multilayer to increase the durability and extend the service life of welded joints of metal structures is analyzed. Using a nickel and copper-based multilayer nanocoating as an example, a notable increase in the durability of the welded joint of up to 300...600% is observed. Corrosion tests reveal that the use of nickel and copper nanostructured metallic multilayer leads to the localization of corrosion processes at the "base metal-nanocoating" boundary. Considering the significant improvement of fatigue characteristics of welded joints and lower corrosion rate compared to welds without lamination, Ni-Cu nanocoatings can be used on offshore structures, provided that the condition of the protective anti-corrosion coating is monitored to mitigate the risk of galvanic corrosion at the base metal-nanolamination boundary.

*Keywords:* nanostructured metallic multilayer; fatigue life; crack growth reduction; welded joints; galvanic corrosion; defect interaction.

## 1. Introduction

Today, welding is the most common method of joining parts in the manufacture of steel structures. It is widely used in conjunction with casting, stamping and special rolling of individual elements of product blanks, almost

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completely replacing complex and expensive all-cast and all-stamped blanks. Various welding technologies find application in the construction of metal structures, with welded joints serving as an economic and reliable method of fastening structural elements.

However, the welding process subjects the structure's metal to thermal influence. The thermal deformation cycle associated with welding involves the simultaneous impact of several adverse factors that comprehensively affect the quality and durability of structures:

- The presence of high residual stresses (due to uneven local heating of the metal of the joint zones by a concentrated heat source), which in some cases reach values close to the yield strength of the metal (250...350 MPa) and cause local deformations and changes in the geometric dimensions of the welded structure;
- Unsatisfactory mechanical properties of the heat affected zone and the weld (due to the formation of heterogeneous metal properties, the appearance of brittle and low-strength metal layers, hydrogenation of weld joint area, etc.), which leads to cracks;
- Presence of stress concentrators due to structural (unsatisfactory shape of the welded product) or technological defects (cracks, pitting, pores, undercuts, etc.).

To minimize the effects of thermal impact and improve operational characteristics, welded joints undergo surface treatment. Treatment methods for welded joints are divided into several groups: thermal, mechanical, deformation, pulse and vibration, special and combined.

Thermal methods at a given heating temperature speed, holding time, and cooling speed are divided into tempering, normalization, thermal rest, austenization, restorative heat treatment, and annealing.

Mechanical methods usually consist of convexity treatment (reinforcement) of welded butt joints with cutters and abrasives grinding wheels. Processing is carried out for elimination stress concentrators, which has a favorable effect on resistance to brittle fractures and increases the limit of endurance under dynamic loads.

Deformation methods carry out plastic deformation of various zones of welded joints by introducing mechanical energy through rolling of welded joints, local plastic deformation, single- and multi-impact tooling, or preloading of welded structures.

Pulse and vibration methods consist of explosive, electrohydro-pulse, magnetic pulse and vibration treatment of welded joints.

Special treatment methods are designed to reduce stress concentrations and protect the metal surface from aggressive environments by applying polymeric and metal coatings to welded joints or structures. polymer and metal coatings on welded joints or structures.

Recently, the utilization of various types of nanocoatings has gained popularity for enhancing material performance. These coatings contribute to increased corrosion resistance and resistance to fatigue loads, etc. (Abdeen et al., 2019; Farag, 2020; Gu et al., 2020). Scientists at the Hamburg University of Technology have developed the latest nanocoatings based on layers of nickel and copper (Brunov & Rutner, 2021). Experimental studies confirmed the effectiveness of nanocoatings as a surface treatment for improving the fatigue characteristics of welded joints. The fatigue life of the nanolaminated specimens was increased up to 600% (Brunow et al., 2021; 2022).

However, the welded joint area, being subject to thermal influence during welding, is a part of construction with high-risk of corrosion development and localization (Garcia et al., 2008; Tsyrul'nyk et al, 2011; Poberezhny et al., 2017; 2019; Kryzhanivskyy et al., 2019; Maksymova et al. 2022; Hutsaylyuk, et al., 2023; Martinez-Galvan et al. 2023). The risks of corrosion damage to metal structures located near the sea and offshore are particularly high. Both components of the developed nanocoatings possess a standard electrode potential nobler than steel, potentially leading to the development of galvanic corrosion.

This study aims to evaluate the possibility of using nanocoatings to improve the performance of welded joints of offshore metal structures, primarily wind power facilities.

## 2. Methodology

The material chosen for the study was S355J2 steel, which is widely used in the construction of various metal structures, including wind power facilities supports.

