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INVITRO CORROSION STUDIES ON NICKEL TITANIUM SUPER ELASTIC ALLOY IN SYNTHETIC URINE IN PRESENCE OF D- GLUCOSE

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Abstract

The aim of this investigation is the study of corrosion behavior of NiTi Superelastic alloy in synthetic urine in presence of D- Glucose at 37˚C. The corrosion inhibition efficiency of NiTi Superelastic alloy in synthetic urine in the absence and presence of D-glucose has been examined by electrochemical studies. It is perceived that the corrosion inhibition efficiency of NiTi Superelastic alloy in synthetic urine rises in presence of D- glucose. This result shows that the protective coating is formed on metal surface than the polished metal surface which is confirmed by the intensification in polarization resistance and diminution in corrosion current density. The surface of the metal was described by scanning electron microscopy, energy dispersive analysis of x-rays and AFM studies which was achieved after the electrochemical tests. The corrosion inhibition efficiency of NiTi Superelastic alloy in synthetic urine in the presence of D-glucose was improved.

Keywords: NiTi Superelastic alloy, synthetic urine, D-Glucose, Polarization study, AC impedance spectroscopy study, SEM, EDAX and AFM

I.INTRODUCTION

NiTi shape memory alloy has been commonly used for medical devices, such as guide wire orthodontic wire and stent. Shape memory alloys have the capacity to remember a preset shape even after severe distortion. Among presently available shape memory alloys, NiTi alloys have greater mechanical properties [1- 4]. These alloys have been employed for selected in vivo applications due to their shape memory effect and superelasticity and also establish an interesting group of smart alloys which appreciate an ever increasing market share as biomaterials. They are most broadly used as stents, orthodontic arch wires etc. NiTi alloys are gorgeous materials that are used for medicine. However, Ni-release may origin allergic reactions in an organism. The Ni-release rate is toughly affected by the surface of the NiTi alloy that is mainly determined by its processing route.

The goal of this research deals with study to the electrochemical behavior of NiTi superelastic alloy in synthetic urine in presence of D-Glucose. This research has been executed using potentiodynamic polarization study, AC impedence spectroscopy study and surface of the metal was studied by SEM with EDAX and AFM.

II. EXPERIMENT

Metal

The NiTi superelastic alloy was selected for the current study. The configuration of NiTi superelastic alloy was (wt%) given in Table. I [5]. The metal sample was compressed in Teflon. The surface area of the uncovered metal surface was 0.0785 cm^2. The metal was polished to mirror finish and degreased with trichloroethylene. The metal was plunged in Synthetic urine (SU) [6], its composition was given in Table.2. The pH of the medium was 6.2.

The experiments were conceded out using Synthetic urine solution. The configuration of this solution has been exposed in Table 2. A custom-made cell was employed to maintain the temperature of the solution at the chosen value. The precision of temperature sustained in the present investigation was ±0.5°C. In electrochemical studies the metal specimen was engaged as working electrode. Synthetic urine was used as the electrolyte. The temperature was maintained at 37±0.1^{0}C.

Table: 1 Composition of NiTi super elastic alloy

NiTi Superelastic alloy	55.6% Ni	44.4% Ti

Table: 2 Composition of Synthetic urine

Solution A		Solution B	
Compound	Composition (g/l)	Compound	Composition(g/l)
$CaCl_2.H_2O$	1.766	$NaH_2PO_4.2H_2O$	2.659
Na_2SO_4	4.861	Na_2HPO_4	0.870
$MgSO_4.7H_2O$	1.463	$C_6H_5Na_3O_7.2H_2O$	1.169
NH_4Cl	4.642	NaCl	13.55
KCl	12.130	-	-

Methodology:

Electrochemical Techniques

The electrochemical techniques were carried out by using potentiostat. A predictable three-electrode set-up involved of NiTi superelastic alloy sample as working electrode, Calomel electrode as reference electrode and a platinum electrode as counter electrode was used for the test. The complete three-electrode assembly was situated in a Faraday cage to limit the noise disturbance.

