

In-situ Corrosion Testing of ENP-PTFE Coatings in Geothermal Environment

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ABSTRACT

Electroless nickel-phosphorus coatings with PTFE (Ni/P-PTFE) have been reported to have excellent corrosion resistance¹. The corrosion behaviour of the Ni/P-PTFE varies depending on the P content in the coating system due to its microstructure. High P (HP) content has been reported to have higher corrosion resistance in acidic environment compared to low P (LP) content due to more amorphous structure².

This work demonstrates the integrity of Ni/P-PTFE top functional coating layer with low and high P content deposited on Ni/P adhesion layer without PTFE both on coupons and U-bend carbon steel samples exposed to geothermal conditions. The samples were tested for three months in-situ geothermal steam at Hellisheiði power plant. The tested samples were taken out after 3 months and evaluated using SEM/EDX analysis. Characterization results revealed a reaction between sulphur (S) from geothermal environment to Ni, resulting in nickel sulphide (NiS) compound generated on the top functional layer. The

results showed stress crack formation in coating possible due to hydrogen released from hydrogen sulphide (H_2S) with reaction to the Ni in the film. In aerated environment where pin hole formed during exposure or production an under film galvanic corrosion was seen.

Key words: Geothermal corrosion, electroless plated nickel coatings, PTFE particles,

INTRODUCTION

Ni/P coatings applied on carbon steel are well-known for its corrosion, wear and abrasion resistance in various environments including geothermal corrosion media such as CO_2 , H_2S and high salinity^{2,1}. However, the coating has been reported to be unsuitable in a corrosive environment with media containing chloride-based product, ferric sulphate and ammonium¹. Coatings in the geothermal condition are exposed to synergy effect of several corrosion species together with high temperature and pressure which is generally not tested for in the lab. The reported research work that have been done on corrosive resistance of electroless nickel coating having individual presence of Cl^- , acid, CO_2 or H_2S at room temperature and ambient pressure³. However recent work done by Chong Sun et al studying demonstrated the importance of investigate the synergy effect which is reported in Unravelling the effect of CO_2 and H_2S on the corrosion behaviour of electroless Ni/P coating in $CO_2/H_2S/Cl^-$ environments at high temperature and pressure demonstrated synergy corrosive effect of CO_2 , H_2S , Cl^- on Ni/P coatings⁴.

One of the main limitations of using Ni/P coatings in geothermal environments is the possibility of adverse effects of corrosion at the coating-substrate interface. The coatings are reported to have strong substrate adhesion. However defects on the interface can initiate corrosion². Furthermore, it has been reported that P diffuses out of Ni/P coatings in a CO_2 environment. S products are known to be high corrosive and is H_2S is known to be corrosive due to hydrogen penetration that embrittles the metal and accelerates corrosion rate. Ni is known to intensively absorb hydrogen promoting volume expansion and crystal damage resulting in a brittle material⁵. H_2S is more corrosive compared to sulphur dioxide (SO_2)⁶. It was reported by Lee et al. that the concentration of 0,1% H_2S results in higher corrosion rate compared to 1 % SO_2 in an aerated environment on carbon steel. Moreover the iron sulphide scale formation is reported to grow fast, to be fragile and to be non-adhering⁶.

Modifying the standard Ni/P coatings with PTFE particle can improve the tribological properties, reduce the friction coefficient, increase wear and corrosion resistance of the coating and providing excellent self-lubricity^{7,8}.

This research work intends to understand the behaviour of Ni/P coating with PTFE particles coated on carbon steel in different geothermal applications. The work consists of two different test conditions with different test purposes:

- A) Geothermal Wellhead environment, common environment in geothermal plant
- B) Aerated environment, oxygen rich and highly corrosive environment.

In the wellhead the coupons both consist of full coating cover of the sample and U-bend sample with induced cracks. The induced cracks create vacancy in the coating resulted in space for volume change of the coating. The aerated environment demonstrated if coating failure or defects reaches the substrate a under film galvanic corrosion will accrue.

EXPERIMENTAL PROCEDURE

The study was done on two different coating types of electroless nickel coating on carbon steel. Both coatings had same adhesion layer, primer, which is high in P. The topcoats contain PTFE particles but

the varies in P. The LP coating contains 4,2 wt% after deposits while HP has 12,9 wt%. The coating was tested in two different environments.

