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Nano-laminated Alloys for Improved Return on Oilfield Assets

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This paper addresses both the up-front cost of deploying nano-laminated alloys that are based on traditional alloy chemistries, configured using novel nanolamination techniques, as well as the lifecycle performance and cost of these new alloy classes. This paper evaluates overall return on assets for conventional alloys versus nano-laminated alloys.

ABSTRACT

Nano-laminated metallic claddings is an emerging technology that is being used to generate products with material property combinations heretofore not possible. Through a patented electrochemical controlled deposition process, Modumetal produces precisely defined configurations of layered metal alloys that can be applied to a variety of substrates or as near net shape parts. The deposition process can be controlled to produce nano-scale layers with unique interfacial properties resulting in corrosion resistance, elastic modulus, strength,

hardness, and fracture toughness combinations uniquely different from conventional material processing.

Oil and gas equipment is constantly exposed to corrosive elements that threaten asset longevity and productivity. Corrosion and wear of equipment such as tubulars, downhole artificial lift systems and pumps, leads to production decline over time and ultimately to expensive repairs and operational downtime, all of which negatively impact companies' bottom lines. Until now, the most common fixes to combat pipeline corrosion required a sacrifice of either performance or cost. On one hand, more corrosion-resistant equipment coated with expensive materials like tungsten carbide coatings or high nickel containing steels can be installed at considerable cost. Alternatively, lower-performance materials like carbon steel or organic coatings can be applied, with the understanding that more frequent replacements will be needed. This paper presents a novel class of materials, called nano-laminated alloys that are based on the same conventional materials used today in galvanizing or metal coatings, but configured into nano-laminated structures that deliver significantly higher performance at a price that is competitive with conventional metals and coatings.

Calling on data from field tests carried out in collaboration with Chevron in various onshore fields in the Mid-Continent Region, this paper illustrates how nano-laminated alloys achieve higher performance than traditional alloys at comparable costs. The presentation will include a performance and economics data-rich comparison of nano-laminated alloy

coating performance and cost with conventional steels and coatings.

Two case studies are presented for downhole tubulars and downhole plunger lift systems. These case studies represent the conclusions of actual field trials. Results of these case studies review the up-front cost of the nano-laminated product installation, performance comparison both in lab and field trials and return on investment calculation for the nano-laminated products in the field environment.

KEY WORDS

Metallic coatings, nano-laminated, nickel, autoclave, pump, valve, tubular, plunger lift systems, corrosion, sour service, chloride resistance, mechanical properties, hydrogen, abrasion, nanotechnology, oilfield cost control, industrial nanomaterials, corrosion resistance, wear resistance

INTRODUCTION

“Nano-laminated materials” refers to a class of materials that are comprised of nanometer-scale particles deposited in layers that vary in composition, phase, material microstructure or a combination of these. Nano-laminated materials have been the subject of extensive research starting in the 1970s¹ and are of particular interest due to the unique performance characteristics that can be tailored through layer composition, layer thickness, microstructure, and other novel control parameters that are not available in the design of homogeneous materials.^{2,3}

For the purposes of this paper nano-laminated claddings are nickel-based metallic alloy systems applied electrochemically, at room temperature, to steel substrates to enhance the wear and corrosion resistance of the base material. The unique metal attributes achieved by nanolamination impart not only improved performance characteristics, but also overcome intrinsic material property tradeoffs (i.e. hardness and toughness, creep and fatigue, corrosion and wear) that are typically encountered in homogeneous materials.⁴ By balancing the trade-offs in conventional material performance, nano-laminated materials have the potential for broad application as surface coatings, claddings, bulk materials or as near-net-shape parts. Furthermore, nano-laminated materials, when properly designed, can possess ultra-high strengths, high resistance to fatigue damage, and resistance to environmental degradation.⁵ Studies involving nano-laminated structures have also demonstrated superior performance in impact toughness, wear resistance, damping, hardness, stiffness,

corrosion protection and other commercially-relevant properties.⁶

By leveraging phenomena that occur in these nano-laminated materials, it is possible to develop products that demonstrate dramatic improvements in structural, corrosion and high temperature performance, using readily available basic raw materials. Modumetal has significantly extended the number of options of these nano-laminated materials in the development of families of nano-laminated alloys for marine corrosion protection, downhole corrosion and wear protection, structural reinforcement and more.

Historically, nano-laminated materials have been produced via sputtering processes, which limited applications to academic research and small scale production. Today, Modumetal is scaling and commercializing production through a patented process that has enabled the commercial production of these materials in coating applications using large-scale manufacturing techniques similar to electroplating operations (US Patent no. 6,547,944). This paper describes the performance and return on investment in applications of a specific nano-laminated, nickel-based cladding used in energy industry applications.

