

## Corrosion Behaviour of Metals in Artificial Sweat

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**Abstract:** Human sweat comes in contact with a number of consumer products. This results in a variety of undesirable effects such as corrosion and malfunction. Corrosion behaviour of three metals, namely, mild steel (MS), galvanized steel (GS) and SS 316 L in artificial sweat (the ISO standard ISO 3160-2) has been studied by polarization study and AC impedance spectra. The study reveals that the decreasing order of corrosion resistance is SS 316 L > MS > GS.

**Keywords:** Corrosion of metals, artificial sweat, SS 316 L, mild steel.

### INTRODUCTION

Human perspiration (sweat) comes in contact with a number of consumer products. Contact can cause a variety of undesirable effects. Dyes can bleed or discolour, components can corrode and/or malfunction, residues can be unsightly.

The problem of metal corrosion resulting from contamination by palmar sweat is common to many industrial occupations. Constant handling of metal parts by some individuals causes an accumulation of rust. In the manufacture of highly finished metal products, for example ball-bearings, and also in subsequent assembling and packing processes, serious consideration must be given to this effect [1].

The corrosive nature of sweat has been known as early as 1919. But few objective investigations on this subject have appeared. Metal ion release from electric guitar strings in artificial sweat has been investigated [2]. Electric guitar strings consisted of two separate parts: Sn-plated steel core wire which has hexagonal in cross section and Ni-plated steel wrap which was round in cross section. Dissolution of Ni<sup>2+</sup>, Si<sup>4+</sup>, Mn<sup>2+</sup>, Sn<sup>2+</sup> and Fe<sup>3+</sup> ions from electric guitar strings E6 and D4 were measured as a function of time in

artificial sweat solution. Among all investigated metal ions, nickel is far the most allergenic.

Corrosion behaviours of electroless plating Ni-P coatings deposited on magnesium alloys in artificial sweat solution have been studied [3]. Magnesium alloys are the optimum shell materials for electronic products. These electronic products inevitably contact with the hands of the user and then are corroded by the sweat solution mainly consisting 0.1% urea, 0.5% NaCl and 0.5% lactic acid. Electroless plating Ni-P coatings can provide protection to the magnesium alloys shell. The study indicated that urea acted as corrosion inhibitor. The inhibiting effect of urea was reduced in NaCl solution or lactic acid solution. Randian [4] has evaluated the corrosion resistance of nickel in artificial sweat and synthetic seawater. The corrosion resistance of nickel 200 has been determined in artificial sweats (perspiration) and in synthetic seawater by several electrochemical methods. Nickel 200 is not stable in the two electrolytes investigated and the attack occurs with the formation of pits. Nickel 200 cannot be used for application where it may be in direct contact with the skin because of its high corrosion rate in oxygenated sweat. The released nickel ion is responsible for contact dermatitis observed in some individuals.

Skin exudates can corrode (oxidize) and possibly dissolve metal surfaces they contact. Their composition varies as a function of physical, pharmacological and

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environmental conditions, gender, age, sweat rate, body site and methods of collection, also in a healthy organism [5].

The corrosion resistance of various nickel-containing alloys was measured in artificial sweat (perspiration) using the Tafel extrapolation method. It was found that Ni, CuNi 25 (coin alloy), NiAl (colored intermetallic compounds), WC + Ni (hard metal), white gold (jewelry alloy), FN42 and Nilo Alby K (controlled expansion alloys), and NiP (electroless nickel coating) are in an active state and dissolve readily in oxygenated artificial sweat. By contrast, austenitic stainless steels, TiC + Mo<sub>2</sub>C + Ni (hard metal), NiTi (shape-memory alloy), Hastelloy  $\chi$  (superalloy), Phydur (precipitation hardening alloy), PdNi and SnNi (nickel-containing coatings) are in a passive state but may pit under certain conditions. Cobalt, Cr, Ti, and some of their alloys were also investigated for the purpose of comparison. Cobalt and its alloys have poor corrosion resistance except for Stellite 20. Chromium and high-chromium ferritic stainless steels have a high pitting potential but the latter are susceptible to crevice corrosion [6].