Coating process methods

Substrate preparation

Carbon steel samples were first put in a hot (~50°C) alkaline solution for 15 min. The samples were cleaned with deionised (DI) water and etched in hot (~50°C) H₂SO₄ solution. The time for etching depended on the thickness of oxide layer present on the sample surface. Once the oxide layer was removed, samples were rinsed in DI water. During etching, samples were removed periodically and rinsed with DI water to ensure that they were not over-etched. A continuous film of water on the surface of the sample after etching indicated that the surface was ready for nickel plating. The samples were then quickly transferred to electroless nickel (EN) bath.

Electroless Nickel plating bath formulation

The type and the amount of chemicals used in the bath depended on the amount of phosphorus targeted in the Ni/P layer. More specifically, the chemical make-up of the baths formulated for low (~4wt% P) and high (>11wt%P) phosphorus in the deposits were different, although they were based on the chemicals shown in Table 1. All chemicals were of analytical grade and purchased from Sigma Aldrich and Fisher Scientific.

Table 1: Key chemicals and their quantity (per litre) used for preparing EN baths.

Chemical	Range
Nickel sulphate	0.1-0.11M
Sodium hypophosphite	0.19-0.28M
Sodium citrate	0.035M
Acetic acid/ammonium hydroxide	Regulating pH (5.5-6.2)

Preparation of aqueous dispersion of PTFE particles:

In order to produce EN composite coatings with a homogeneous dispersion of PTFE particles, an aqueous dispersion of PTFE particles was prepared. PTFE particles, due to their hydrophobic nature, cannot be dispersed homogeneously in water. Therefore, a procedure was developed for preparing an aqueous dispersion of PTFE particles. Specifically, 10gm of PTFE (particle size <0.5µm; Sigma Aldrich) and ~100gm of surfactant (CTAB) were mixed in 100ml of DI water and stirred using a magnetic stirrer for 2 hours. After this step, the solution was subjected to ultrasonic treatment for 3 hours. This step de-agglomerated the PTFE particles and produced a homogeneous aqueous dispersion. This was confirmed by the particle size distribution, which was obtained using dynamic light scattering method (instrument: Malvern ZetaSizer Nano-S). A unimodal distribution was seen with the average size of PTFE particles of around 307nm. This PTFE aqueous dispersion was then mixed in the different EN baths to produce Ni/P coatings with low and high P, with a homogeneous PTFE particle distribution (i.e. low P + PTFE and high P + PTFE).

Production of duplex coatings

All EN plating trials were performed in a fumehood. Beakers containing EN plating solution were placed on a multi-hot plate kit. The hot plates were also capable of magnetically stirring the EN plating solution that was placed in the beakers. For the production of duplex coatings with Ni/P undercoat and Ni/P-PTFE topcoat on carbon steel substrates, two beakers, one with EN solution (for undercoat) and the other with EN+PTFE dispersion (for topcoat), were heated simultaneously. In order to produce specimens with duplex coating, the samples that were etched were first immersed in the EN bath to deposit Ni/P layer (undercoat). After a specific time, which depended on the rate of deposition, the specimens were quickly transferred into the second bath consisting of plating solution that resulted in deposits containing PTFE

particles homogeneously distributed in Ni/P matrix (topcoat). During both depositions, temperature of the solutions was maintained above 60°C while the pH was maintained between 5.5 and 6.2 (depending on the phosphorus content) along with agitating the solution with a magnetic stirrer.

Test exposure

The testing was done at ON at Hellisheiði geothermal plant in two different geothermal conditions.

- 1) Downhole exposure test connection to a wellhead, HE-23
- 2) In aerated fluid connected to separator water from the power plant.

The coated sample was exposed to three different testing purposes as seen in

Table 2. The tests conditions are described in two separated chapters below.

Table 2: An overview of the test exposure and purpose.

Test number	Test location	Sample	Purpose
1	Wellhead-23	Coupon-with coating	Understanding coating behaviour in geothermal wellhead environment
2	Wellhead-23	U-bend- with a cracked coating	Understanding the coating-substrate behaviour where there are defects. The defect allows for volume expansion on the material reducing stress build.
3	Aerated test location	Coupon-with coating	Understanding coating behaviour in oxygen-rich environment

Wellhead-23

In the wellhead, the test conditions of the wellhead were 194 °C and pressure of 12.6 bars. The chemical in the environment is shown in Table 3

Table 3: Chemical analysis of the environment.