EVALUATED MATERIALS

Nano-laminated test coupons and parts were produced by immersing metallic test coupons into a formulated electrolyte containing nickel and other metal constituents. The nano-laminated cladding profiled in this paper is based on a single, nickel-based nano-laminated alloy configuration. Traditional and proprietary metal finishing equipment and techniques were employed, including proprietary power delivery systems. A modulated electric field control system is used to deposit micron to millimeter thick coatings in nanometer thick sub-layers of alternating nickel-alloys through the coating thickness as seen in the cross-section Figure 1.

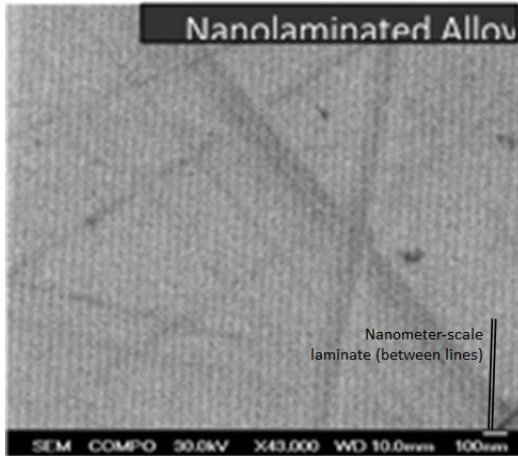


Figure 1: Cross section image of nanometer sublayer within nickel based nano-laminated test sample.

EXPERIMENTAL PERFORMANCE RESULTS

Prior to field evaluation, performance testing was carried out on the nano-laminated nickel alloys in order to establish suitability of use and to establish expected performance margins over conventional steels and corrosion-resistant alloy coatings. The following sections outline a subset of the performance tests that were carried out.

1.) Cladding Adhesion

In order to characterize the adhesion quality of nickel based nano-laminated claddings, bend adhesion testing was performed in accordance with ASTM B571 "Standard Practice for Qualitative Adhesion Testing of Metallic Coatings" Method 3.⁷ Three (3) 2" x 0.5" nano-laminated clad samples were loaded into a cylindrical mandrel bend tester with a 1/4" diameter mandrel. The test samples were then bent until a 0t bend was achieved then repeatedly back and forth until fracture of the substrate was achieved. Visual examination showed no signs of delamination between cladding and substrate. After the samples were further subjected to peeling and prying, visual examination of the samples at 10x magnification showed no signs of the delamination between the cladding and the substrate.

2.) Hardness Properties

Microhardness testing was performed in accordance with ASTM E384 "Standard Test Method for Knoop and Vickers Hardness of Materials".⁸ A 1cm² test specimen was cut from three (3) nickel nano-laminated clad samples and cast into epoxy at 300°F prior to being polished with 1600 grit Silicon-

Carbide paper. Vickers microhardness test was then performed on these specimens in accordance with ASTM E384, using a 50 gram load with a 10 second dwell time. The material hardness average for the nano-laminated claddings was calculated to be 562.5 ± 11 HV0.05. For purposes of comparison, the maximum microhardness of API grades J55 and L80 is 255 HV.

3.) Abrasive (Taber) Wear Resistance

The resistance of the nickel based nano-laminated claddings to taber abrasion was measured relative to electroless nickel and cold rolled steel on a rotating taber abrader according to ASTM D4060 "Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser"⁹ Annex X.1. Testing was setup using a 1000g load per wheel and type CS-17 taber wheels.

The graph in Figure 2 represents the compiled Taber wear index figures of various materials, including electroless nickel cladding. The nano-laminated claddings had the lowest average Taber wear index. Data for Nickel 200, electroless nickel⁹, SAE 1008 steel and Stainless Steel 316 are reported values.

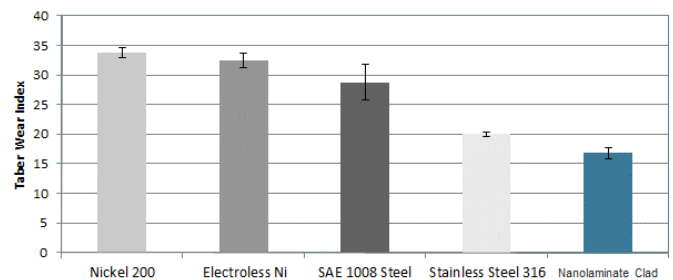


Figure 2: Taber wear index for Metallic coatings and steels.

4.) Erosive (Sand) Wear Resistance

The resistance of the nickel based nano-laminated claddings to particle impingement erosion was measured relative to Stellite-6®, Ultamet® and other treated steels. The erosion test was carried out in accordance with ASTM G76 entitled "Erosion Testing by Particle Impingement". Testing was setup using 50 micron sand at a 2" standoff distance and 30 degree impingement angle. 1.25 pounds of sand was used in each test for a duration of 2 minutes. Figure 3 shows the enhanced performance of the nano-laminated cladding when compared with conventional wear resistant claddings and surface treatment methods.