Scanning Electron Microscopic Studies (SEM)

To identify the surface morphology of the alloy after linear anodic potentiodynamic polarization test, the specimen was ultrasonically cleaned in deionized water, dried under an air stream, and then inspected by a scanning electron microscopy. To implement this study by JOEL-6390 computer-controlled scanning electron microscope. The assembly is equipped with a system complete of microanalyse X and with a detector of back-scattered electrons. The analyzed volume is of the order of μm^3.

Atomic Force Microscopy Characterization (AFM):

The metal specimen was immersed in blank and in the glucose solution for a period of one day and it was removed, rinsed with double distilled water, dried and exposed to the surface examination. Atomic force microscope was used to perceive the sample surface in tapping mode using cantilever with linear tips. The scanning area in the image was 5 μm × 5 μm and the scan rate was 0.6Hz.

III.RESULT AND DISCUSSION

Polarization study

This study has been used to authorize the formation of protective film made on the metal surface during corrosion inhibition process. If a protective layer is formed on the metal surface, the linear polarization resistance values (LPR) rises and the corrosion current value ($I_{corr)}$ drops [7-9].Figure.1.shows the polarization curves of NiTi superelastic alloy dipped in SU in the absence and presence of D- Glucose. Table.3 comprises the corrosion parameters namely LPR, I_{corr}, E_{corr}, Tafel slopes (b_c = cathodic, b_a = anodic).

When NiTi superelastic alloy submerged in SU, the corrosion potential is -435mV vs SCE. The system consisting of SU with 50 ppm of D-Glucose and 100 ppm of D-Glucose, the corrosion potentials were -426mV vs SCE and -344mV vs SCE. It is perceived that the corrosion potential is lifted to the cathodic side. Hence it is decided that the additive system predominantly controls the cathodic reaction. The

LPR value for NiTi superelastic alloy in SU system with 50ppm D-Glucose drops from 1.87 x 10^7 to 7.30 x 10^6 ohmcm^2 and the corrosion current (I_{corr}) value rise from 1.90 x 10^{-9} to 4.70 x 10^{-9} A/cm^2 and the system consisting of 100 ppm of D-Glucose in SU, the LPR value rise from 7.30 x 10^6 to 1.03 x 10^7 ohmcm^2 and the corrosion current (I_{corr}) value drops to 2.70 x 10^{-9} A/cm^2. In common it is perceived that the LPR value rises with fall in corrosion current which shows that adsorption of additive on the metal surface to block the active sites and hinders the corrosion and diminish the corrosion rate. From the above data it accomplishes that the corrosion resistance of NiTi superelastic alloy in SU increases in the presence of D-Glucose at high concentration.

Table: 3: Polarization study of NiTi super elastic alloy dipped in SU in absence and presence of D - Glucose

System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR ohmcm^2	I_{corr} A/cm^2
NiTi + SU	-0.435	128	212	1.87 x 10^7	1.90 x 10^{-9}
NiTi + SU + 50 ppm Glucose	-0.426	153	158	7.30 x 10^6	4.70 x 10^{-9}
NiTi + SU + 100 ppm glucose	-0.344	144	130	1.03 x 10^7	2.70 x 10^{-9}

Analysis of AC impedance spectra

AC impedance spectra have been used to authorize the formation of protective film on the metal surface and it was confirmed by the rise of charge transfer resistance (R_t), fall of double layer capacitance value (C_{dl}) and rise of impedance log (z/ohm) value. The Nyquist plots of NiTi superelastic alloy dipped in various solutions are displayed in Figure.2. Table.4. comprises AC impedance parameters namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}). The AC impedance spectra are shown in Figure.2 (a,b,c) (Nyquist plots), Figure.3 (a,b,c) (Bode plots).

