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#### D4.4: Influence of heat treatments on mechanical and chemical properties of PTFE based composite coatings

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# GEO-COAT

DEVELOPMENT OF NOVEL AND COST-EFFECTIVE CORROSION RESISTANT COATINGS  
FOR HIGH TEMPERATURE GEOTHERMAL APPLICATIONS



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## SUMMARY

This report provides details of the effect of heat treatments on the properties of polytetrafluoroethylene (PTFE) based electroless nickel-phosphorus (Ni-P) composite coatings on mild steel substrates. Duplex coatings containing low (~4%), medium (6-8%), and high (>11%) phosphorus were produced by altering bath chemistry and subjecting coatings to two different heat treatments: 8 hours at 250°C and 2 hours at 300°C. Both heat treatments resulted in the formation of hard Ni<sub>3</sub>P phase, which was confirmed from X-ray diffraction (XRD) data of high P deposits. The volume fraction of Ni<sub>3</sub>P phase in low and medium P deposits was below the detection limit of laboratory XRD, and its presence was inferred indirectly from the hardness measurements. Variations in the hardness values as a result of the heat treatments did not follow a specific trend, potentially due to the differences in the amounts of soft PTFE particles and hard Ni<sub>3</sub>P phase, in addition to the likely differences in the thickness of the deposits. For low P duplex coatings, heat treatment at 300°C resulted in an increase in hardness from 288±45 HV<sub>0.5</sub> to 502±82 HV<sub>0.5</sub>, while for high P duplex coatings, the hardness increased from 255±34 HV<sub>0.5</sub> to 261±34 HV<sub>0.5</sub>, compared with the as-deposited condition. Heat treatment at 300°C resulted in a decrease in the wear rate from 1.2E-05mm<sup>3</sup>/Nm in the as-deposited state to 1.03E-05mm<sup>3</sup>/Nm in the heat treated condition for low P duplex deposits. For the high P deposits, the wear rate decreased from 3.34E-04mm<sup>3</sup>/Nm in the as-deposited condition to 6.57E-06mm<sup>3</sup>/Nm when heat treated at 300°C.

Corrosion performance deteriorated as a result of the heat treatments while the wear rate decreased suggesting that the two properties are mutually exclusive. It was concluded that for the intended application (coatings for heat exchangers), in order to have superior corrosion performance, low P and high P duplex coatings will be tested in the simulated and actual geothermal conditions in the as-deposited condition.

## Objectives Met

The current deliverable contributes towards the following work package objectives:

- To study the effect of heat treatment on mechanical and chemical properties of PTFE based composite coatings

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## 1. INTRODUCTION

Heat exchanger materials used in geothermal power plants are subjected to degradation mechanisms such as corrosion, fouling, scaling, and wear. Coatings can be used in order to mitigate these effects, which can potentially extend the time between cleaning cycles and increase the operating life of heat exchangers. Deposition of coating materials allows the usage of cheaper structural materials (e.g. less expensive steel grades as opposed to more expensive corrosion resistant alloys) for manufacturing the heat exchangers, which in-turn results in significant cost savings and aligns with our efforts towards sustainable manufacturing. Within the Geo-Coat project, composite electroless nickel coatings were proposed for evaluating their suitability to improve the operating efficiency and decrease the costs associated with manufacturing and heat exchangers.

Within the Work Package 4 (WP4) of Geo-Coat project, tasks 4.2, 4.4, and 4.5 involve development of the electroless nickel plating (ENP) process for the production of polytetrafluoroethylene (PTFE) based composite coatings on mild steel substrates. Task 4.5 specifically involves the development of suitable post-deposition heat treatments in order to optimise the corrosion performance and tribological properties of the coatings. EN coatings based on nickel-phosphorus (Ni-P) binary alloy are widely used in various industries such as oil and gas, automotive, etc [1], and were therefore considered for development in this project. While Ni-P coatings have superior corrosion and wear resistance properties, additional functionalities such as anti-fouling and anti-scaling, which are important for heat exchanger application, can be imparted by incorporating suitable nanoparticles in the coated matrix. Specifically, by incorporating sub-micron sized PTFE particles in the Ni-P matrix, the surface energy of the coatings can be markedly reduced which make the coatings hydrophobic (water contact angle greater than 90°) and also reduce the coefficient of friction. Additional advantages of PTFE include chemical inertness and relatively high melting point (~326°C). Optimising the alloy chemistry, volume fraction of PTFE particles, and post-deposition heat treatment procedures can potentially alleviate the problem of corrosion, wear, fouling and scaling in heat exchangers.

## 2. OBJECTIVE

The main objective of the present work was to perform heat treatments on the EN-PTFE composite coatings deposited on mild steel substrate, and understand their effect on the microstructural development, mechanical, and tribological properties. This work builds on the body of work carried out in Task 4.2 and Task 4.4, which involved the development of EN-PTFE composite coatings on mild steel substrates. Coating process development activities and the results obtained were described in deliverable reports D4.1 and D4.3.

## 3. WORK CARRIED OUT

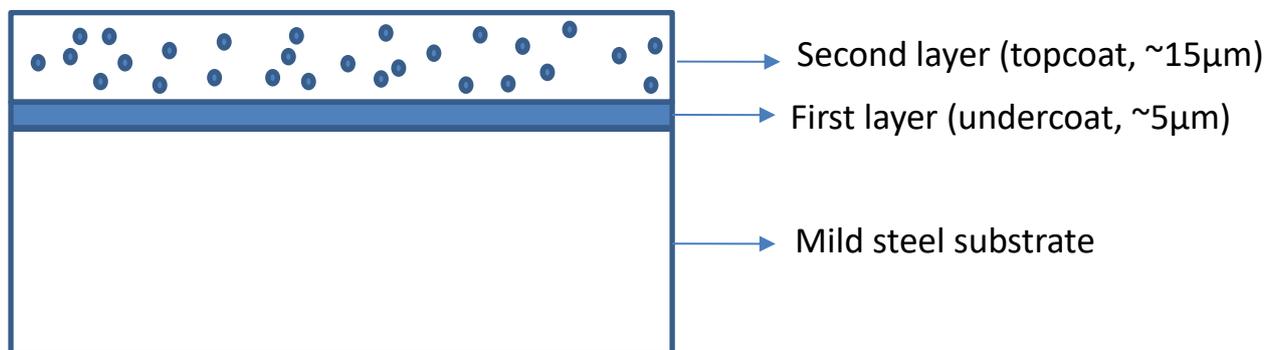
Duplex electroless nickel coatings (i.e, ~5µm thick Ni-P undercoat and ~15µm thick Ni-P topcoat with homogeneous distribution of PTFE particles) with varying phosphorus contents (i.e 4-5wt%, 6-8wt%, and >11wt% P) were produced, and subjected to two different heat treatments. A schematic of the duplex coatings produced in this work is reproduced (Figure 1) in this report from deliverable report D4.3 for clarity. The coated specimens were heat treated at 250°C for 8 hours and 300°C for 2 hours under vacuum ( $5 \times 10^{-4}$  mbar or better). Electron microscopy, X-ray diffraction (XRD), microhardness, tribological, and corrosion tests were performed on the specimens to understand the effect of the two

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heat treatment regimes on their microstructure, hardness and tribological properties, and corrosion resistance.