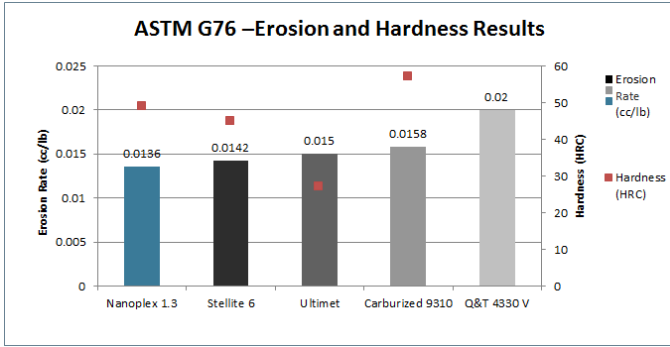


Figure 3: Erosion and Hardness of Nano-laminated Cladding.

5.) Pin on Disk Lubricity

Pin-on-disk testing was performed on nickel based nano-laminated cladded samples in accordance with ASTM G99 “Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus”¹⁰. The wear resistance measurements were performed by pressing a stainless steel pin with a 1.8” diameter hemispherical tip at a 1,656 gram load perpendicular to a flat rotating disk. The disk rotated at a rate of 163 rpm for four minutes and created a circular wear path on the disk due to the position of the pin. The results of pin on disk testing are summarized in Table 1. The nano-laminated cladding showed good resistance to sliding wear in losing 0.015g ±0.001 mass. Also, cross section comparison of the wear and non-wear paths show that the cladding integrity was not compromised during testing.

Table 1: ASTM G99 Pin on Disk Wear Test Results.

Nano-laminated Pin On Disk (ASTM G99)			
Sample Description	Pin Mass Loss (g)	Disk Mass Loss (g)	Avg. Mass Loss (g)
Nano-laminated Clad # 1	0.009	0.016	0.015
Nano-laminated Clad # 2	0.006	0.016	±0.001
Nano-laminated Clad # 3	0.005	0.013	

6.) Adhesive (Block on Ring) Wear Resistance

Adhesive wear testing was performed on nano-laminated claddings, Electroless Nickel (E-Ni) and bare steel samples in accordance with ASTM G77 “Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test”¹¹. Testing was setup using a test block of sample material loaded with 90 lbf against a test ring

of sample material. The ring was then spun against the block at a rate of 72 rpm for a given number of revolutions.

The total volumetric wear rate of the block and ring, calculated from the block scar width and ring scar width, and the mass loss rate of the block and ring are reported in Figure 4. The nano-laminated cladding outperformed the other systems and measured, on average a volumetric wear rate of 0.0113 ±0.0030 mm³/s.

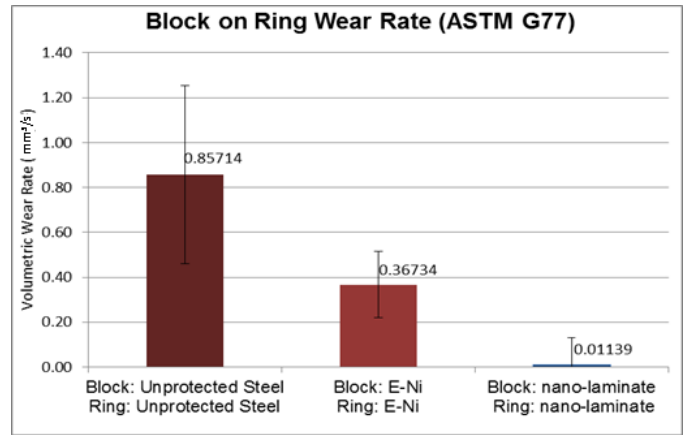


Figure 4: ASTM G77 Block on ring volumetric wear rate.

7.) Porosity Resistance (Salt Fog Evaluation)

Salt fog performance tests were used as a method to evaluate cladding for pin holes, porosity and defects. Testing was carried out on nano-laminated cladded steel panels relative to Electroless Nickel and run in accordance with ASTM B117 “Standard Practice for Operating Salt Spray (Fog) Apparatus”¹². Samples were evaluated every seven days over a period of 30 days. For every evaluation the samples were removed, photographed and graded in accordance with ASTM D610 “Standard Test Method for Evaluating Degree of Rusting on Painted Surfaces.”

After 30 days of salt fog exposure, the nano-laminated cladded samples visually outperformed the Electroless Nickel group as shown in Figure 5. The E-Ni samples were rated 4-General (~10% red rust coverage) and 5-General (~3% red rust coverage) whereas the nano-laminated samples ranged between 10 (No Rust) to 7 (~0.3% red rust coverage).

