# EFFECT OF CR ADDITION ON TI-BASE SHAPE MEMORY IMPLANT

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## ABSTRACT

Shape Memory Alloys (SMAs) have been considered as one of the most Promising smart materials. They can provide novel solution in several fields, for various applications. Shape Memory Alloys demonstrate a unique ability to recover their initial shape after deformation through a reversible thermo-elastic phase transformation, the effect of Cr addition on mechanical properties and biocompatibility of the Ti-Ta shape memory implant are investigated, many test was done on prepared samples that produced by powder metallurgy technique, and the results shows that all prepared sample consist of two phases α and β ,also the transformation temperature of the alloy decrease when Cr is added at different percentage, and there is a remarkable decrease in hardness (108.8Hv) due to the increase in porosity percentage(7.6%) when Cr is added ,finally the corrosion behavior of the alloy in general is improved as Cr content increase which mean that the alloy attractive to use in human body as implants.

**Keywords : smart materials, Ti –base, biocompatibility, Ti-Ta shape memory alloys, powder metallurgy technique.**

# تأثير إضافة الكروم على سبائك ذاكرة الشكل الطبية المزروعة ذات أساس من التيتانيوم

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## الخلاصة :

تعتبر سبائك ذاكرة الشكل من أهم المواد الذكية في الوقت الحاضر، والتي توفر حلول لكثير من المشاكل في الوقت الحاضر. وتعرف سبائك ذاكرة الشكل أنها المواد التي لها القدرة على استرجاع شكلها الأصلي بواسطة التحول ألطوري . في هذا البحث تم دراسة تأثير إضافة عنصر الكروم على كل من التوافقية والخصائص الميكانيكية لسبيكة ذاكرة الشكل (التيتانيوم –التانتالوم) وقد أظهرت النتائج أن جميع السبائك المحضرة بواسطة تكنولوجيا المساحيق مكونة من طورين أساسيين هما طور إلفا وطور بيتا وكذلك أظهرت أن إضافة عنصر الكروم تؤدي إلى خفض درجة حرارة التحول ألطوري ولوحظ انخفاض كبير في قيمة الصلادة (108.8Hv) عند إضافة الكروم نظرا لارتفاع المسامية (7.6%) نتيجة لعمليه التصنيع وأخيرا أظهرت النتائج أن سلوك التآكل قد تحسن نوعا ما عند زيادة نسبه الكروم مما يجعل السبيكة قابلة للاستخدام داخل جسم الإنسان كمزروعة .

## 1. INTRODUCTION :

In recent years there has been an increasing attention to the development and research of so-called "smart materials". These new kind of materials appeared as a result of the synthesis of structural and functional materials combined with the integration of a control mechanism. Some of the most interesting materials in this class are shape memory alloys (SMA).which refers to any materials that demonstrate the ability to return to some previously defined shape or size when subjected to the appropriate thermal procedure. Generally, these materials can be plastically deformed at some relatively low temperature, and upon exposure to some higher temperature will return to their shape prior to the deformation. **[Shuichi Miyazaki2009]**

NiTi alloys (Nitinol), are widely used as shape memory alloy and have been successfully applied as biomaterials, however, it has been pointed out that pure Ni is a toxic element and causes Ni-hypersensitivity due to its toxic nature when used inside human body **[ASM 1990]**, therefor recent studies tends to developed new shape memory systems in order to provide safety implants for a long period of time inside the body. Ni-free ,Ti-base shape memory alloys becomes a promising solution for biocompatibility problems of shape memory implants**[Yan Li 2008]** , Recently the β -type Ti base shape memory alloys which exhibit excellent cold workability has been extensively investigated. For example the shape memory behavior of β-type Ti-base alloys, such as Ti-Mo [T. Maeshima 2006, H.Y. Kim2006], Ti-Nb [H.Y. Kim 2006- H. Matsumoto2005] and Ti-Ta [T. Inamura2005] alloys, has been reported.

The aim of this research is to prepare Ti-Ta shape memory alloys samples by powder metallurgy technique and study the effect chromium additions on the hardness, porosity percentage, transformation temperature, and corrosion rate in different solutions artificial such as; saliva, simulated body fluid( i.e. Ringer's solution) and blood plasma.

## 2. EXPERIMENTAL WORK

The experimental work includes method by which the samples were prepared, in addition the characterization process and types of tests that were adopted in this work. The preparation of master sample (Ti-Ta) and the samples with addition of Cr in different percentage by using powder metallurgy technique as shows in table (1).

After selecting the weighted percentages for each sample the material powder was weighted by using the sensitive balance type (DENVER INSTRUMENT) (4 deg.) and the total weight of each sample is 5gm.
In order to obtained a homogenous distribution of the powders and to achieve good mixing between each elements, the samples' powders are mixed in a boll mill type (BAIRD & TATLOCK) for two hour at high level of speed to each sample, Finally we obtain homogenous powders ready for pressing process, which involves compact the powder of each samples by using the Punch and die (made from D2 tool steel) with die diameter of 15 mm.

The powder was pressed under pressure 850 MPa for 10 min by using the hydraulic press machine type (RAJCO), and thus we obtained samples with diameter 15mm and 4mm in height. The final step in sample preparation is sintering process it was carried out by using electrical furnace at temperature 1000 °C for 9 hours under controlled atmosphere (argon gas) to impede the samples oxidation.

This process was doing in two stages due to the inability to make this process in one stage for 9hours so we separate this process for two stages. After sintering process we obtained the Ti-Ta alloys with and without Cr addition these samples are ready for inspection and test.