Table: 4: AC impedance spectra of NiTi super elastic alloy dipped in SU in absence and presence of D - Glucose

System	Nyquist plot		Bode plot
	R_t ohmcm^2	C_{dl} (F cm^{-2})	Log Z/ohm
NiTi + SU	3.48 x 10^5	1.50 x 10^{-11}	6.32
NiTi + SU + 50 ppm glucose	4.30 x 10^4	1.92 x 10^{-10}	5.40
NiTi + SU + 100 ppm glucose	4.87 x10^4	1.10 x 10^{-10}	5.51

It is detected from the table that when D-Glucose is added to SU the R_t value drops and then rises, the C_{dl} value rises and then drops for increasing the concentration of D-Glucose. This indicates that in presence of D-Glucose at high concentration, the corrosion inhibition efficiency of NiTi superelastic alloy increases. This is in agreement with the results of polarization studies. This is further maintained that in presence of D-Glucose the impedance value (Log Z/ohm) rises and the phase angle value rises (Bode plots) [10-12].

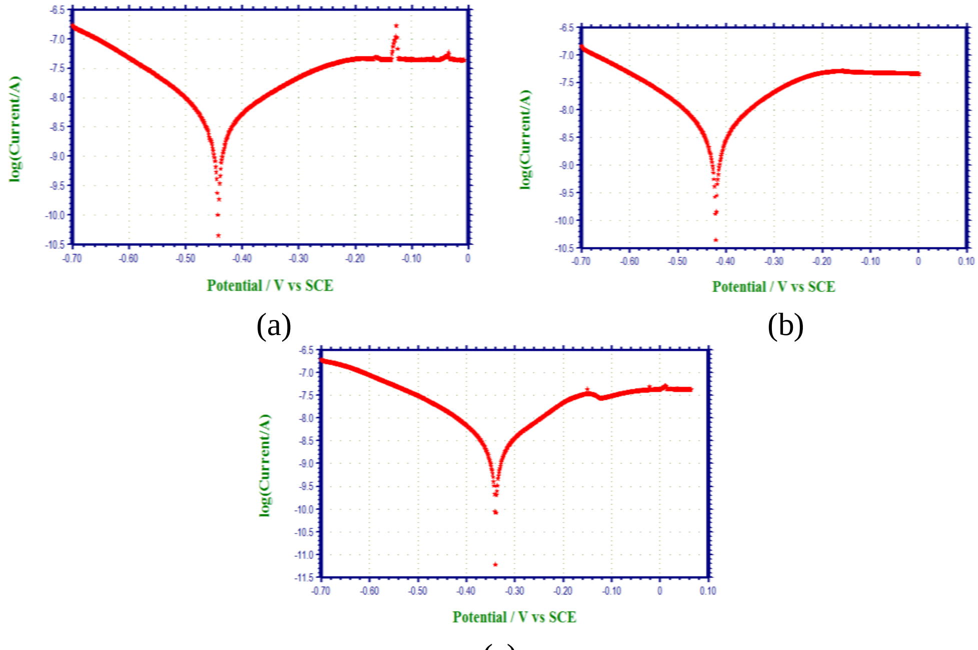


Figure.1 Polarization curves of NiTi Super elastic in various test solutions.
a) NiTi +SU b) NiTi + SU+ 50 ppm of glucose c) NiTi + SU+ 100 ppm of glucose

