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CORROSION BEHAVIOR OF BIOCOMPATIBLE (CP-TI) AND (TI-SI) ALLOYS

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ABSTRACT

The porous Titanium is characterized by high permeability which can assure ingrowth of bone tissue, and consequently result in good bonding between metallic implant and bone. In this research, all the samples are prepared using powder metallurgy technique and the preparation process included adding Silicon element to the commercially pure Titanium at different weight percents of (2, 4, 6, 8 and 10) to investigate the effect of adding Silicon element to the commercially pure Titanium on the porosity percentage, microstructure and corrosion behaviour of the resulted samples. Microstructure analysis stated that at (Si) content lower than (2 wt%) the alloy is single phase (α- Ti alloy), as the Silicon content increased, in addition to (α-phase), (Ti5Si3) intermetallic compound developed in the alloy microstructure. Porosity measurement results showed that the porosity percentage increases with the increase in Silicon content. The corrosion results showed improved resistance with increasing the Silicon content in the two testing solutions (Blood Plasma and Ringer's solutions).

INTRODUCTION

For a long period of time, Titanium and Titanium alloys have confirmed to be cost effective materials and technically superiors for extensive ranges of applications including marine industries, aerospace industries and even more commercial products, due to their good combination of mechanical characteristics (stiffness and superior specific strength) and their immunity to corrosive attack for extensive ranges of acidic and neutral water media, atmosphere of marine and saltwater. It also showed remarkable resistance to an extensive range of industrial chemicals, acids, natural waters and alkalis. Ti-alloys also display superior resistance to cavitation, erosion or impingement attacks in the environment over an extensive range of aggressiveness, and importantly their accepted mechanical properties at high temperatures together with an intrinsic ability to resist and safely function at high temperatures. These noticeable attractive properties of Titanium alloys have encouraged their selection and enhanced use in marine and a spectrum of other critical performance applications **[1]**.

(Titanium-Silicon) alloys are new type of rapidly developing Titanium alloys. Their low processing cost and good formability make them a very promising alloy for casting. The (Titanium-Silicon) alloys strengthening mechanism is greatly different from the strengthening mechanism of traditional Titanium alloys. It consists of (Titanium matrix) as a continuous ductile phase and (Ti_5Si_3 reinforcing phase) as a second brittle phase **[2]**.

Silicon alloyed Titanium provides a low cost production method because of the lower melting point of Silicon as compared to pure Titanium. In general, the influence of an alloying element on the corrosion behavior involves: (I) its oxide ability to bind with another oxide, (II) the stability of the alloying element oxides, such as the dependence of the dissolution rate on the pH, (III) the effect on the oxides defect structures of the of the major element and (IV) the coefficients of ion diffusion in the alloying element oxides. For (Ti–Si) alloys, the effect of Silicon on the corrosion behavior is related to the (SiO_2/TiO_2) ratio, the dissolution rate of Silicon oxide, the probable Silicon-doping on Titanium oxide and the diffusion coefficient of oxygen in Silicon oxide. Previous work on the Titanium alloys showed the surface protection of these alloys by a highly insoluble adherent passive film **[3]**.

Yong Ryeolet. al, [4**],** assessed the effect of gold addition on the microstructure, and corrosion behavior of commercially pure Titanium (CP-Ti). The results indicated that the (Ti–xAu) alloys containing up to (15 wt% Au) showed a hexagonal close-packed (α) structure, whereas the (Ti–xAu) alloys containing more than (20 wt% Au) were mainly composed of the (α-phase) and (Ti_3Au) intermetallic phase, the electrochemical results showed that the (Ti–xAu) alloys exhibited improved corrosion resistance than that of the (CP-Ti).

Jinwen Lu et. al, [5], evaluated the corrosion behavior of new high strength (Ti-1300) beta Titanium alloy with different microstructure compared to (Ti64) alloy. The microstructure results indicated that the (Ti-1300) and (Ti64) alloy consist of two phases (alpha and beta), without any other phases or intermetallic compounds. After immersion test the (Ti-1300) alloy SEM observation indicates that alpha phase and (alpha and beta) inter-phase boundary act as the preferential dissolution locations, the accumulation of beta stabilizing elements within the beta phase in addition to the formation micro-galvanic cells are the chief factors influencing the (Ti-1300) alloy corrosion performance

Grzegorz Dercz et. al, [6], assessed the possibility of producing porous (50Ti-50Ta) alloys using powder metallurgy by characterizing the corrosion behaviour of the alloy in ringer's solution. The corrosion results show that better resistance to corrosion was exhibited by (Ti-50Ta) when compared with the corrosion resistance of Titanium or tantalum pure samples.

