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HEAT TREATMENT OF ELECTROLESS Ni-P LAYERS ON AN AUSTENITIC STAINLESS-STEEL SUBSTRATE

TOPLOTNA OBDELAVA KEMIJSKO NANEŠENE PLASTI Ni-P NA PODLAGI IZ AVSTENITNEGA NERJAVNEGA JEKLA

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Properties of electroless deposited nickel-phosphorous coatings on an austenitic stainless-steel substrate were investigated. The main study was focused on the influence of heat treatment on the microhardness and microstructure analysis of electroless Ni-P coatings. A nickel-phosphorous coating was deposited without nickel-strike pre-coating treatment. An electroless Ni-P layer was deposited on a stainless-steel substrate. Sodium hypophosphite was used as the reducing agent. The microstructure and morphology of heat-treated electroless specimens were analyzed with optical and scanning electron microscopy. Adhesivity was estimated with a Vickers indenter. Based on the experimental results, it can be concluded that heat-treated electroless nickel-phosphorous coatings have a higher microhardness than non-heat-treated electroless nickel-phosphorous coatings. An analysis of the Vickers indentation results showed that the proposed electroless process gives satisfactory results.

Keywords: electroless, deposition, coatings, heat treatment, stainless steel, micro-hardness

Preiskovane so bila lastnosti kemijsko nanešene plasti nikelj – fosfor, na podlagi iz avtenitnega nerjavnega jekla. Glavni študij je bil usmerjen na vpliv toplotne obdelave na mikrotrdoto in analizo mikrostrukture kemijsko nanešenega Ni-P nanosa. Nanos nikelj –fosfor je bil nanešen brez predhodnega premaza. Kemijski nanos Ni-P je bil nanešen na osnovo iz nerjavnega jekla. Natrijev hipofosfid je bil uporabljen kot redukcijsko sredstvo. Mikrostruktura in morfologija kemijsko nanešenega vzorca je bila analizirana s svetlobno in z vrstično mikroskopijo. Adhezivnost je bila določena z vtiskovanjem po Vickers piramidi. Na osnovi rezultatov preizkusov je mogoče zaključiti, da ima toplotno obdelan kemijski nanos nikelj – fosfor višjo trdoto kot neobdelan kemijski nanos nikelj – fosfor. Analiza rezultatov Vickers vtiskov je pokazala, da predlagani kemijski postopek daje zadovoljive rezultate.

Ključne besede: brez pomoči električnega toka, nanašanje, nanosi, toplotna obdelava, nerjavno jeklo, mikrotrdota

1 INTRODUCTION

Electroless deposited coatings have a more uniform thickness on complex-shaped objects in comparison to electroplated deposits. This uniform thickness and composition of a coating results in uniform mechanical and physical properties of the surface layer.[1,2,3] Besides, Ni-P coatings deposited with the electroless process can have good anticorrosive properties, wear resistance and high hardness.[4–6] An electroless Ni–P coating has a higher hardness and a better corrosion resistance than the AISI 316 stainless steel.[7]

Since it is very difficult to form a Ni-P deposit on an austenitic stainless-steel substrate using the electroless process, the activation with a weak acid etch, i.e., nickel strike should be applied.[8] Nickel-strike pre-coating treatment makes the Ni-P coating deposition on stainless steel more complicated in comparison to the other similar electroless depositions on other types of steel, aluminium alloys and so on. Ni-P alloy coatings should be heat treated, mainly to increase the hardness of Ni-P alloy coatings; the heat treatment should be applied after the electroless coating process.[8]

Generally, the microstructure of the Ni-P coatings deposited with the electroless process depends on the phosphorous content. Electroless deposited Ni-P coatings are crystalline if the phosphorus content is between 1–5 % mass fraction (low phosphorus). If the content of phosphorous is between 6–9 % mass fraction (medium phosphorous), the Ni-P coatings deposited with the electroless process have mixed, amorphous and crystalline structures. If the content of phosphorous is between 10–13 % mass fraction (high phosphorus), the Ni-P coatings deposited with the electroless process are amorphous.[1,9–12]

To achieve high adhesion, a thorough surface preparation, or a removal of foreign contaminants from the base-metal surface and elimination of mechanically distorted surface layers, resulting in a clean, healthy surface structure, is required.[13] With a prolonged heat treatment, i.e., aging at high temperatures, electroless deposited nickel-phosphorous coatings begin to crystallize and lose their preferable amorphous character.[14] At the same time, a higher hardness of the stainless steel is obtained. As suggested by the authors of reference[14], this effect is probably due to the diffusion of phosphorus from the region near the interface with the substrate. With the prolonged heat treatment at high temperatures, the nickel-phosphide particles conglomerate and the

