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MICROHARDNESS AND CORROSION BEHAVIOR ELECTROLESS NI-P COATED ON STAINLESS STEEL 304 IN GAMMA RADIATION ENVIRONMENT

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In the research, electroless Ni-9%P and Ni-12%P coatings were deposited on stainless steel AISI 304. Deposits have been irradiated in 30% H_2O_2 environment with a ^{60}Co gamma source at a dose rate of 0.48 Gy/s at ambient temperature for 70 hours. Results showed that gamma radiation has not essential effect on corrosion potential of stainless steel 304 and Ni-P deposited. However, corrosion rate at T=373°K decreased 10 times following gamma radiation.

Keywords: *Ni-P, corrosion rate, gamma- radiation, microhardness*

The Ni-P alloys with phosphorus content of 7-15% in the form of coating deposited on surfaces of different materials are used as an anticorrosion protection and a means of raising hardness of these surfaces. Due to their amorphous structure, these deposits have higher hardness than uncoated steels. Electroless plating is made via the redox reaction of an oxidizer and a reductant in an electrolyte solution. It is an autocatalytic process, which is widely used for the production of uniform, less porous, adherent deposit. Note that this deposit is applied for many industrial purposes [1]. Electroless plating is a chemical reduction process, which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of the metal without the use of electrical energy [2]. Electroless nickel coatings have gained popularity due to their inherent properties like excellent corrosion, wear and abrasion resistance [3]. In particular, electroless nickel – phosphorous 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 as nuclear engineering, aerospace, automotive, oil petrochemicals, textiles, etc. Nuclear reactor parts are coated with electroless nickel as an engineering coating for improvement of 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 corrosion and surface characterization of stainless steels which are extensively used in the water-cooled nuclear reactors [7-9]. Based on studies, there is no study reported on the effect of gamma radiation on the surface characteristics and corrosion behavior of electroless Ni-P deposition. From scientific and technological point of view, surface characterization of coatings has of great importance because in any application or use it is the surface of the material which is in contact with the surroundings [10]. In this experiment we investigated the effect of gamma radiation-induced changes on the surface morphology, corrosion behavior and microhardness of electroless Ni-P coated AISI 304 stainless steel using Scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX) system, polarization method and a Vickers micro hardness tester.

Experimental procedure:

Electroless Ni-P coatings were deposited on specimens made of stainless steel AISI 304 with dimensions of 15mm × 10mm × 0.35mm. Prior to coating deposition the surfaces of the specimens were ground with abrasive paper of 400–1200 grit. Then 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. Then the specimen was activated for 2-3 seconds in 10% HCl and 90% H_2SO_4 solution, washed with distilled water and immediately subjected to the electroless nickel-phosphorous deposition process for 2h. The contents of chemicals for the electroless plating baths were nickel sulfate (21.2 g/lit), sodium hypophosphite (24 g/lit) lactic acid (23 ml/lit), and propionic acid (1.8 ml/lit). The pH value of the plating bath related to content of P coating was fixed at 4.2 (Ni-12%P) and 4.6 (Ni-9%P) and adjusted with 20 vol. % H_2SO_4 and 50 vol. % NH_4OH solutions. Chemical composition of the electroless nickel plating bath and operation condition has been shown in table1. The samples of Ni-P before to gamma irradiation first cleaned with Aston then rinsed in distilled water and with inert gas. After this stage samples immerse in H_2O_2 30% solution in guards ampoules and vacuumed until $P=10^{-3}$ Pa by method of thermo-vacum pumps, the samples are irradiated with cobalt-60 irradiator for 10, 30, 70 h at a dose rate of 0.48 Gy/s at ambient temperature.

The microstructure and chemical composition of the surface layer were characterized by SEM (Model SSI, CSEM) equipped with EDX. A Vickers microhardness tester was employed to study the hardness of the surface after gamma radiation. In order to evaluate corrosion behavior of the deposits, polarization measurements were carried out at a room temperature and in hot water solution to obtain corrosion rate.