## 3. RESULTS AND DISCUSSION :

### 3.1 X-Ray Diffraction :

In order to know the composition and the phase identification of each sample the XRD test was done by use shimadzu x-ray diffractometer xrd- 6000/7000.

The phases produced as a result of the sintering process it can be seen in Fig. (1), that there are probably no pure metals present which proves that the sintering time and temperature used in this work result in complete sintering reaction.

X-ray diffraction showed that all the samples alloys has consist mainly of two phases ($\alpha + \beta$) biphasic structure; the martensitic phase ($\alpha$- phase) orthorhombic structure and the austenitic phase ($\beta$- phase) B.c.c. structure. It is noteworthy that the volume fractions of $\beta$ -phase increases along with the increase of alloy Ta content.

### 3.2 Transformation Temperature:

DSC is the most widely used technique to determine the transformation temperatures and to get the energy of transformations of shape memory alloys.

The DSC measurements have been employed, at constant rate 10 °C/min of heating and cooling cycle for all samples. The measurements are carried out in the temperature range from (-50°C to 200°C).

Fig. (2) shows the transformation temperature of the master sample, we can see that during the heating cycle we have one peak which refers to one phase transformation from 36.0 °C to 44.0°C. While during the cooling cycle of the alloy from austenite to martensite will occurs in to stage (two peaks), at temperature (-16.5°C to -16.2 °C and 11.2 °C to 19.9°C). The transformation temperature from an alpha-beta phase or all-alpha phase to all beta is known as the beta transition temperature. The beta transition is defined as the lowest equilibrium temperature at which the material is 100% beta. Below the beta transition temperature, titanium will be a mixture of $\alpha + \beta$ if the material contains some beta stabilizers or it will be all alpha phase if it contains no beta stabilizers. The beta transition is important, because processing and heat treatment are often carried out with reference to some incremental temperature above or below the beta transition.

From Figs (3to5) we can see that with increase the Cr percentage cause decreasing in the transformation temperature especially at the cooling cycle where the transformation is occur at very low temperature, at 2%Cr the transformation start (-17.3°C) and with 3%Cr the transformation start at (-25.8°C) this refer that the Cr is effected on the alloy even at minus which refer that also the Cr lowest the beta transition temperature (beta stabilizer elements) by their eutectoid system. The beta isomorphism group consists of elements that are miscible in the beta phase, including molybdenum, vanadium, tantalum, and niobium. The other group forms eutectoid systems with titanium, having eutectoid temperatures as much as 333 °C (600 °F) below the transformation temperature of unalloyed titanium.

### 3.3. Microstructure:

#### 3.3.1 Scanning Electron Microscope (SEM):

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as conductivity. The device type CAM SCAN MV2300. The magnification applied samples was (50X and 5000X). Figs. (6 to 9) show the results of SEM of the master sample and the samples with different Cr percentage.

#### 3.3.2 Optical Microstructure:

The microstructure was studied by optical microscope in order to show the grains and the phases existing, after the samples were ground, polished, and etched in a solution of (8 ml HF, 10 ml HNO3and 82 $H_2O$) and the magnification applied was (200X, 400X, 600X and 800 X).

Microstructures of Ti–Ta alloys with and without Cr addition have been taken using scanning electron microscopy and light optical microscope with digital camera. The microstructure observed that all the samples alloys has consist mainly of two phases ($\alpha + \beta$) structure as shown in figs. (10 and 11). The beta fleck is a result of the local composition with a higher beta-stabilizer content that results in a local beta transition lower than that of the bulk material. Beta flecks occur if the temperature is above the transition in the “flecked” region. A beta fleck could go undetected if the final processing and heat treatment are conducted at a temperature low enough that the beta transition suppression is not sufficient to cause a microstructure perturbation. Beta flecks are more of a problem with near-beta alloys; they are observed macroscopically as shiny spots or flecks. Their appearance is similar in (α + β) alloys. The beta-stabilizer enrichment in the flecked regions of beta alloys, however, is sufficient to stabilize the beta down to room temperature. To guarantee material that will be fleck-free, producers must solution treat samples at a certain temperature below the beta transition, assuring the user that the material will not form beta flecks if heat treated to a temperature up to or below the test temperature. The material will then form alpha, but beta fleck regions will be above or much nearer the transition. Therefore, they will be void of alpha or contain a significantly lower volume fraction of alpha upon cooling to room temperature. These regions in beta alloys will be harder, will have higher strength and lower ductility, and will have lower low-cycle fatigue strength than the bulk material.

In alpha-beta and beta alloys, some equilibrium beta is present at room temperature. A non-equilibrium, or metastable, beta phase can be produced in alpha-beta alloys that contain enough beta-stabilizing elements to retain the beta phase at room temperature on rapid cooling from high in the α + β phase field. The composition of the alloy must be such that the temperature for the start of martensite formation is depressed to below room temperature. One hundred percent beta can be retained by air cooling beta alloys. The decomposition of this retained beta (or martensite) is the basis for heat treating titanium alloys to higher strengths.

### 3.4 Vickers micro hardness:

Hardness measurements were made for master sample and these values will be compared with those of the prepared samples with Cr additives. The hardness of these alloys was taken by using vickers micro hardness tester type (TP μP-A, HV-1000), where the average of 5 readings was taken. All hardness values were taken at a load of 1Kg.

From the Fig. (12) show that measurement hardness value of master sample higher than that for samples with Cr additives in hardness may be attributed to some phases and pores localized on the surface and can be attributed to the fact that sample has more porosity than master sample.

