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Influence of Nitrogen Ion Implantation on the Structure and Corrosion Resistance of Stainless Steel Substrates Coated with Ni Nanolayer

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ABSTRACT

Ion implantation is a surface modification technology that produces new materials on the surface by impingement of high energy ions from the ion accelerator. In this work, AISI 304 stainless steels were coated with 90 nm Ni film by electron beam deposition and implanted by a flow of 5×10^{17} $N^{+}cm^{-2}$ at 400 K with different implantation energies of 10, 20, 30 and 40 keV. The corrosion behavior of prepared samples was tested in 3.5% NaCl solution using potentiodynamic polarization technique. Crystallographic and morphological structure of the samples was analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. A clear correlation was achieved between the physical analyses (XRD and SEM) and the potentiodynamic results. The highest corrosion resistance was achieved with a corrosion current density of 0.172 µA cm^{-2} in the case of sample which was N^{+} ion implanted at 20 keV. Prog. Color Colorants Coat. 9 (2016), 77-83 © Institute for Color Science and Technology.

1. Introduction

AISI 304 stainless steels (SS) are one of the most important alloys used in corroding environments and have received special attention in the last few years. A wide variety of surface modification methods of austenitic SSs such as physical vapor deposition, gas nitriding, ion nitriding and ion implantation have been studied to improve corrosion properties [1-5]. Ion implantation is a surface modification technology which produces new materials on the surface by impingement of high energy ions from an ion accelerator. The ion implantation technique introduces atomic species in a material in order to modify its mechanical, optical and structural properties [6-9]. The beam of species is accelerated through an electric field and thus bombards the target material with an electron-volt to mega-electron-volt energy range. The implantation energy represents the energy acquired by ions under the acceleration of the electric field. The

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properties of the target material which lead to different applications are modified depending on the nature of the ions, their quantity and energy [10, 11].

Stainless steels contain a number of different alloying elements. Thus, the properties of a specific steel grade are determined by the combined effect of the alloying and trace elements in that specific grade. Therefore, by changing the amount of each element in the alloy composition, it is possible to obtain different corrosion behavior. Nickel is the basis of an important group of materials employed for corrosion inhibition. Nickel content not only enhances the corrosion inhibition behavior of stainless steel but also improves its physical and mechanical properties. The main reason for adding nickel is to promote an austenitic structure. Nickel generally increases ductility and toughness. In precipitation-hardening steels, nickel is also used to form the intermetallic compounds to increase the strength of the steel [11].

Nitrogen is a very strong austenite former. It also substantially increases the mechanical strength of steel and enhances its resistance to localized corrosion [12]. Implantation of nitrogen into the stainless steel produces a hard, corrosion and wear resistant surface. At implantation temperature close to 673 K, nitrogen diffuses into solid solution in the steel structure without the formation of nitrides of chromium and iron. Chromium nitride can be very detrimental in terms of corrosion behavior [13, 14].

The effect of nitrogen ion implantation on corrosion resistance of stainless steel has been studied by many researchers [15-19]. The implantation step and the choice of the implantation parameters are crucial to obtain a successful nitride layer. In the work described here, we aim at enhancing the surface properties of stainless steel by introducing nitrogen ion implantation prior to the deposition of nickel.

2. Experimental

Specimens with dimension of 20 mm×20 mm×0.7 mm were cut from sheets of AISI 304 stainless steel. The specimens were subsequently cleaned ultrasonically in heated acetone (CH_3COCH_3) and then ethanol (C_2H_5OH). Nickel films of 90 nm thicknesses were deposited on 304 stainless steel samples by electron beam evaporation (PVD-EB, E19A3 Edwards model, England) at room temperature with a base pressure of 2×10^{-7} mbar. The purity of nickel was 99.98%. Nitrogen ion implantation of the samples was performed at 400 K with a fluence of 5×10^{17} N^+ cm^{-2} at four different energies of 10, 20, 30 and 40 keV.

The crystallographic structure of the films was determined using a STOE model STADI MP Diffractometer (CuKα radiation) with a step size of 0.02° and count time of 1.0 s per step. The surface physical morphology was obtained using a scanning electron microscope (SEM: LEO 440i).

