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Scientific paper
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Corrosion behaviour of metals in artificial blood plasma in presence of glucose

Electrochemical behavior of seven metals namely, mild steel, (super elastic) Ni, Ti, Ni-Cr, SS316, Cu-Ni-Ti, 22 Carat gold, 24 Carat gold have been evaluated in artificial plasma in presence of glucose. Pontentiodynamic polarizations study and AC impedance spectra have been used to investigate the corrosion behavior of these metals. Among these seven metals SS316 and Ni-Cr are showing very good corrosion resistance. Rest of the metals shows good corrosion resistance when very small amount of glucose is present. Generally for diabetes the glucose level is not stable. Glucose level will increase or decrease. For them some metallic materials are used as implants in reconstructive surgery to replace bones or joining of bones. The metals may contact the blood during the blood circulation when human blood is circulate the diabetes body the implant metals such as mild steel, super elastic, Ni- Cr, SS316, Cu Ni-Ti, 22 Carat gold and 24 Carat gold even in presence of glucose also control the corrosion resistance. The metals such as SS316 and Ni-Cr are showing very good corrosion resistance even in presence of 0.05 g amount of glucose. Electrochemical studies were carried out in a CHI – Electrochemical workstation with impedance, model 660A. The instrument was used for polarization study and to record AC impedance spectra. The cell setup was also the same. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies.

Key words: *Corrosion, artificial plasma, SS316L, Ni-Cr, glucose*

INTRODUCTION

As the global population increases in age, there is a parallel increase in the number of implantation procedures. The performance of any material in the human body is controlled by two sets of characteristics: biofunctionality and biocompatibility. There are wide ranges of materials available for implantation. It is relatively easy to satisfy the requirements for mechanical and physical functionality of implantable devices. The selection of materials for medical applications is usually based on considerations of biocompatibility [1]. When metals are considered, the susceptibility of the material to corrosion and the effect of the corrosion on the tissue are the central aspects of biocompatibility. The human body is not an environment that one would consider hospitable for an implanted metal alloy [2]. The materials for the devices generate less concern in their biocompatibility with human body than those for implants [3]. The basic knowledge of metal composition, microstructure and processing is necessary to select a metallic material for a specific application [4]. Metallic materials can have serious corrosion problems in aqueous solution, such as in contact with physiological fluids [5]. Corrosion results in releasing toxic metals ions to body and also weakening implants.

An electrochemical reaction involves removing electrons from the anodic to the cathode [6]. When the metal is surrounded by an aqueous solution, oxidation may occur at the location on the metal surface [7]. For the past hundred years various metals are used for implantation in the human body, such as aluminum, copper, zinc, iron and carbon steels, silver, nickel, and magnesium [8, 9]. Corrosion resistance of implant materials may involve qualitative measurements or quantitative electrochemical measurements in simulated body fluid [10]. Now a day's various alloys and metallic materials are found and are used as implantation material in human body for long period. Corrosion is one of the major issues resulting in the failure of biomedical implant devices. The nature of the passive oxide films formed, and the mechanical properties of the materials form some of the essential criteria for selection of alternative or development of new materials.

Commercially available D-Glucose (Indian pharmacopeias grade) was used in this study. 0.05 g and 0.10 g of glucose was used in artificial plasma (AP). The present work was undertaken to study the corrosion behaviour of seven metals, namely, mild steel (super elastic) Ni-Ti, Ni- Cr ,SS 316, Cu-Ni-Ti, 22 Carat gold 24 Carat gold in artificial plasma in the absence of and presence of glucose, by polarization study and AC impedance spectra. Corrosion parameter such as corrosion potential, corrosion current, linear polarization resistance, charge transfer resistance and double layer capacitance have been derived from these studies.

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MATERIALS AND METHODS

The metal specimens, namely, mild steel super elastic Ni- Cr, SS316, Cu-Ni-Ti, and 22 Carat gold, 24 Carat gold were chosen for the present study. The composition of mild steel is (wt %) 0.026 S, 0.06 P, 0.4 Mn, 0.1C and balance iron [11, 12]. The composition of SS 316L is (wt %) 18 Cr, 12 Ni, 2.5 Mo, < 0.03 C and balance iron [13]. The metal specimens were encapsulated in Teflon. The metal specimens were polished to mirror finish and degreased with trichloroethylene. The metal specimens were immersed in artificial plasma. The chemical composition of the artificial plasma according to PN-EN ISO 10993-15 standard [14] (g/l distilled water) was NaCl 6.8, $CaCl_2$ 0.200, KCl 0.4, $MgSO_4$ 0.1, $NaHCO_3$ 2.2, Na_2HPO_4 0.126, NaH_2PO_4 0.026. In electrochemical studies the metal specimens were used as working plasma was used as electrolyte (10 ml). The temperature was maintained at 37.0 °C.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic, b_a and cathodic, b_c) were calculated.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell setup was also the same. The real part (Z’) and imaginary part (Z”) of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated from Nyquist plots, impedance log (Z/ohm) value was calculated from bode plots.