### 3.5 Porosity :

Duo to the use of powder metallurgy method to produced samples, this test become necessary to see the effect of this method on the porosity of samples and the effect of porosity on shape memory property. The porosity percentage was measured by using Archimedes method. This method include measuring the weight of dry samples, then the samples immerse in water for 24 hours, then we weight the samples after cleaning their surface by cloth, and finally we weight the samples while they placed in basket and immersed in water. The porosity is measured according to this Formula:

Porosity% = [(Ws –Wd) / (Ws –Wn)] *100 (1)

Where:

Wd: weight of dry sample.

Ws: weight of saturated samples.

Wn: weight of immersed sample

From Fig. (13) we can see that the porosity percentage of the sample increase with increasing Cr content that is mean the porosity of the master sample is lower than that of samples with Cr this is agree with the hardness results and is due to the manufacture and preparation procedure since the particle size of the Cr powder is almost have similar size of master sample which may cause non suitable particle size distribution that result in increased the porosity percentage as the amount of Cr increased .

### 3.6. Corrosion Test:

Because of the importance of the Ti-base shape memory alloys and their use in important regions within the human body we had make the corrosion test on the research samples in order to know the corrosion behavior of these samples and to determine the period of validity in human body. In this test we use three different body solutions; artificial saliva, Ringer's solution and synthetic blood plasma as show in table (2).

The corrosion test was conducted on the samples at temperature 37°C with 1.76 $Cm^2$ in area. The test was conduct by using these steps:

1- Mounting of samples.

2- Grinding and polishing, each sample grinded with SiC emery paper different grits started from 120,600, 1200 grit to get flat and scratch free surface and finally these samples were polished with smooth cloth.

3- Calculation the OCP (open circuit potential) of each sample in the three different solutions, the open circuit potential measurement was maintained up to5 minute with reading every10 second.

4- calculation of corrosion rate by using this formula:

Rmpy = 0.13* Icorr. * Equivalent weight of alloy/ alloy density (2)

The corrosion resistance of a pure metal or an alloy strongly depends on the environment where it is exposed, the chemical composition, temperature, velocity and so forth. The excellent corrosion resistance of pure Ti and its alloys results from the formation of very stable, continuous, highly adherent, self- rehealed and protective oxide films (mainly $TiO_2$) on metal surfaces within milliseconds in a wide range of corrosive media with all pH ranges, and the outstanding corrosion capacity of Ta and its alloys are by contrast because of the formation of the protective oxide films (mainly pentoxide$Ta_2O_5$). Thus, those$TiO_2$ and$Ta_2O_5$ oxide films can definitely result in the expected superior corrosion resistance of Ti–Ta alloys.

Ti-30% Ta alloys have current densities smaller than those of the other materials, which indicates that the oxide films (mainly $Ta_2O_5$) formed on the surfaces of Ti–30% Ta alloys can more effectively prevent an exchange of electrons and ions than those (mainly $TiO_2$) formed on the surfaces of the other materials, and thus the $Ta_2O_5$ oxide film is stronger and more stable than the $TiO_2$ oxide film. The compositions of the corrosion products formed on the surfaces of studied Ti-Ta alloys change predominately from $TiO_2$ to $Ta_2O_5$ and the negative free energy of $Ta_2O_5$ is relatively higher than that of $TiO_2$ oxide, which are related to the noble shift of anodic polarization curves of studied Ti-Ta alloys with increasing Ta content according to the relationship between free energy and electrochemical potential. As mentioned above, the $TiO_2$ oxides have been extensively observed on the surfaces of Ti and its alloys when exposed in the moist media with the air or moisture.

Figs. (12 to14) shows the corrosion behavior and the corrosion rate of all samples which were tested by using three different body solutions (artificial saliva, Ringer's solution and Synthetic blood plasma) Generally, addition of alloying elements such as Cr decreases the corrosion current density of master alloy. It is known that any factor that enhances the value of ($i_{corr}$) results in an enhanced value of the corrosion rate on pure kinetic ground. The rate ($C_R$ mpy) of corrosion in a given environment is directly proportional with its corrosion current density ($i_{corr}$). The decreasing in corrosion rate was enhanced with the decreasing in cathodic and anodic tafel slopes. These results show the possibility of using Ti-Ta alloys in the dentistry. Corrosion test in all solutions for Ti-Ta alloys gives variation in corrosion parameters such as $E_{oc}$, $E_{corr}$, $i_{corr}$ and tafel slopes. But the decreasing in corrosion current density noted when Cr element was added to master alloy, i.e. the decreasing in corrosion rate was occur in Ti-Ta alloy with 1, 2 and 3% Cr in Ringer solution. This means that the later alloy was used in human body as implant. it is also important to know that the reason of increase in corrosion rate when adding Cr to the master sample is due to Cr is corroded more and the bulk is protected, But though the activity of Cr is less than that of Ti, the Ti from a protective oxide film helps in keeping the corrosion rate not to influenced by the Cr addition.

## 4. CONCLUSIONS :

From the result of adding the chromium to Ti-Ta shape memory alloy we can conclude that:

1. The samples consist of two phases (α and β) this was conclude from XRD and microstructure investigation.
2. From the transformation temperature result we conclude that the addition of Cr result in reduce phase transformation temperature at all percentage.
3. There is a remarkable decrease in hardness due to the increase in porosity percentage when Cr is added.
4. Finally the corrosion behavior of the alloy in general is improved as Cr content increase which means that the alloy attractive to use in human body as implants.