**Figure 1** Schematic showing the mild steel substrate along with Ni-P undercoat and Ni-P+PTFE topcoat. Solid blue features in the topcoat represent PTFE particles.

## 4. MATERIALS AND METHODS

The procedure for producing Ni-P and PTFE based composite coatings was described in detail in deliverable report D4.3. Here, only a brief description is provided. Mild steel substrates were first put in a hot ( $\sim 50^{\circ}\text{C}$ ) alkaline solution for 15 min, cleaned with deionised (DI) water, and then etched in hot ( $\sim 50^{\circ}\text{C}$ ) sulphuric acid ( $\text{H}_2\text{SO}_4$ ) solution to remove the surface oxide layer. Once etched, the samples were immediately transferred into successive electroless nickel plating (ENP) baths for depositing the Ni-P coatings (i.e. first, ENP bath for undercoat and then ENP+PTFE bath for top coat, Figure 1). The coatings produced contained low ( $\sim 4\text{wt}\%$  P), medium (6-8wt% P) and high ( $>11\text{wt}\%$  P) phosphorus in the deposits. Three baths were developed for undercoat (i.e. low P, medium P, and high P) and three baths for top coat (low P + PTFE, medium P + PTFE, and high P + PTFE), making a total of six different baths. The average size of PTFE particles was around 307nm.

Chemical compositions of the baths were tailored to produce the desired amount of phosphorus, and were based on chemicals such as nickel sulphate, sodium hypophosphite, and sodium citrate. The plating conditions were as described in D4.3. It is pointed out that medium P specimens were not considered for further evaluation (i.e. for WP6 and WP8 where the samples are being tested under simulated and actual geothermal conditions, respectively) due to their poor corrosion performance (results reported in deliverable D5.3), although some characterisation has been performed to observe the trends as a function of the phosphorus content in the deposit.

The coatings were subjected to two different heat treatments:  $250^{\circ}\text{C}$  for 8 hours and  $300^{\circ}\text{C}$  for 2 hours under vacuum ( $5 \times 10^{-4}$  mbar or better). The specimens produced for this study and the nomenclature used to identify the specimens are shown in Table 1. Specimens were further characterised using electron microscopy, XRD, Vickers micro hardness, and pin-on-disc tests. For electron microscopy, cross-sections of the specimens were obtained by sectioning them using a low speed diamond saw. They were mounted in Bakelite, ground and polished to  $0.25\mu\text{m}$  finish using standard metallographic procedures. Backscattered electron (BSE) images were obtained on a field emission gun scanning electron microscope (FEG-SEM). XRD data were collected using Bruker D8 Advance equipped with a copper source. Patterns were obtained with a step size of  $0.02^{\circ}$  and a dwell time of 1 second. Quantitative phase analysis using the Rietveld method was not attempted, and the data were only used for qualitatively identifying the presence of potential phases based on Ni-P phase diagram. Vickers microhardness tests were performed on the coatings using 500gm load and reported as an

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average of five readings. While the load used was high for coatings, values below 500gm did not give indents useful for extracting hardness data. It is also emphasised that the hardness values in this case will be of the composite (i.e. of the substrate and the coating) and not of the coatings alone. While the absolute values do not reflect the actual hardness of the coatings, the relative changes in the hardness values can be inferred.

**Table 1** The specimen nomenclature along with their description produced in this work.

Specimen nomenclature	Description
LP	Low phosphorus Ni-P deposit.
MP	Medium phosphorus Ni-P deposit.
HP	High phosphorus Ni-P deposit.
LP250	Low phosphorus Ni-P deposit heat treated at 250°C for 8 hours.
MP250	Medium phosphorus Ni-P deposit heat treated at 250°C for 8 hours.
HP250	High phosphorus Ni-P deposit heat treated at 250°C for 8 hours.
LP300	Low phosphorus Ni-P deposit heat treated at 300°C for 2 hours.
MP300	Medium phosphorus Ni-P deposit heat treated at 300°C for 2 hours.
HP300	High phosphorus Ni-P deposit heat treated at 300°C for 2 hours.
LP-PTFE	Low phosphorus Ni-P topcoat with PTFE particles in the deposit. The undercoat had high phosphorus deposit.
MP-PTFE	Medium phosphorus Ni-P topcoat with PTFE particles in the deposit. The undercoat had medium phosphorus deposit.
HP-PTFE	High phosphorus Ni-P topcoat with PTFE particles in the deposit. The undercoat had high phosphorus deposit.
LP-PTFE250	LP-PTFE deposit heat treated at 250°C for 8 hours.
MP-PTFE250	MP-PTFE deposit heat treated at 250°C for 8 hours.
HP-PTFE250	HP-PTFE deposit heat treated at 250°C for 8 hours.
LP-PTFE300	LP-PTFE deposit heat treated at 300°C for 2 hours.
MP-PTFE300	MP-PTFE deposit heat treated at 300°C for 2 hours.
HP-PTFE300	HP-PTFE deposit heat treated at 300°C for 2 hours.

Tribological testing was performed using Anton Paar® TRB<sup>3</sup> tribometer with a ball-on-disc configuration as per ASTM G99 standard. The 6mm diameter ball, made up of chromium steel (100Cr6), was pressed on the coated specimen at an applied load of 5N. Radius of the wear track was varied between 5mm and 20mm. In order to generate the same number of cycles, the velocity was varied linearly depending on the size of the sample and the distance covered. All tests were performed at a motor speed of 200rpm and for a duration of 3600 seconds. Wear rate was calculated from the 3D images generated using an optical profilometer. A Solarius® SD-V100-3219 optical profilometer

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was used to obtain 3D profiles of worn surfaces and cross-sectional profiles were used for determining the wear volume. The wear rate  $w$  ( $\text{mm}^3/\text{Nm}$ ) was determined from the wear volume ( $V$ , in  $\text{mm}^3$ ), applied load ( $F$ , in  $\text{N}$ ), and the distance covered ( $L$ , in  $\text{m}$ ) during the test:

