Material mechanisms of Cu/Ni nanolaminate coatings resulting in lifetime extensions of welded joints

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Abstract

In this paper nanolaminate coatings are introduced as a new approach in post-weld treatment methods. Welded joints are often the weakest link for steel constructions under cyclic loading. The weld introduces small geometrical deficiencies that increase the stress intensities near to the weld. Combined with material related deficiencies, which reduce the toughness of the steel in the heat-affected zone, this leads to a decreased fatigue resistance. A Cu/Ni nanolaminate coating is deposited electrochemically from a single Cu/Ni citrate bath onto a butt-welded tension-tension fatigue specimen. The nanolaminate coating with a total thickness of 9560 nm consists of a 1000 nm Ni base layer and 160 alternating Cu and Ni layers with thicknesses of 40 nm and 67 nm, respectively. The specimen are tested in tension-tension fatigue with a load factor R of 0.015 and a stress range close to the yield strength of the specimen. This first study revealed surprisingly high lifetime extensions of welded joints. The tested specimens are thoroughly examined using different microscopy techniques. With Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM) and Transmission Electron Microscopy (TEM) the structure and composition of the nanolaminate are studied while local roughness measurements are carried out with an atomic force microscope (AFM). This led to observations on crack behavior of nanostructured Cu/Ni multilayers on steel substrates. The Cu layers show initial multi crack building, the length of those cracks is limited by the Cu lamina thickness and the cracks arrest at the interface towards the Ni layers. The Ni layers bridge those cracks and each Ni layer will tear individually. The results are discussed and a hypothesis is formed on how and why nanostructured coatings can extend the crack initiation phase and prolong the lifetime of welded joints as well as other specimens.

Keywords: nanostructured materials, nanolaminate, thin film, coating, fatigue, post-weld treatment, welding

More often than not, the weak link of a structure exposed to fatigue loading is a joint. In the case of steel constructions, the welded joint is a notch that is generating fatigue stress concentrations under cyclic loading. Additionally, the toughness of the material is lowered inside the heat affected zone, which results in a higher susceptibility for crack growth, because the crack tip cannot be blunted by strain hardening in the areas with reduced toughness.

Different methods to prolong the crack initiation phase in welded joints have been established as post-weld treatment methods [1]. Brunow and Rutner [2] introduced the nanolaminate coating as a novel post-weld treatment method and raised the question on the mechanics of nanolaminate coatings for fatigue resistance on welded joints. The results of [2] are presented and hypotheses on the fatigue mechanics are presented and discussed herein.

Nanostructured materials and nanostructured metal multilayers have been known to possess superior material properties in comparison to bulk materials, like increased strength, wear resistance, corrosion resistance, fatigue resistance and magnetic properties [3–7]. These superior properties have been attributed to the Hall-Petch effect and to the number of coherent or incoherent interfaces, which act as barriers, impeding the propagation of deformation carriers such as dislocations, phase transformation bands and shear bands, as investigated in [8–10]. But there have also been reports of reduced thermal stability in nanolaminate structures due to melting point depression [11–13].

Electrodeposition, which is used for the bottom-up fabrication of nanostructured materials, exhibits advantages and disadvantages compared to vapor deposition techniques, like PVD, CVD or ALD [7,14]. The electrodeposition process is prone to quality variations in the produced coatings, due to small changes in the preparation process, as it can be seen in [15]. The variety of electroplated nanolaminate material combinations is limited by the materials, which can successfully be electroplated and is even smaller for materials that can be electroplated from a single bath process [14]. The single-bath process utilizes the difference in electrode potential and mass composition by pulsing the current between a high and a low current for deposition of different metals from one single electrolyte [14]. However, the low costs and the scalability of the electrodeposition process in comparison to vapor deposition processes makes it suitable for a large scale or even in-situ application like a post-weld treatment method.