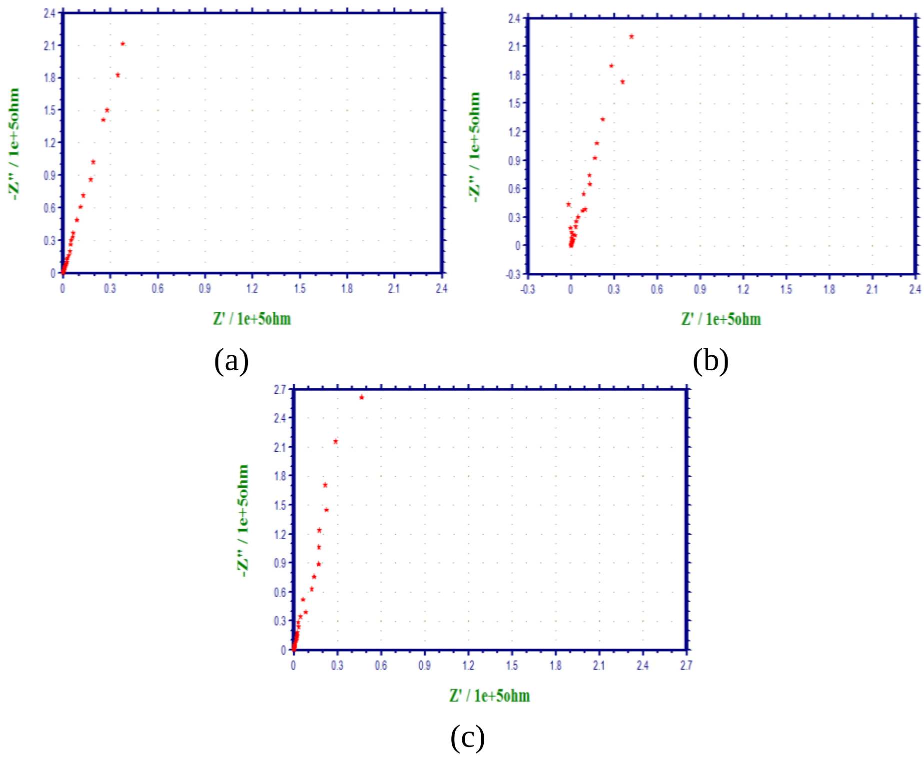


Figure.2 AC impedance spectra (Nyquist plots)
a) NiTi super elastic dipped in SU b) NiTi super elastic dipped in SU + 50 ppm glucose
c) NiTi super elastic dipped in SU + 100 ppm glucose