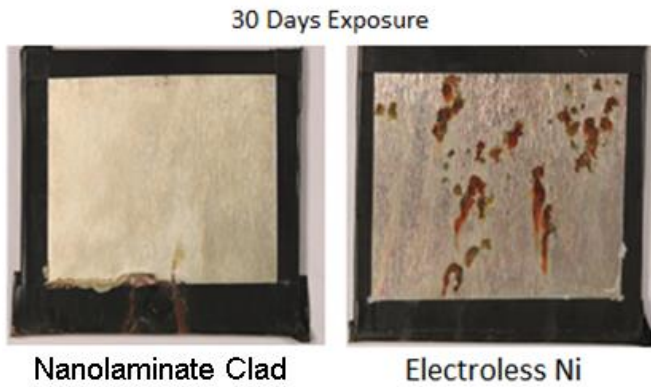


Figure 5: Representative performance of Nano-laminated clad and Electroless nickel panels after B117 testing.

8.) Hydrochloric Acid (15% (vol.)) Resistance

Resistance corrosion via chloride attack was performed on nano-laminated clad steel panels relative to Electroless nickel in accordance with ASTM G31/NACE TM0169 “Standard Guide for Laboratory Immersion Corrosion Testing of Metals”¹³ in a solution of 15% (vol) Hydrochloric Acid at 25°C. After 30 days of immersion in 15% Hydrochloric acid. The mass loss data, surface roughness and visual comparison are summarized in Figures 6 and 7.

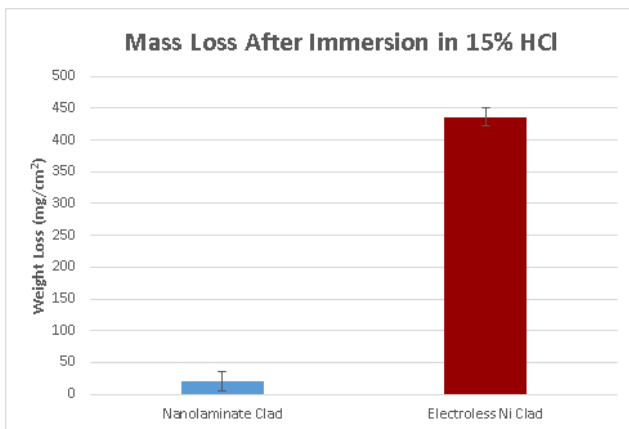


Figure 6: Mass loss of Nano-laminated and Electroless Ni clad samples after immersion.

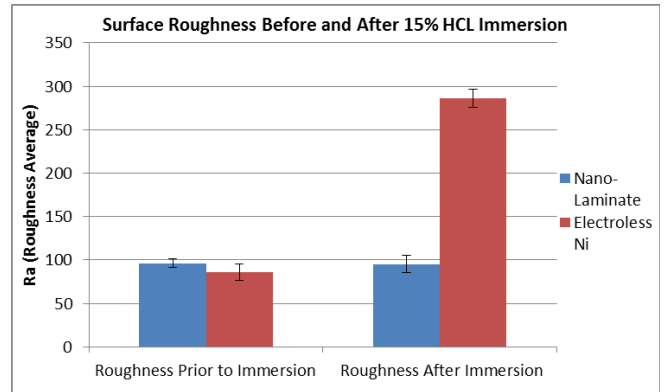


Figure 7: Surface roughness before and after immersion in 15% HCl.

9.) Autoclave Corrosion Resistance (100% CO₂)

Autoclave testing in accordance with guidelines provided by NACE TM0185¹⁴ was performed on nano-laminated clad steel test coupons, stand-alone nano-laminated cladding and unprotected steel coupons. Testing was performed in the two phase system with individual samples being exposed exclusively to a single phase. The aqueous phase consisted of an 8% sodium chloride solution at a starting pH of 3.5. The gas phase consisted of 100% carbon dioxide with sufficient gas to achieve 1000 psi. Samples were exposed to their respective phases for a period of 30 days at a temperature of 250°F

After the 30 day exposure, samples were removed from test, cleaned, and evaluated for mass loss. Nano-laminated clad samples and free-standing nano-laminated material as shown in Figure 8.