In a 2001 study from Stoudt, Ricker and Cammarata [16] a nanolaminate coating was used to engineer the surface deformation behavior of copper samples in fatigue tests, showing significant lifetime improvements. Since all coated samples were declared as run-outs no statement could be made towards the failure mechanisms of nanolaminate coatings. These results could be replicated by Kaneko et al. in 2007 [17] and were attributed to the suppression of dislocation structure evolution. To our knowledge these two instances were the only time electrodeposited metal multilayers were used as coatings to enhance the fatigue resistance of specimen. This is supported by the 2021 review of Aliofkhazraei et al. on recent developments in electrodeposited multilayer coatings [7]. Even further, a practical implementation of Cu/Ni nanolaminate coatings is unknown to us, which would make the study presented here the first practical utilization of nanolaminate coatings as a post-weld-treatment against fatigue.

To test the fatigue resistance of welded joints, two 8 mm S235 flat steel bars with a measured yield strength of 271 MPa were prepared with a double v groove and joined with a butt weld. To reduce inconsistencies between the samples a collaborative welding robot was used for welding. The used filler material is a SG3 (G4Si1) with a strength of 460 MPa which led to a joint with a much higher yield strength, then the base material. The joined flat steel bars were cut into tensile test samples with a length of 135 mm a width of 10 mm and a thickness of 8 mm, as it is shown in Figure 1a.

To coat the sample with a Cu/Ni nanolaminate patch a single bath electroplating process was used with a pulsed direct current method. The electrolyte was a Cu/Ni citrate bath according to [18] and used with mean current densities of 0,4 mA/cm² for Cu deposition and 50 mA/cm² for Ni deposition. The used coating has a thickness of 9650 nm and consists of a 1000 nm Ni base layer and 160 Cu/Ni bilayers with thicknesses of 40 nm and 67 nm respectively. The Ni base layer was found to be important for two reasons. Firstly, the adhesion between copper and steel is not sufficient and using a Ni base layer for buttering fixes this problem. Secondly, electrodeposition of Ni has a leveling effect on the surface roughness as it can be clearly seen in the middle of figure 1c, where a notch in the steel substrate is filled with Ni and is no longer present at the interface between the Ni base layer and the nanolaminate coating.