**Table (1): illustrates purity and composition of alloying elements.**

| Alloying Element | purity | Percentage % | Result Alloy at% |
|---|---|---|---|
| Ti | 99.9 | 70 | Master alloy |
| Ta | 99.9 | 30 | |
| Cr | 99.8 | 1%<br>2%<br>3% | 69Ti-30Ta-1Cr<br>68Ti-30Ta-2Cr<br>67Ti-30Ta-3Cr |

**Table (2): Chemical composition of different body solutions**

| Solution type | Chemical composition |
|---|---|
| Artificial saliva | NaCl (0.4g/L), KCl (o.4g/L), $CaCl_2$ (0.78g/L), $NaH_2PO_4$. $H_2O$ (0.69g/L), $Na_2S$. $9H_2O$ (0.005g\L), KSCN (0.3g\L), Urea (1g\L). |
| Ringer's solution | Adding Ringer tablet to o.5 liter of distillated water and heating the solution to temperature 120°C for 15 min. and leaving it to cool .then $Na_2HCo_3$ was added to obtain pH of 7.4.Ringer tablet were obtain from Merck Company Germany. |
| Synthetic Blood plasma | NaCl (6.8g\L), KCl(0.4g\L), $CaCl_2$(o.2), $NaHCO_3$ (2.2g\L), $Na_2HPO_4$ (1.126g\L), $NaH_2PO_4$ (0.026g\L), $MgSO_4$ (0.1g\L). |

**Table (3): Corrosion parameters of alloys in artificial saliva**

| **Alloy composition at%** | **-Ocp mV** | **$-E_{corr.}$ mV** | **$i_{corr.}$ $mA.cm^2$** | **$-b_c$ $mv.dec^{-1}$** | **+ ba $mv.dec^{-1}$** | **Corrosion rate mpy ($*10^{-6}$)** |
|---|---|---|---|---|---|---|
| Master (70Ti-30Ta) | 312 | 342.6 | 0.22 | 100.4 | 90.3 | 0.073 |
| (69Ti-30Ta-1Cr) | 267 | 388.4 | 3.75 | 122.7 | 63.2 | 0.744 |
| (68Ti-30Ta-2Cr) | 285 | 331.5 | 2.03 | 103.8 | 72.1 | 0.6708 |
| (67Ti-30Ta-3Cr) | 308 | 340 | 1.82 | 78 | 83.6 | 0.6014 |

**Table (4): Corrosion parameters of alloys in Ringer solution**

| Alloy composition wt% | -ocp mV | $-E_{corr.}$ mV | $i_{corr.}$ $mA/cm^2$ | $-b_c$ $mv.dec^{-1}$ | + ba $mv.dec^{-1}$ | Corrosion rate mpy ($*10^{-6}$) |
|---|---|---|---|---|---|---|
| Master(70Ti-30Ta) | 144 | 221.1 | 4.31 | 74.7 | 108.5 | 1.4240 |
| (69Ti-30Ta-1Cr) | 143 | 355.3 | 0.56 | 65.2 | 112.3 | 0.185 |
| (68Ti-30Ta-2Cr) | 178 | 264.0 | 1.96 | 78.2 | 99.4 | 0.647 |
| (67Ti-30Ta-3Cr) | 211 | 272.1 | 2.16 | 89.8 | 75.8 | 0.7137 |

**Table (5): Corrosion parameters of alloys in blood plasma solution**

| **Alloy composition wt%** | **-ocp mV** | **$-E_{corr.}$ mV** | **$i_{corr.}$ $mA/cm^2$** | **$-b_c$ $mv.dec^{-1}$** | **+ba $mv.dec^{-1}$** | **Corrosion rate mpy ($*10^{-6}$)** |
|---|---|---|---|---|---|---|
| Master(70Ti-30Ta) | 437 | 440.1 | 4.31 | 110.4 | 103.0 | 1.424 |
| (69Ti-30Ta-1Cr) | 765 | 654.4 | 17.19 | 162.5 | 66.6 | 5.680 |
| (68Ti-30Ta-2Cr) | 702 | 679.2 | 13.5 | 144.6 | 73.8 | 4.4610 |
| (67Ti-30Ta-3Cr) | 600 | 681.8 | 7.79 | 92.3 | 136.0 | 2.574 |