Copper and its alloys are subject to chemical reactions on exposure to environmental or physiological factors, whereby products are potentially generated which become diffusible through mammalian skin. The chemistry of oxidation is reviewed as well as the factors contributing to corrosion. Skin exudates (sweat and sebum) can react with metal surfaces they come in contact with, but even in the healthy organism their composition is variable, as a function of physical, pharmacological and environmental conditions, gender, age, sweat rate or body site. This overview addresses sweat and sebum composition, and discusses components which determine the skin's corrosive action: chloride ion, low-molecular-weight acids and amino acids in sweat, and fatty acids in sebum, which hold the potential to solubilize copper-containing metal objects. These components can form copper salts and soaps whose molecular characteristics (size and polarity) will determine the rate and route of cutaneous penetration [7].

The present work is undertaken to study the corrosion behaviour of three metals, namely, mild steel, galvanized steel and SS 316 L, in artificial sweat by polarization study and AC impedance spectra. Corrosion parameters such as corrosion potential, corrosion current, linear polarization resistance, charge transfer resistance and double layer capacitance have been derived from these studies.

## MATERIALS AND METHODOLOGY

Three metal specimens, namely, mild steel, mild steel coated with zinc (commercial galvanized steel) and SS316L were chosen for the present study. The composition of mild steel is (wt %) 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron [8]. The composition of SS316L is (wt %): 18 Cr, 12 Ni, 2.5 Mo, <0.03 C and balance iron [9]. The metal specimens were encapsulated in Teflon. The surface area of the exposed metal surface was 0.00785 cm<sup>2</sup>. The metal specimens were polished to mirror finish and degreased with trichloroethylene. The metal specimens were immersed in artificial sweat (the ISO standard ISO 3160-2), whose composition was : 20g/l NaCl, 17.5 g/l NH<sub>4</sub>Cl, 5g/l acetic

acid and 15 g/l d,l lactic acid with the pH adjusted to 4.7 by NaOH.

In electrochemical studies, the metal specimens were used as working electrodes. Artificial sweat (AS) was used as the electrolyte (10 ml). The temperature was maintained at 37 ± 0.1°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 one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. The details of the experimental conditions are as follows: Hold Time at E<sub>f</sub> (s) = 0; Scan Rate (v/s) = 0.005; Quiet Time (s) = 2.

From the polarization study, corrosion parameters such as corrosion potential (E<sub>corr</sub>), corrosion current (I<sub>corr</sub>) and Tafel slopes (anodic = b<sub>a</sub> and cathodic = b<sub>c</sub>) and linear polarization resistance (LPR) were calculated. LPR monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream allows the calculation of corrosion current. If the electrodes are corroding at high rate with the metal ions passing into solution, a small potential applied between the electrodes will produce a high current, and therefore a low polarization resistance. This corresponds to a high corrosion rate [10, 11].

## 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. The details of the experimental conditions are as follows: Initial E (V) = 0; High frequency (Hz) = 1 x 10<sup>5</sup>; Low frequency (Hz) = 10; Amplitude (V) = 0.005; Quiet Time (s) = 2. Values of the charge transfer resistance (R<sub>t</sub>) and the double layer capacitance (C<sub>dl</sub>) were calculated.

## RESULTS AND DISCUSSION

### Potentiodynamic Polarization Study

The potentiodynamic polarization curves of various metals (MS, GS and SS 316 L) immersed in artificial sweat solution is shown in Figs. (1-3). The corrosion parameters, namely, corrosion potential (E<sub>corr</sub>), Tafel slopes (b<sub>c</sub>=cathodic; b<sub>a</sub> = anodic), linear polarization resistance (LPR) and corrosion current (I<sub>corr</sub>) are given in Table 1.