RESULTS AND DISCUSSION

Analysis of potentiodynamic polarization curves

The corrosion parameters of various metals such as, mild steel (super elastic) Ni-Ti, Ni- Cr,SS316, Cu-Ni-Ti, 22 Carat gold and 24 Carat gold, immersed in artificial plasma (AP) are given in Table 1. The potentiodynamic polarization curves are shown in Figs. 1 and 2.

Table 1 - Corrosion parameters of metals immersed in artificial plasma (AP) in the absence and presence of glucose, obtained by polarization study

Metal	System	E_{corr}/mV vs SCE	b_c, mV/dec	b_a, mV/dec	LPR, ohm cm^2	I_{corr}, A
MS	AP	-0.677	154	243	7743.8	5.302×10^{-6}
	AP + 0.05g glucose	-0.670	156	245	8517.5	4.865×10^{-6}
Ni-Ti (Super Elastic)	AP	-0.518	171	161	7028663.0	5.138×10^{-9}
	AP + 0.05g Glu	-0.490	145	310	39057156.0	1.101×10^{-9}
Ni-Cr	AP	-0.507	172	178	6787915.5	5.616×10^{-9}
	AP + 0.05g Glu	-0.553	150	292	11561834.0	3.731×10^{-9}
SS 316 L	AP	-0.410	154	461	823792.8	6.097×10^{-8}
	AP + 0.05g Glu	-0.429	153	523	999271.8	5.144×10^{-8}
Cu-Ni-Ti	AP	-0.421	145	290	6974095.5	6.037×10^{-9}
	AP + 0.05g glucose	-0.510	130	402	16081520.0	2.661×10^{-9}
22 Gold	AP	-0.127	116	332	2158306.8	1.724×10^{-8}
	AP + 0.05g glucose	-0.196	154	249	723853.5	5.718×10^{-8}
24 Gold	AP	-0.127	116	325	2158306.8	1.724×10^{-8}
	AP + 0.05g glucose	-0.148	113	240	1014141.8	3.303×10^{-8}

Analysis of SS316 in artificial plasma solution

When SS 316L is immersed in AP the corrosion potential is shifted to the noble side (-0.410 mV vs SCE). This suggests that a protective film is formed on the metal surface, when it is immersed in AP. The LPR value is very high and it is 0.824 ohm cm^2. The corrosion current decreases to a great extent (7.69×10^{-4} mA cm^{-2}). The values of Tafel slopes (b_a = 461 mV/dec; b_c=153 mV/dec.) indicate that the rate of change of current with potential is higher during anodic polarization than during cathodic polarization.

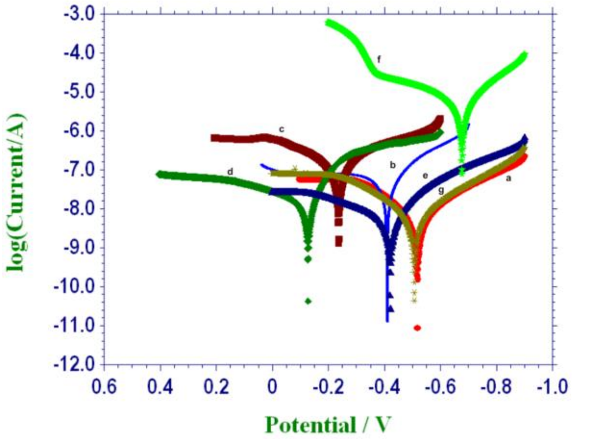

Fig.1: Polarization curves of various metals immersed in various test solutions: a) AP + Super Elastic, b) AP + SS 316 L, c) AP + 22 Cr Gold, d) AP + 24 Cr Gold, e) AP + Cu-Ni-Ti, f) AP + MS, g) AP + Ni-Cr