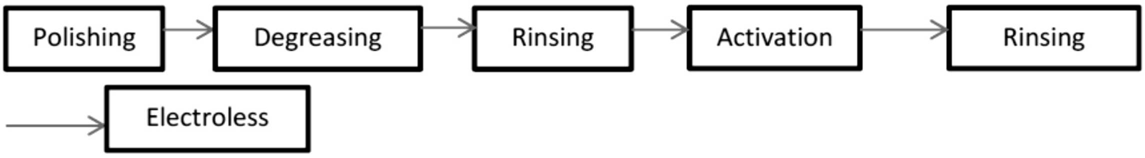

Figure 1: Flow-chart diagram of the electroless process of nickel plating on an austenitic-steel AISI 316 substrate
Slika 1: Potek kemijskega procesa nanašanja niklja na podlago iz avstenitnega nerjavnega jekla AISI 316

matrix of Ni_3P forms due to the continued heating.[14] The hardness of the coating can increase with the appearance of the intermetallic Ni_3P phase and with a higher crystallinity of the nickel-phosphorous coatings.[8–10,15] Moreover, the hardness of the electroless deposited nickel-phosphorous coatings can increase because of the precipitation of the Ni_3P phase.[15] The maximum hardness can be obtained if the phosphorus content is around 4 % mass fraction.[1,9–12]

The application of an appropriate heat treatment of Ni-P coatings deposited with the electroless process can have a significant impact on their hardness.[1–5] The microhardness of Ni-P coatings deposited with the electroless process depends on the heat treatment of the coatings, the content of phosphorus in the coatings and on the contents of other alloying elements in the coatings.[9]

Nickel with an amorphous structure has a lower hardness than nickel with a crystalline structure.[4,10–12,16–28] After the heat treatment, the structure of the coating is more crystalline; moreover, the intermetallic nickel phosphide (Ni_3P) phase appears.[9,10,15] The hardness of coatings can increase with the appearance of the intermetallic Ni_3P phase and a higher crystallinity of nickel-phosphorous coatings.[8–10,15]

The grain size of Ni-P composite coatings deposited with the electroless process can have a significant influence on the hardness.[20]

In this work, the adhesivity related to the optimization of heat-treatment processes was estimated with a Vickers indenter.

2 EXPERIMENTAL PART

In the applied experimental procedure, cylindrical specimens of austenitic steel AISI 316 were used as the substrate. The chemical composition of steel specimens is shown in **Table 1**. The diameter of cylindrical specimens was 8 mm and their length was 50 mm. Before the electroless process, the surfaces of specimens were cleaned to eliminate all types of surface contamination. At first, specimens were mechanically polished using Kemipol T-12, with Al_2O_3 grains of 14 μm. This was followed by degreasing the surfaces of the samples with the cleaning agent UNICLEAN 253, which is composed of silicate, hydroxide and biodegradable surfactants. After that, the substrate surfaces were washed and activated in the activation agent UNICLEAN 675. Additional activation was done with chemical pre-coating treatment. After rinsing, the main electroless-deposition process was applied (**Figure 1**). The electroless nickel-plating process was carried out using a Nikora nickel bath (a registered trademark of Schering AG, Berlin). It is known that the Nikora nickel bath is based on an aqueous solution of sodium hypophosphite. The chemical composition of the electroless plating bath was not studied.

Table 1: Chemical composition of steel substrate
Tabela 1: Kemijska sestava jekla iz podlage

Chemical composition in mass fraction (*w*/%)							
C	Si	Mn	P	S	Cr	Mo	Ni
0.07	0.71	1.36	0.031	0.021	17.1	2.42	11.6

After the electroless processing, some samples were heat treated by aging them at 500 °C for 60 min in an air-furnace atmosphere.[18] Other specimens were not heat treated after the electroless processing. The heat treatment was not longer than 24 h, applied after the electroless processing of the specimens.

Ni-P coating layers of the non-heat-treated samples and heat-treated samples were tested with the microhardness indentation technique. The Vickers microhardness of each sample was determined as the average of five test results obtained with the Vickers tester Struers Duramin 2. A microstructure analysis of the Ni-P coating layers was carried out with an Olympus BX51 optical microscope and scanning electron microscope FEG FEI QUANTA 250 SEM. An X-ray diffraction (XRD) analysis of the heat-treated electroless coating was carried out with a BRUKER AXS D8–Advance instrument and Vertical Theta–Theta goniometer with Co radiation.