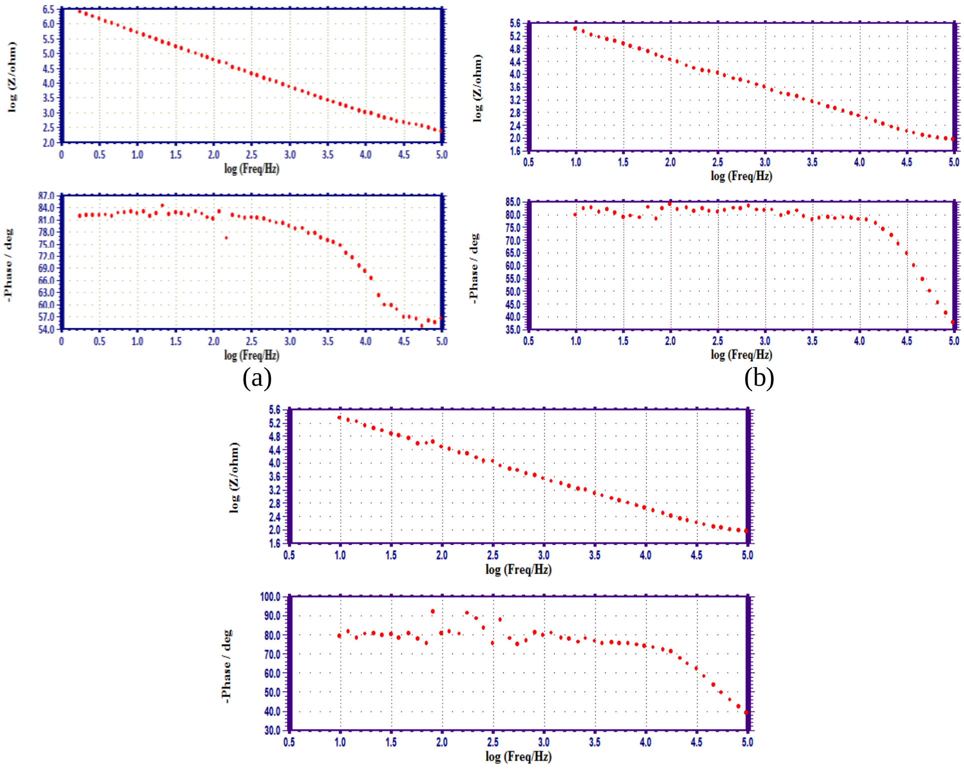


Figure.3. AC impedance spectra (Bode plots) of

a) NiTi super elastic alloy dipped in SU b) NiTi super elastic dipped in SU + 50 ppm glucose

c) NiTi super elastic dipped in SU + 100 ppm glucose

SEM Analysis of Metal Surface

SEM offers a pictorial representation of the surface. To know the nature of the surface film in the absence and the presence of additive and the magnitude of corrosion of NiTi super elastic alloy, the SEM micrographs of the surface are inspected [15-17]. The SEM image of polished NiTi super elastic alloy are shown in Figure.4a shows the smooth surface of the metal. This indicates the absence of any corrosion products on the metal surface. The SEM image of NiTi super elastic alloy immersed in SU are shown in Figure.4b.shows the slight roughness of the surface which indicates the corrosion of NiTi super elastic alloy in SU. Figure.4c shows that in the presence of 100 ppm of glucose in SU, the surface coverage upturns due to the formation of insoluble complex on the metal surface which effectively controls the dissolution of the NiTi super elastic alloy.

Analysis of Energy Dispersive Analysis of X-rays (EDAX)

EDAX spectra were used to conclude the elements present on the NiTi super elastic alloy surface before and after exposure to the additive system. To achieve this goal, EDAX examinations of the metal surface was performed in the absence and presence of an additive system.[16]

The EDAX spectra of polished NiTi super elastic alloy is shown in Figure.5a. This designates the presence of Nickel (Ni), Titanium (Ti), Carbon (C) and Oxygen (O) on the metal surface. Figure.5b shows the EDAX spectra of NiTi super elastic alloy surface dipped in SU. The analysis indicates the presence of characteristic peaks of corrosion product elements. Figure.5c represents the EDAX spectra of NiTi super elastic alloy dipped in SU containing 100 ppm of glucose. The analysis indicates the presence of peaks of C, O which could be attributed to the presence of some elements in the metal surface, forming a film which is protective in nature. The surface of the NiTi super elastic alloy is preserved to a large extent due to formation of the protective film by additive molecule as indicated by the rise of Titanium peak in Figure.5c. This outcome recommends that glucose is coordinated with $Ni^{2+}$and Ti^{2+}, resulting in the creation of complex on the anodic sites of the metal surface and some of the compounds are triggered on the cathodic sites of the metal surface and it is stable and more resistance towards corrosion.

Atomic Force Microscopy Characterization

Atomic Force Microscopy (AFM) is a commanding technique for collecting of roughness statistics from a variety of surfaces. The three dimensional (3D) AFM morphologies for polished NiTi super elastic alloy surface, NiTi super elastic alloy surface dipped in SU and NiTi super elastic alloy dipped in SU containing 100 ppm of glucose are shown in Figure.6 [17-19].

Root-Mean-square Roughness, Average roughness and Peak- to- peak valley value

AFM analysis was performed to attain the average roughness, R_a, root-mean-square roughness, R_q and the maximum peak-to-valley (p-v) height values. The $R_{q,}$ $R_{a,}$ and p-v values for NiTi super elastic alloy surface immersed in different environment are concise in Table.5.

In Figure.6a the surface topography of polished metal surface is shown. The values of Rq, Ra, and p-v height for the polished NiTi super elastic alloy are 32.5 nm, 24.0 nm and 403.4 nm respectively. The data indicates the surface is homogeneous. The slight roughness detected in the polished NiTi super elastic alloy is due to atmospheric corrosion. [13-15].