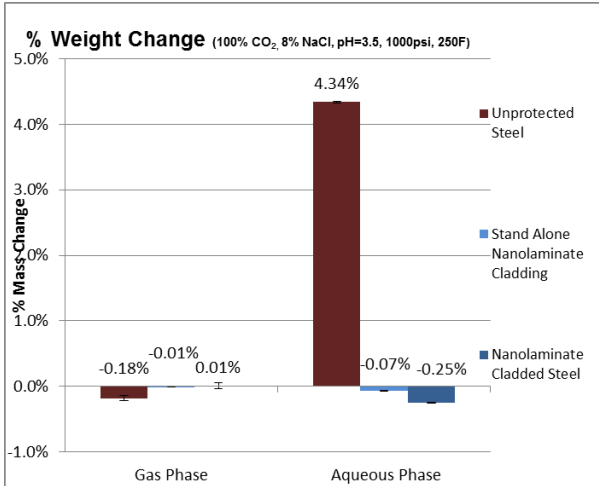


Figure 8: 100% CO₂ exposure (NACE TM0185) test results.

10.) Autoclave Corrosion Resistance (5% H₂S, 5% CO₂)

Additional autoclave testing in accordance with guidelines provided by NACE TM0185¹⁴ was performed on nano-laminated clad steel test coupons and unprotected steel coupons. The aqueous phase consisted of an 8% sodium chloride solution at starting pH of 3.5. The hydrocarbon phase consisted of a 1:1 mixture of kerosene and toluene. And the gaseous phase consisted of a 5% hydrogen sulfide and 5% carbon dioxide mixture (with balance methane). Sufficient gas mixture was introduced to achieve 1000 psi within the vessel. Samples were exposed to their respective phases for a period of 96 hours at a temperature of 250°F.

After the 96-hour exposure, samples were removed from test, cleaned, and evaluated for mass loss. Figure 8 compares the corrosion resistance of the two sample types and shows the approximate 15 times performance improvement of nano-laminated clad samples over unprotected steel systems.

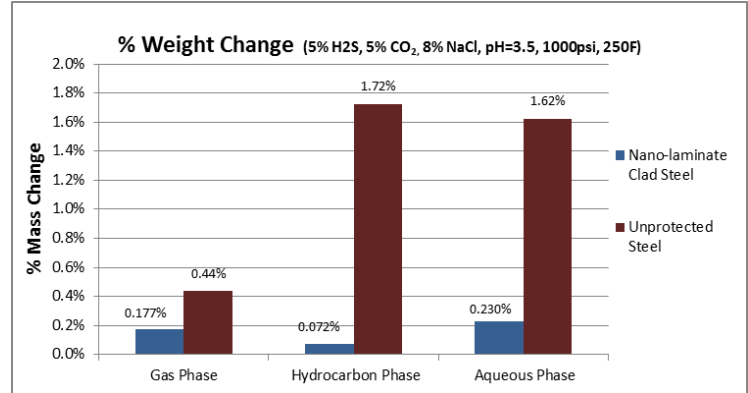


Figure 9: 5% H₂S, 5% CO₂ exposure (NACE TM0185) test results.

The nano-laminated clad demonstrated significant improvement in corrosion, wear and structural performance when compared both with conventional 4130 steel grades as well as when compared with conventional metal cladding systems.

FIELD TRIAL RESULTS AND RETURN ON INVESTMENT

The following section shows the field performance as the result of trials carried out in Chevron’s Mid-Continent Business Unit (MCBU), USA. MCBU is one of Chevron’s producing business entities that manages a large resource base of oil and liquids-rich gas opportunities within the central United States. MCBU places strong focus on cost efficient production. One of the main challenges is to extend well and downhole artificial lift life experiencing erosion/corrosion problems. Nano-laminated alloy coating materials were evaluated and selected for field trials due to cost competitiveness and performance compared to the existing materials

1.) Plunger lift system application

Plunger lift system field trials were specifically carried out in one of Chevron’s fields in Texas and Oklahoma areas, where 25% of the wells are using plunger lift systems. These wells experience plunger lift challenges. Typically, the plunger lift has to be replaced every two (2) months due to corrosion/erosion. The plunger pistons in these wells typically run 20-30 trips per day at an average travel speed of 700 ft/min. Failure of the plunger lift systems is typically a result of adhesive wear and loss of dimensionality of the plunger piston causing loss of system pressure and production rate.

Figure 10 illustrates plunger lift components. 4-6 mils of nano-laminated nickel alloy was cladded on the plunger piston, over the carbon steel based material.

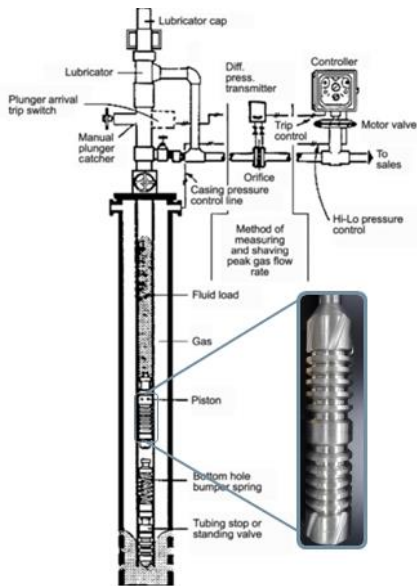


Figure 10: Plunger lift system lift schematic and an example Nano-laminated clad piston/plunger lift system component.¹⁵

When considering the relatively thin coating thickness and associated wear rate of steel versus the nano-laminated alloy, it is important to note that this nano-laminated nickel alloy coating was chosen for its resistance to adhesive wear and hardness. A high hardness material which does not wear in the environment is alternatively not desirable as this would result in wearing of the production tubular, a more expensive replacement.