In this study, a single bath electroplating process using a pulsed direct current method was utilized to coat a sample with a Cu/Ni nanolaminate (Fig. 1). The electrolyte used was a Cu/Ni citrate bath, as described in (Bonhote & Landolt, 1997), and the mean current densities for Cu and Ni deposition were 0.4 $mA/cm^2$ and 50 $mA/cm^2$, respectively. The duration of the pulse for Ni and Cu deposition was 5 s and 320 s, respectively, with a one-second off time during current pulses. The coating applied had a total thickness of approximately 7.5 µm and was composed of a 1 µm thick Ni base layer and 160 Cu/Ni bilayers, with a thickness of 39 nm and 47 nm, respectively. The thickness measurements of individual layers were made possible using element mapping with Cu-K and Ni-K x-rays (8.04 and 7.47 keV). The utilization of a Ni base layer was found to be significant for two reasons. Firstly, the adhesion between copper and steel was insufficient and using a Ni base layer for coupling resolved this issue. Secondly, electrodeposition of Ni had a leveling effect on the surface roughness (Brunow et al., 2022).

For electrochemical tests, 4 types of samples were made:

- Fully nanolaminated with an outer layer of nickel (BM-Ni);
- Fully nanolaminated with an outer layer of copper (BM-Ni-Cu);
- Partially laminated (only the welded joint zone + 2 cm on each side) with an outer layer of nickel, working area located on the boundary of nanolamination (Bound-Ni);
- Partially laminated with an outer layer of copper and the same working area location (Bound-Cu).

The electrochemical part of the study included measurements of the Open Circuit Potential (OCP) and potentiodynamic tests, using a three-electrode clamp cell (Fig. 1, b). The area of the working electrode surface was 0.2 and 0.5 $cm^2$. Scan rate – 0.5; 0.25; 0.166 mV/s. The reference electrode is an Ag/AgCl electrode. Electrochemical tests were carried out with the potentiostat Gamry Interface 1010B. Before conducting electrochemical tests, the working surface was cleaned with acetone. In the case of partially laminated specimens, the working electrode surface was positioned at the "Nanolamination – Base Metal (BM)" boundary, with half of the working surface area being laminated and the other half was not.

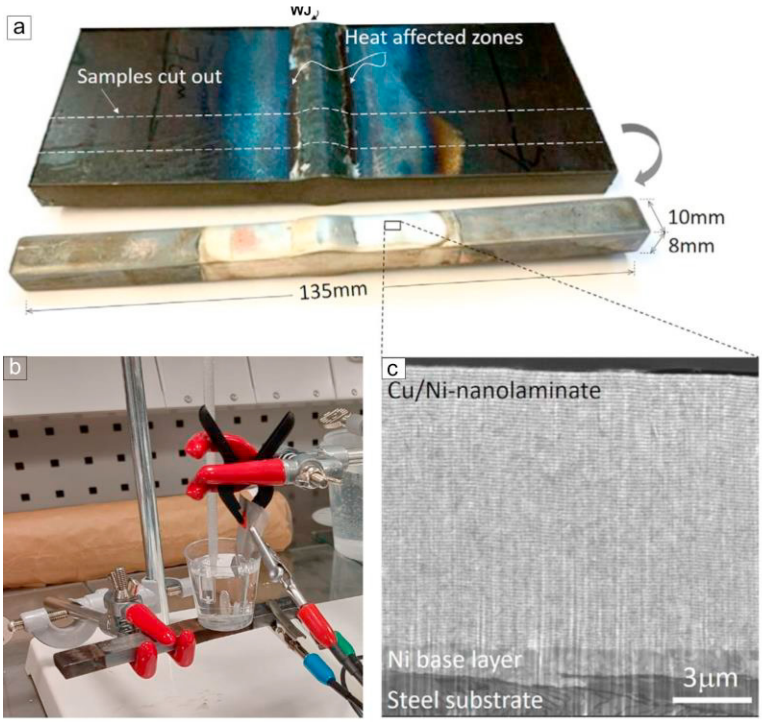

Fig. 1. Specimen preparation for corrosion tests: (a) cut out and lamination (Brunow et al., 2022); (b) clamp on electrochemical cell installation; (c) nanolaminate structure (Brunow et al., 2022).

## 3. Results and discussion

Analyzing the kinetics of the electrode potential reveals that after 4 hours of exposure to 3.5% NaCl solution, it approaches stability (Fig. 2). Notably, there is a significant difference (291mV) between the OCP value for stranded copper wire and nanolaminate with a copper outer layer. This difference may stem from the interaction with the Ni underlayer of the nanolaminate through microdefects and pores in the outer Cu layer. The specimens with the working area on the "BM-Nanolamination" boundary exhibit the lowest OCP levels, indicating the highest corrosion risk. The difference between OCP is 80 and 96 mV for Ni-laminated and Ni-Cu laminated specimens, respectively.