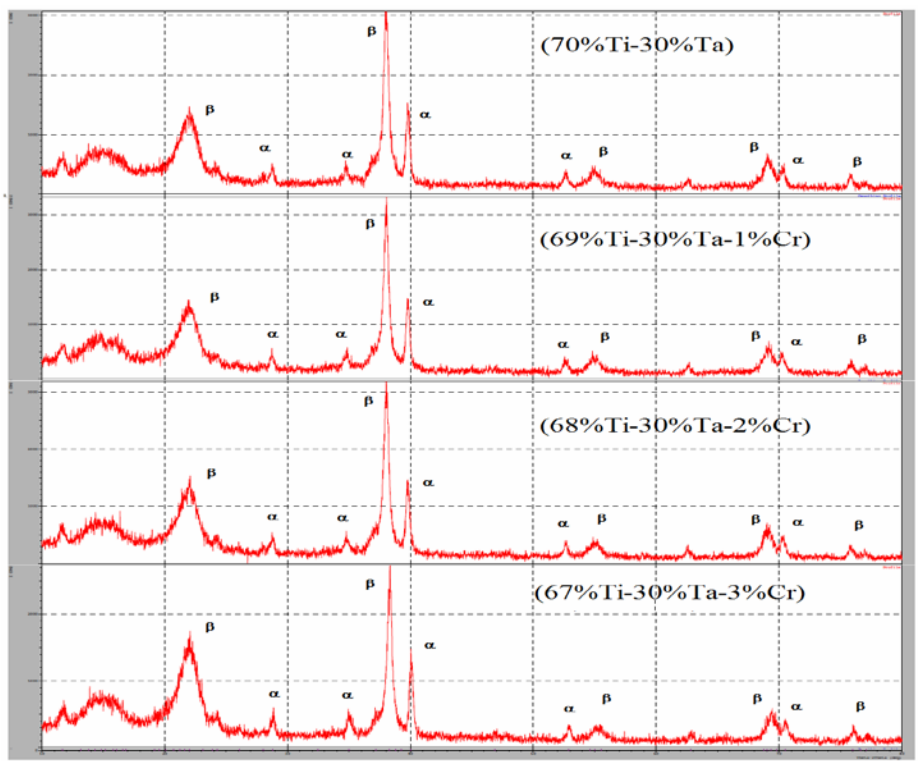



**Fig. (1): XRD pattern of samples with and without Cr addition.**

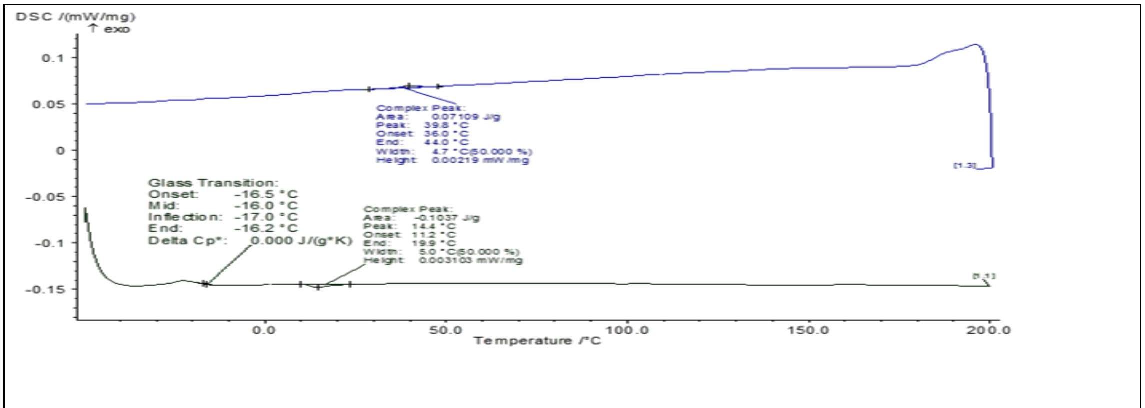



**Fig. (2): Transformation temperature of master sample (70%Ti-30%Ta)**

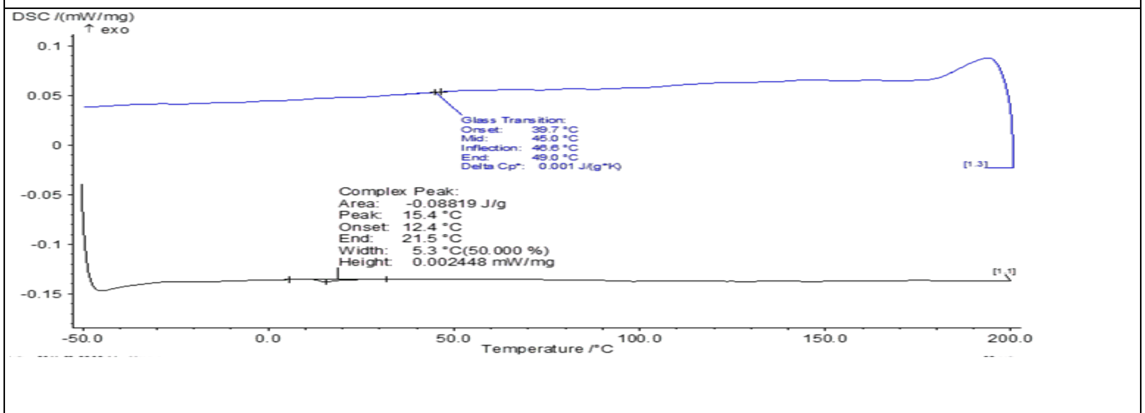



**Fig. (3): Transformation temperature of the sample (69%Ti-30%Ta-1% Cr)**