Nano-laminated clad plunger lift systems were installed in three (3) wells. The results reported herein are analyzed from one well, referred to as “Well W.”

A nano-laminated clad clean-out type plunger lift system was deployed in the Well W and was evaluated for dimensional changes to the outside diameter (OD) after 98 days and 135 days. A non-clad, clean-out plunger lift system was deployed immediately in the same well and was evaluated after 62 days in service at which time it was deemed to have reached the end of its service life as it was out of tolerance (Figure 11).

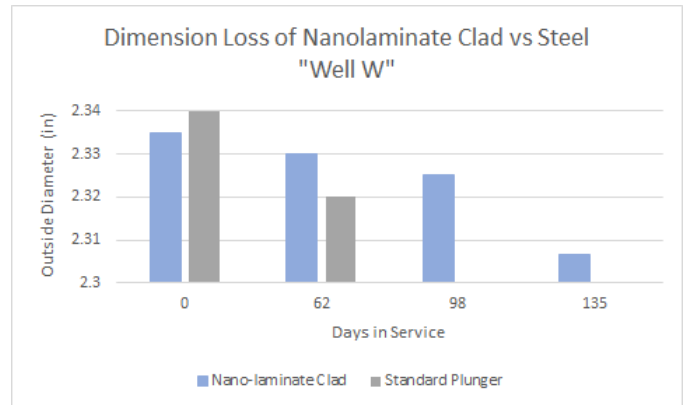


Figure 11: Dimensional changes of Nano-laminated clad plunger lift system vs. Steel plunger lift system (Note: performance of the nano-laminated clad plunger lift system is estimated at the 62 day point).

The relative wear rate of the steel clean-out plunger lift system compared with the nano-laminated nickel clad plunger lift system is illustrated in

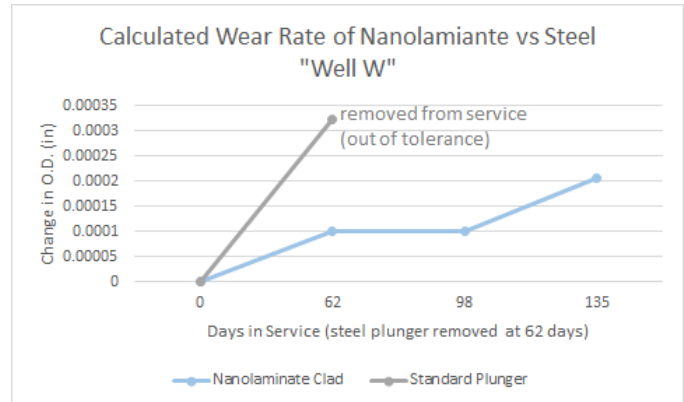


Figure 12. It appears that in the range of 100-130 days, the thin-layer of nano-laminated cladding was starting to wear and the substrate steel was being exposed to wear in some areas. This was corroborated by post-trial analysis of the nano-laminated plunger lift system dimensions, which showed some wearing only at the edges of the piston (after 135 days) as illustrated in Figure 13.

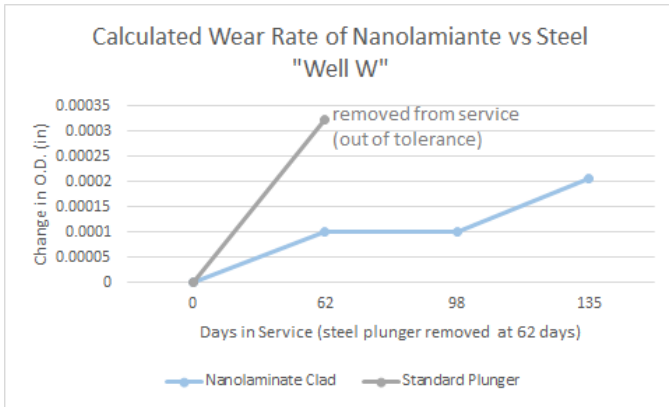


Figure 12: Wear rate comparison of Nano-laminated clad plunger lift system versus Steel.