Figure.6b shows the pitted, corroded NiTi super elastic alloy in the absence of additive placed in SU. The $R_{q,}$ $R_{a,}$ and p-v height values for the NiTi super elastic alloy surface are 48.2 nm, 36.4 nm, and 546.3 nm respectively. These data recommends that surface has a greater roughness than the polished NiTi super elastic alloy.

Figure.6c shows the NiTi super elastic alloy in SU containing 100ppm glucose. The $R_{q,}$ $R_{a,}$ and p-v height values for the NiTi super elastic alloy surface are 70.7 nm, 53.1 nm and 651.1 nm respectively. The $R_{q,}$ $R_{a,}$ and p-v height values are noticeably high in the presence of D-Glucose than in absence. These factors confirm that the surface is smooth. The surface of the metal is enclosed by strong protective layer.

Entropy

The entropy values for polished NiTi super elastic alloy, NiTi super elastic alloy dipped in SU and NiTi super elastic alloy dipped in SU containing glucose decreases gradually. It shows that the corrosion efficiency of the metal is increase.

Skewness

Surface skewness (S_{sk}) is a statistical parameter to explain the amplitude distribution function (ADF) which indicates the probability that a profile of the surface has a certain height at any position. Surfaces with negative Skewness, it shows a porous surface, have fairly deep valleys in a smoother plateau for polished NiTi super elastic alloy, NiTi super elastic alloy dipped in SU. Surfaces with positive Skewness, it shows a raised surface, have fairly high spikes that protrude above a flatter average for NiTi super elastic alloy is dipped in SU containing glucose.

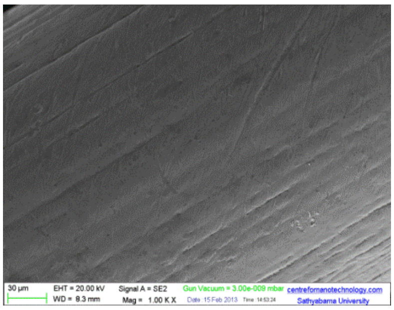
Kurtosis

Kurtosis relates to the uniformity of the ADF or to the spikiness of the profile. The R_{ku} <3 the distribution has few high peaks and low valleys, which means a comparatively flat surface for polished NiTi super elastic alloy, NiTi super elastic alloy dipped in SU and NiTi super elastic alloy dipped in SU containing glucose. It is decided that NiTi super elastic alloy dipped in SU containing glucose is more corrosion resistance than the polished NiTi super elastic alloy, NiTi super elastic alloy dipped in SU.

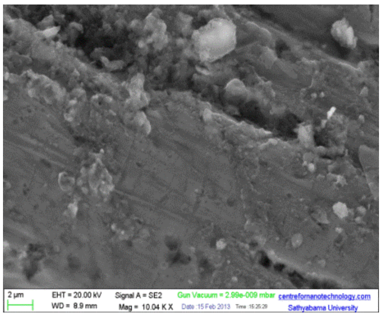
Table: 5 : AFM data for NiTi super elastic alloy surface dipped in absence and presence of D-Glucose

Samples	RMS (Rq) Roughness (nm)	Average (Ra) Roughness (nm)	Maximum Peak-to valley Height (nm)	Kurtosis (R_{ku})	Entropy	Surface skewness (S_{sk})
Polished NiTi	31.7	23.0	410.5	2.25	10.10	-0.135

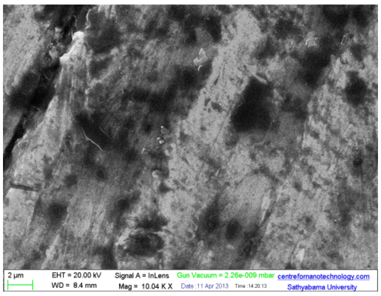
NiTi dipped in SU	49.6	37.4	552.3	1.24	11.23	-0.028
NiTi dipped in SU + glucose	73.7	56.2	671.1	1.36	10.41	0.076