The electrochemical behavior of the samples was studied using a potentiodynamic method with a potentiostat coupled to a PC (EG&G273A). All electrochemical experiments were performed in a 3.5% wt NaCl solution at room temperature. The exposed surface area of the samples was 1.0±0.05 cm^2. A saturated calomel reference electrode (SCE) and a platinum counter electrode were used for the three-electrode setup. The samples were polarized from -600 mV vs. open circuit potential at a scan rate of 1 mVs^{-1}. All the potentials presented in this work are referenced to SCE.

3. Results

3.1. XRD Results

Figure 1 shows the X-ray diffraction (XRD) patterns of the as deposited and nitrogen implanted Ni/SS (AISI 304) samples with a fluence of 5×10^{17} N^+cm^{-2} at 400 K with different implantation energies of 10, 20, 30 and 40 keV. The XRD pattern of the bare stainless steel shows the presence of austenite peaks at $2\theta = 43.71°$, 50.78°, 74.81° and 90.08° that correspond to γ-Fe(111), γ-Fe(200), γ-Fe(220) and γ-Fe(311), respectively.

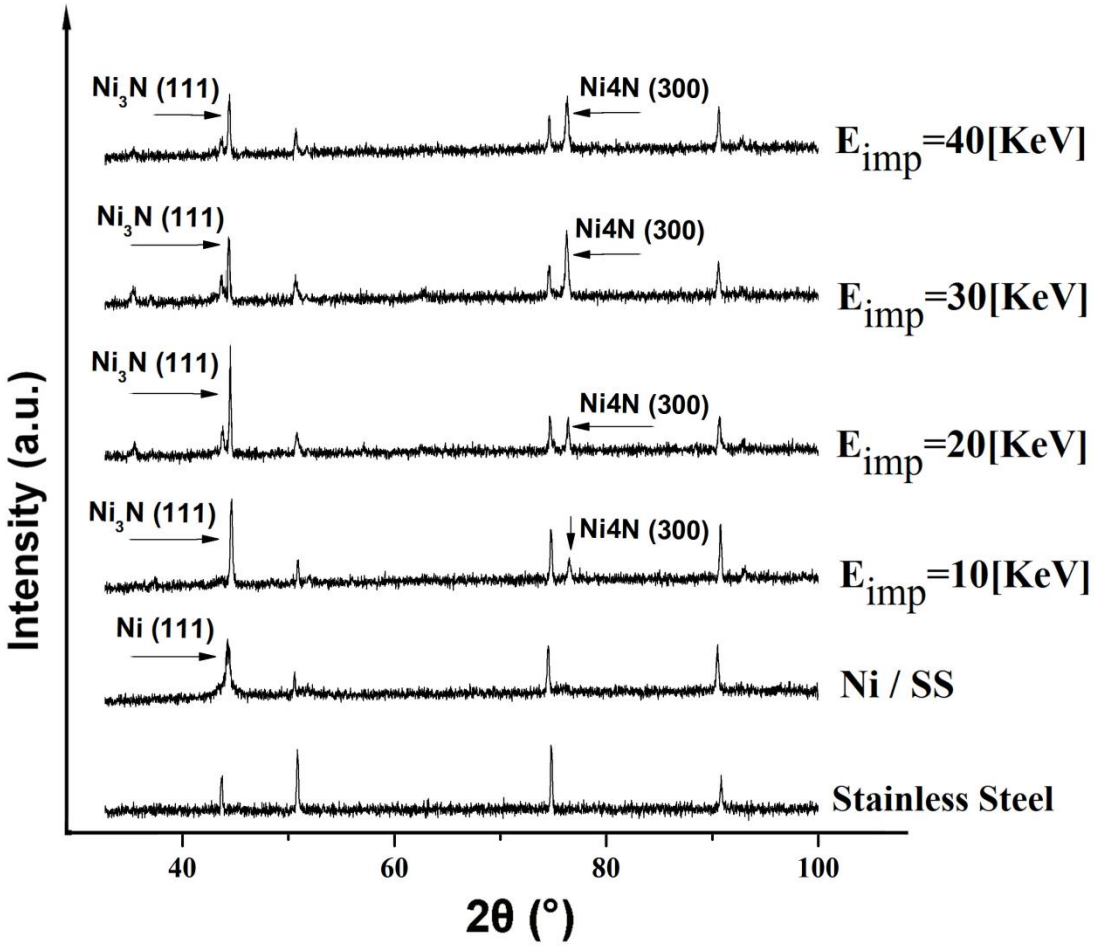

Figure1: XRD patterns of AISI 304 Stainless Steel, nickel coated and implanted samples with different nitrogen ion energies.