In the present work, the corrosion behavior of (CP-Ti) and (Ti–Si) alloys in which the contents of Silicon are (2, 4, 6, 8 and 10 wt%) have been investigated via the electrochemical techniques, together with microstructure analysis (optical microscope and (SEM) scanning electron microscope) and the porosity measurement which carried out by Archimedes method.

MATERIALS AND METHODS

Materials

In this work, Commercially Pure Titanium (CP-Ti) powder of (98.5% purity and 0.785µm particle size) and Silicon powder of (99.0% purity and 250 µm particle size) were used to prepare (CP-Ti) and a series of (Ti-Si) alloys of (0, 2, 4, 6, 8 and 10 wt% Si) samples of (13mm diameter), using Powder Metallurgy technique.

Methods

The starting powders were weighed (8 gm) for each sample then blended and homogenized for (20 min.) in a ball mill type (CAPCO-9VS), shown in **Figure (1)**. After Blending, the powders were cold pressed at (3 tons for 2 min.) using hydraulic Press type (MEGA-KPD-50E), shown in **figure (2)**, the sintering process of the compacted samples was carries out under high-purity argon atmosphere at (900℃ and 10℃/sec heating rate for 2 hrs.) to get improved bonding among the green sample particles.

Figure (1): Ball mill type (CAPCO-9VS).

Figure (2): Hydraulic Press type (MEGA-KPD-50E).

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For Surface preparation, the Bakelite mounted specimens were grounded using (400, 600, 800, 1000 to 1200) grit emery paper to get a flat surface free from scratches and polished by using diamond paste. Samples were then etched to reveal their microstructure using a reagent that is a solution mixture of (5 ml) of nitric acid (HNO_3), (10 ml) of hydrofluoric acid (HF) and (85 ml) of water (H_2O) **[7]**.

The surface morphology of the samples was analyzed using SEM (VEGA II SBH MS 12), shown in **figure (3),** and optical microscope (Model - MTM - 1A, BEL - ITALY, SN/1380), shown in **figure (4),** and the porosity measurements of the sintered samples was determined by the Archimedes method (RADWAG PS 360/C/1), shown in **figure (5)**.

Figure (3): SEM type (VEGA II SBH MS 12).

Figure (4): Optical Microscope type (BEL-ITALY).

Figure (5): Porosity measurement device type (RADWAG PS 360/C/1).

The corrosion behavior of the samples was determined by measuring the corrosion rate of the samples in two different body solutions (Ringer's solution and synthetic blood plasma), to determine the period of validity of these samples in the human body. The corrosion cell involved three electrodes connected to a potentiostat (X MTD-2MA), shown in **figure (6)**, a saturated calomel electrode (SCE) as a reference electrode, a platinum rod as a counter electrode and a working electrode.

Figure (6): Corrosion rate device type (X MTD-2MA).

The working electrode was made by attaching the mounted and surface prepared sample to copper wire to get electrical contact. The open circuit potential measurement takes up to (5 minutes) with reading every (10 seconds) at scanning rate of (10 V/sec). The chemical composition of the testing solutions are listed in **table (1).**

Table (1): Chemical composition of the testing solutions.

Solution type	**Chemical composition**
Simulated body fluid (Ringer's solution)	Adding Ringer tablet to (0.5) liter of distillated water and heating the solution to a temperature of (120°C) for (15 min.) and leaving it to cool, then Na_2HCO_3 was added to obtain pH of (7.4). Ringer tablet was obtained from Merck Company Germany.
Synthetic blood plasma **[8]**	NaCl (6.8g\L), KCl (0.4g\L), $CaCl_2$(0.2) $NaHCO_3$ (2.2g\L), Na_2HPO_4 (1.126g\L), NaH_2PO_4(0.026g\L), $MgSO_4$ (0.1g\L).