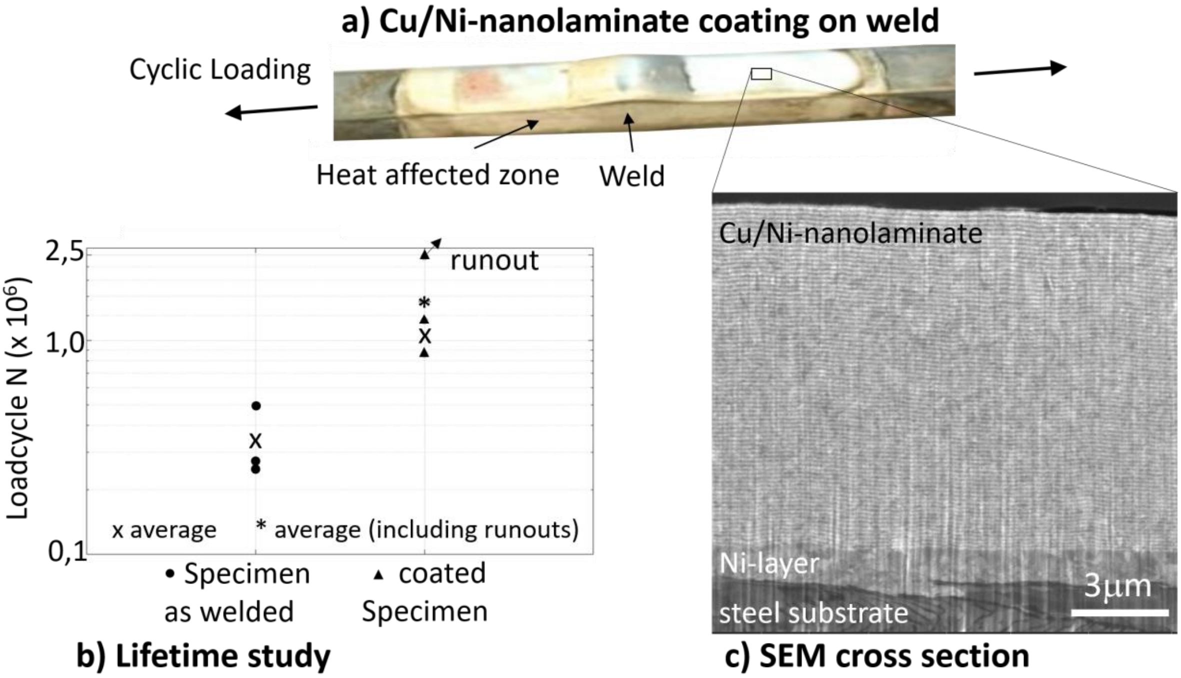

Figure 1. a) Tensile test sample with Cu/Ni-nanolaminate coating covering weld, heat affected zone and part of the base material; b) Lifetime extension of specimen with Cu/Ni-nanolaminate compared to specimen as welded, σ/fy=0,94 R=0,015; c) SEM cross section scan of the applied Cu/Ni-nanolaminate coating.

The samples were tested in tension-tension fatigue with a stress range of 255 MPa, which is 94% of the measured yield strength of the samples (271 MPa). The ratio between minimum peak stress and maximum peak stress was R = 0,015.

As shown in Figure 1b three as welded specimen are tested with an average lifetime under fatigue loading of 341.238 cycles and three samples with nanolaminate coating were tested. Since only three samples have been tested, all at the same stress level, the runout is considered as an additional measuring point and listed in a second average value for the lifetime of the coated specimen. Therefore, the average of the coated samples is 1047896 (or1.515264 considering the runout). This means that the lifetime of butt-welded joints can be extended by the factor 3 (or 4.5 considering the runout). Both Stoudt, Ricker et al. and Kaneko et al. have seen comparable or even higher lifetime extensions for uniform copper specimen without a defined notch [16,17]. Our results confirm the findings that the nanolaminate coating is effectively extending the fatigue resistance of specimen and we have shown for the first time that this effect can be used selectively on notches and joints of metal specimen.

In the following SEM and TEM investigations into the cracking mechanism of the fatigued samples are shown. The cross sections shown in figure 2 are all from the same area of one fatigue-tested specimen. The cross section in figure 2a is produced by cutting into the surface of the coated sample with a focused ion beam (FIB). Subsequently, the crack is followed by FIB-tomography and essentially a TEM Lamella (figure 2d, e) is taken from the crack tip to investigate the crack propagation behavior in the nanolaminate structure.