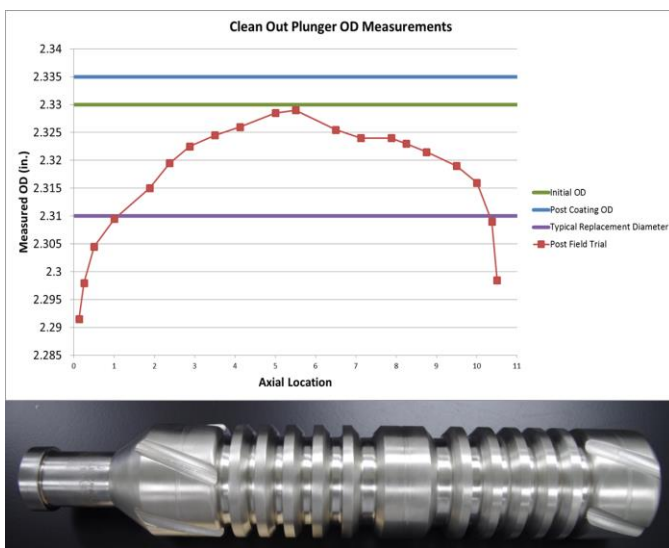


Figure 13: Dimensions of Nano-laminated clad plunger lift system following field trial (Note: out of tolerance only reached at leading and trailing edges).

The reduced wear rate of the nano-laminated nickel alloy is a good combination of lower wear rate without transference to a tubular wear mechanism.

As demonstrated in the Well W example, only 0.002" (2 mils) of the nano-laminated coating on the surface of the plunger has extended the run life of the system over two (2) times.

2.) Production Tubular Application

In MCBU, the mean time before failures (MTBF) of the wells are varied depending on, for example, type of reservoir fluids, artificial lift methods, etc. Typically, in this area the MTBF of J55 grade tubular is 5-7 years. However, some of these wells have short MTBF, 1.5-2 years, due to microbial induced corrosion (MIC) or corrosion due to produced water and dissolved gas breakout. The MTBF is shorter, less than 1.5

years, if the wells are having MIC and mechanical wear from artificial lift.

Tubular field trials were carried out in 4 wells. This field trial provides results for the Well V. The Well V experiences both MIC problems and tubing wear (the latter due to rod pump operations). The 2-7/8" J-55 10' pup joint was clad using the nano-laminated nickel alloy. The pup joint was deployed in a segment of the well, where it was previously shown that prior failures had initiated. The parameters of the deployment are outlined in Table 2.

Table 2: Nano-laminated clad tubular dimensions & deployment information.

Unit	Measure
Diameter	2 7/8"
Length	10'
Weight (before cladding)	6.5 ppf
Nano-laminated clad thickness	0.8 mm
Tested Depth	2,564'



Figure 14: Installation of nano-laminated clad pup joint to improve corrosion performance and reduce rod wear.

With a nano-laminated pup joint this well has demonstrated a run life of over a year. This is compared with the previous mean time to failure of 175 days for this well. The nano-laminated pup joint has been in the well since November, 2014 without interruption of operation, resulting in both workover cost savings and no lost production opportunity due to well downtime.

In addition to direct maintenance costs, the frequent replacement schedule also drives the need for an additional

rig, and reduces production during the workover operation. The appropriate nano-laminated thickness was used in the calculation.

The nano-laminated clad tubular cost is correlated to cladding thickness and substrate diameter, which is defined based on specific well parameters. Figure 15 illustrates the relative cost of nano-laminated clad tubulars in comparison with conventional corrosion resistant tubular options. This comparison illustrates the cost differential between a nano-laminated clad, J55 tubular string and the next best option for corrosion mitigation, which is a 13% chromium or “super” 13% chromium tubular alloy type.

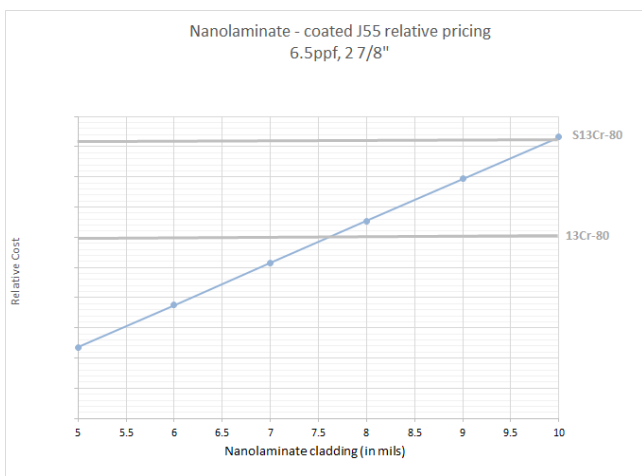


Figure 15: Nano-laminated clad tubular relative pricing analysis (NOTE: The 13% chromium alloy grades are not available in a J-55, 55 ksi option and are shown here for an 80 ksi, L-80 steel grade.).