RESULTS AND DISCUSSION

I. SEM and Optical Microscopic Analysis

The SEM and optical microstructure images of the (CP-Ti) and (Ti–Si) alloys samples are shown in **figure (7)** and **figure (8**). From the microstructure analysis, at Silicon content (0 and 2 wt%) the sample was comprises of a single phase (α-phase), with increasing the Silicon content to (4,6,8 and 10 wt%) an intermetallic compound (Ti_5Si_3) begins to form in addition to the (α-phase), and this agrees with binary (Ti–Si) phase diagram **[9]**. It is obvious that the use of powders with large differences in their particle size causes formation of highly porous alloys after the sintering process which may affect many main properties. The addition of Silicon element led to the production of single phase alloys with a high chance of producing intermetallic compound which changes the physical and chemical properties of the alloys according to the Silicon content.

Also from the microstructures, the corrosion behaviour of samples must be correlated to (α-phase) and (Ti_5Si_3) intermetallic compound.

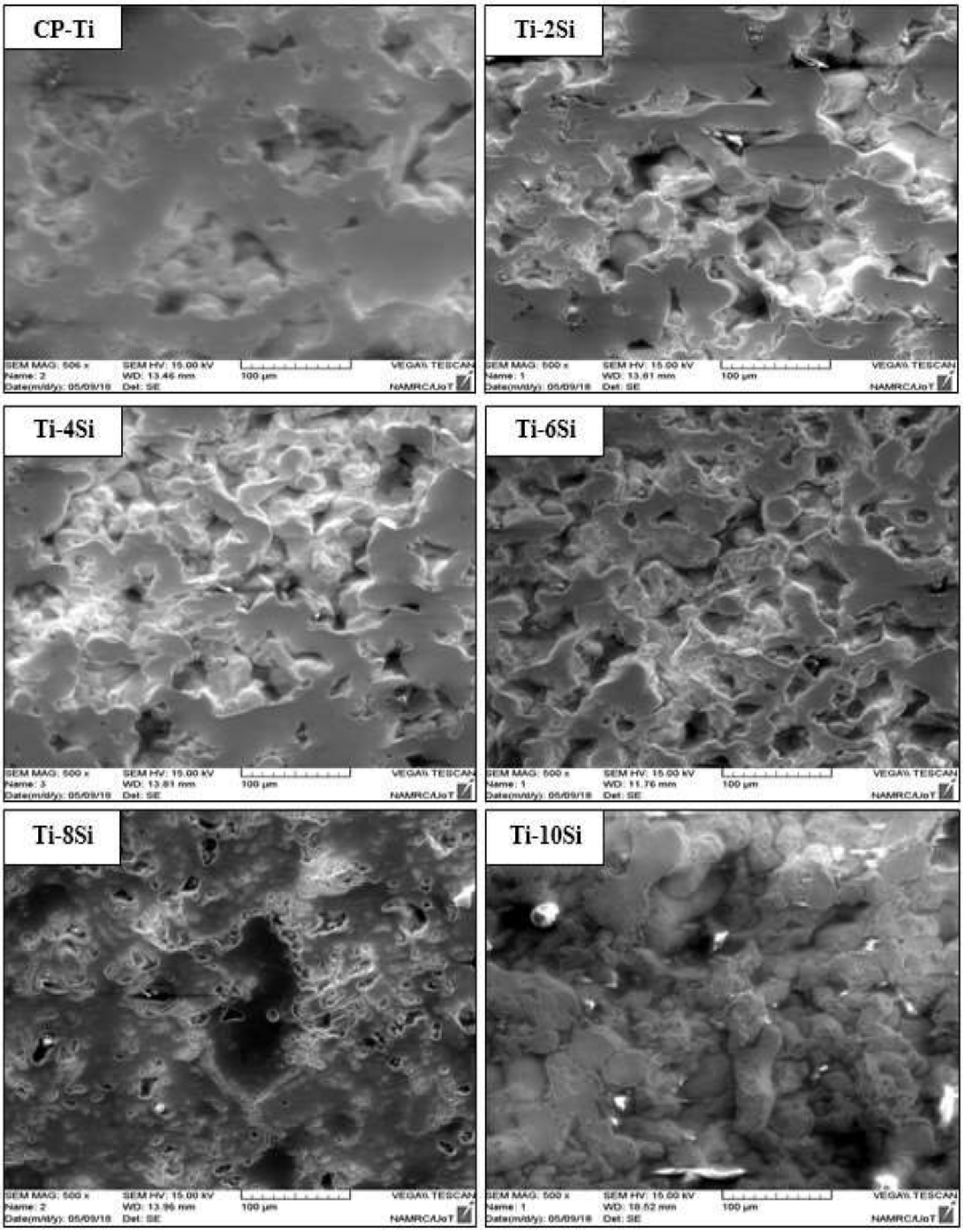

Figure (7): SEM images of the (CP-Ti) and (Ti–Si) alloys samples.

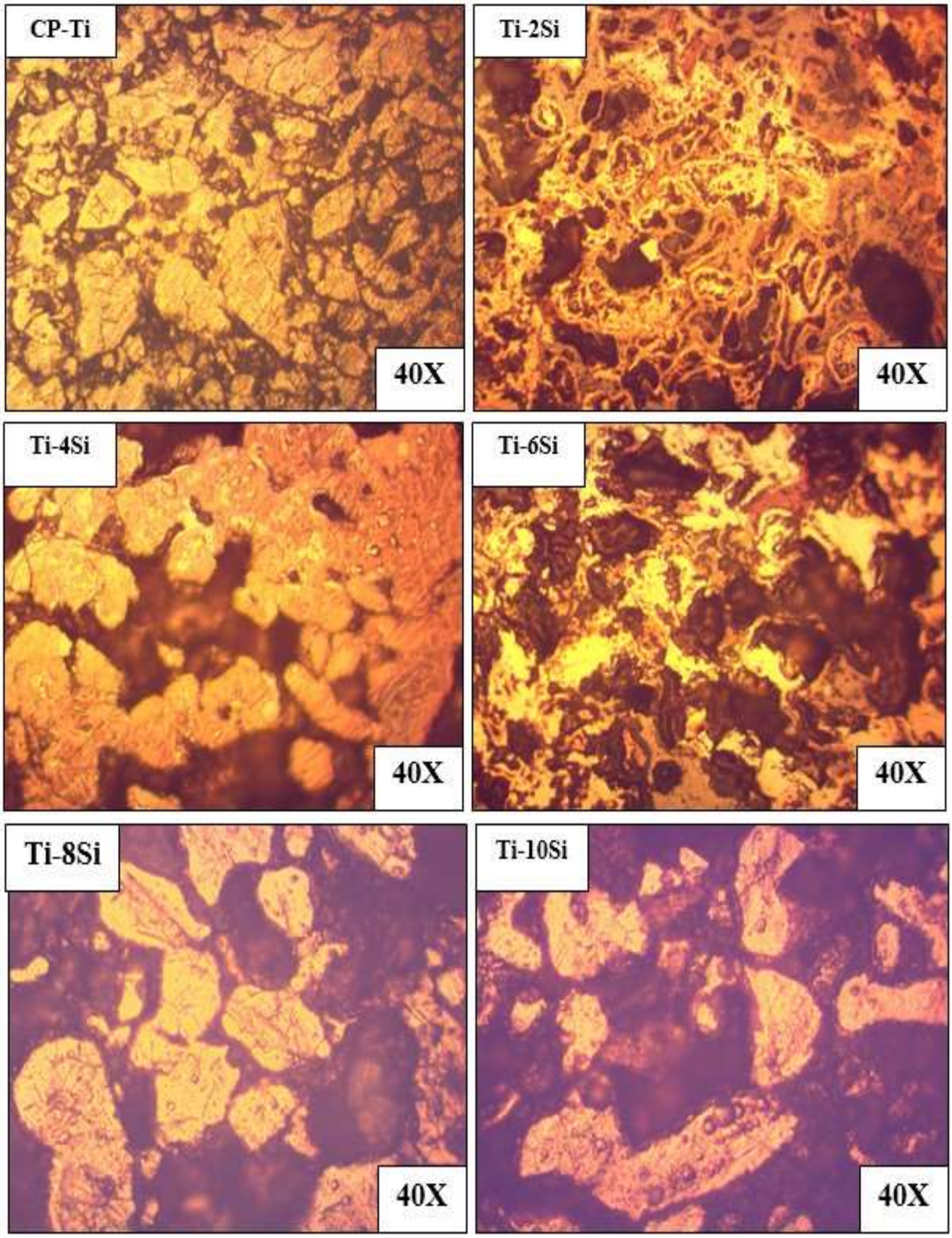

Figure (8): Optical microstructure images of the (CP-Ti) and (Ti–Si) alloys samples.