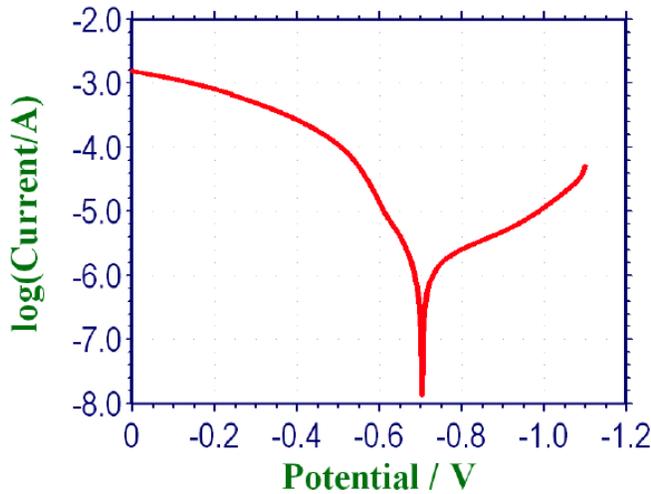
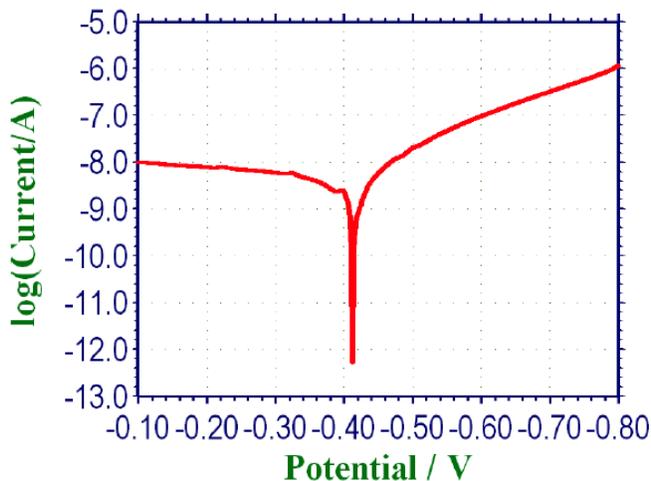
When mild steel (MS) is immersed in AS solution (Fig. 1) the corrosion potential is -704 mV vs SCE. The cathodic Tafel slope (b<sub>c</sub>) is 328 mV/decade and the anodic Tafel slope is 87 mV/decade. It is inferred that the change of current with change in potential is less during anodic polarization than during cathodic polarization. The LPR value is 2.138 x 10<sup>4</sup> ohm cm<sup>2</sup> and the corrosion current is 181 x 10<sup>-6</sup> A/cm<sup>2</sup>.

When galvanized steel (GS) is immersed in AS solution (Fig. 2). The corrosion potential is shifted to the noble side (anodic side, -412 mV vs SCE) (relative to MS). This suggests that a protective film is formed on the metal

**Table 1. Corrosion Parameters of Metals Immersed Artificial Sweat (AS) Obtained from Polarization Study**

Metal	$E_{\text{corr}}$ mV vs SCE	$b_c$ mV/Decade	$b_a$ mV/Decade	LPR ohm cm <sup>2</sup>	$I_{\text{corr}}$ A/cm <sup>2</sup>
MS + AS	-704	328	89	$2.138 \times 10^4$	$181 \times 10^{-6}$
GS + AS	-412	128	126	$6.568 \times 10^6$	$877 \times 10^{-9}$
SS 316 L + AS	-443	134	665	$5.054 \times 10^5$	$1224 \times 10^{-8}$

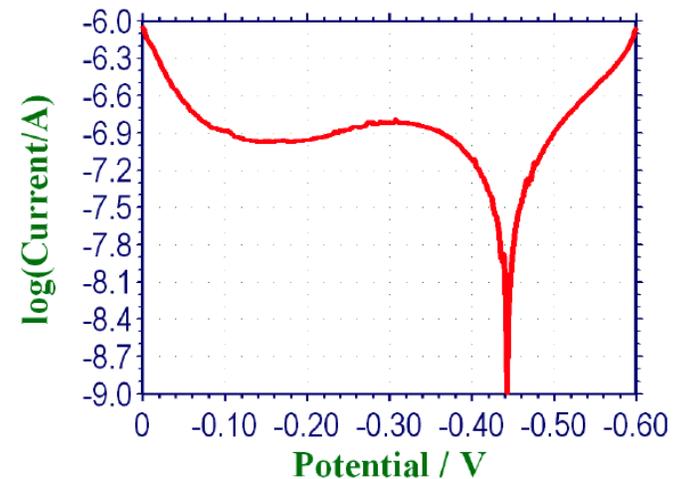
surface. The cathodic and anodic Tafel slopes are almost equal (128 and 126 mV/decade). This indicates that the change of current during change of potential is more or less equal during anodic and cathodic polarization.

**Fig. (1).** Polarization curve of MS immersed in artificial sweat.**Fig. (2).** Polarization curve of GS immersed in artificial sweat.