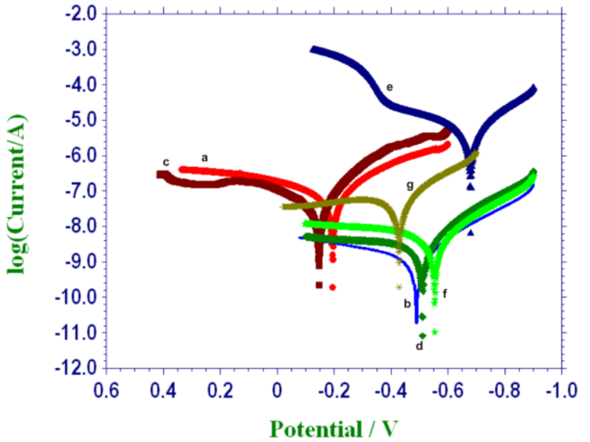

Fig.2. Polarization curves of various metals immersed in various test solutions: a) AP + 22 Cr Gold + Glucose 0.5g, b) AP + Super Elastic + Glucose 0.5g, c) AP + 24 Cr Gold + Glucose 0.5g, d) AP + Cu-Ni-Ti + Glucose 0.5g, e) AP + MS + Glucose 0.5g, f) AP + Ni-Cr + Glucose 0.5g, g) AP + SS 316 L + Glucose 0.5g

Analysis of Ni-Cr in artificial plasma solution

Ni-Cr is immersed in artificial plasma (AP), the corrosion potential is -0.507 mV vs SCE (Fig.1a). The linear polarization resistance (LPR) is 6.79 × 10^{10} ohm cm^2 and the corrosion current (j_{orr}) is 0.715 mA cm^{-2}. When Ni-Cr is immersed in AP, with 0.05 g glucose the corrosion potential shifts to the cathodic side (Fig.2a). The LPR value increase to 11.56 × 10^{10} ohm cm^2 and the corrosion current density decreases up to 4.75 × 10^{-4} mA cm^{-2}. These observations indicate that mild steel is more corrosion resistant when in presence of glucose than itself. A protective layer is formed on the metal surface. In the case of Ni-Cr coated in AP with 0.05 g glucose, the cathodic Tafel slope is 150 mV/dec and the anodic Tafel slope is 292 mV/dec. These values suggest that during anodic polarization, the rate of change of corrosion current with potential is high, and it is less during the cathodic polarization. A comparison of LPR values and corrosion current values of the seven metals investigated reveals that SS 316 L, Ni-Cr are the better candidates to be used in implantation.

Corrosion behavior of metals in artificial plasma containing glucose

When SS316 is immersed in AP, containing glucose, the corrosion potential is slightly shifted to the cathodic side (when compared with the behaviour of SS316 in AP; Fig.1b) the Tafel slopes are not affected very much. However, it is observed that the cathodic Tafel slope is slightly influenced. It is interesting to note that in the presence of glucose, the LPR value increases and the corrosion current decreases. It seems that a protective layer is formed on the metal surface which controls the rate of corrosion in the presence of glucose.

Table 2 - Corrosion parameters of metals immersed in artificial plasma (AP) in the absence and presence of glucose obtained from AC impedance spectra

Metal	System	Nyquist plot	
		R_t, ohm cm^2	C_{dl}, μF/cm^2
MS	AP	260	1.9615
	AP + 0.05 g glucose	240	2.125
Ni-Ti (Super Elastic)	AP	1.4	364.285
	AP + 0.05 g glucose	0.4	1275.0
Ni-Cr	AP	1.5	340.0
	AP + 0.05 g glucose	2.7	188.88
SS 316 L	AP	1.3	392.30
	AP + 0.05 g glucose	1.7	300.0
Cu-Ni-Ti	AP	0.58	879.310
	AP + 0.05 g glucose	1.08	472.22
22 Cr Gold	AP	2.42	210.743
	AP + 0.05 g glucose	5.42	94.0959
24 Cr Gold	AP	0.35	1457.14
	AP + 0.05 g glucose	5.0	102.0

AC impedance spectra

AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) (derived from Nyquist plots) and impedance value log (z/ohm) (derived from Bode plots), of various metals immersed in artificial plasma and artificial plasma containing glucose are given in Table 2. The AC impedance spectra are shown in Figs. 3 and 4.

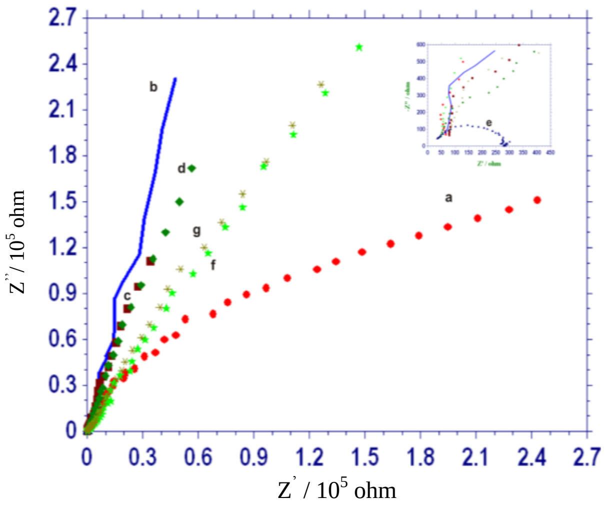

Fig.3: AC impedance spectra (Nyquist plot) of various metals immer sed in various test solutions: a) AP + 22 Cr Gold, b) AP + Super Elastic, c) AP + 24 Cr Gold, d) AP + Cu-Ni-Ti, e) AP + MS, f) AP + Ni-Cr, g) AP + SS 316 L