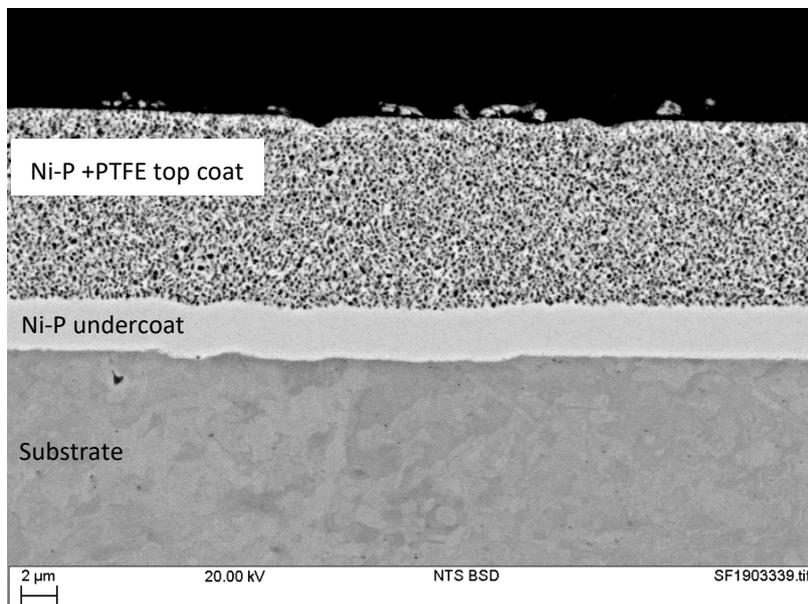
$$W = \frac{V}{F.L}$$

Additional results such as images from optical profilometer and SEM, and the wear mechanisms will be reported in deliverable D6.4. Corrosion performance was evaluated by potentiodynamic polarisation resistance and Tafel scan measurements as per ASTM G102-89 standard. Both acidic and alkaline solutions with  $\text{pH} = 4$  and  $\text{pH} = 8$ , respectively, were used to evaluate the coatings' corrosion performance, and the results are reported in deliverable D5.3. In this report, only a brief summary of the results is provided.

## 5. RESULTS

### 5.1 Microstructures

A representative image of the cross-section of as-deposited microstructure of the coating is shown in Figure 2. The phosphorus content in the coating (both undercoat and topcoat) was  $>11\%$ , and corresponded to high P EN coating. It was seen that the PTFE particles were distributed homogeneously in the topcoat. Moreover, no macroscopic defects were observed in the coatings. Similar microstructures were observed for coatings containing low ( $\sim 4\%$ ) and medium phosphorus (6-8%).



**Figure 2** A representative BSE image of cross-section of duplex EN deposit with undercoat and topcoat on mild steel substrate. Both undercoat and topcoat had high P. PTFE particles were dispersed very homogeneously in the topcoat.

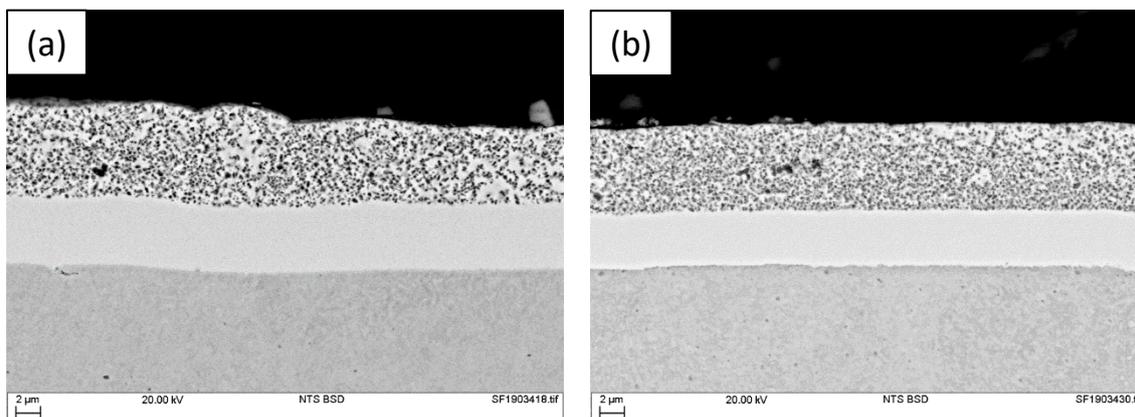
Electroless Ni-P deposits are usually heat treated in the  $345^{\circ}\text{C}$  to  $400^{\circ}\text{C}$  temperature range in order to increase their hardness and improve wear resistance, the most common being one hour at  $400^{\circ}\text{C}$  [1].

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As the melting point of PTFE is around 326°C, the heat treatments for duplex coatings produced in this work were carried out at lower temperatures, i.e. 250°C for 8 hours and 300°C for 2 hours under vacuum ( $5 \times 10^{-4}$  mbar or better). Representative BSE images of the microstructures of the specimens subjected to the two heat treatments are shown in Figure 3a and Figure 3b, respectively. The phosphorus content in topcoat and undercoat in both specimens was >11%. It was seen that the PTFE particles did not undergo any decomposition.



**Figure 3** Representative BSE images of cross-section of duplex EN deposits heat treated at (a) 250°C for 8 hours and (b) 300°C for 2 hours. No decomposition of PTFE particles was observed as a result of the heat treatments.

## 5.2 X-ray Diffraction

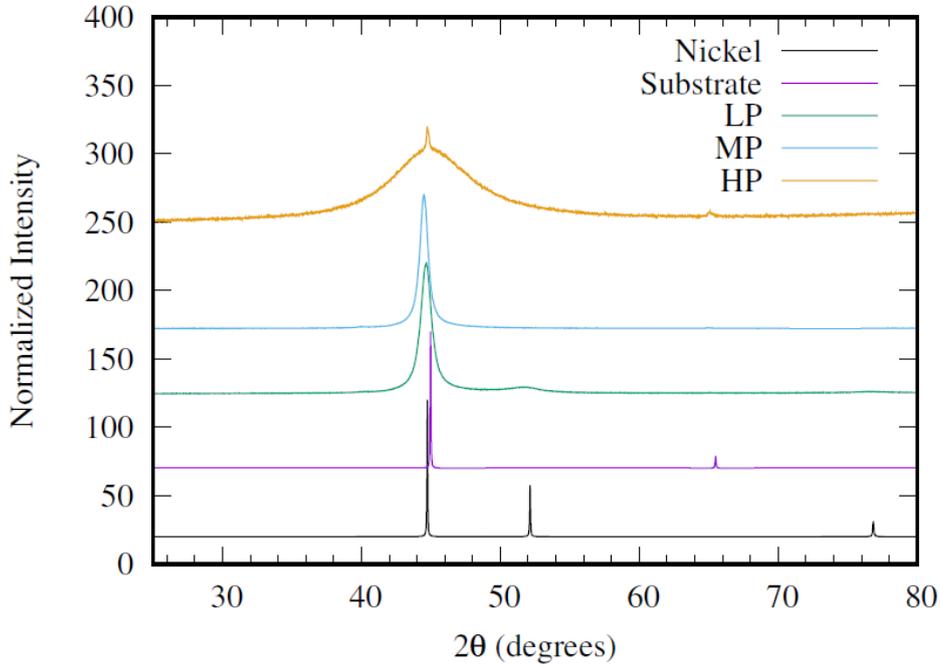
### 5.2.1 Overview

Depending on the amount of phosphorus content in the Ni-P deposits, the as-deposited coatings can vary from being nanostructured to being amorphous. Specifically, the low phosphorus deposits have been shown to be nanostructured with grain size between 5nm-10nm while the medium and high P deposits were reported to be amorphous [2, 3]. In this work, XRD patterns were collected on the as-deposited and heat treated specimens of EN and composite coatings (i.e. Ni-P and Ni-P-PTFE deposits, respectively) to complement the results from electron microscopy in order to understand the microstructural changes occurring as a result of the heat treatments.