The LPR value increases from  $2.138 \times 10^4$  to  $6.568 \times 10^6$  ohm cm<sup>2</sup>. The corrosion current value decreases from  $181 \times 10^{-6}$  to  $877 \times 10^{-9}$  A/cm<sup>2</sup>. These results suggest that mild steel coated with zinc is more corrosion resistant than mild steel. This may be due to the cathodic protective nature of zinc. Zinc undergoes corrosion protecting mild steel. Zinc is often referred to as sacrificial anode [12].

When SS 316 L is immersed in AS solution, the corrosion potential is shifted to -443 mV vs SCE (Fig. 3). It is anodic (noble) when compared with mild steel and it is cathodic (active) when compared with mild steel coated with

zinc. That is, SS 316 L is more corrosion resistant than mild steel and less corrosion resistant than mild coated with zinc. This view is supported by the fact that the LPR value is  $5.054 \times 10^5$  ohm cm<sup>2</sup>, when SS 316 L is immersed in AS solution. This value is higher when compared with the value of mild steel and it is lower when compared with the value of mild steel coated with zinc. This is further supported by the corrosion current value ( $1224 \times 10^{-8}$  A/cm<sup>2</sup>), which is lower than that of mild steel and which is higher than that of mild steel coated with zinc. An increase in LPR value and a decrease in corrosion current value are indications of more corrosion resistant nature of a metal in a medium. It is observed that the value of current remains almost constant in the potential range -382 to -100 mV vs SCE. This indicates that the film formed on the metal surface is stable in this potential range. Then the film is broken and the current passing through the metal increases.

**Fig. (3).** Polarization curve of SS 316 L immersed in artificial sweat.

Polarization study leads to the conclusion that the decreasing order of corrosion resistance in artificial sweat is  $GS > SS\ 316\ L > MS$ .

### AC Impedance Spectra

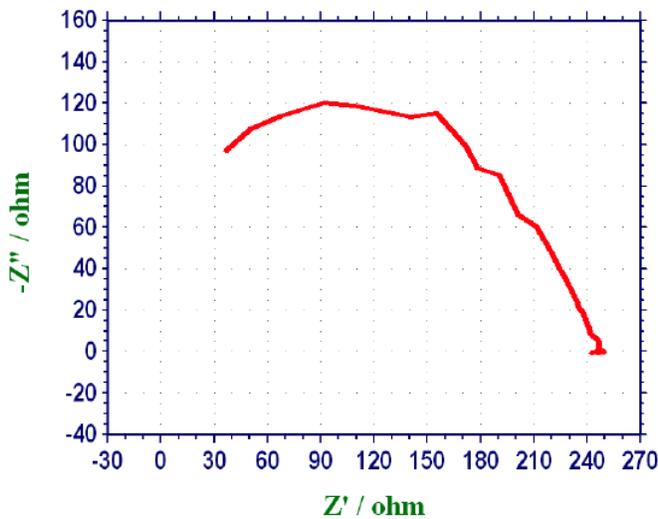
AC impedance spectra of metals immersed in artificial sweat (AS) solution are shown in Figs. (4-12). Nyquist plots are shown in Figs. (4-6) and the bode plots are shown in Figs. (7-12). The charge transfer resistance ( $R_t$ ) and double layer capacitance ( $C_{dl}$ ) values (derived from Nyquist plots) and the impedance,  $\log(Z/\text{ohm})$ , values derived from bode plots are given in Table 2.

When mild steel is immersed in AS solution, the charge transfer resistance is 217 ohm cm<sup>2</sup> and the double layer capacitance is  $299 \times 10^{-8}$  F/cm<sup>2</sup> (Fig. 4). The impedance,  $\log(Z/\text{ohm})$ , value is 2.378 (Fig. 7).

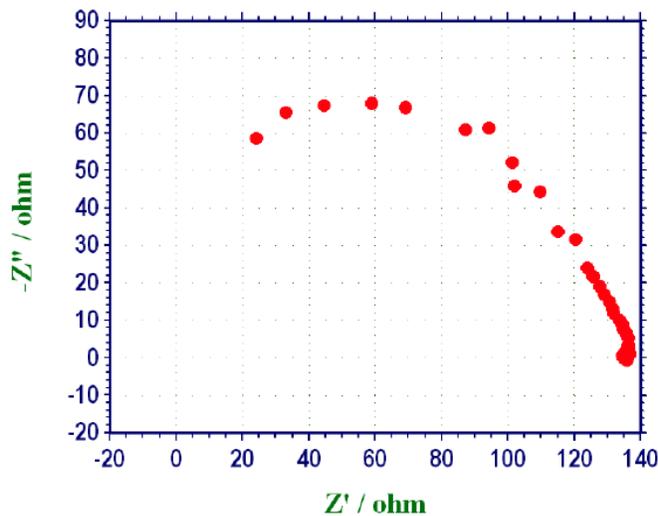
**Table 2. Corrosion Parameters of Metals Immersed in Artificial Sweat Obtained from AC Impedance Spectral Study**

