Effect of Gamma Radiation on Oxidation of Electroless Ni-P Deposited on Stainless Steel st. 304

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The given work deals with the effect of gamma-irradiation on the oxidation process of the Ni-P chemical deposition on the surface of the stainless steel marked 304. The methods used are scanning electron microscopy and X-ray analysis. As a result, it has been found out that after gamma-irradiation the surface of the Ni-P layer is completely covered with cracks, and on the surface of this layer a high content of oxygen and phosphor has been detected because of formation of the P_2O_5 oxide.

Keywords: Ni-P layer, surface morphology, gamma-radiation, structure.

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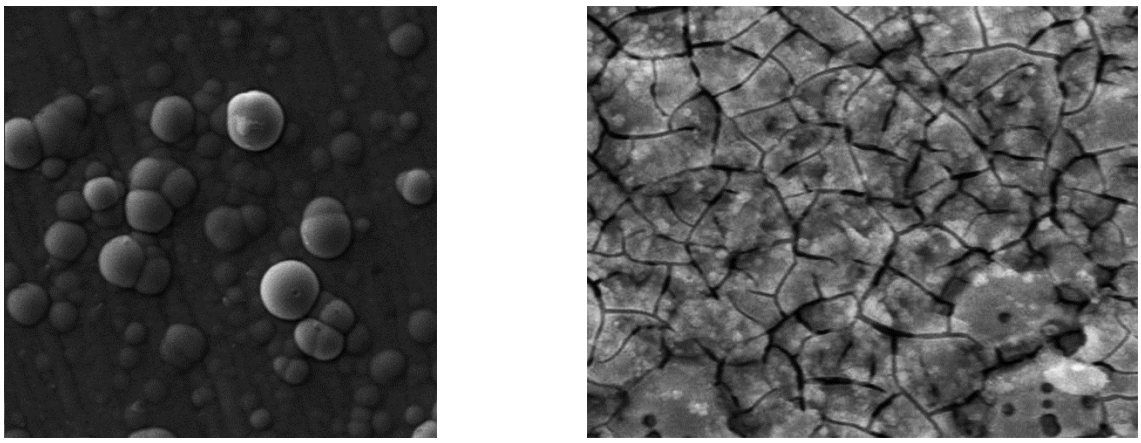
INTRODUCTION

Electroless plating is carried out via the redox reaction of an oxidizer and a reductant in an electrolyte solution. It is an autocatalytic process widely used for the production of uniform, less porous, adherent deposit for many industrial applications [1]. Electroless plating is a chemical reduction process that depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of a metal without the use of electrical energy [2]. Electroless nickel coatings have gained popularity due to their inherent properties like excellent resistance to corrosion, wear and abrasion [3]. In particular, electroless nickel – phosphorus plating has been used as a functional coating due to the advantage of corrosion [4]. Electroless nickel, as an engineering coating, is used in many industrial applications, for instance, nuclear engineering, aerospace, automotive, oil petrochemicals, textiles, etc. Nuclear reactor parts are coated with electroless nickel, as an engineering coating, so as to improve their corrosion and wear resistance [2]. The radiolysis of the primary coolant water by gamma radiation in the water-cooled nuclear reactors is often related to corrosion problems. The interaction of gamma radiation with aqueous solutions produces a host of transient radicals, ion and stable molecular species. In addition to unstable radicals, hydrogen peroxide is the most stable molecular species generated by water radiolysis [5–6]. Various studies have been done on the effect of H_2O_2 induced change on the surface characterization of stainless steels extensively used in the water-cooled nuclear reactors [7–9]. So far, there is no reported study on the effect of gamma radiation on the surface characteristics of electroless Ni-P deposition. From scientific and technological points of view, surface characterization of coatings has of great importance because in any application it is the surface of the material that is in contact with the surroundings [10]. In the given paper we have investigated the effect of gamma radiation induced change on the surface morphology of electroless Ni-P deposited on stainless steel st. 304. The methods used are: Scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX) system and Atomic Force Microscopy (AFM). Chemical characterization of the surface was performed by the X-ray photoelectron spectroscopy (XPS).