3 RESULTS AND DISCUSSION

The obtained microhardness of the non-heat-treated electroless Ni-P coating on the austenitic stainless-steel AISI 316 substrate was 429±17 HV0.01, while the hardness of the heat-treated electroless Ni-P coating was 853±26 HV0.01.

The adhesivity related to the studied electroless process was compared with the adhesivity achieved with the electroless process, in which chemical activation was not applied. The adhesivity was estimated with a Vickers indenter. In **Figure 2**, it can be seen that the delamination of the deposited layer did not appear on the specimen treated with chemical pre-coating.

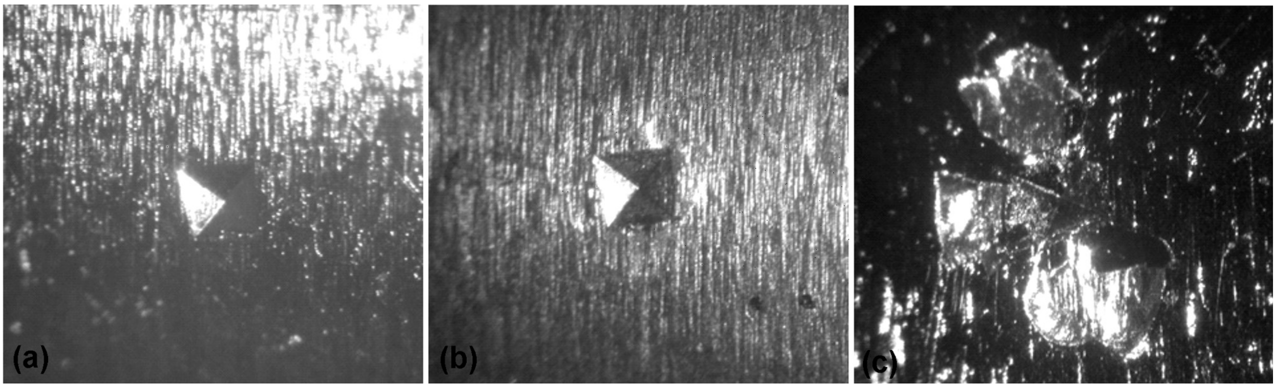

Figure 2: Indentation results for adhesivity of Ni-P electroless coatings, mag. 35:1: a) chemical pre-coating treatment of the surface + electroless coating, b) pre-coating treatment of the surface + electroless coating + aging at 500 °C, c) electroless coating + aging at 500 °C

Slika 2: Rezultati vtiskovanja za adhezivnost kemijskega Ni-P nanosa: 35-kratna povečava: a) kemijska predobdelava površine s kemijskim nanosom, b) kemijska predobdelava površine s kemijskim nanosom in staranjem na 500 °C, c) nanos in staranje na 500 °C

A metallographic analysis of the Ni-P coating layers was performed on the cross-sections of both parts of the samples (**Figure 3**).

From **Figure 3a**, it is evident that the electroless Ni-P coating follows the surface morphology and surface roughness of the substrate. **Figure 3a** shows that the coating exists but shows failures that can be explained with the cracking of the brittle coating during the specimen preparation for the micro-analysis.

The deposited Ni-P coating of a heat-treated specimen is shown in **Figure 3b**. The heat treatment, i.e., the aging of specimens was applied after the main electroless process. No failures in the Ni-P coating were observed on the heat-treated specimens.

No relevant differences between the thicknesses of these two Ni-P coatings were detected. The thickness of the non-heat-treated Ni-P coating is 8.11±0.18 μm while the thickness of the heat-treated Ni-P coating is 7.52±0.18 μm.