Metal	Nyquist Plot		Bode Plot
	$R_t$ ohm cm <sup>2</sup>	$C_{dl}$ F/ cm <sup>2</sup>	Impedance, log(Z/ohm)
MS + AS	217	$299 \times 10^{-8}$	2.378
GS + AS	115	$565 \times 10^{-8}$	2.130
SS 316 L + AS	17900 (very high)	$317 \times 10^{-10}$	4.799

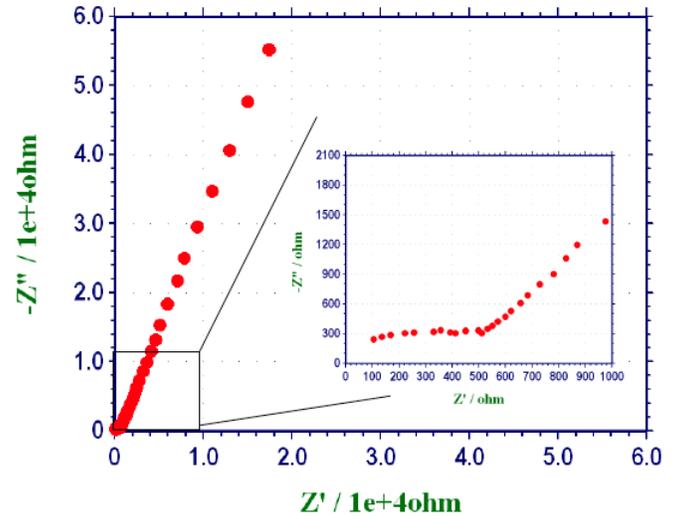
When galvanized steel is immersed in AS solution the charge transfer resistance decrease from 217 ohm cm<sup>2</sup> to 115 ohm cm<sup>2</sup> and the double layer capacitance value increases from  $299 \times 10^{-8}$  to  $565 \times 10^{-8}$  F/ cm<sup>2</sup> (Fig. 5). The impedance value decreases from 2.378 to 2.130. This indicates that mild steel coated with zinc less corrosion resistant than mild steel.



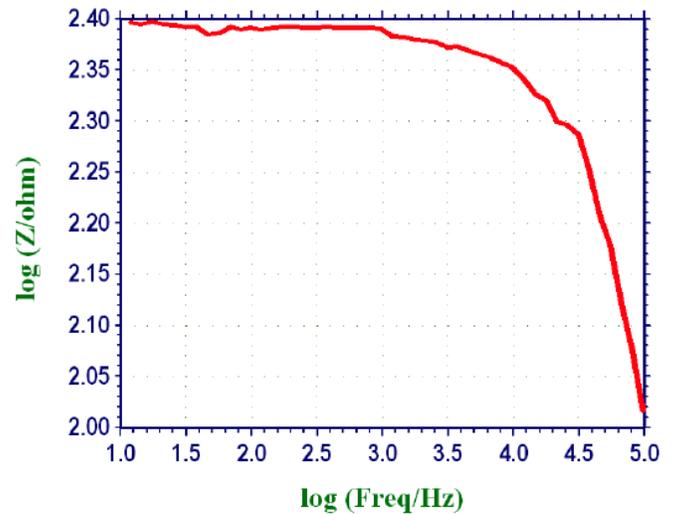
**Fig. (4).** AC impedance spectrum (Nyquist plot) of MS immersed in artificial sweat.