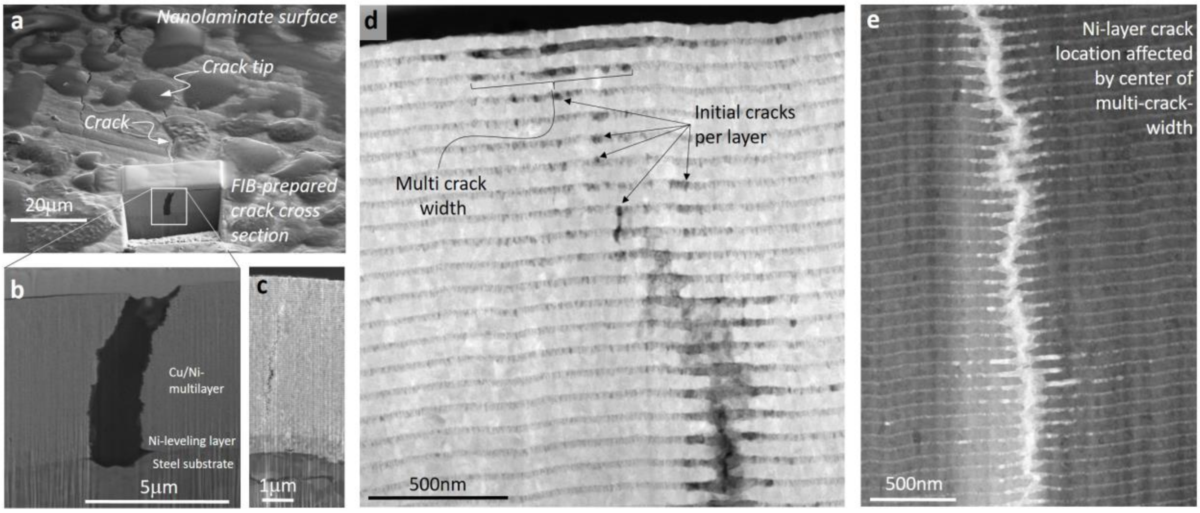

Figure 2. a) Trench of the FIB-tomography following the crack; b) FIB cross section with a wide crack through the nanolaminate; c) FIB cross section of the closing crack tip; d) scan of the crack tip closure in the top part of the TEM-lamella with multi cracks forming in the Cu-layers; e) scan in the middle part of the TEM-lamella showing the single cracks in the Ni-layers as well as multi-cracks in the Cu-layers

The figure 2b shows the crack in an area with a high local substrate strain. Figure 2c shows a SEM image of the crack tip which is taken out as a TEM-lamella. As can be seen the crack is closing towards the surface as well as in the steel substrate and the Ni base layer. A local strain difference in the substrate has to be transferred as stress through the coating making the local plastic deformation work against the high strength nanolaminate first, before a crack opening in the steel substrate can occur. This leads to a crack bridging effect (cf. figure 3), where shear forces transfer some of the load into the coating, which reduces the crack propagation into the substrate by decreasing the stress intensities at the crack tip, while simultaneously keeping the crack width limited until the whole nanolaminate ruptures (or fails?).

The crack propagation through the nanolaminate is controlled by initial cracks in the Cu layers and subsequent multi-cracks forming in the Cu-layer (cf. figure 2d and 3). The creation of multiple cracks per Cu-layer spreading over a certain width, rather than a pileup of dislocations leading to a single crack, are caused by the barrier strength and the mismatch of tensile strength of the constituents. The formation of multi-cracks needs more energy than a single crack. The Ni-layers connect the two crack flanks. Each layer has to rupture individually under necking and strain hardening. This combination of decoupling the crack propagation into two different mechanisms at the interfaces with a higher energy dissipation and strain hardening behavior might be the reason for the superior fatigue resistance. These mechanisms lead to unique crack flank pattern with outreaching Ni-layers and retracted or missing Cu-layers, as observed in figure 2e and shown in figure 3. Wang, Misra and Hoagland [19] show SEM scans with similar crack patterns for freestanding, fatigued Cu/Nb nanolamiantes, without going into details of the crack propagation mechanisms.