Results and discussion

Fig. 1 - 3 shows the SEM surface morphology of electroless Ni–P deposit and stainless steel substrate before and after radiation. The surface morphology of Ni–P deposit shows the hemispherical nodular structure which indicates typical amorphous structure of deposit. The diameter of the biggest nodule size on the surface reached about 100 nm. No micro crack was observed on the surface of the deposit. After radiation, the surface morphology of Ni-P deposit shows the completely cracked structure and no hemispheres were found on the surface. While any changes are manifest in surface morphology of stainless steel after radiation but there is O peak as identified in EDX analysis (fig4).

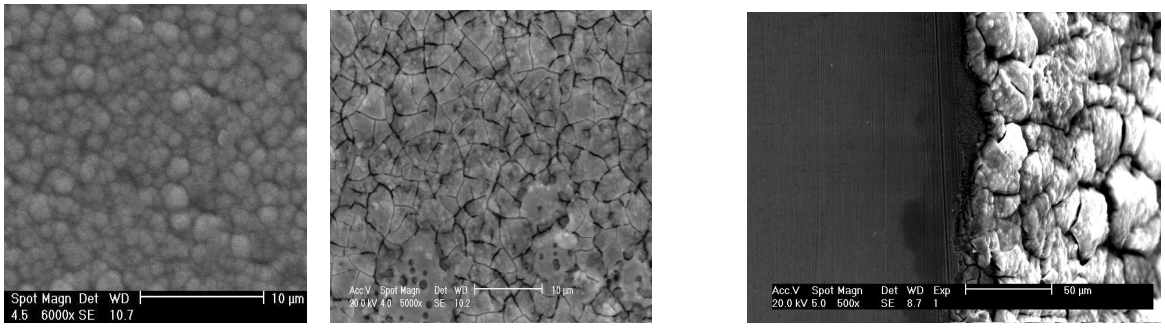
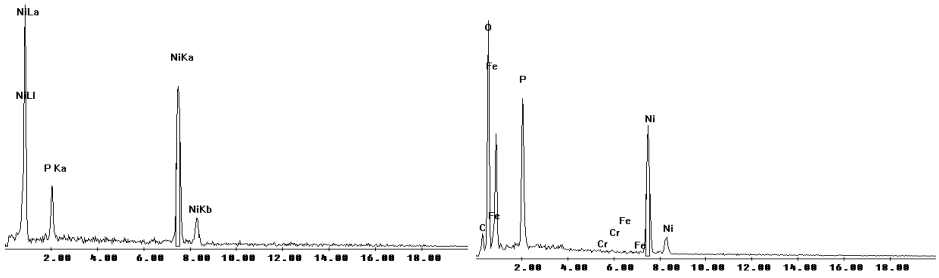


Fig.1. SEM of Ni-P (a) before and (b) after gamma irradiation (c) cross section of Ni-P after gamma irradiation



(a) (b)

Fig. 2. EDX pattern of the electroless Ni-P deposit before and after gamma radiation

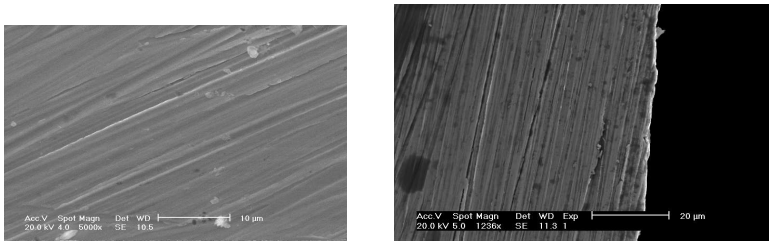
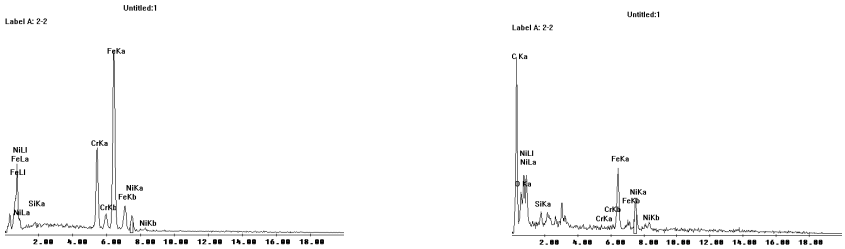


Fig.3. SEM of surface stainless steel after gamma irradiation



(a) (b)