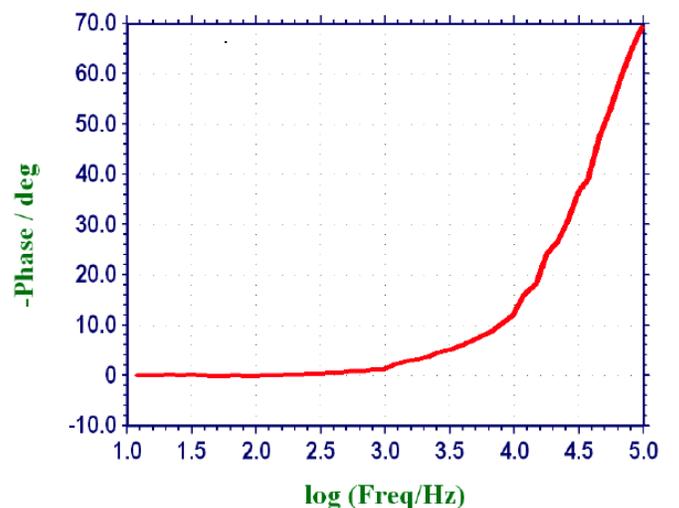
**Fig. (5).** AC impedance spectrum (Nyquist plot) of GS immersed in artificial sweat.



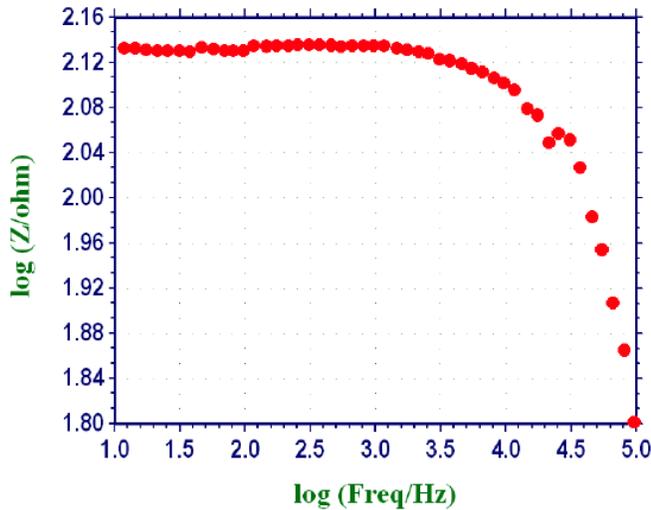
**Fig. (6).** AC impedance spectrum (Nyquist plot) of SS 316 L immersed in artificial sweat.



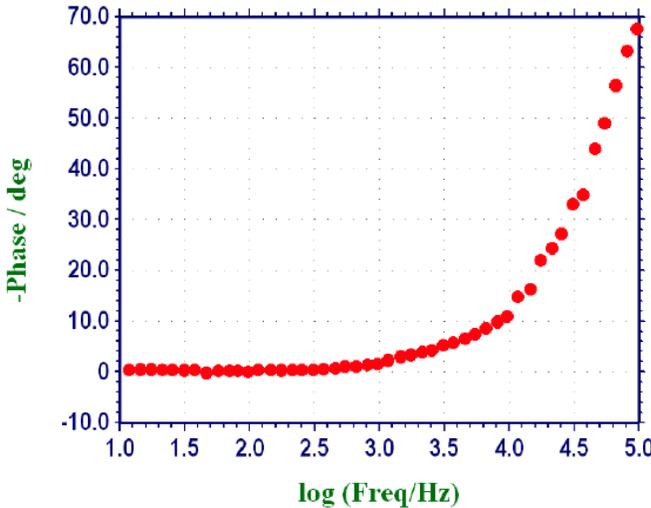
**Fig. (7).** AC impedance spectrum (Bode frequency plot) of MS immersed in artificial sweat.



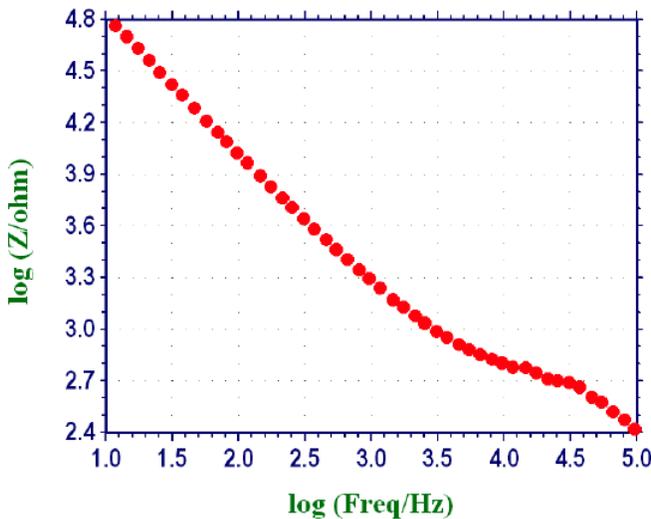
**Fig. (8).** AC impedance spectrum (Bode phase plot) of MS immersed in artificial sweat.