A model was run to estimate the projected return on a marginal production scenario based on this well’s depth and previous MTBF characteristics. Return is presented as return on the tubular Assets (ROA), where ROA is calculated as:

$$ROA = \frac{\text{Cumulative Margin} - \text{Cumulative Asset Cost}}{\text{Cumulative Asset Cost}}$$

These scenarios are intended to reflect production rates and margins for “trouble” wells that may be best shut-in rather than operated in present market conditions. Table 3 outlines the assumptions were made to support this estimate scenario.

Table 3: Return on Assets Model Assumptions.

Model Parameter	Value	Units
Well depth	2564	feet
\$/ft J55	5.80	USD

\$/ft NL-clad J55 (6 mil)	20.00	USD
MTBF J55	175	days
MTBF NL-clad J55	700	days
Cost of Workover	60,000	USD
Time for Workover	5	days
Production Rate	50	barrels/day

This scenario assumes that the entire tubular string is clad with the nano-laminated material, which likely over-estimates the cost of the installation itself as likely only troubled sections of the well would need to deploy the nano-laminated cladding.

Based on the projected cost of a J55 tubular, clad with the nano-laminated alloy, the cumulative ROA in the nano-laminated clad tubular assets to date is well over 5.5 times that of the J55 tubulars as shown in Figure 16.

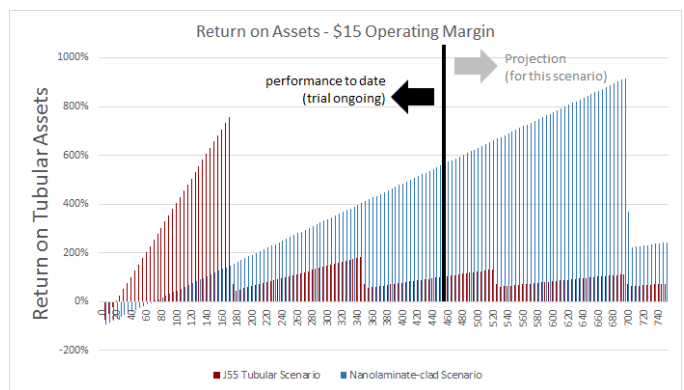


Figure 16: ROA comparison between J-55 and Nano-laminated tubulars at \$15 operating margin.

The impact of this return on asset and asset maintenance cost is even more compelling when considering a less profitable market environment. In a low rate production well, operating in a \$5/barrel margin environment, the nano-laminated clad tubular could mean the difference between a well that generates return and one that does not ever reach a positive ROA condition as shown in Figure 17.

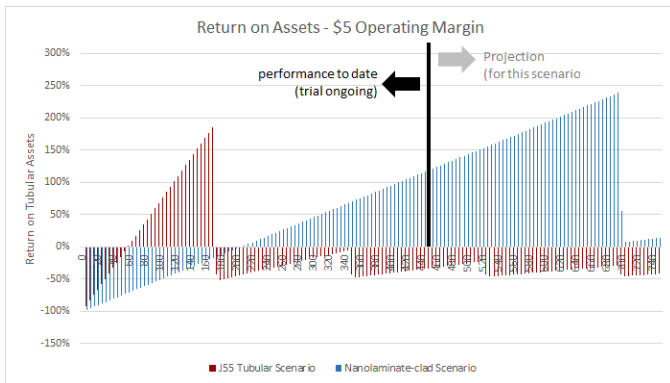


Figure 17: ROA comparison between J-55 and Nano-laminated tubulars at \$5 operating margin.

Nano-laminated clad alloy improves return on assets, especially in a low operating environment, by reducing downtime due to fewer workovers. This can result in a 2% increase in revenue for a given well.

DISCUSSION

The unique and impressive combination of properties offered by the nickel-based nano-laminated cladding is attributed to interactions that occur uniquely at the interfaces between laminates. Today, Modumetal has fielded parts that are clad with nano-laminated nickel-based applications in downhole environments on artificial lift systems and tubulars.

This paper has demonstrated characteristics and applications of nano-laminated claddings for downhole corrosion and wear prevention and the implications of the return on assets realized in artificial lift and tubular applications of the nano-laminated claddings, especially important in the current low-margin production environment.

Surface modification to enhance or repress the interaction of corrosive operating environments with the metallic (typically steel) surfaces found in the majority of the oil and gas production and processing assets has the potential to offer a step change in the cost of development and operation.

Nano-laminated technique offers significant corrosion, wear and erosion protection in hydrocarbon producing environments at a fraction of what conventional alloy alternatives would cost. This can have a significant impact on reducing production operating costs, increasing asset longevity, and improving overall safety

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