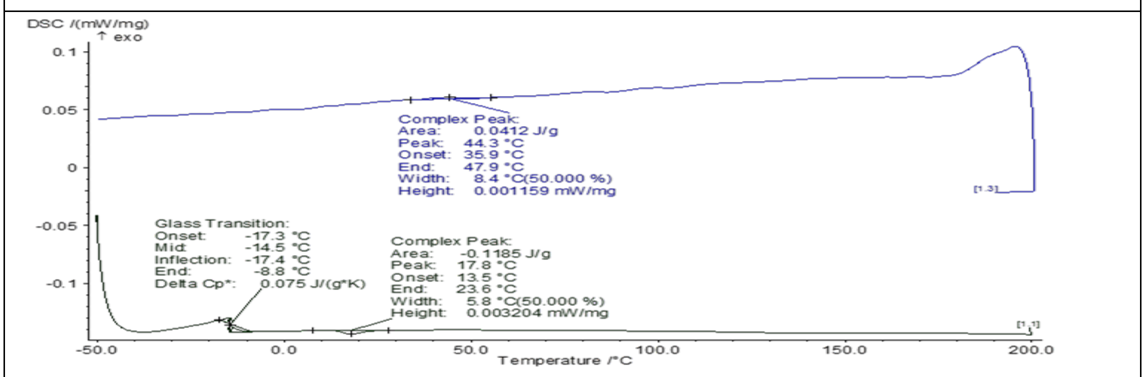



**Fig. (4): Transformation temperature of the sample (68%Ti-30%Ta-2%Cr)**

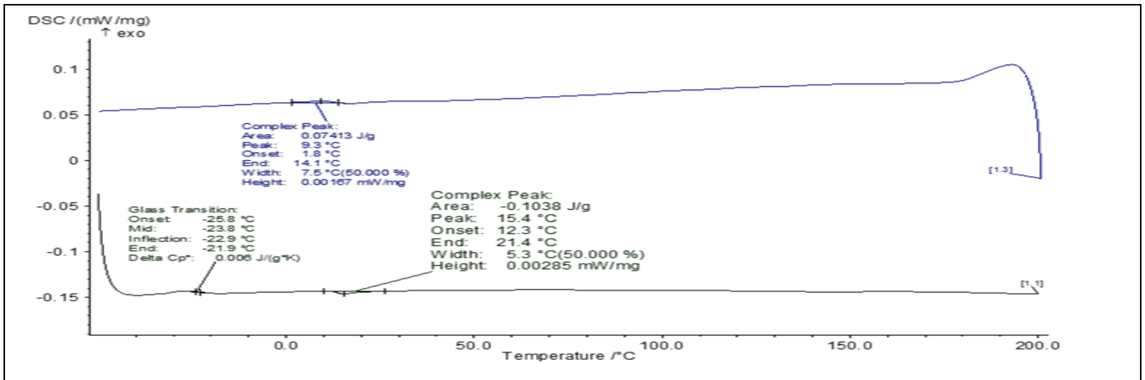



**Fig. (5): Transformation temperature of the sample (67%Ti-30%Ta-3%Cr)**

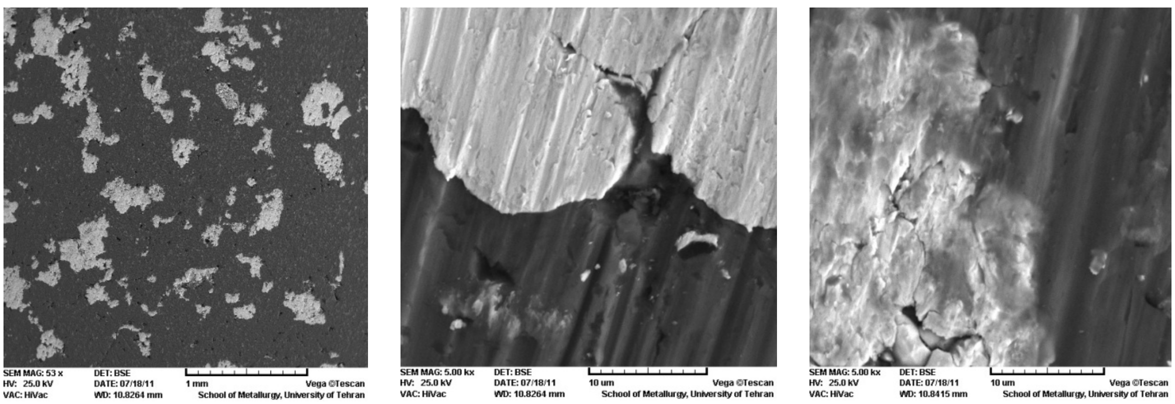



**Fig. (6): SEM of Master sample (70%Ti-30%Ta)**

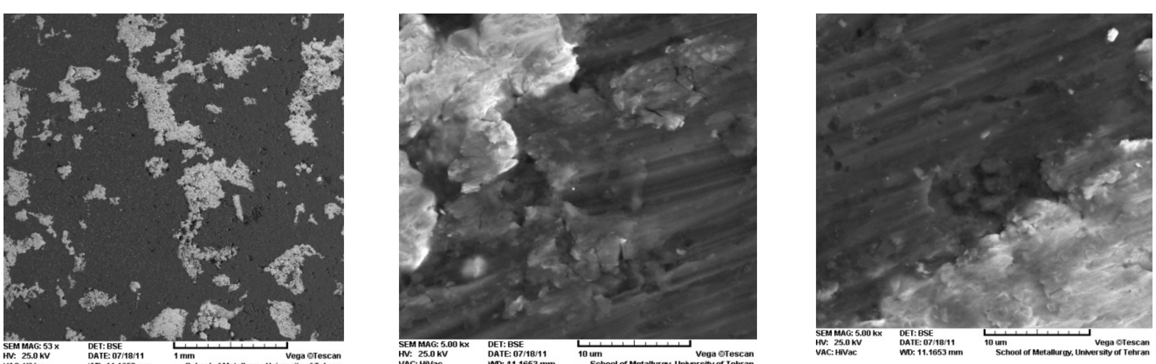