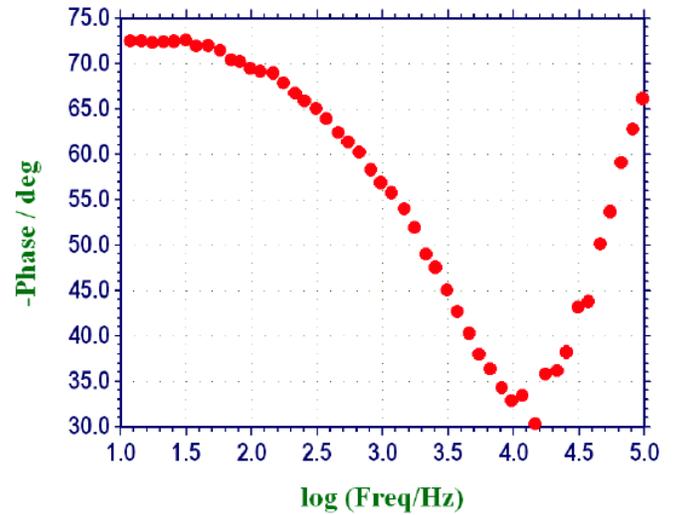
**Fig. (9).** AC impedance spectrum (Bode frequency plot) of GS immersed in artificial sweat.



**Fig. (10).** AC impedance spectrum (Bode Phase plot) of MS immersed in artificial sweat.



**Fig. (11).** AC impedance spectrum (Bode Frequency plot) of MS immersed in artificial sweat.



**Fig. (12).** AC impedance spectrum (Bode Phase plot) of MS immersed in artificial sweat.

It is interesting to note that according to polarization study, galvanized steel (GS) is more corrosion resistant than mild steel (MS). But according to AC impedance spectra, GS is less corrosion resistant than MS.

This can be explained by the fact that the film formed on the metal surface (GS) is amorphous and porous; it is broken by the aggressive ions present in the AS solution. Hence the charge transfer resistance decreases and double layer capacitance value increases.

When SS 316 L is immersed in AS solution the charge transfer resistance value is very high. The double layer capacitance value decreases (Fig. 6). The impedance value increases (Fig. 9). These observations indicate that SS 316 L is more corrosion resistant than other metals under investigation.

The very small semicircle (Fig. 5 inset) in the Nyquist plot suggests the formation of chromium oxide film on the metal surface to a very small extent. Afterwards there is no transfer of electrons from the metal surface. Hence the charge transfer resistance value is very high; the impedance value,  $\log(Z/\text{ohm})$  is also relatively high (4.799).

Thus, AC impedance spectra lead to the conclusion that the decreasing order of corrosion resistance of metals in artificial sweat is as follows:

$$\text{SS 316 L} > \text{MS} > \text{GS}$$

The difference in conclusion derived from polarization study and AC impedance spectra may be attributed by the fact that AC impedance spectra reveal that the close-packedness and compactness of the protective film formed on the metal surfaces is as follows  $\text{SS 316 L} > \text{MS} > \text{GS}$ . The corrosion behaviour of the protective films appears to be governed by a complex interrelated ensemble of chemical, structural, textural, morphological and electronic characteristics of the films.

**Analysis of Bode Plots**

**Mild Steel in Artificial Sweat Solution**

Analysis of  $\log(\text{Freq}/\text{Hz})$  vs  $\log(Z/\text{ohm})$  plot reveals that when  $\log(\text{Freq}/\text{Hz})$  value is 1,  $\log(Z/\text{ohm})$  value is

maximum (2.399) (Fig. 7). As the value of frequency increases, impedance value almost remains constant upto 3.0. Afterwards, as the value of frequency increases, the impedance value decreases. When the log (Freq/Hz) is 5.0, the log (Z/ohm) value is minimum, namely 2.017.