II. Porosity Measurements

The porosity percentages results of (CP-Ti) and (Ti-Si) alloys are graphically represented in **figure (9).** The graph shows an increasing in porosity percentage with the increase in Silicon content, as a result of using different powders (Ti, Si) with a large difference in their particle size, the particle size of Titanium powder was (0.785) µm while the particle size of Silicon was (250) µm.

The minimum value of porosity percentage was obtained in (CP-Ti) sample (with no Si content) (12.4%) while the maximum value was obtained in the (Ti-Si) sample of (10% Si content), (30%).

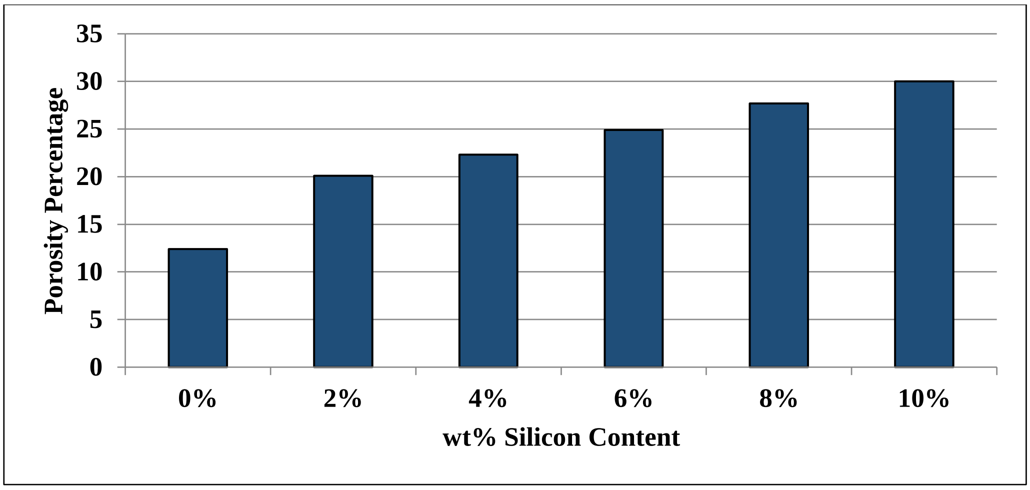

Figure (9): Porosity percentages.

III. Corrosion Behavior

a. Corrosion Behavior in Blood Plasma Solution

The results showed a sudden decrease in corrosion resistance when (2 wt%) Silicon is added to the (CP-Ti), as shown in **figure (10)**, this can be attributed to the sudden increase in porosity percentage from (12.4 to 20.1), then the corrosion rate values begin to decrease continuously and this is because the (TiO_2 and SiO_2) oxides would form simultaneously on the sample surface when exposed to the body solution and the higher resistance to corrosion provided by the more stable (SiO_2) over that of the (TiO_2) Oxide.