The contents of the iron, chromium, nickel and phosphorus of the non-heat-treated sample were evaluated with SEM and EDS mapping. A map of the contents of

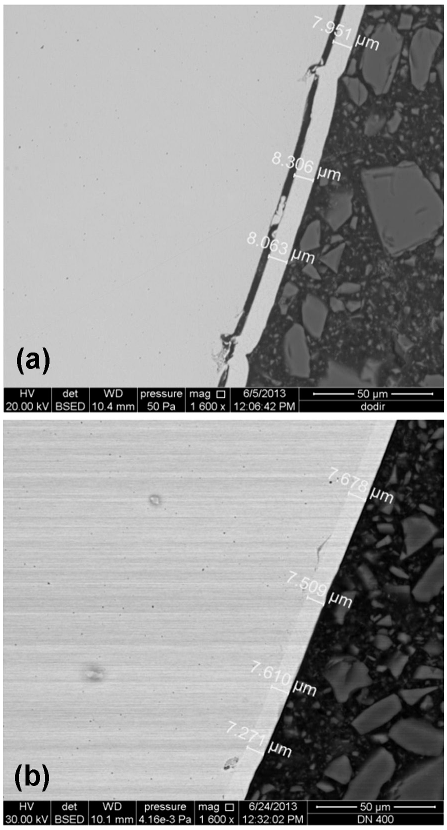

Figure 3: Micrographs of the cross-sections of Ni-P coatings on: a) non-heat-treated austenitic stainless-steel AISI 316 substrate, b) heat-treated austenitic stainless-steel AISI 316 substrate

Slika 3: Posnetka preseka Ni-P nanosa na podlagi iz avstenitnega nerjavnega jekla AISI 316: a) toplotno neobdelano, b) toplotno obdelano

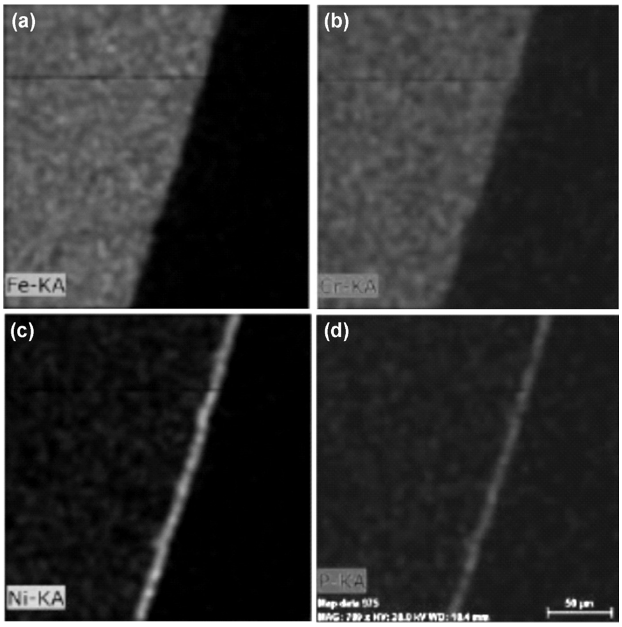

Figure 4: SEM and EDS mapping of the iron, chromium, nickel and phosphorus of the non-heat-treated samples

Slika 4: SEM- in EDS-prikaz razporeditve železa, niklja in fosforja na toplotno neobdelanem vzorcu

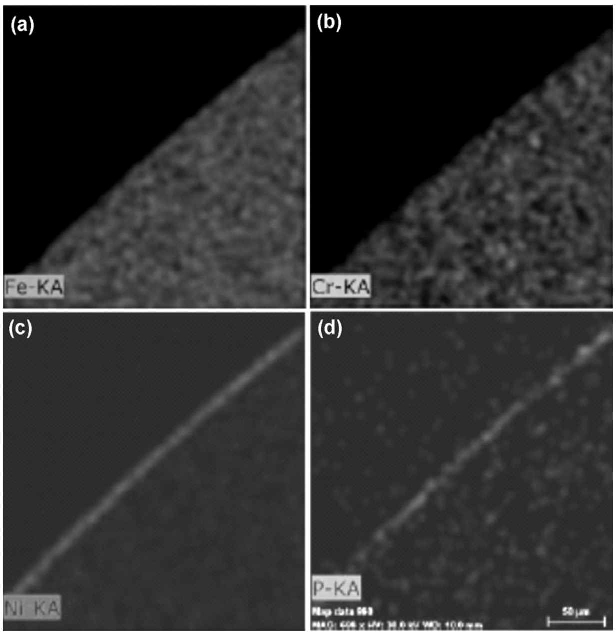

Figure 5: Content of the iron, chromium, nickel and phosphorus present on the cross-sections of Ni-P coatings deposited with the electroless process on austenitic stainless-steel AISI 316 substrate of the heat-treated sample, obtained with SEM and EDS mapping

Slika 5: SEM- in EDS-prikaz razporeditve železa, niklja in fosforja na toplotno obdelanem vzorcu

iron, chromium, nickel and phosphorus is shown in **Figure 4**. It is evident that nickel (**Figure 4c**) and phosphorous (**Figure 4d**) are located in both the coating and the substrate. Iron (**Figure 4a**) and chromium (**Figure 4b**) are located only in the substrate. Phosphorous is uniformly distributed in the Ni-P coating.