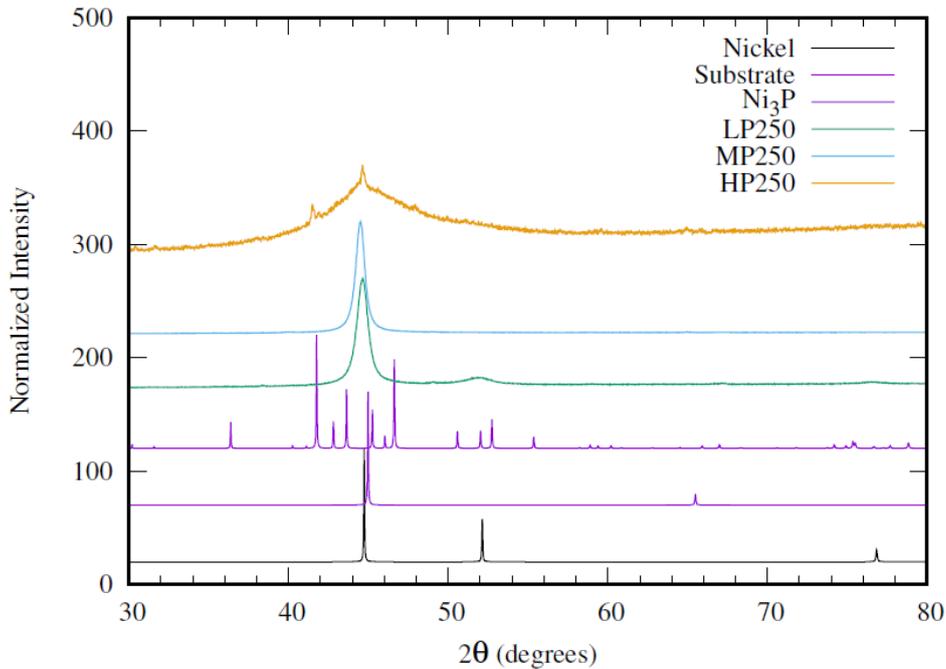
### 5.2.2 Undercoat (Ni-P deposits)

Figure 4 shows the XRD patterns of low P, medium P, and high P electroless Ni-P deposits in the as-deposited condition (i.e. undercoat, without any PTFE particle dispersion). Reference patterns for nickel and mild steel (body centred cubic iron) are also shown. The intensities were normalised to the highest peak intensity of each pattern and were shifted in the vertical axis for clarity. For the low P specimen, the data suggest that the as-deposited microstructure was mostly crystalline, although the peak broadening observed for the reflections around 52° and 76° suggests that the deposit has an amorphous character to a certain extent. For medium P specimen, the XRD pattern was similar to that observed for the low P specimen, suggesting that the deposit was mostly crystalline. However, for high P specimen, the peaks were very broad, with sharp peaks superimposed on them (at ~45° Figure 4). Broad peaks suggest amorphous nature of the coatings, consistent with previously published literature [2, 3]. The presence of the sharp peak superimposed on the broad peak suggests that it is from the substrate material (mild steel), presumably due to lower thickness of the high P coating. It is pointed

out that these coatings were deposited for 1 hour and the deposition rate of high P coatings is lower (~10 $\mu\text{m/hr}$ ) compared with low P and medium P coatings (~15 $\mu\text{m/hr}$ ).

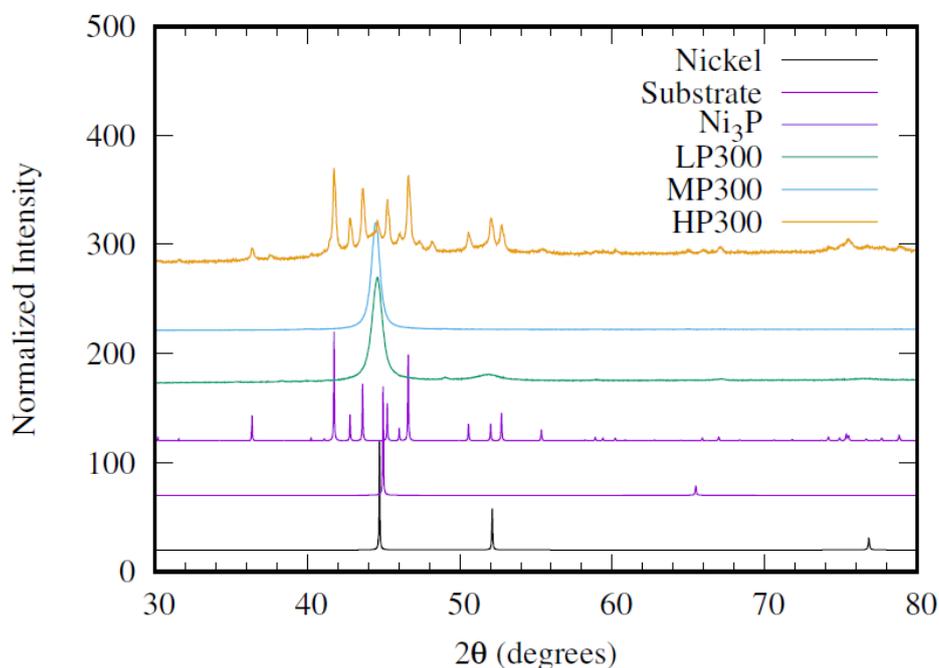


**Figure 4** XRD patterns of undercoat deposits along with the simulated patterns of nickel and the substrate. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.



**Figure 5** XRD patterns of undercoat deposits heat treated at 250°C along with the simulated patterns of nickel, substrate, and Ni<sub>3</sub>P. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.