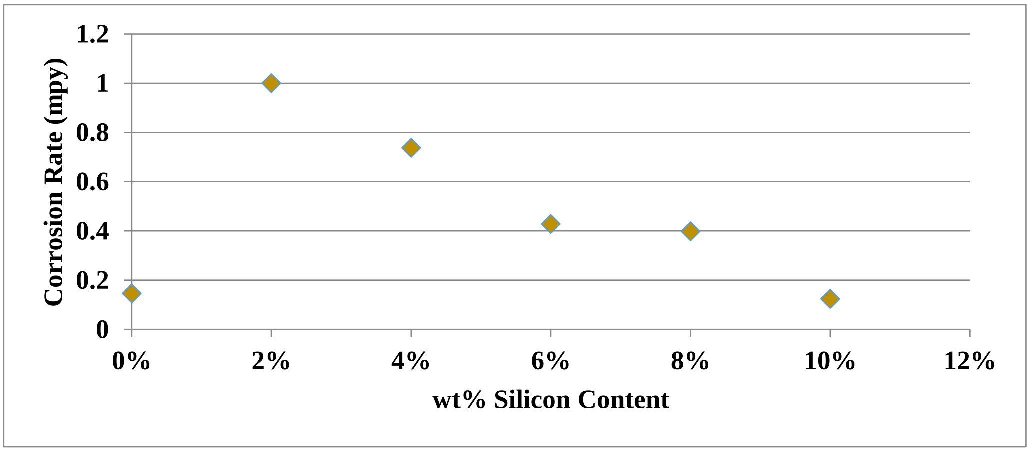

Figure (10): The relationship between corrosion rate and Silicon content in Blood plasma solution.

a. Corrosion Behavior in Ringer's Solution

The results showed that the corrosion rate rapidly increases to (0.56 mpy) by addition of (2 wt%) Silicon, as shown in **figure (11)**, samples with increased Silicon content of (4, 6, 8 and 10 wt%)) exhibit improved corrosion rates due to the higher stability, higher corrosion resistance, of (SiO_2) oxide over (TiO_2) oxide.

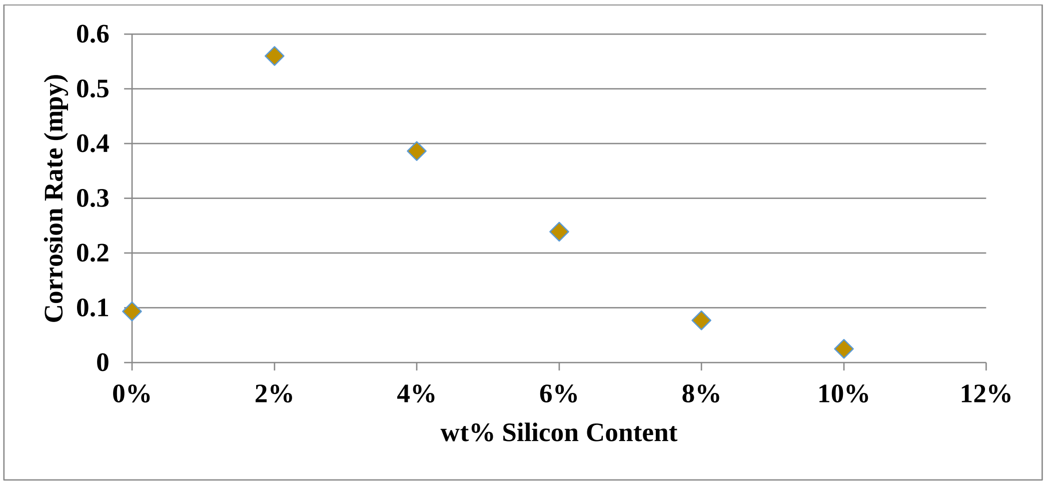

Figure (11): The relationship between corrosion rate and Silicon content in Ringer's Solution.

It is extensively accepted that the protective passivity films on the metals and alloys surfaces show a bilayer structure, i.e., an inner layer of oxide and an outer layer of hydroxide. Based on the bilayer structure, the (Ti–Si) alloys passive films might consist of an inner layer of (Si–$TiO_{1.993-1.996}$) and an outer layer of ($TiO_2 \cdot nH_2O$). While the inner oxide layer is formed through (Ti and Ti_5Si_3) oxidation, precipitation of some of the dissolved oxides on the surface results in the formation of an outer hydroxide layer. Because of the lower dissolution rate of (SiO_2) than TiO_2), (TiO_2) will selectively dissolve from the (SiO_2/TiO_2) layer, leaving (SiO_2) behind **[3]**.

CONCLUSION

(1) Using powders with large differences in their particle size causes formation of highly porous alloys after the sintering process which may affect many main properties.
(2) The microstructures of the samples with Silicon content of (0 and 2 wt%) comprise of single phase (α-phase), with increasing the Silicon content to (4, 6, 8 and 10 wt%) the alloy comprises (α-phase) and (Ti5Si3) intermetallic compound.
(3) The porosity percentage increase with the increase in Silicon content.
(4) The corrosion resistance improves with increasing the Silicon content in the two solutions (Blood Plasma and Ringer's solutions).

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