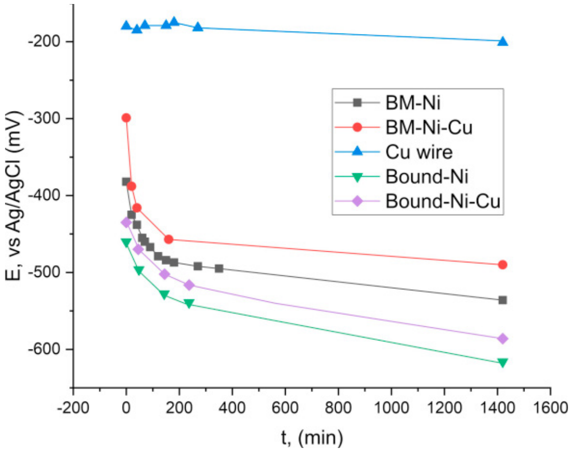

Fig. 2. OCP kinetic curves for laminated specimens and Cu stranded wire.

When comparing the results of the potentiodynamic test of the laminated specimens after exposition in 3.5% NaCl (Fig. 3), on the anode branch for specimens with BM-Ni-Cu lamination (outer layer is Cu) corrosion products layer formation after 120 and 300 min of exposition in solution is in the same potential range (-0.05…0.05V). The corrosion products layer remains present after 300 minutes and is more pronounced. The corrosion rate between 120 and 300 min exposition in 3.5% NaCl solution increases up to 6.5 times (Table 1).

In contrast, for BM-Ni laminated specimen on the anode branch formation of corrosion products layer is not observed (Fig. 3,a). The corrosion potential for two potentiodynamic measurements with 80 min interval differs by 100 mV.

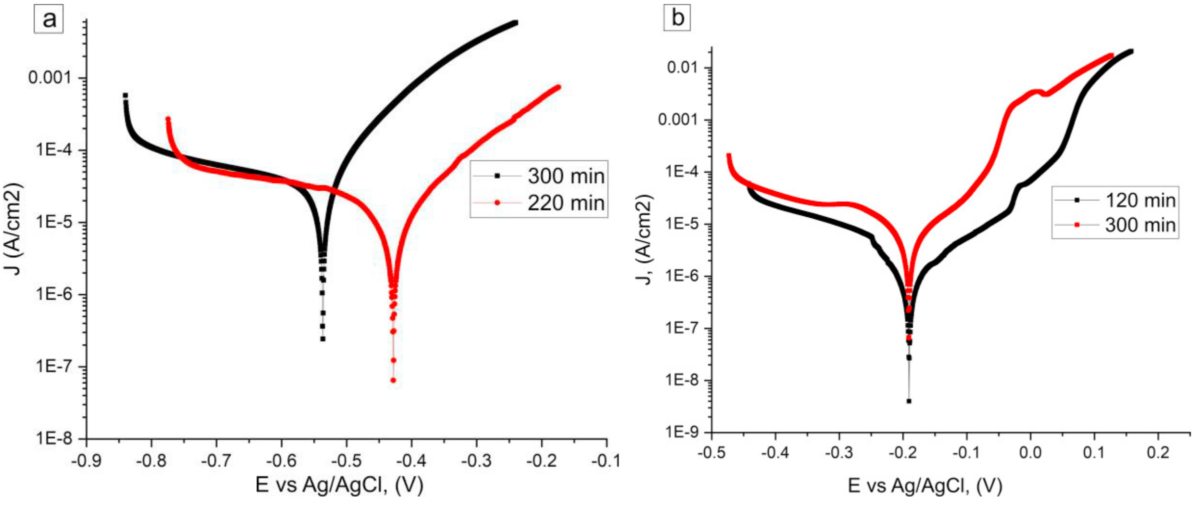

Fig. 3. Potentiodynamic curves for specimens after exposition in 3.5% NaCl solution: (a) BM-Ni; (b) BM-Ni-Cu. Scan rate – 0.5mV/s.

The corrosion rate after 300 min in 3.5% NaCl solution is 5.5 times higher than for the BM-Ni-Cu laminated specimen (Table 1). Corrosion potential is stable between two potentiodynamic measurements with 180 min interval.