**Fig. (7): SEM of (69%Ti-30%Ta-1%Cr)**

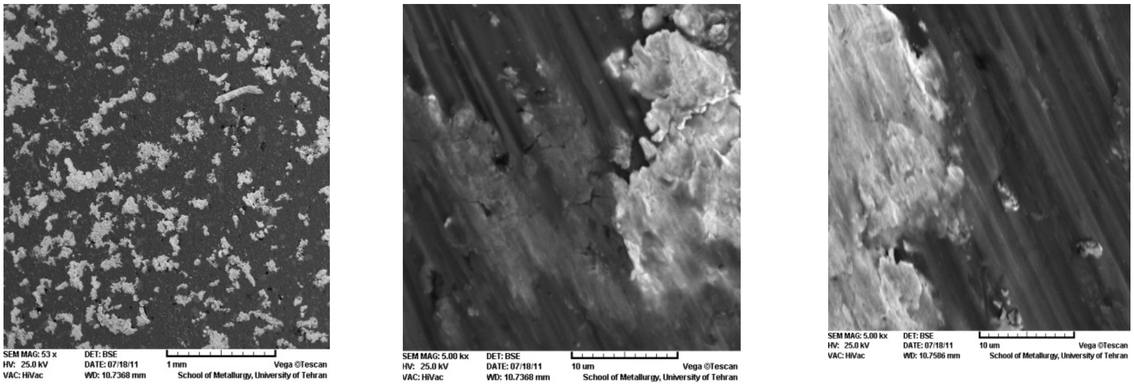


**Fig. (8): SEM of (68%Ti -30%Ta-2%Cr)**

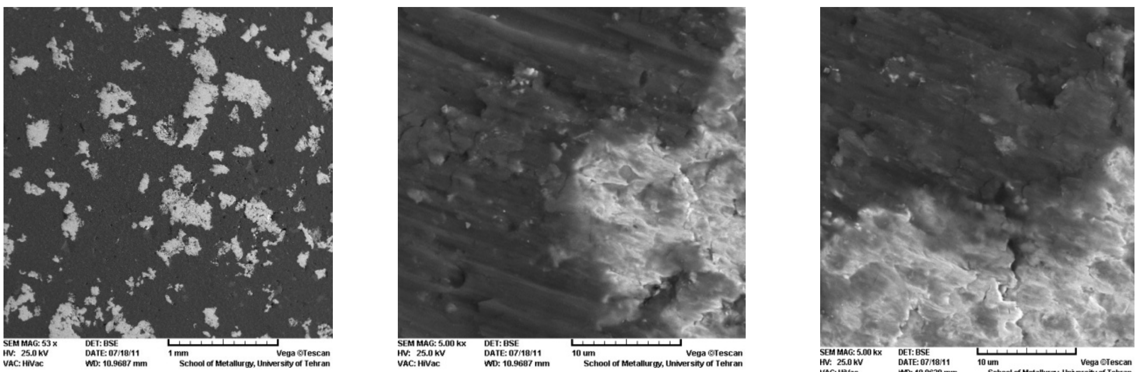


**Fig. (9): SEM of (67%Ti-30%Ta-3%Cr)**

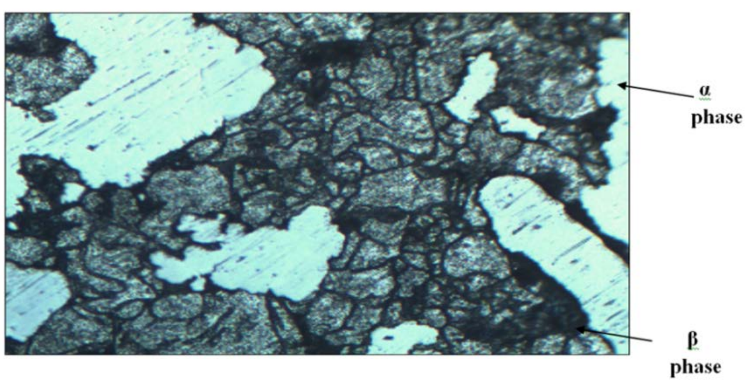
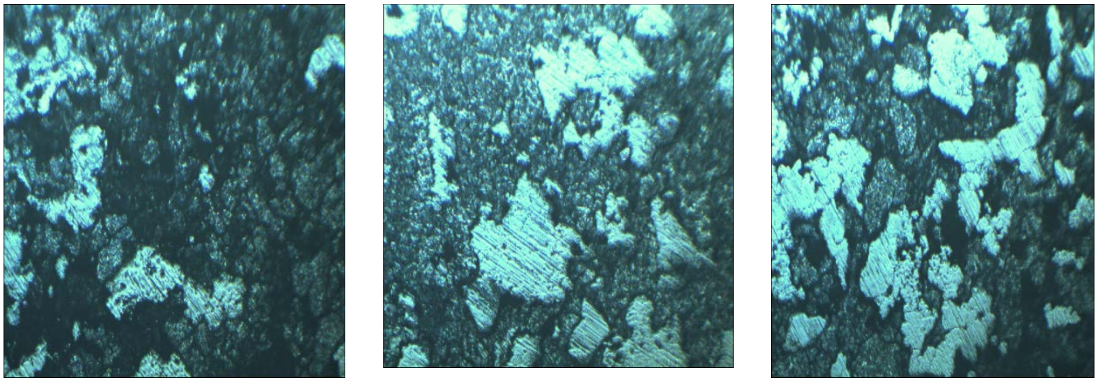