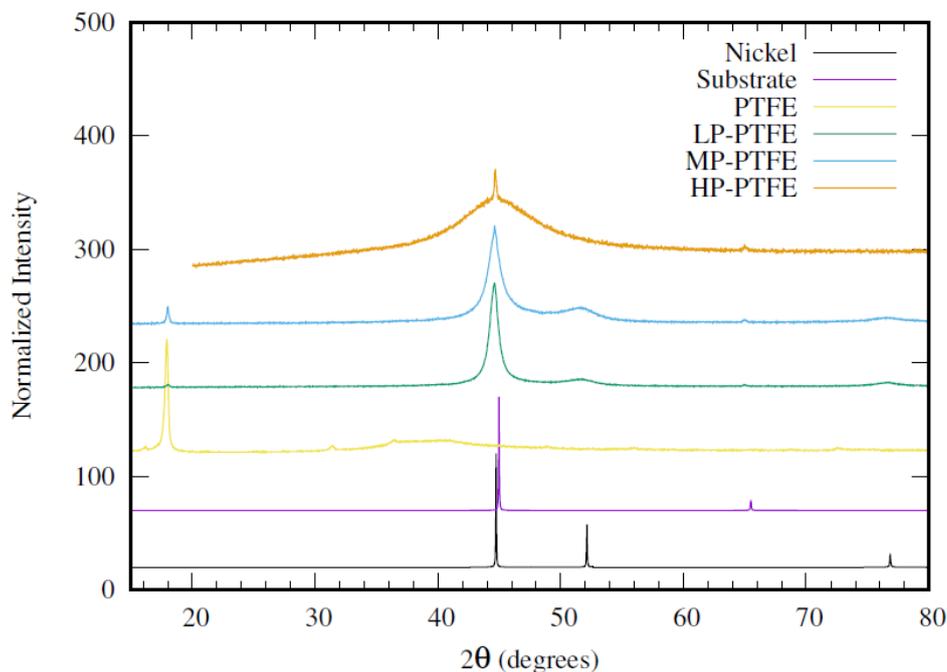
Figure 5 shows the XRD patterns of the specimens annealed at 250°C for 8 hours. Also included are the peak positions for nickel, substrate material (i.e. mild steel), and Ni<sub>3</sub>P. It was seen that the peaks became sharper, and no additional peaks that correspond to the intermetallic phase, Ni<sub>3</sub>P, were observed for low P and medium P specimens (LP250 and MP250, respectively). This suggests that either the annealing conditions were not adequate for the nucleation of these phases or the amount of phosphorus was too low, such that the volume fraction of Ni<sub>3</sub>P nucleated was below the detection limit of laboratory XRD. However, for high P specimens (HP250), additional peaks were observed indicating the presence of Ni<sub>3</sub>P. This further suggests Ni<sub>3</sub>P phase nucleates under these annealing conditions (i.e. 8 hours at 250°C), and the amount of phosphorus was too low in low P and medium P specimens for the volume fraction of Ni<sub>3</sub>P to be detected using the laboratory XRD technique.



**Figure 6** XRD patterns of undercoat deposits heat treated at 300°C along with the simulated patterns of nickel, substrate, and Ni<sub>3</sub>P. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.

Figure 6 shows the XRD patterns of the specimens annealed at 300°C for 2 hours. Similar to the XRD data of the specimens that were annealed at 250°C, no additional peaks for low P and medium P specimens were observed (LP300 and MP300, respectively). However, for the high P specimen (HP300), new peaks were seen, which correspond to the Ni<sub>3</sub>P phase. Also, comparing the patterns for two high P heat treated specimens, it was evident that the number and strength of the reflections of the Ni<sub>3</sub>P phase have increased when annealed at 300°C compared with those at 250°C (Figure 5 and Figure 6). This suggests that the equilibrium condition was not reached for the specimen heat treated at 250°C.

### 5.2.3 Duplex coatings (undercoat and topcoat)

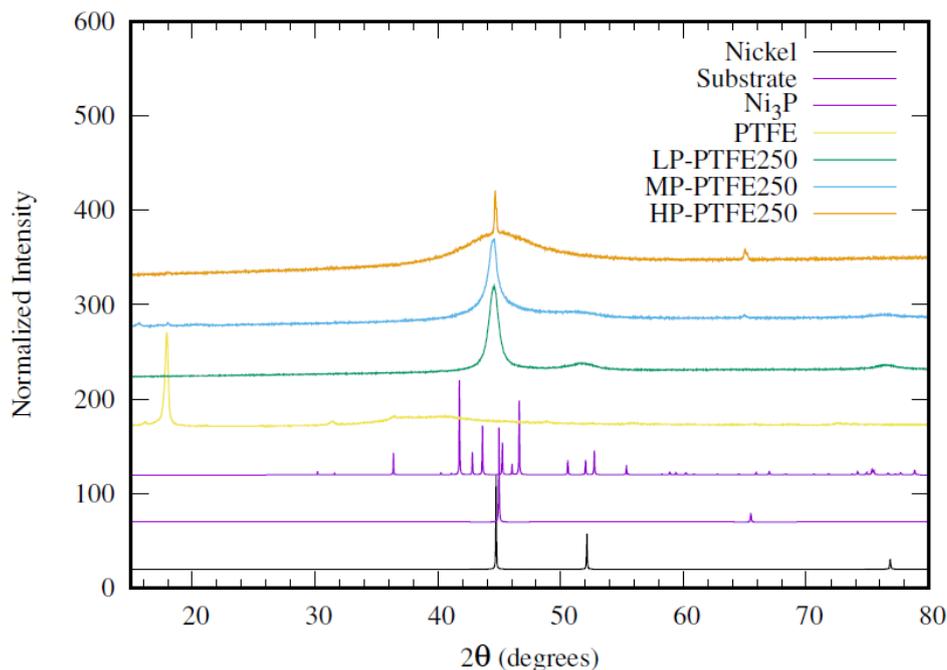


**Figure 7** XRD patterns of duplex coatings in the as-deposited condition and PTFE powder along with the simulated patterns of nickel and the substrate. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.

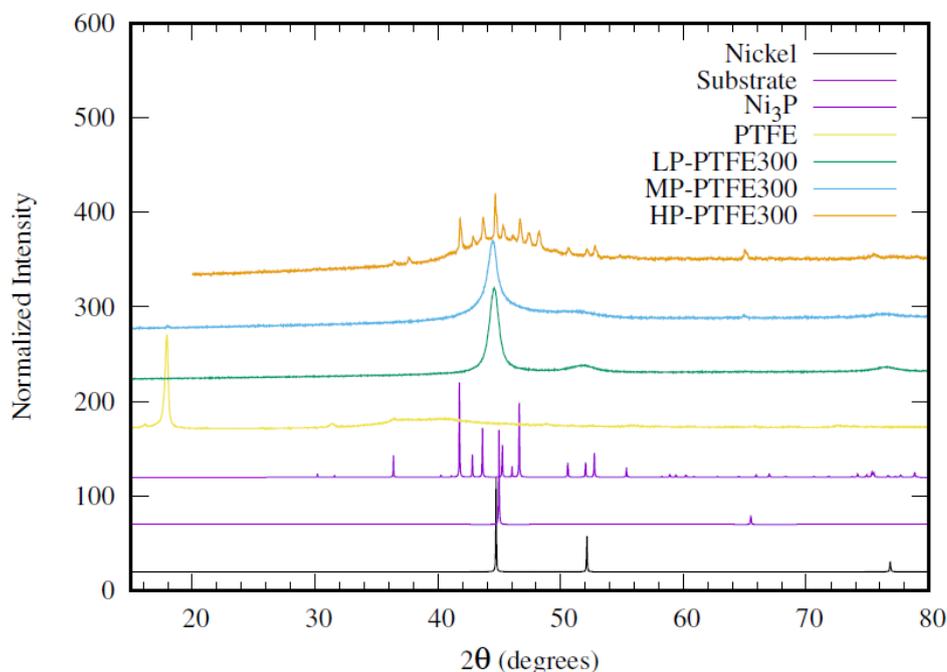
Figure 7 shows the XRD patterns of the duplex coatings in the as-plated condition and of the PTFE powder that was used for deposition. Also shown are the simulated patterns of nickel and mild steel. It was seen that for the LP-PTFE specimens, a peak corresponding to PTFE (at  $\sim 18^\circ$ ) was seen, in addition to the nickel peaks. It is pointed out that this peak has the highest intensity, as can be seen from the pattern of the PTFE powder. Absence of other peaks of PTFE in the duplex coated specimens can be attributed to the combination of its volume fraction in the coatings and their smaller intensity (compared with the one at  $\sim 18^\circ$ ). Similarly, for the MP-PTFE specimen, a peak confirming the presence of PTFE particles was seen, although for the HP-PTFE specimen, the lower limit of the scan ( $30^\circ$ ) was higher than the expected peak position of the largest intensity peak of PTFE powder ( $\sim 18^\circ$ ). However, the microstructures confirmed its presence (a representative image showing PTFE particles is shown in Figure 2. Additional images are shown in deliverable report D4.3).