SEM and EDS mapping of the contents of the iron, chromium, nickel and phosphorus in the heat-treated samples is shown in **Figure 5**. It is evident that the distribution of chemical elements in the coating and the substrate is similar to the distribution of chemical elements in the non-heat-treated specimen. Nickel (**Figure 5c**) and phosphorous (**Figure 5d**) are found in the coating and in the substrate, but iron (**Figure 5a**) and chromium (**Figure 5b**) are found only in the substrate.

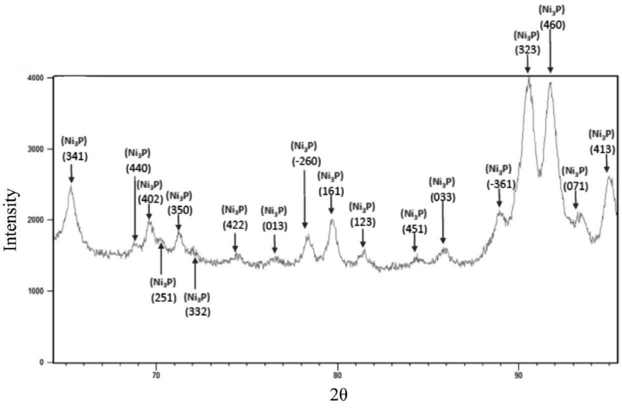

Figure 6: X-ray spectra of the heat-treated electroless nickel-phosphorous coating

Slika 6: Rentgenogram toplotno obdelanega, kemijsko nanešenega nanosa nikelj-fosfor

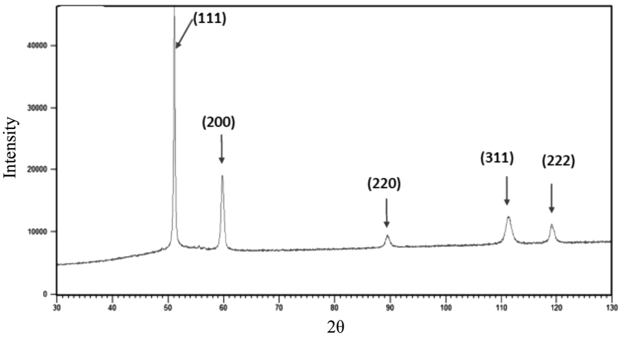

Figure 7: X-ray spectra of the non-heat-treated electroless nickel-phosphorous coating

Slika 7: Rentgenogram toplotno neobdelanega kemijsko nanešenega nanosa nikelj-fosfor

It was found that the heat-treated and non-heat-treated specimens have about 9 % of phosphorous. Distributions of phosphorous in the coatings are similar in both the heat-treated and non-heat-treated specimens, but it is known that the non-heat-treated coating with 9 % of phosphorous has a mixed, amorphous and crystalline structure.[8]

For a more precise definition of a possible mechanism of hardening the coating with heat treatment, a further study of the electroless nickel-phosphorous coatings was done using an X-ray diffraction analysis. The X-ray diffraction analysis was performed on both types of samples, i.e., the heat-treated and non-heat-treated electroless nickel-phosphorous coatings. In **Figure 6,** the results of the X-ray diffraction analysis of a heat-treated electroless coating are shown. It can be seen that the Ni_3P phase is formed in the heat-treated electroless coating. **Figure 7** shows the X-ray diffraction analysis of a non-heat-treated electroless coating. The Ni_3P phase was not formed on the non-heat-treated electroless coating.

4 CONCLUSION

Application of the Ni-P coatings deposited with the electroless process on the austenitic steel AISI 316 was analyzed.

Surfaces of the austenitic-steel AISI 316 substrate were prepared before depositing the Ni-P coatings with the electroless process. The investigated coatings follow the surface morphology of the samples. Uniform Ni-P coatings deposited with the electroless process were formed.

With the X-ray diffraction analysis, it was determined that the Ni_3P phase was formed due to the heat treatment of the samples. At the same time, it was found that a substantial increase in the hardness of an electroless Ni-P coating is achieved by applying the heat treatment. The thickness of the non-heat-treated Ni-P coating is 8 μm while the thickness of the heat-treated Ni-P coating is 7.5 μm.

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