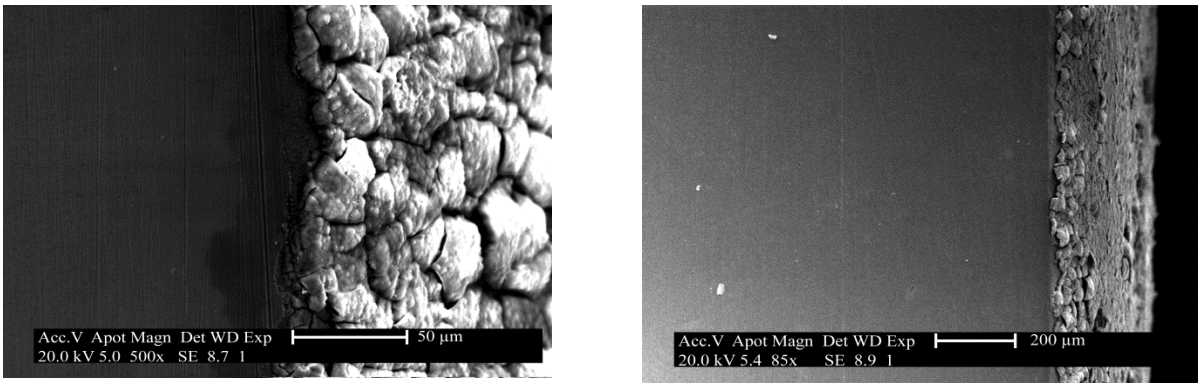
EXPERIMENTAL PROCEDURE

Electroless Ni-P coatings were deposited on specimens made of stainless steel st. 304 with dimensions of 15 mm × 10 mm × 0.35 mm. Prior to the coating deposition, the surfaces of the specimens were ground with abrasive paper of 400–1200 grit. After that the specimens were cleaned with alkaline solution at 60–80°C for 10–20 min and then rinsed with water. Subsequently the specimens were immersed for 2 min in 37% HCl at 30°C and then washed in cold running water and in distilled water. Next, the specimens were activated for 2–3 seconds in the 10% HCl and 90% H_2SO_4 solution, washed with distilled water and immediately subjected to the electroless nickel-phosphorus deposition process. The contents of chemicals for the electroless plating baths were nickel sulfate (21.2 g/l), sodium hypophosphite (24 g/l), lactic acid (23 ml/l), and propionic acid (1.8 ml/l). The pH value of the plating bath was fixed at 4.2 and adjusted with 20 vol. % H_2SO_4 and 50 vol. % NH_4OH solutions. The Ni-P deposits were irradiated in the 30% H_2O_2 environment with a ^{60}Co gamma source at a dose rate of 0.48 Gy/s at ambient temperature. The microstructure and chemical composition of the surface layer were characterized with SEM (Model SSI, CSEM) equipped with EDX. XPS was used to



(a) (b)

Fig. 1. SEM surface morphology of electroless Ni-P deposit: (a) before and (b) after radiation.



(a) (b)

Fig. 2. Cross sectional SEM micrograph of Ni-P deposit to gamma radiation influence: (a) 500X, and (b) 85X magnifications.

study the structure of the surface after gamma radiation. In order to analyze the surface topography of the deposits, AFM measurements were carried out at room temperature to obtain surface topological images of the samples within the scale of 10 µm × 10 µm.

RESULTS AND CONCLUSION

Figs. 1a and b show the SEM surface morphology of the electroless Ni-P deposit before and after radiation. The surface morphology of the Ni-P deposit shows the hemispherical nodular structure, which indicates a typical amorphous structure of the deposit. The diameter of the biggest nodule size on the surface reached about 100 nm. No micro crack was observed at the surface of the deposit. After radiation, the surface morphology of the Ni-P deposit showed a completely cracked structure; no hemispheres were found on the surface.

Figs. 2a and b display the cross sectional SEM micrographs of the Ni-P deposit to gamma radiation influence. As seen, the Ni-P deposit is completely fragmented. Fragments near the surface have been detached from the surface most probably due to a polishing process.

The chemical composition of the electroless Ni-P deposit before and after gamma radiation is presented in Table. The Ni-P deposit contains 12.6 wt.% phosphorus and 87.4 wt.% nickel, which indicates the amorphous structure of the Ni-P deposit. The P content in the Ni-P layer is very important because it allows to easily control the properties of the Ni-P alloy [11]. In general, the electroless Ni-P deposits can be classified as low (1–5 wt.% P), medium (5–8 wt.% P) and high (9 wt.% P and more) phosphorus deposits, based on their phosphorus contents. It has been shown that a low phosphorus content in coatings is crystalline whe-reas the coatings with a higher phosphorus content are amorphous [12]. After gamma radiation the surface of the Ni-P deposit showed a considerable oxygen concentration (38.6 wt.%). Also the Ni content decreased from 87.4 wt.% to 48.6 wt.% after radiation.