Figure 8 shows XRD patterns of the duplex coatings heat treated at  $250^\circ\text{C}$  for 8 hours. It can be seen that for the LP-PTFE<sub>250</sub> specimen, neither the peaks corresponding to  $\text{Ni}_3\text{P}$  nor PTFE were observed. Absence of  $\text{Ni}_3\text{P}$  peaks is consistent with the specimen with low P undercoat (i.e. LP<sub>250</sub>) that was heat treated under similar conditions (Figure 5), however, the absence of peaks associated with PTFE suggests that its volume fraction in the matrix is low. For the MP-PTFE<sub>250</sub> specimen, peaks corresponding to PTFE in addition to the nickel peaks were seen, although peaks corresponding to  $\text{Ni}_3\text{P}$  phase were not observed. This result is consistent with the medium P undercoat specimen heat treated under similar conditions (i.e. MP<sub>250</sub> in Figure 5). For the HP-250 specimen, while the PTFE peak was seen, no peaks for the  $\text{Ni}_3\text{P}$  phase were observed, which is in contrast with the HP<sub>250</sub> specimen (Figure 5). It is likely that the volume fraction of  $\text{Ni}_3\text{P}$  is below the detection limit of XRD.

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**Figure 8** XRD patterns of duplex deposits heat treated at 250°C and PTFE powder along with the simulated patterns of nickel, substrate, and Ni<sub>3</sub>P. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.



**Figure 9** XRD patterns of duplex deposits heat treated at 300°C and PTFE powder along with the simulated patterns of nickel, substrate, and Ni<sub>3</sub>P. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.

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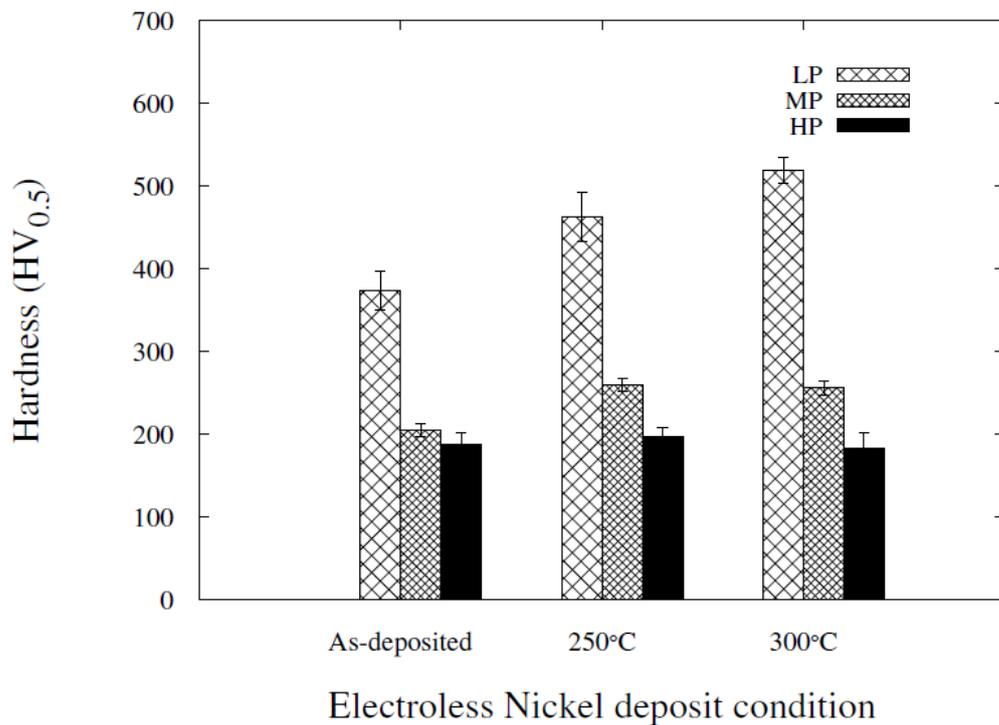
Figure 9 shows XRD patterns of the duplex coatings heat treated at 300°C for 2 hours. The pattern for LP-PTFE300 is similar to the low P duplex coating heat treated at 250°C (i.e. the LP-PTFE250 specimen, Figure 8) suggesting low volume fractions of PTFE and Ni<sub>3</sub>P phase. The pattern for the MP-PTFE300 specimen does not contain peaks for the Ni<sub>3</sub>P phase, similar to the MP-PTFE250, MP250 and MP300 specimens. An additional peak corresponding to PTFE was seen, confirming its presence. The pattern for the HP-PTFE300 specimen has peaks corresponding to nickel and the Ni<sub>3</sub>P phase. However, the lower limit of the scan (30°) was higher than the scan position of the highest intensity peak for PTFE (~18°), although the presence of PTFE was confirmed from the BSE images of heat treated high P specimens (Figure 3).