In addition to the peaks for stainless steel, XRD patterns of Ni/SS sample showed Ni(111) diffraction peak of nickel at 2θ = 44.521° (JCPDS 00-045-1027). The broadness of this peak overlaps the original SS peak at 2θ = 44.521°.

All ion implanted samples with different energies at the same dose of 5×10^{17} N^+ cm^{-2} and temperature of 400 K show two peaks which can be designed to $Ni_3N(111)$ and $Ni_4N(300)$ with reference to 2θ = 44.485° and 2θ = 76.08° (JCPDS 00-010-0280), respectively. It is clear that by the increase of implantation energy from 10 to 20 keV, nickel nitride peaks namely $Ni_3N(111)$ and $Ni_4N(300)$ are intensified. For implantation energies of 30 and 40 keV, the intensity of nickel nitride peaks are slightly decreased, so the maximum nickel nitride peaks are obtained by the sample implanted at 20 keV.

3.2. Polarization Results

Potentiodynamic polarization curves of the untreated and the nitrogen implanted Ni coated stainless steel with different energies in 3.5% NaCl solution are shown in Figure 2. None of these samples showed active passive behavior. The polarization plots illustrate that the deposition of nickel and N^+ implantation increases stainless steel resistance against corrosion. A remarkable tendency to corrosion

protection for the treated SS samples can be observed in Figure 2 with the polarization curves shifting towards lower corrosion current densities and higher corrosion potentials such that for sample implanted with 20 keV, the optimum corrosion current density and corrosion potential are obtained as 0.172 µA/cm^2 and -0.07 V vs. SCE, respectively, while these quantities for bare AISI 304 substrate are 13.948 µA/cm^2 and -0.42 V vs. SCE. The quantitative values of corrosion related parameters obtained from the polarization plots are given in Table 1.

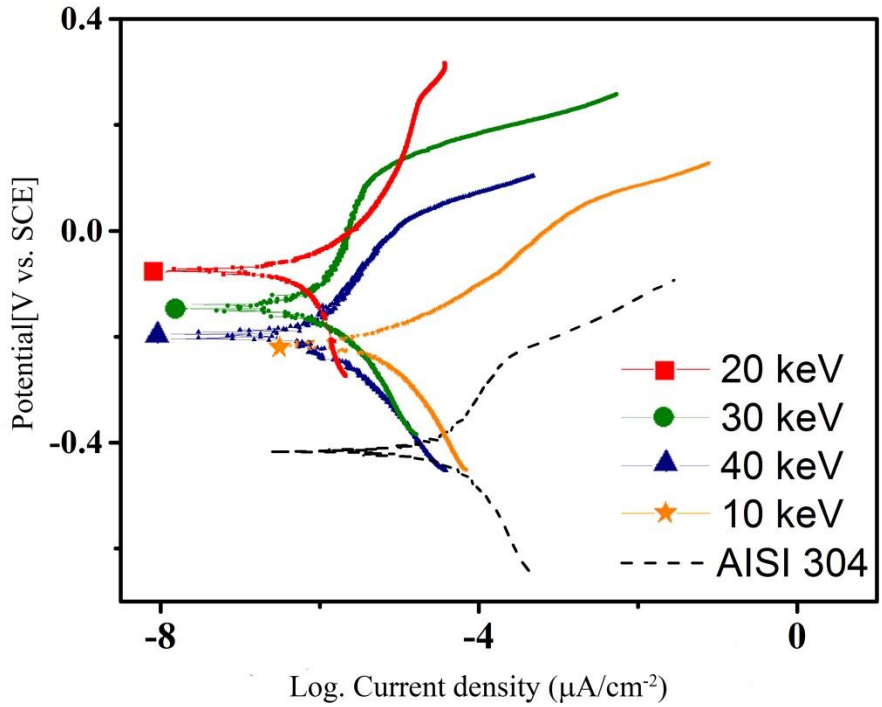

Figure 2: Polarization curves obtained for AISI 304 Stainless Steel and implanted samples using NaCl (3.5%) solution as the corroding environment at room temperature.