Fig.4. EDX of stainless steel before (a) and after (b) gamma irradiation

Chemical Composition of the electroless Ni-P deposit before and after gamma radiation is shown in table 1. The Ni–P deposit contains 12.6 wt. % phosphorous and 87.4 wt. % nickels which indicates to the amorphous structure of Ni-P deposit. The P content in the EN–P layer is very important because it allows easy control over properties of the EN–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 revealed that the low content in phosphorous coatings is crystalline whereas the coatings with higher phosphorous content are amorphous [12]. Following the gamma radiation, the surface of Ni-P deposit showed considerable oxygen concentration (38.6 wt %). Also, nickel content fell from 87.4 wt% to 48.6 wt% after radiation. High oxygen content of the Ni-P deposit after gamma radiation is most likely due to the oxidation of the Ni-P deposit in H_2O_2 environment.

Table 1: Chemical composition of the electroless Ni-P deposit before and after gamma radiation

Element	Before radiation (wt %)	After radiation (wt %)
Ni	87.4 91	48.6 60
P	12.6 9	11.8 8
O	0 0	38.6 32

Fig. 5 shows the microhardness behavior of Ni-9%P and Ni-12%P coated and uncoated with stainless steel substrate using a Vickers micro hardness tester under a load of 100gr with loading time 15 s before and after gamma radiation in H_2O_2 environment at 10,30,70 hours. Results showed that gamma radiation had not considerable effect on microhardness of stainless steel substrate but microhardness of both Ni-9%P and Ni-12%P coatings decreased with the increase of gamma radiation time until 70 hours, however, at 70 h radiation time its values rose suddenly. This increscent of microhardness at 70 hours radiation time was due to two reasons: first, to the formation of two bright and dark phases on the surface according to microscope results(fig 1b) which the bright phase had high microhardness and the dark one had low microhardness; second, to the fall of phosphorous content coating to 8% .The point is that Yan et al [13-15] have found that the hardness of electroless Ni-P coatings is dependent on the phosphorous content and at first it grows with the increase in phosphorous content up to 8% and then goes down . The maximum hardness electroless Ni-P is attained by means of deposited coating with 8%P.

It concludes that as per SEM and EDX results the gamma radiation causes changes in the chemical composition of the electroless Ni-P deposit and formation of oxides and phosphide phases where these phases act as barriers to dislocate the motion, thereby increasing the hardness. However, the hardness of Ni-P films degrades with excessive annealing due to the grain coarsening that leads to the surface brittleness and enhanced dislocation propagation [16].

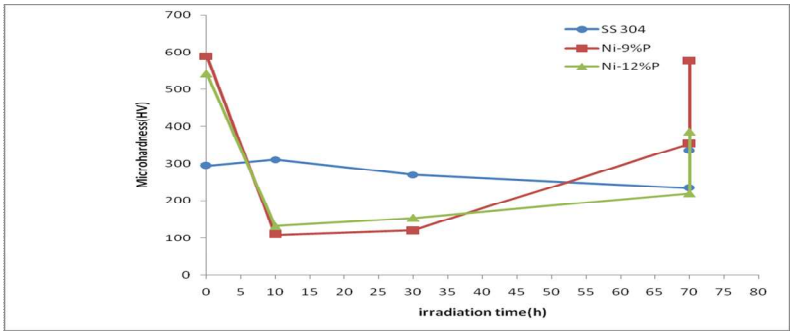


Fig. 5. Values of microhardness of substrate - stainless steel 304 ,Ni-9%P and Ni-12%P coated on stainless steel at different gamma irradiation times

Polarization curves of Ni-P deposits with 9 and 12 w % of P and uncoated substrate stainless steel before and after gamma irradiation measured in a ionize water solution at 1 mVs^{-1} in room and boiling water temperature are shown in fig.6, 7 respectively. Note that on curves of fig 6a (room tempuraure water) the corrosion potential (E_{corr}) of Ni-12%P deposit and stainless steel substrate have negative values (table 2).