### 5.3 Corrosion performance

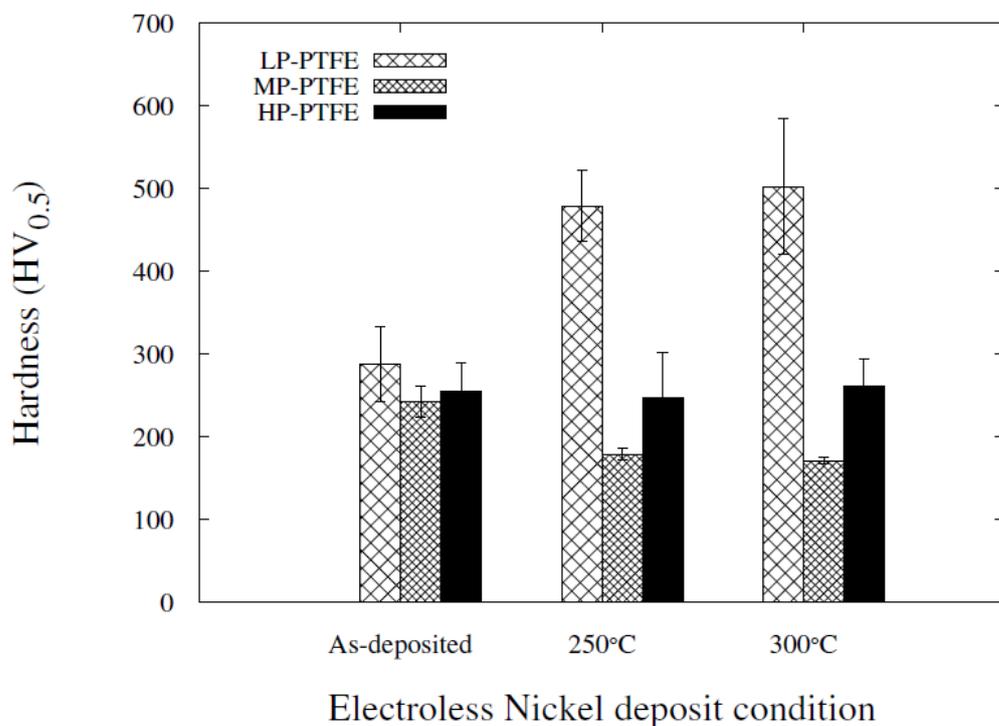
Corrosion performance of the electroless nickel deposits was evaluated as part of the down-selection process, and the results were reported in deliverable report D5.3. Briefly, it was found that deposits with medium P showed very poor corrosion resistance compared with low P and high P deposits. Moreover, the pH of the solution had a strong effect on the performance of low P and high P deposits. In general, high P deposits had excellent corrosion resistance while low P deposits showed good corrosion resistance in an acidic environment. Both heat treatments (i.e. 8 hours at 250°C and 2 hours at 300°C) were found to degrade the corrosion performance. Therefore, two sets of specimens for WP6 and WP8 (i.e. for testing under simulated and actual geothermal environments) were produced with low P and high P topcoat, respectively, with PTFE dispersion. The undercoat in both cases had high P.

### 5.4 Microhardness

Microhardness (i.e. HV<sub>0.5</sub>) of low P, medium P, and high P coatings in the as-deposited condition and heat treated conditions is shown in Figure 10. The error bars shown in the figure correspond to the standard deviation of the five hardness measurements. It was seen that in the as-deposited state, low P coatings have the highest hardness (374±24) followed by medium P coatings (205±8), while the high P coatings had the lowest hardness (188±14). This trend is consistent with the published literature [1], although the values measured were lower. The hardness of the substrate was measured to be 107±6 HV<sub>0.5</sub>. It is again emphasised that the hardness values reported here correspond to that of the composite (i.e. coating and mild steel substrate), and the actual hardness of the coatings will be much higher than the values reported here. Upon heat treating the deposits for 8 hours at 250°C, the hardness of the low P deposit increased by 24% (to 463±29) while for medium P and high P deposits the increase was 27% and 5%, respectively (260±8 and 198±11, respectively). On heat treating the coatings for 2 hours at 300°C, the hardness of low P deposit, compared with the as-deposited state, increased by 39% (to 519±16) and for the medium P deposit it increased by 25% (256±9). However, the hardness of the high P deposit decreased by 3% (to 183±19), although it was seen that the value is quite close to the as-deposited state, considering the error associated (i.e. ±19HV<sub>0.5</sub>) with the measurements.



**Figure 10** Hardness values of Ni-P coatings (i.e. undercoat) in the as-deposited condition. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.



**Figure 11** Hardness values of duplex coatings in the as-deposited condition. LP is low phosphorus, MP is medium phosphorus, and HP is high phosphorus.

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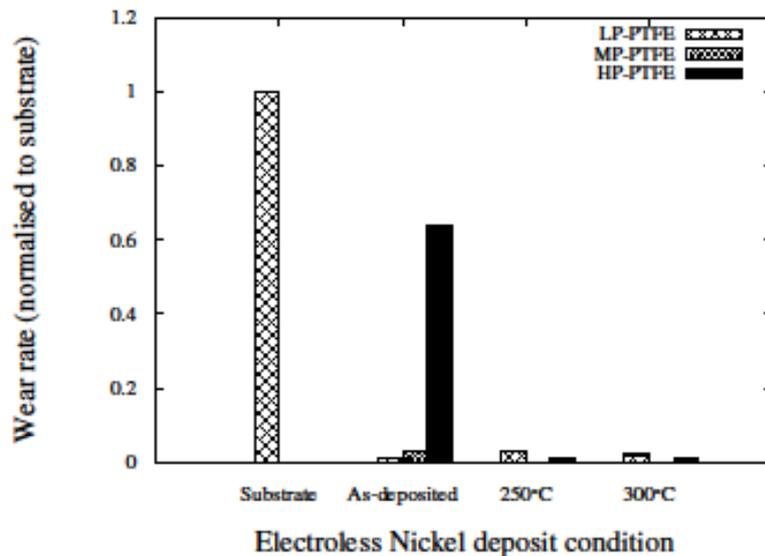
For the duplex coatings, in the as-deposited state, the LP-PTFE specimen had a hardness of  $288\pm 45$  while MP-PTFE and HP-PTFE deposits had a hardness of  $243\pm 19$  and  $255\pm 34$ , respectively (Figure 11). The error bars shown in the figure correspond to the standard deviation of the five hardness measurements. It was observed that, compared with the hardness values of the undercoat (i.e. without any PTFE particles), addition of PTFE particles to the low P topcoat resulted in a 23% decrease in its hardness. However, for medium P and high P deposits, addition of PTFE particles resulted in an increase in hardness by 19% and 36%, respectively. It is worth noting that the duplex coatings have an undercoat layer deposited on the substrate, and therefore, the hardness values will be of the composite (substrate+undercoat+topcoat). On heat treating the duplex coatings for 8 hours at  $250^{\circ}\text{C}$ , the hardness of the low P deposit (i.e. LP-PTFE250) increased by 66% compared with LP-PTFE, and for medium P deposits (i.e. MP-PTFE250), the hardness decreased by 26% compared with the MP-PTFE specimen. For the high P deposit, the hardness decreased by 3%. On heat treating the duplex coatings for 2 hours at  $300^{\circ}\text{C}$ , hardness of low P deposits (i.e. LP-PTFE300) increased by 74% (compared with LP-PTFE), while for the medium P deposits (MP-PTFE300), it decreased by 30% (compared with MP-PTFE). For high P duplex coatings, an increase in the hardness by 2% over the as-deposited condition (i.e. HP-PTFE) was observed.

## 5.5 Wear properties

The wear rates obtained using pin-on-disc tests for various duplex coatings are shown in Figure 12. The data were expressed as the fraction of the normalised wear rate of the substrate material. Compared to the substrate, all coatings had lower rates. It was seen that in the as-deposited state, low P coatings (i.e. LP-PTFE) had the lowest wear rate, followed by medium P (i.e. MP-PTFE) and high P coatings (i.e. HP-PTFE). Compared with high P coatings, the low P coatings had an order of magnitude lower wear rate. As stated previously, medium P coatings were not down-selected based on their corrosion performance. Specifically, they had poor corrosion resistance compared with low P and high P deposits, and hence were not tested further for tribological performance under heat-treated conditions; data were only obtained in as-deposited state.