Chemical composition of the electroless Ni-P deposit before and after gamma radiation

Element	Before radiation (wt.%)	After radiation (wt.%)
Ni	87.4	48.6
P	12.6	11.8
O	–	38.6

The EDX spectra of the electroless Ni-P deposit before and after gamma radiation are shown in Figs. 3a and b.

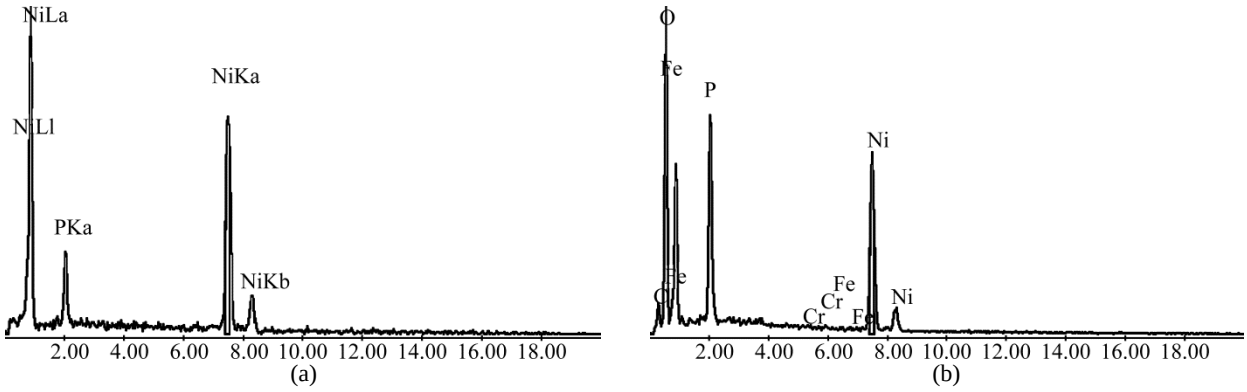


Fig. 3. EDX pattern of the electroless Ni-P deposit before and after gamma radiation.

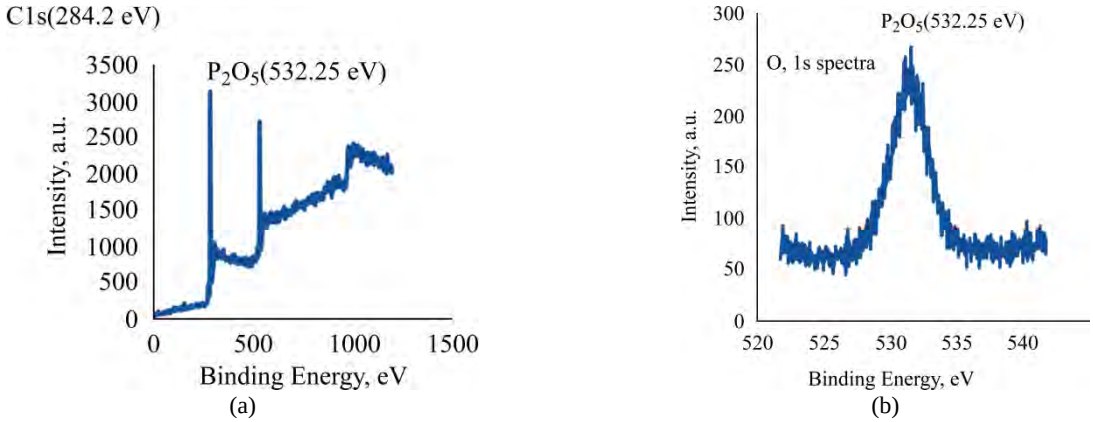


Fig. 4. XPS spectra: (a) full scan spectra of the surface of Ni-P film, and (b) narrow scan analysis of the surface element of O after gamma radiation.