Table 1: Corrosion parameters of AISI 304 stainless steel and N^+ implanted samples of Ni/AISI 304 with different energies.

Sample		Energy (keV)	Corrosion current density (µA cm^{-2})	Corrosion potential (V vs. SCE)
AISI 304 SS		---	13.948	-0.42
Implanted samples	1	10	2.436	-0.22
	2	20	0.172	-0.07
	3	30	0.259	-0.14
	4	40	0.435	-0.20

3.3. SEM Results

Surface morphology of samples after corrosion test is presented in Figure 3. Comparison of Figure 3(a) obtained from uncoated stainless steel with nickel coated and implanted samples (Figure 3(b-e)) clearly shows that the most corroded and damaged sample after corrosion test is the bare stainless steel. This can be observed by the extent of damage occurred on samples after corrosion test. In addition, it can also be observed that the SEM image of the sample implanted at 20 keV (Figure 3(c)) shows the least amount of corrosion effects on its surface which is also consistent with the polarization results according to the discussion in Section 3.2 above.

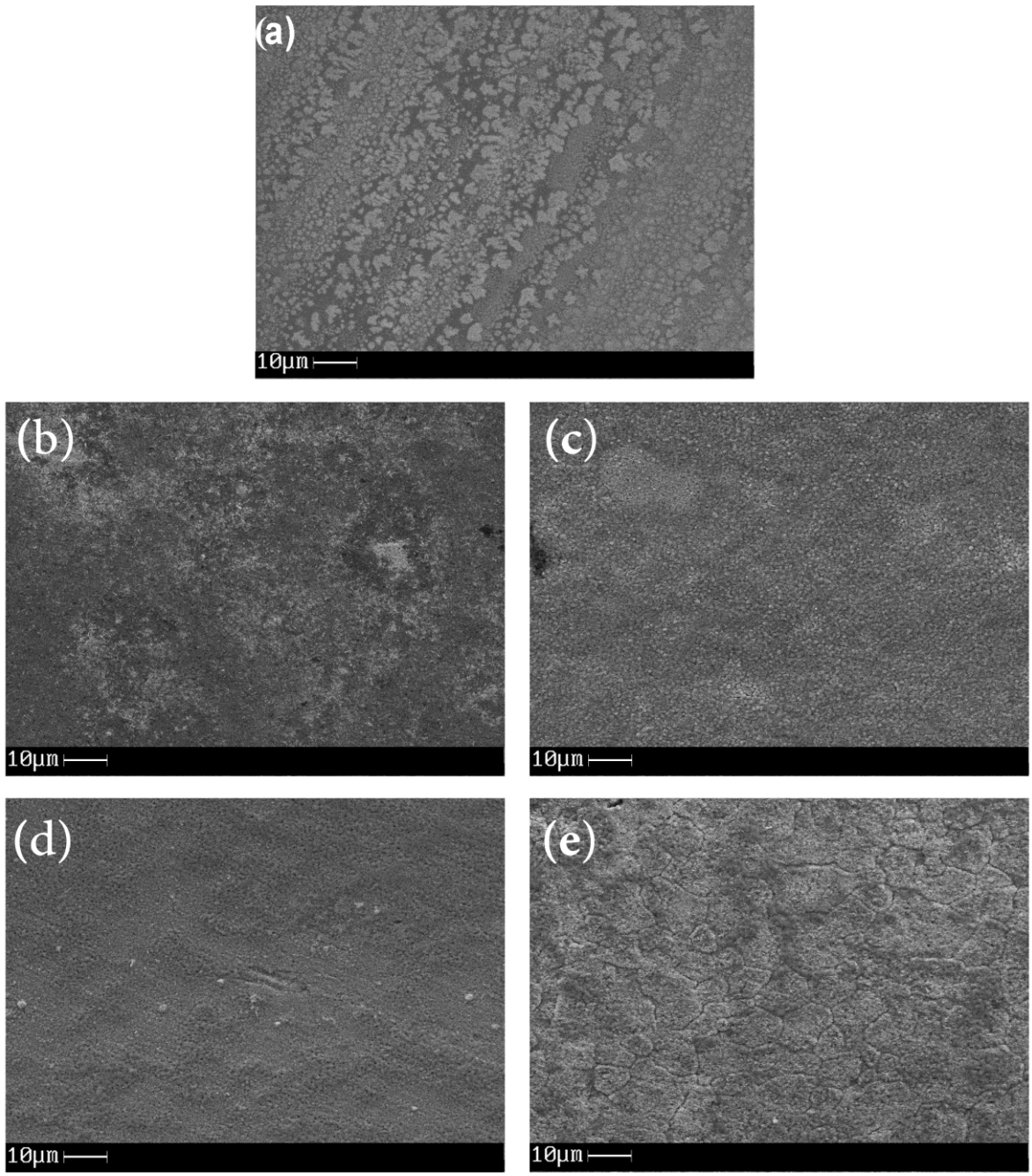

Figure 3: SEM electron micrographs of a) AISI 304 stainless steel and implanted samples at: b)10 ,c) 20, d)30, and e) 40 keV.

The implantation process for 20N-Ni/SS sample was simulated using TRIM2008 (transport of ions in matter) code in order to theoretically estimate N^+ ions distribution in Ni thin film coated on 304 stainless steel. TRIM is Monte Carlo computer program that calculates the interactions of energetic ions with targets. It is a group of programs that calculate the stopping power, average projected range ions (10eV–2GeV/amu) and other parameters in the process of implantation using a quantum mechanical treatment of ion-atom collisions. The nominal N^+ ion average projected range (R_p = 19.1 nm), straggling (ΔR_p=10.5 nm), maximum/peak nitrogen concentration (C_p = 2.7 × 1023 atoms cm^{-3}) and the expected sputtering rate (Rs = 2.42 atoms ion^{-1}) at the end of implantation process (i.e., after 99999 ions implanted), were obtained from TRIM2008 calculations.

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4. Discussion

XRD analysis was used for crystallographic examination of the samples before corrosion test, while SEM was implemented after corrosion test. All investigations showed a clear correlation between the physical analyses and the potentiodynamic results.