**Fig. (10): Optical microstructure master sample (70%Ti-30%Ta)**



**(69%Ti-30%Ta-1%Cr) (68%Ti-30%Ta-2%Cr) (67%Ti-30%Ta-3%Cr)**

**Fig. (11): Optical microstructure of the sample with Cr addition**

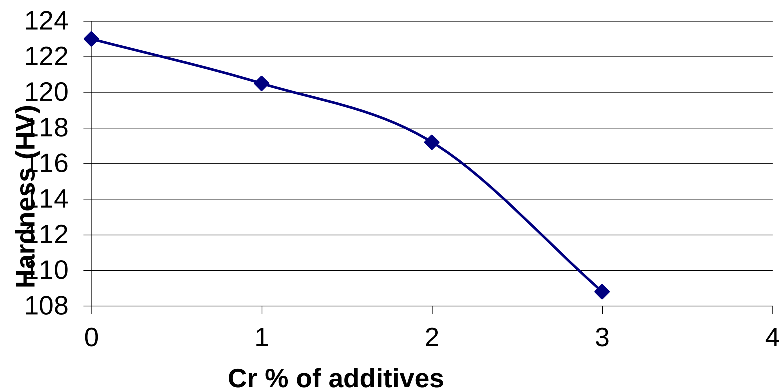



**Fig. (12): Hardness values for the sample with and without Cr addition**

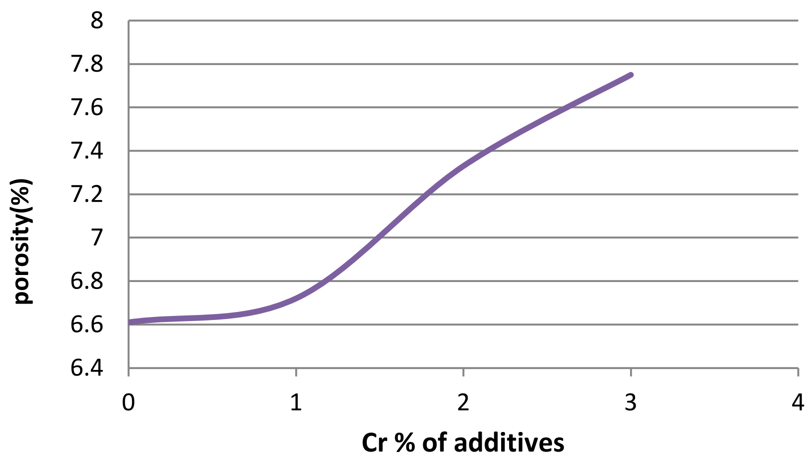



**Fig. (13): Porosity percentage for the samples with and without Cr addition**

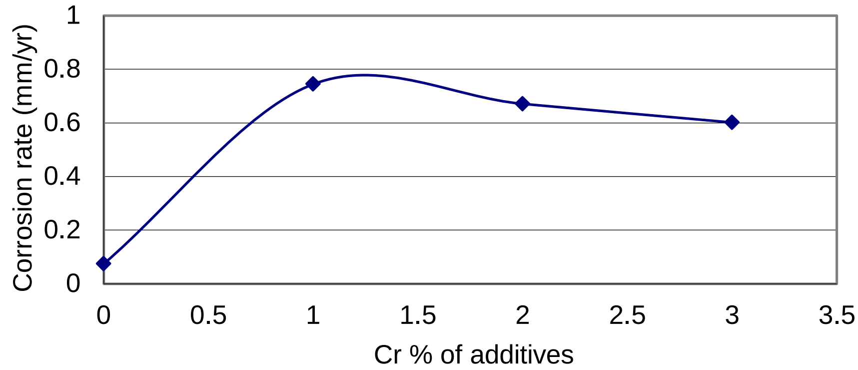



**Fig. (14): Corrosion rate (mm/yr) for the samples with and without Cr additives in saliva Solution**

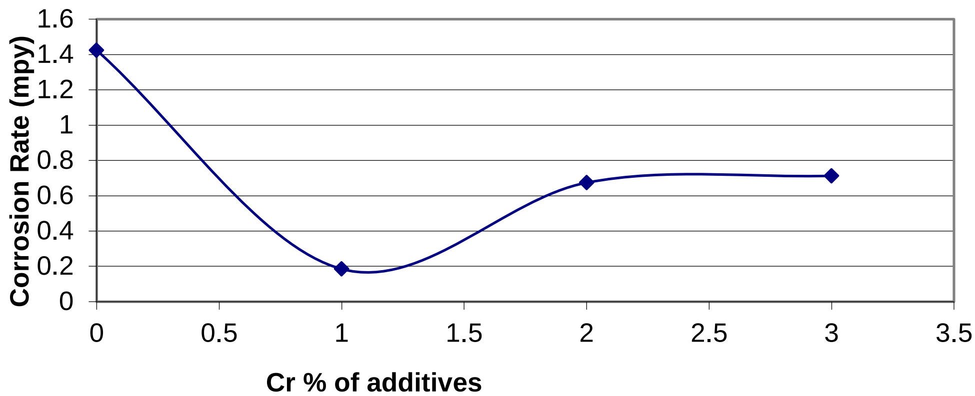



**Fig. (15): Corrosion rate (mm/yr) for the samples with and without Cr additives in Ringer Solution**

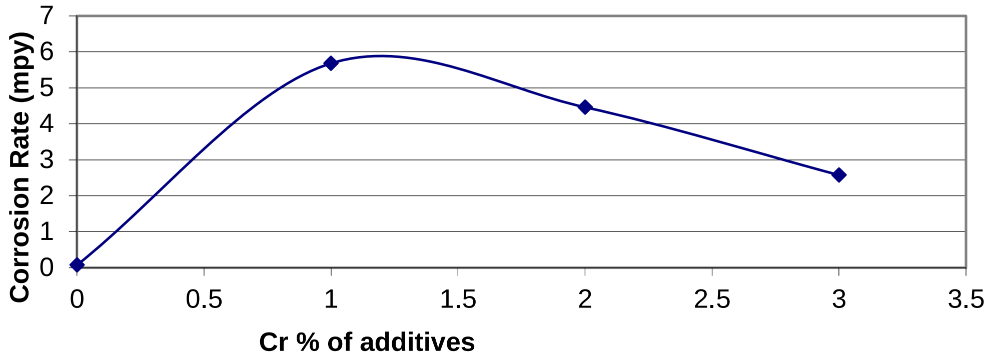



**Fig. (16): Corrosion rate (mm/yr) for the samples with and without Cr additives in blood plasma Solution**

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