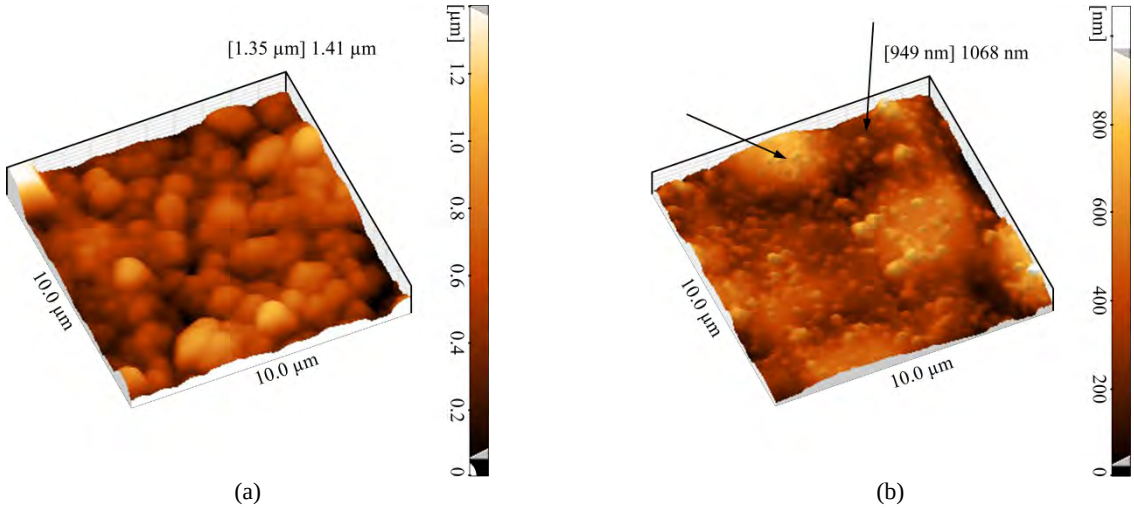


Fig. 5. Three dimensional AFM images of Ni-P deposit: (a): before and (b) after gamma radiation.

High oxygen content of the Ni-P deposit after gamma radiation most likely originated from the oxidation of the Ni-P deposit in the H_2O_2 environment. The XPS full scan spectra of the Ni-P deposit and narrow scan spectra of oxygen on the Ni-P surface after gamma irradiation are depicted in Figs. 4a and b. As is seen, the surface of the Ni-P deposit after gamma irradiation contained elements of oxygen and carbon (Fig. 4a), with the main peak from C(1S) at 284.2 eV as a reference and a peak from O(1s) at 532.2 eV energy (Fig. 4b), which is related to the (O-P) formation visible in the XPS spectra [12]. There were not any peaks from Ni (2p3/2) in Ni, Ni-P, NiO, and $Ni(OH)_2$ in the XPS spectra, respectively (Fig. 4a).

This fact indicates a preferential segregation of P to the surface, which could be due to its low heat of evaporation or due to the strain energy. The heat of evaporation of P is 2.97 Kcal/g-atom, while that of Ni is 91Kcal/g-atom [13]. That might be the cause for the predominant formation of (O-P) on the surface of the deposit after gamma irradiation in the H_2O_2 environment.

Three dimensional AFM images of the Ni-P deposit before and after gamma radiation are shown in Fig. 5. As is seen, the surface of the Ni-P deposit

before radiation (Fig. 5a) is relatively regular and consists of typical hemispherical nodules distributed over the scanned area. After radiation the surface of the Ni-P deposit shows a clustered structure. Each cluster consists of small nodules agglomerated together. Breaking off of positions was observed between the clusters that illuminate the cracked structure of the surface, as shown by arrows.

CONCLUSION

This investigation has found out that gamma radiation has a considerable effect on the electroless Ni-P deposit. Gamma radiation of electroless Ni-P deposits in the 30% H_2O_2 environment caused a complete fragmentation of the Ni-P deposit. This most probably was due to the oxidation of the Ni-P deposit in the H_2O_2 environment during gamma radiation. Expansion of the Ni-P deposit followed by the preferential formation of P_2O_5 oxide during gamma radiation resulted in the formation of an intensive residual stress in the structure of the Ni-P deposit, thus leading to the fragmentation of this deposit after gamma radiation. The preferential segregation of P to the surface, probably due to its low heat of evaporation or due to the strain energy, caused the preferential formation of the P_2O_5 oxide on the surface of the deposit. There were not observed any compositions from Ni (2p3/2) in Ni, Ni-P, NiO, and $Ni(OH)_2$ in the XPS spectra of the Ni-P deposit.

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Реферат

В настоящей работе исследовано влияние γ-излучения на процесс окисления Ni-P химически осажденного покрытия на нержавеющей стали марки 304 методом сканирующей электронной микроскопии (SEM) и рентгеновского анализа (EDX). Установлено, что после γ-излучения поверхность Ni-P слоя была полностью покрыта трещинами, и на поверхности Ni-P слоя обнаружено высокое содержание кислорода и фосфора из-за образования оксида P_2O_5.

Ключевые слова: слой Ni-P, морфология поверхности, гамма-облучение, структура.