The changes observed in the intensity of the XRD peaks can be correlated to the results obtained from the potentiodynamic tests. The XRD results also show that the highest intensity of nickel nitride peaks correspond to the sample implanted at 20 keV, hence it can also be concluded that the volume of nickel nitride formed on this sample is more than those produced at lower and higher energies.

Many researchers have dealt with the role of N^+ ion in enhancing the corrosion resistance of stainless steel [20, 21]. As a result of crevice corrosion of stainless steel in the electrolyte solution, nitrogen becomes concentrated in form of NH_3 and NH_4^+ at the interface between metal and the passive layer, which acts as an important factor for the formation and protection of passive layer. These are formed as a result of reaction of nitrogen with H^+ ions (protons) which in turn are the product of reactions of hydrolysis of metal ions. Of course, this will happen when the passive layer is locally broken and the metal is dissolved. It is worthwhile to mention that this reaction prevents the decrease of pH in the pits. Hence it can be concluded that the amount of detected H^+ in the solution for formation of NH_4^+ in the pit should correspond to the amount of nitrogen in the dissolved metal. Therefore, it is suggested that formation of NH_4^+ controls the local decrease of pH by the decrease of acidity and increase of pH in the pits, and promotes the re-passivation.

On the other hand, the highest corrosion resistance was achieved at 20 keV implantation energy with corrosion current density of 0.172 μA/cm^2. In addition, it can also be observed that the SEM image of the sample implanted at 20 keV shows the least amount of corrosion effects on its surface. Therefore, all the above mentioned discussions show a correlation between the reported results in this work.

5. Conclusions

We clarified that nickel coating and nitrogen implantation have a prominent effect on corrosion protection. Crystallographic examination using XRD revealed formation of nickel nitride peaks for treated samples such that the maximum intensity of nickel nitride peaks are belong to the sample implanted at 20 keV. It is also observed from polarization plots that there is an optimum implantation energy as 20 keV with the highest corrosion resistance. SEM images taken after corrosion test demonstrated a great protective surface for the sample implanted at 20 keV energy.

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