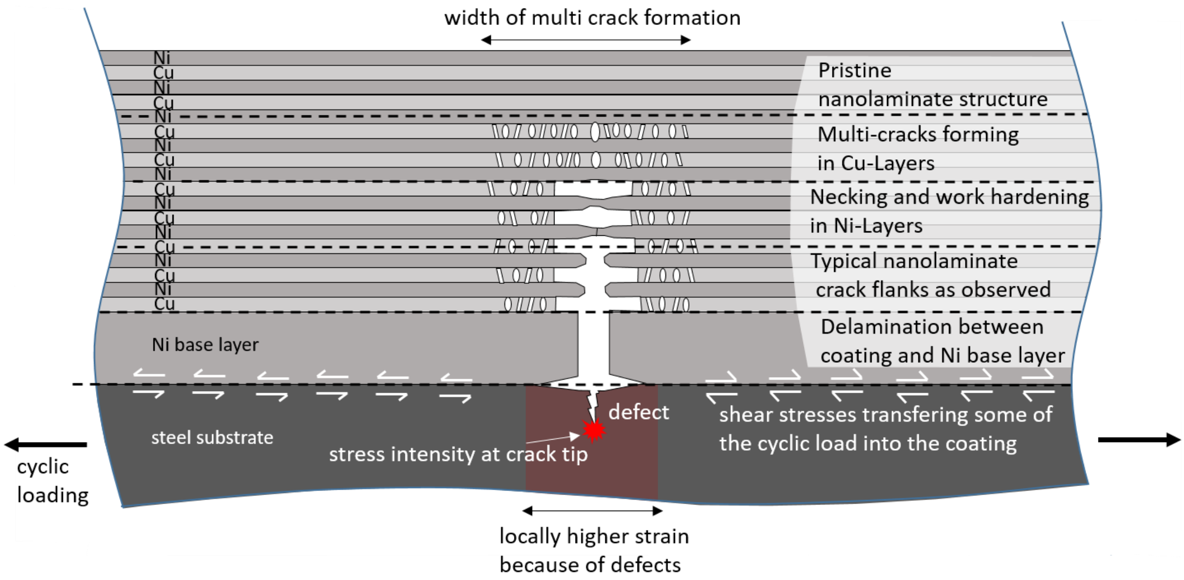

Figure 3. Schematic crack bridging behavior and crack propagation behavior of steel with a nanolaminate coating. The crack is growing from the site of an initial defect into the substrate, locally increasing the strain which results in a crack growth into the nanolaminate towards the surface

In figure 3, the different crack stages are shown schematically and annotated on the right-hand side of the figure, from the pristine nanolaminate layup, to multi cracks forming in the Cu-layers, necking and work hardening of separated Ni-layers and finally crack opening above an area with higher strain. Defects like a micro-crack in the substrate might be responsible for the higher strain in the substrate, nonetheless other reasons for the high strain are possible, but the key mechanisms in the nanolaminate stay the same.

The average local roughness of the specimen in the heat affected zone, around the weld, is measured before and after testing with one as-welded specimen and one coated specimen using atomic force microscopy (AFM). The determined average roughness is the mean value of the measured height information for each pixel. The investigated areas are with 10 x 10 µm² and 70 x 70 µm² relatively small compared to the whole specimen. With this measurement the average surface roughness without macroscopic artefacts from the welding and polishing process is determined. In figure 4 the 3D surface reconstructions of the uncoated (left) steel and the nanolaminate (right) are shown. From this image the difference in roughness can be clearly seen. At the end of their lifetime, the nanolaminate shows significant smaller roughness than the steel.

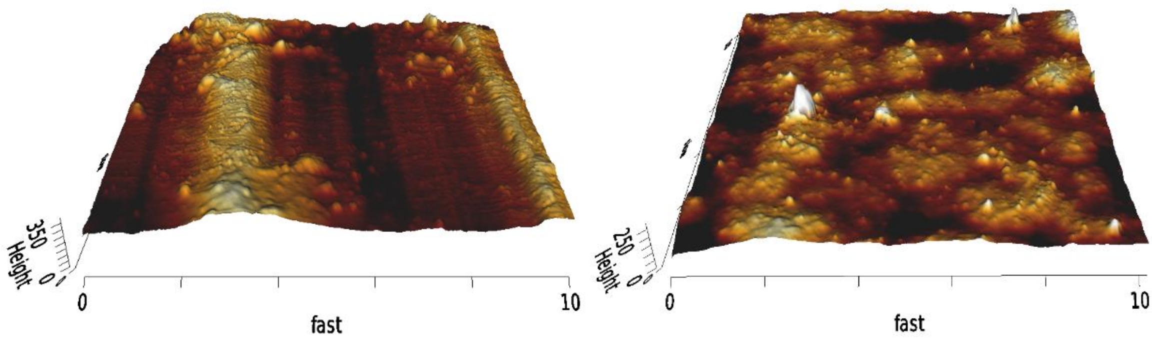

Figure 4. Left: 3D-surface reconstruction of an uncoated steel specimen at the end of its lifetime; Right: 3D Surface topology of a nanolaminate coated specimen at the end of lifetime; the selected areas are 10 µm x 10 µm and the measured heights are up to 350 nm

Table 1 sums up the values for the average roughness for polished steel and the coated specimen at the beginning, as welded, and at the end of lifetime.
For both an increase in roughness can be seen, but the absolute values for the nanolaminate remain on a comparable small level.