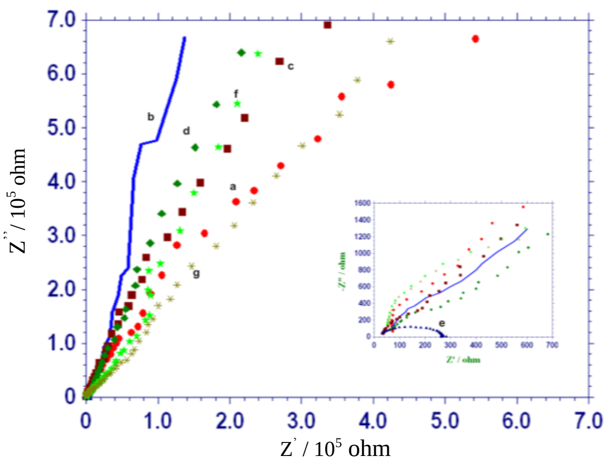

Fig.4: AC impedance spectra (Nyquist plot) of various metals immersed in various test solutions: a) AP + 22 Cr Gold + Glucose 0.5g, b) AP + Super Elastic + Glucose 0.5g, c) AP + 24 Cr Gold + Glucose 0.5g, d) AP + Cu-Ni-Ti + Glucose 0.5g, e) AP + MS + Glucose 0.5g, f) AP + Ni-Cr + Glucose 0.5g, g) AP + SS 316 L + Glucose 0.5g

When SS316 is immersed in AS (Fig.4a), the charge transfers resistance is 1.3 ohm cm^2. The double layer capacitance is 5.0×10^{-5} µF cm^{-2}. The impedance value [log(Z/ohm)] is 2.92. In presence of spirulina (Fig.4b), R_t value increases and C_{dl} value decreases. There is increase in the value of impedance [log(Z/ohm)]. These observations indicate that in the presence of glucose in artificial plasma, the corrosion rate of SS316 is reduced, due to the formation of protective film formed on the metal surface. The protective film, probably, consists of oxides of iron. When SS316 is immersed in AS with 0.05 g glucose, the charge transfer resistance is 1.7 ohm cm^2. The double layer capacitance is 3.82×10^{-5} µF cm^{-2}. The impedance value log (z/ohm) is 300. When these values are compared with the values of SS316, it is observed that compared with other metals it shows less corrosion resistant (in artificial plasma). That is the oxide film formed on the metal surface is less stable and easily broken by the ions present in AP. Similar observation is made when Ni-Cr is immersed in AS containing 0.05 g glucose. The R_t value increases from 1.5 to 2.7 ohm cm^2, the C_{dl} value decreases from 4.33×10^{-5} to 2.41×10^{-5} µF cm^{-2}; and the impedance value, log(z/ohm), decreases to 3.20×10^2. This observation suggests that the film formed on Ni-Cr in AP, in the presence of glucose is less stable and easily broken by the ions present in AP.

CONCLUSIONS

Corrosion behaviour of seven metals namely mild steel super elastic Ni- Cr, SS316, Cu-Ni-Ti, 22 Carat gold 24 Carat gold in plasma in presence of glucose have been evaluated by electrochemical studies of polarization and AC Impedance spectra. Electrochemical study reveals that corrosion resistance of materials is studied in artificial plasma in presence of glucose is SS316 and Ni-Cr are showing very good corrosion resistance than the rest. The rest of the metals show good corrosion resistance when very less amount of 0.01 g glucose is present.

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IZVOD

KOROZIONO PONAŠANJE METALA U VEŠTAČKOJ KRVNOJ PLAZMI U PRISUSTVU GLUKOZE

Elektrohemijsko ponašanje nekih metala i legura (meki čelik), Ni, Ti, Ni-Cr, SS316, Cu-Ni-Ti, 22 i 24-karatno zlato je bilo ispitano u veštačkoj plazmi u prisustvu glukoze. Potenciodinamičko polarizaciono ispitivanje i AC impedancijski spektri su bili korišćeni da se istraži koroziono ponašanje ovih metala i legura. Medju njima, SS316 i Ni-Cr pokazuju veoma dobro korozionu otpornost. Ostatak metala i legura pokazuje dobru korozionu otpornost kada veoma mala količina glukoze je prisutna.

Ključne reči: *korozija, veštačka plazma, SS316L, Ni-Cr, glukoza*

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