Table 1. Electrochemical characteristics from potentiodynamic data

| Electrochemical parameter | BM-Ni lamination 220/300 min in 3.5% NaCl | BM-Ni-Cu lamination 120/300 min in 3.5% NaCl | Bound-Ni 24h in 3.5% NaCl | Bound-Cu 24h in 3.5% NaCl |
|---|---|---|---|---|
| $E_{cor}$ vs Ag/AgCl, V | -0.431/-0.532 | -0.194 | -0.633 | -0.577 |
| $J_{cor}$, μA/cm$^2$ | 19.95/22.38 | 0.68/4.07 | 42.7 | 63 |
| $V_{cor}$, mm/year | 0.235/0.264 | 0.0075/0.048 | 0.503 | 0.742 |
| $b_c$, V/dec | 0.398/0.778 | 0.073/0.077 | 0.412 | 0.321 |
| $b_a$, V/dec | 0.0896/0.173 | 0.093/0.105 | 0.082 | 0.068 |

Results from potentiodynamic tests on partially nanolaminated specimens with a working electrode surface containing a “BM-nanolayer boundary” (Fig. 4) show a shift of the corrosion potential to more negative values than fully laminated specimens. This shift occurs because half of the working surface is a base metal surface with more negative potential than laminated area. After 20 h of exposition in 3.5% NaCl corrosion rate for Bound-Cu specimen is higher than for Bound-Ni, due to the higher potential difference between base metal and copper nanolayer.

In the future, investigating the corrosion behavior at the metal-nanocoating boundary at a longer exposure to a corrosive environment, as well as in the presence of cathodic protection, would be of interest.

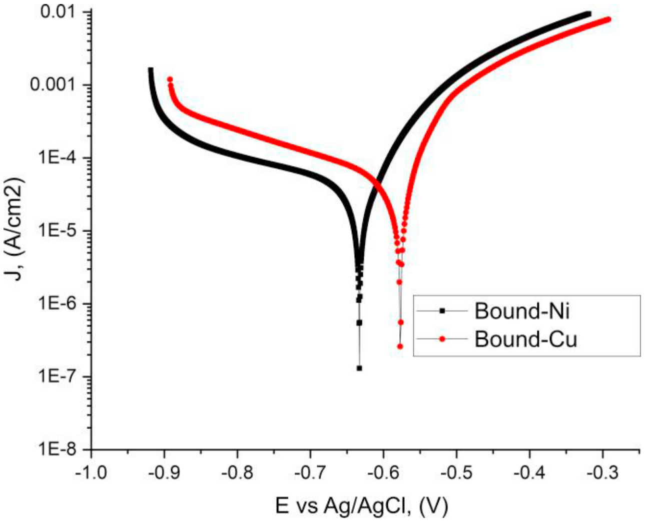

Fig. 4. Potentiodynamic curves for Bound-Ni and Bound-Cu specimens, after 20 h in 3.5 NaCl solution; Scan rate 0.167 mV/s.

The next stage of the corrosion tests scrutinizes the working surface in the initial and corroded state using a metallographic microscope Leica DM4 P. The initial state of the surfaces of the specimens is shown in Fig. 5. There are many surface defects over lamination, which can play a role of pitting corrosion centers.

For partially Ni-laminated specimens, after 24 h exposition in air, corrosion processes are localized on boundary “BM-nanolamination” (Fig. 6, a). Also, on the Ni surface spot corrosion damage was detected (Fig. 6, b). On the laminated part of the working surface after the potentiodynamic test in 3.5% NaCl solution a large number of corrosion spots were detected. Corrosion is more uniform on the part of the "base metal" of the work surface (Fig. 6, c).

Fig. 5. Initial state of the specimens' surface: (a) – base metal; (b) BM-Ni-Cu lamination; (c) BM-Ni lamination.

Fig. 6. Ni laminated specimen surface after corrosion: (a) 24 h in air; (b) boundary of working area; (c) BM-lamination boundary.

Figure 7 shows corrosion damages of the different parts of the Ni-Cu partially laminated specimen. As for the Ni-laminated specimen, after 24 h oh air, corrosion localized on the boundary "base metal-nanolamination". In the working area, corrosion is mainly uniform but also presents few notch defects.

Fig. 7. Ni-Cu laminated specimen surface after corrosion: (a) 24 h in air; (b) boundary of working area; (c) BM-lamination boundary.

## 4. Conclusions

The developed Ni-Cu nanolaminate coatings improve the fatigue characteristics of welded joints and hold promising potential for use as a surface treatment for new and existing metal structures. The inclusion of copper in the nanolaminate improves the resistance to biocorrosion, and the nickel layers can prevent hydrogenation.

Corrosion tests were conducted on S355J2 steel samples with welded joints protected by Ni-Cu nanolaminate coating. According to the results of tests of partially nanolaminated specimens indicated the localization of corrosion processes on the "base metal – nanolamination" boundary. Inspection of the surface of the laminated samples shows defects that are possible points of corrosion initiation. This observation provides a plausible explanation for the difference in potential values due to the probability of contact between the corrosive medium with the metal beneath the nanolayer.

Considering the significant improvement in the fatigue characteristics of welded joints and lower corrosion rate compared to welds without lamination, Ni-Cu nanocoatings can be used on offshore structures. However, it is crucial to monitor the condition of the protective anti-corrosion coating to mitigate the risk of galvanic corrosion at the BM-nanolamination boundary.

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