On heat treating the coatings for 8 hours at  $250^{\circ}\text{C}$ , the wear rate for low P deposits (i.e. LP-PTFE250) increased by around 26% (compared with LP-PTFE coatings) while for high P deposits (i.e. HP-PTFE250), the wear rate decreased by 96% (compared with HP-PTFE coatings). On heat treating the coatings for 2 hours at  $300^{\circ}\text{C}$ , the wear rate for low P deposits (i.e. LP-PTFE300) decreased by 14% (compared with LP-PTFE coatings) while for the high P deposits (i.e. HP-PTFE300), the wear rate decreased by about 96% (compared with HP-PTFE coatings).

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**Figure12** Wear data of various duplex coatings obtained using 5N load expressed as fraction of the highest wear rate.

## 6. DISCUSSION

The effects of the presence of PTFE particles in various nickel-phosphorus deposits on mild steel substrates and two different heat treatments on the microstructural evolution and some of the properties such as hardness, corrosion, and wear rate were studied in this task. The chemistry of the deposits was controlled by changing the chemical make-up of the electroless nickel bath. Specifically, the phosphorus content in the deposits was varied, which resulted in the deposits containing low (~4%), medium (6-8%), and high phosphorus (>11%). First, the effect of two different heat treatments (8 hours at 250°C and 2 hours at 300°C) on the microstructure, hardness and wear rate of the deposits (also referred to as undercoat) was studied. Duplex coatings were then produced on a mild steel substrate, first with an undercoat containing a thin layer of nickel-phosphorus alloy (targeted thickness of 5µm), and an additional layer with a homogeneous distribution of PTFE particles in a Ni-P matrix. The effect of the two heat treatments on the microstructure, hardness, corrosion performance, and wear rate was studied.

As mentioned previously, electroless Ni-P coatings are usually heat treated in 345°C to 400°C temperature range in order to increase their hardness and improve wear resistance, the most common being one hour at 400°C. However, as the duplex coatings contained PTFE particles, and because PTFE decomposes at around 326°C, the heat treatments were carried out at lower temperatures (250°C and 300°C). It was seen that the microstructure of the deposits changed from being nano-crystalline (low phosphorus) to amorphous (high phosphorus), Figure 4. The change in the microstructure as a function of the alloying content of the deposits can be rationalised based on thermodynamics [4]. In a single component system, the total free energy of the system is reduced by increasing its grain size,

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producing the driving force for grain growth. However, for a two-component system, there is a possibility to lower the free energy of the system by segregating one of the elements to the grain boundaries thereby reducing the grain boundary energy and the tendency for grain growth. Such a stability is a consequence of the strong relationship between the number of high-energy grain boundary sites for the grain size, and the solute content. The principle of grain boundary segregation to stabilise the nano-crystalline structure has been previously used to produce Ni-P coatings with tailored properties [5, 6]. One of the important results in these studies was the reduction in grain size with increase in the amount of phosphorus content in the deposit, owing to the strong tendency of phosphorus to segregate to grain boundaries. Results from the present study are consistent with the published literature.

Heat treating the Ni-P deposits at 250°C for 8 hours resulted in the formation of Ni<sub>3</sub>P phase, although from XRD data it was seen that for low and medium P deposits, its volume fraction was below the detection limit of the laboratory XRD technique while for high P deposit, peaks corresponding to Ni<sub>3</sub>P were observed (Figure 5). There was a concomitant increase in the hardness (Figure 10), which can be attributed to the presence of Ni<sub>3</sub>P. Increase in the hardness of the deposits upon heat treating them at 300°C for 2 hours was observed (Figure 10) due to the presence of Ni<sub>3</sub>P, which was confirmed by XRD data (Figure 6).

For the duplex coatings, changes observed in the hardness were more complex due to the effect from the substrate and the undercoat. The hardness of the duplex coatings is affected by the changes in the microstructure of the undercoat due to heat treatment. The presence of PTFE particles in the topcoat of low P specimens resulted in a decrease in the as-deposited hardness while for MP-PTFE and HP-PTFE deposits, there was a marginal increase in the hardness. This can be attributed to the potential differences in the incorporation of PTFE particles within the Ni-P matrix as a function of the bath chemistry, and the presence of a thin undercoat layer. On heat treatment, considerable increase in the hardness was observed for LP-PTFE250 and LP-PTFE300 coatings. This was likely due to the lower incorporation of PTFE particles in the deposits and also the effect of undercoat layer. While the presence of soft PTFE particles in the matrix should reduce the hardness, Ni<sub>3</sub>P phase should have the opposite effect (i.e. increase the hardness). Therefore, any differences or changes in the level of incorporation of PTFE particles and the amount Ni<sub>3</sub>P phase present due to batch-to-batch variations (in a particular batch, only two or three specimens could be produced) affects the hardness of the duplex coatings.

While the wear rate for duplex coatings in the heat treated state was lower than the as-deposited condition (due to the presence of the hard Ni<sub>3</sub>P phase), the corrosion performance was observed to be the opposite, with heat treatment resulting in poor corrosion resistance (results reported in deliverable report D5.3). Therefore, no heat treatment was performed on the specimens that were produced for further testing in simulated and actual geothermal conditions (i.e. for WP6 and WP8).

## 7. CONCLUSIONS

In this task, electroless nickel coatings with and without PTFE particles were subjected to two different heat treatments, and the effect on the microstructural development, hardness, tribological properties, and corrosion performance was studied. The main findings are summarised as follows:

- For the undercoat specimens, on heat treating the coatings for 8 hours at 250°C and 2 hours at 300°C formation of hard Ni<sub>3</sub>P was observed only in high P deposits using XRD data. However, it is likely that this phase formed in low P and medium P deposits because of the increased hardness observed compared with the as-deposited condition. Absence of Ni<sub>3</sub>P peaks in the

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XRD data was attributed to the lower amount of phosphorus in the deposits, which likely resulted in lower volume fraction of Ni<sub>3</sub>P, below the detection limit of laboratory XRD.

- For the duplex coatings, heat treatments resulted in the formation of Ni<sub>3</sub>P phase, although the changes observed in hardness data were complex. This was attributed to the likely differences in the volume fractions of soft PTFE particles and hard Ni<sub>3</sub>P phase, and the thickness of the deposits. While the hardness increase in the case of low P specimens was high (i.e. LP-PTFE vs LP-PTFE250 and LP-PTFE300), the changes were not so pronounced for high P deposits (HP-PTFE vs HP-PTFE250 and HP-PTFE300). For medium P deposits, a decrease in hardness was observed on heat treatments.
- Compared with the as-deposited state, the wear rate for duplex coatings decreased with the heat treatments. This was attributed to the presence of Ni<sub>3</sub>P phase.
- The corrosion performance of duplex coatings deteriorated with heat treatments.

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