Table 1: Comparison of the Average Roughness R_a for two specimens with and without nanolaminate coating before and after testing and different AFM image sizes

	Average Roughness R_a [nm]			
AFM Imagesize	*70x70 [µm²]*		*10x10 [µm²]*	
lifetime	*As welded*	*End of lifetime*	*As welded*	*End of lifetime*
Polished steel	235.0 nm	286.4 nm	37.98 nm	41.68 nm
Nanolaminate	94.74 nm	152.3 nm	13.23 nm	15.00 nm

It is remarkable, that the roughness at the end of lifetime for the nanolaminate is smoother than the one of the steel before testing. Figure 4 shows two effects of the nanolaminate coating on the surface roughness of samples essentially contributing to extended lifetime. Firstly, the surface roughness of the pristine steel weld with nanolaminate coating is lower than of the uncoated as-welded sample, which can be attributed to the leveling effect of the Ni base layer as discussed earlier. Secondly, the surface roughness does not change significantly over time, in contrast to the as-welded samples, which show an increase in surface roughness, as expected for metal samples that normally form intrusions and extrusions as a result of dislocation pile-ups at the surface [20]. This shows that the nanolaminate coating changes the tribology parameters of the sample no longer allowing dislocations to wander freely through the crystal lattice, but instead imposing a new boundary condition at surface level, meaning the dislocations have to level out internally. This is in accordance with the findings of Stoudt et al. [16] who reported that the surface roughness of nanolaminated copper samples stayed the same under cyclic loading.

The literature provides mechanisms of nano multilayers for different test setups i.e. on a substrate and investigated by nanoindentation [21] or bending of cantilever beams [22] or nanocompression testing of pillars [23]. A variety of test setups, samples, bilayer combinations produced by various fabrication methods have been tested, hence a variety of failure mechanisms have been detected. Crack initiation in the study presented herein is local axial straining because of fatigue loading and subsequent failure progression of the multilayer coating. The mechanisms identified are partly mechanisms discussed in the science community. The crack does not occur in an unstable manner with the crack tip propagating several multilayers, as found in Cu/Ni multilayers in in situ TEM straining experiments [24]. Further, no shear bands spreading across the nano-multilayers, as described by Wang et al, 2017 [21], are found. In addition, interface crossing is not the governing mechanism, although Cu/Ni nanolaminates have a coherent interface. The crack progression visible in Figure 2d is not a crack progression from layer to the adjacent layer due to shear instability [25]. Crack tip blunting is occurring however delamination and immediate reinitiation in the adjacent layer [26] does not occur. Foecke and Kramer found that after Cu and Ni layers fracture the Cu/Ni interfaces stay intact [24], which is consistent with findings in this study. Wang et al. [22] describe the crack bridging as part of the failure mechanism in Ag/Cu-Zr laminate cantilevers subjected to lateral force. Crack bridging occurs in the Ag-layers with a single crack per Cu-Zr-layer.

From the observations and the discussion in context with the literature, we build the following hypotheses on how and why nanolaminate coatings increase the fatigue resistance of metal specimen:

1. Reduced surface roughness – the leveling effect of the Ni base layer reduces the roughness and decreases the stress peaks near the surface
2. Micro-crack bridging – small defects in the metal substrate can be bridged by the high strength film on top of the surface offering alternate load paths and effectively reducing the stresses in the crack tip
3. Energy dissipation – instead of one crack that grows through the nanolaminate there are multiple cracks growing inside of the Cu layers
4. Crack arrest at interfaces – cracks will not grow across the Cu/Ni interface, but instead get arrested at the interface and reinitiate in the Cu layers ahead of the crack tip while Ni layers stay intact, leading to a prolonged crack propagation through the coating
5. Surface Boundary Condition – the pile up of dislocations as intrusions and extrusions on the surface is hindered by the high strength coating, changing the tribology parameters

These findings are in accordance with the literature and mostly match the five perquisites defined by Stoudt, Ricker and Cammarata for an effective surface treatment against fatigue loadings, namely hardness, toughness, cyclic work hardenability, residual compressive stresses, and adherence [16]. Even so residual compressive stresses clearly increase the fatigue resistance, we did not find this mechanism to be essential for Cu/Ni nanolaminate coatings. The yield strength of the coating is important, which is linked with the hardness, the cyclic work hardenability and toughness correspond to the energy dissipation. Adherence of the coating is clearly a perquisite because the coating needs to transfer some of the stresses.

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