Analysis of log (Freq/Hz) vs  $-$ phase/deg reveals that the value of  $-$ phase/deg remains at zero upto log (Freq/Hz) value of 3.0 (Fig. 8). Then upto 4.0, it slowly increases. Afterwards, a sudden increase is noticed. The maximum  $-$ phase/deg is 70.0 when log (Freq/Hz) is 5.0.

#### Galvanized Steel in Artificial Sweat Solution

Analysis of log (Freq/Hz) vs log (Z/ohm) plot reveals that when log (Freq/Hz) value is 1.0, the value of log (Z/ohm), (impedance), is highest (2.130) (Fig. 9). It almost remains constant upto 3.0. Afterwards the impedance value slowly decreases upto 4.0. Afterwards the decrease is rapid. The minimum value for impedance is 1.025 when frequency value is 5.0.

Analysis of log (Freq/Hz) vs  $-$ phase/deg plot reveals that the value of  $-$ phase/deg is zero, when log (Freq/Hz) value is 1.0 (Fig. 10). It remains at zero upto 2.522 [log (Freq/Hz)]. Afterwards it increases slowly upto 4.0. Then it increases rapidly and reaches a maximum of 68.45 at the frequency value of 5.0.

#### SS 316 L in Artificial Sweat Solution

Analysis of log (Freq/Hz) vs log (Z/ohm) plot reveals that when the value of frequency is 1.0, the value of impedance [log (Z/ohm)] is the highest, namely, 4.799 (Fig. 11). As the value of frequency increases the value of impedance decreases sharply upto the frequency value of 3.5 Hz, when the corresponding impedance value is 3.0 ohm. Afterwards the impedance value decreases slowly and reaches a minimum value of 2.4 ohm when the log (Freq/Hz) value is 5.0.

Analysis of log (Freq/Hz) vs  $-$ phase/deg plot reveals that when log frequency value is 1.0 Hz, the  $-$ phase/deg value is 72.81 (Fig. 12). As the log frequency value increases, it remains constant upto 1.5 Hz. Afterwards it decreases sharply and reaches a minimum value of  $-$ phase/deg 30.0 at log (Freq/Hz) value of 4.156. As the value of frequency increases, the value of  $-$ phase/deg increases. When log (Freq/Hz) is 5.0, the value of  $-$ phase/deg is 66.77.

Analysis of the log (Freq/Hz) vs log (Z/ohm) plots is summarized in Table 3.

Analysis of the log (Freq/Hz) vs  $-$ phase/deg plots is summarized in Table 4.

#### CONCLUSION

- Corrosion behaviour of three materials namely, mild steel, mild steel coated with zinc (galvanized steel) and SS 316 L in artificial sweat has been evaluated by polarization study and AC impedance spectra.
- Polarization study reveals that corrosion resistance of the materials studied, in artificial sweat is GS > SS 316 L > MS.

- AC impedance spectra reveal that the corrosion resistance of the materials in artificial sweat is SS 316 L > MS > GS.
- AC impedance spectra also reveal that the close-packedness and compactness of the protective film formed on the materials is SS 316 L > MS > GS.
- SS 316L is a better candidate for making ornaments, such as wrist watch, which come in contact with sweat.

**Table 3. Analysis of Log (Freq/Hz) vs Log (Z/ohm) Plots when Metals are Immersed in Artificial Sweat Solution**

log (Freq/Hz)	Log (Z/ohm)
<b>Mild Steel</b>	
1.0	2.399
5.0	2.017
1 to 3	Remains constant (2.399)
<b>Galvanized Steel</b>	
1.0	2.130
5.0	1.025
1 to 3	Remains constant (2.130)
<b>SS 316 L</b>	
1.0	4.799
5.0	2.4
1 to 3	Sharp decrease to 3.0

**Table 4. Analysis of Log (Freq/Hz) vs  $-$ Phase/Deg Lots, when Metals are Immersed in Artificial Sweat Solution**

log (Freq/Hz)	$-$ Phase/Deg
<b>Mild steel</b>	
1 to 3	Zero
3 to 4	Slow increase
5	70.0
<b>Galvanized steel</b>	
1 to 2.522	Zero
2.522 to 4	Slow increase
5.0	68.45
<b>SS 316 L</b>	
1	72.81
1 to 1.5	Remains constant 72.81
1.5 to 4.156	Sudden decrease to 30.0
4.156 to 5	Increases to 66.77

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