Parameter	HE-23
Test	Test A
Date of sampling	8th July 2009
T [°C] well top	194
P [bar, gauge]	12.6
GAS - Steam analysis:	
CO ₂ base [mg/kg]	15017
H ₂ S base [mg/kg]	1363.4
Cl ⁻ [mg/kg]	62.1
SO ₄ ²⁻ [mg/kg]	58.44

The tested samples were coupons and U-bend samples. The coupon samples and U-bend samples were placed on a rack and into the geothermal wellhead seen in Figure 1 A. The wellhead during exposure is shown in Figure 1. The test duration was 3 months. The microstructure analysis was done with BES/EDX. The EDX results show the elements over 0.5% due to measurements uncertainty. Samples were cross-sectioned 12 mm from the bottom of the samples.

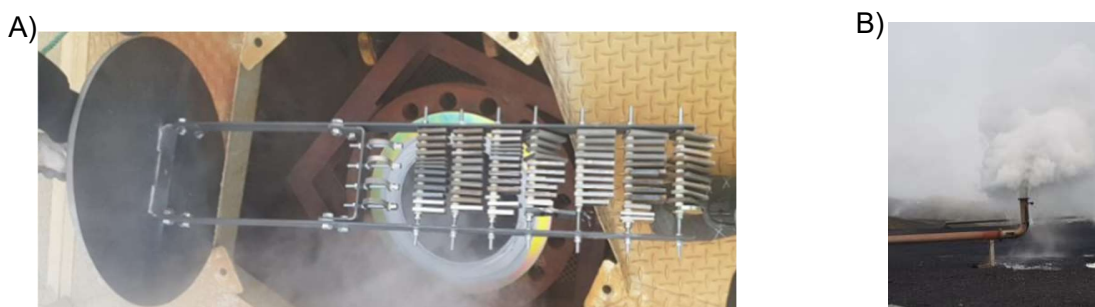


Figure 1: A) The exposed sample on a sample holder and the inlet to the wellhead, B) the wellhead where the samples are exposed.

Aerated testing unit

The aerated testing equipment simulates the environment of the suction of the condenser where the steam mix with high in humidity air. The equipment was manufacture to test coating in oxygen rich environment where sulphuric acid is formed and there is reduction in pH. There are possibilities for S and another dissolved element to be present in the simulated environment. For simulating the harsh environment test set-up was build shown in Figure 2

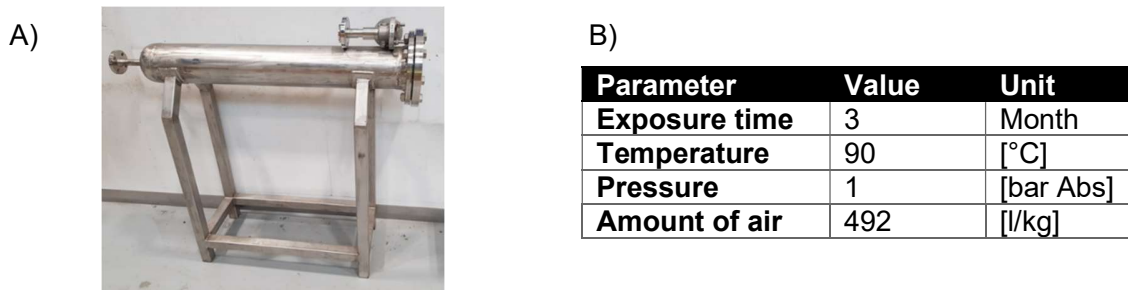


Figure 2: A) Aerated testing equipment, B) the test conditions of the testing.

RESULTS

Wellhead testing

Coupons

The visual corrosion inspection in wellhead 23 of Ni/P-PTFE coating show less corrosion compared to carbon steel tested in the same environment as reported in (a reference to our substrate paper). The environment consists largely of H_2S which is by far more corrosive compared to SO_2

The coupon for both high and low containing phosphor in Ni coating showed corrosion spot and the sample side deposits indicated galvanic corrosion between the coating and the carbon steel substrate as seen in Figure 3A and Figure 6A. The results chapters are divided after coating high in P and low P.

Ni/P-PTFE-HP

The optical microscopic image in figure 3B shows colour difference indicating corrosion spots. The back-scatter images (BES) shows surface texture Ni sulphate, the surface seems to be uniform. The cross-