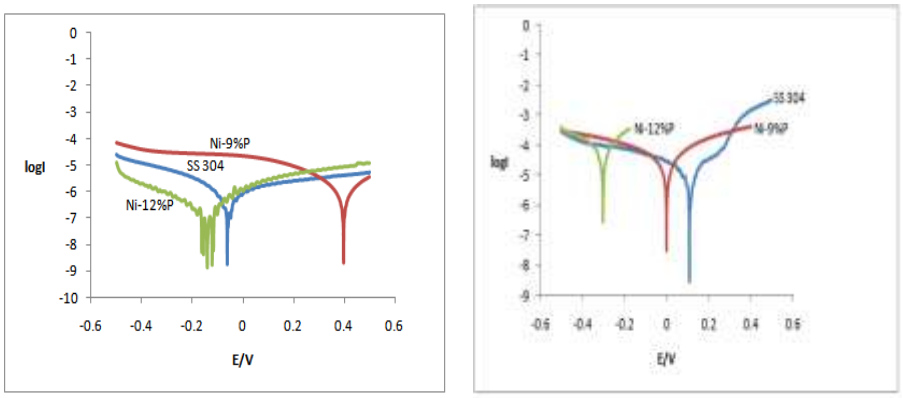


Fig. 6. Polarization curves of steel 304, Ni-9%P and Ni-12%P coatings before radiation in ionized water at (a): T=300°K (b) T=373°K

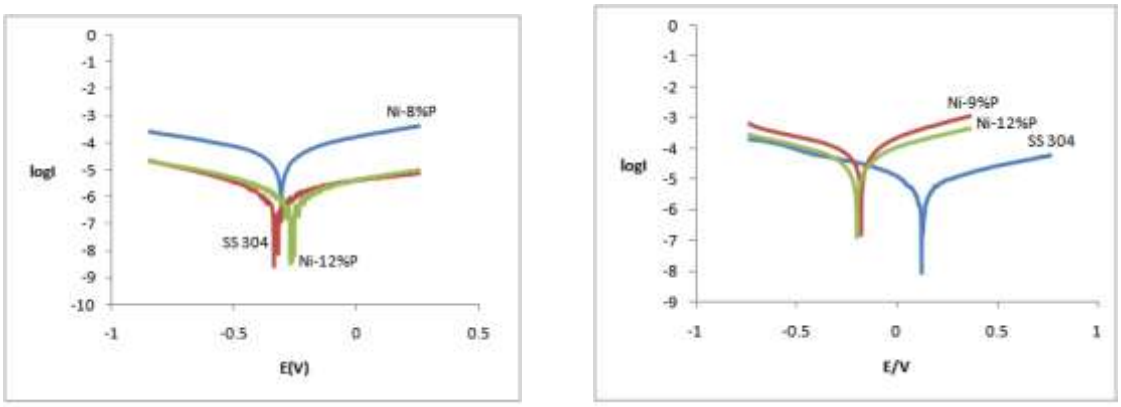


Fig.7. Polarization curves of stainless steel 304, Ni-9%P and Ni-12%P coatings in ionized water after radiation at (a) T=300°K and (b) T=373°K.

Table 2. Corrosion resistance of 304 stainless steel, Ni-9%P and Ni-12%P in ionized water by potentiodynamic polarization studies

System studied	Corrosion rate (mm/year)	E_{corr}(V)	i_{corr} (A cm^{-2})
304 steel before radiation at T=300 ^{0}K	4.48×10^{-3}	-0.062	4.115E-7
304 steel after radiation at T=300 ^{0}K	4.48×10^{-3}	-0.196	3.73E-7
304 steel before radiation at T=373 ^{0}K	5.65×10^{-2}	0.109	5.186E-6
304 steel after radiation at T=373 ^{0}K	3.10×10^{-3}	0.123	2.755E-7
Ni-9%P coating before radiation at T=300 ^{0}K	4.11×10^{-3}	0.40	3.904E-7
Ni-9%P coating after radiation at T=300 ^{0}K	4×10^{-4}	0.363	4.42E-8
Ni-9%P coating before radiation at T=373 ^{0}K	8.59×10^{-2}	-0.26	8.165E-6
Ni-9%P coating after radiation at T=373 ^{0}K	4.39×10^{-2}	0.387	4.169E-6
Ni-12%P coating before radiation at T=300 ^{0}K	6.49×10^{-5}	0.117	5.953E-9
Ni-12%P coating after radiation at T=300 ^{0}K	8.28×10^{-5}	0.31	7.864E-9
Ni-12%P coating before radiation at T=373 ^{0}K	3.78×10^{-2}	0.302	3.467E-6
Ni-12%P coating after radiation at T=373 ^{0}K	9.37×10^{-2}	0.306	8.906E-6