(a)



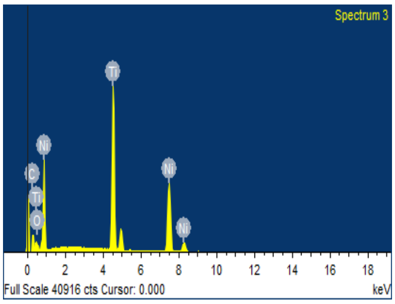
(b)



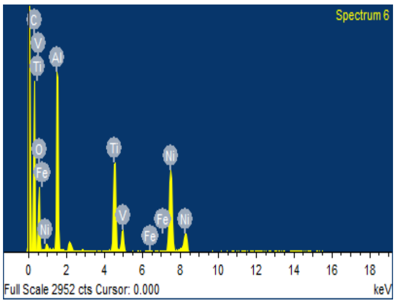
(c)

Figure.4.SEM image

a) Polished NiTi super elastic alloy b) NiTi super elastic alloy dipped in SU c) NiTi super elastic alloy dipped in SU containing 100 ppm of glucose



(a)



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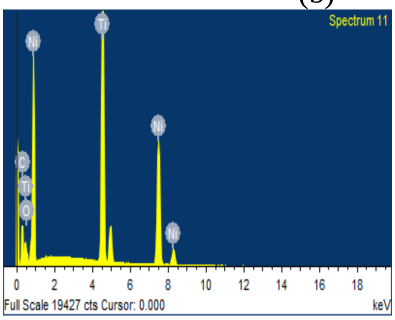
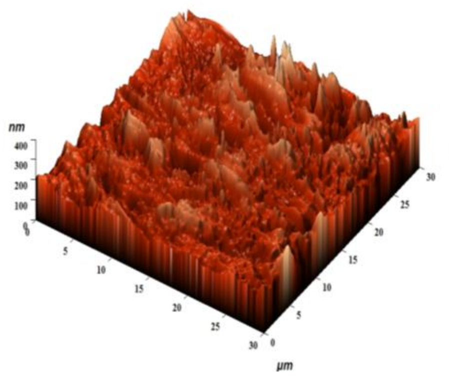


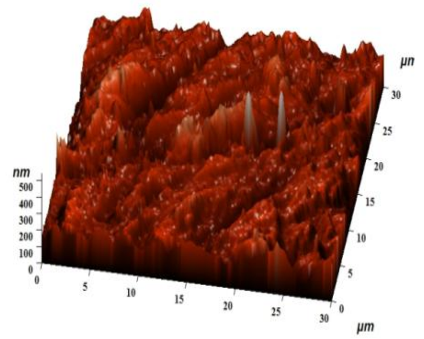
(c)

Figure.5. EDAX spectra

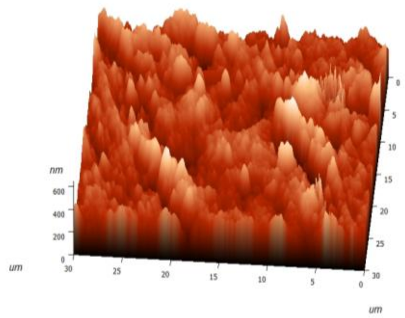
a) Polished NiTi super elastic alloy b) NiTi super elastic alloy dipped in SU c) NiTi super elastic alloy dipped in SU containing 100 ppm of glucose



(a)



(b)



(c)

Figure.7.3D AFM image

a) Polished NiTi super elastic alloy b) NiTi super elastic alloy dipped in SU c) NiTi super elastic alloy dipped in SU containing 100 ppm of glucose

IV. CONCLUSION

Under the different experimental conditions of this study, the following conclusions were drawn:

At low concentration of glucose the corrosion resistance of Ni-Ti super elastic alloy was decreased in electrochemical study and SEM, EDAX and AFM. In higher concentration the resistance of the metal was increased.

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