In the meanwhile, no passive phenomenon is found where the corrosion potential (E_{corr}) of Ni-9%P deposit is positive. This positive shift in Ecorr indicates the good anticorrosive property of medium phosphorous deposits at room tempurature water. The curves of Fig. 6b

(boiling water tempuraure) the corrosion potential (E_{corr}) of Ni-12%P and Ni-9%P deposits are negative while E_{corr} stainless steel substrate has positive value (Table 2). Thus, the Ni-P deposits are expected to be of weaker anticorrosive coating in the high temperature water than stainless steel substrate. From comparsion of curves fig 7 it is conculod that gamma irradiation has not considerable effect on the corrosion potential(E_{corr}) of Ni-P deposits and stainless steel substrate, however, the gamma irradiation reduces corrosion rate of stainless steel. The question is that the environment of oxidant radiation causes the formation of compact and addisive oxide layer on the stainless steel surface while oxide layer on the surface of Ni-P deposit after radiation broke into fragments and the solution diffused in it and results in the growth both of corrosion current (i_{corr}) and corrosion rate (table 2). The corrosion resistance is calculated on the basis of the following equation.

$$R_{corr} = dE/di|_{E=Eocp} \approx \Delta E/\Delta i$$

Note that the corrosion resistance is based on the slope of the regression line, which may sometimes deviate from the average value of the slope(i.e. $\Delta E/\Delta i$). [11]. It may be inferred that Ni-P coating is not eligible for the use in terms of environment where there exists ionizing radiation with this gamma ray, yet, it may be used in case of the lack of radiation rays due to high hardness, good corrosion and wear resistance.

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ВЛИЯНИЕ ГАММА-ИЗЛУЧЕНИЯ НА МИКРОТВЕРДОСТЬ И КОРРОЗИОННОЕ ПОВЕДЕНИЕ НЕРЖАВЕЮЩЕЙ СТАЛИ МАРКИ AISI 304, ПОКРЫТОЙ ХИМИЧЕСКИ ОСАЖДЕННЫМ Ni-P

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На нержавеющую сталь марки AISI 304 было нанесено покрытие состава Ni-9%P и Ni-12%P. Полученные образцы подверглись облучению мощностью дозы в 0.48 Gy/s от ^{60}Co гамма-источника в течение 70 часов, при температуре окружающей среды в среде 30% H_2O_2 . Полученные результаты свидетельствуют о том, что гамма-облучение не оказывает существенного влияния на коррозионный потенциал полученных образцов, однако скорость коррозии при T=373°K уменьшается в 10 раз.

Ключевые слова: *скорость коррозии, гамма-облучение, микротвердость.*

Ni-P ÖRTÜKLÜ 304 MARKALI PASLANMAYAN POLADIN MİKROSƏRTLİYİ VƏ KORROZİYASINA γ-ŞÜALARININ TƏSİRİ

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Səthi elektrokimyəvi metodla Ni- 9%P və Ni-12%P təbəqəsilə örtülmüş 304 markalı paslanmayan polad nümunələri tədqiq edilmişdir. Nümunələr H_2O_2 mühitində 70 saat ərzində otaq temperaturunda dD/dt=0.78 Qr/s doza gücündə ^{60}Co qamma izotop mənbəyində şüalandırılmışdır. Şüalandırılmış nümunələrin müxtəlif temperaturda (T=300-373K) mikrosərtliyi və korroziya sürəti öyrənilmişdir. Müəyyən edilmişdir ki, γ-şüaları 304 markalı paslanmayan poladın fosforla örtülmüş səthinə T=300K-də korroziya sürətinə təsir etmir, lakin T=373K-də isə korroziya sürəti təqribən ~8÷10 dəfə azalır.

Açar sözlər*: korroziya sürəti, qamma- şüalanma, mikrosərtlik.*

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