Effect of Tungsten additions on Microstructure and Corrosion resistance of F75 alloy.

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Abstract. For many surgical applications such as knee implant, metal-to-metal Hip jointing and dental implants, CoCrMo alloys are the main choice. The present study aims to study the effect of Tungsten on Microstructure and Corrosion resistance of CoCrMo (F75) alloy. Tungsten has been added to the base alloy in various weight ratios (0.5, 1 and 1.5 wt. percent). The alloys have been made using powder metallurgy which has been sintered with two stages at 500°C (2 h) and 850°C (6 h) under Argon atmosphere. Microstructures observation, Corrosion resistance, open circuit potential and Brinell macro-hardness, have been performed. In the microstructure test this phase (CoCr and CoCrMo) was appeared. Corrosion test results have shown that with the addition of (1.5% W) the highest corrosion resistance was found, which gives the lowest rate of corrosion (4.310 mpy) in Ringer's solution. The hardness of F75 alloy improve after the addition of tungsten in Ringer's solution, also hardness increases as tungsten additives increase, which have the highest percentage (1.5% W) gave the highest hardness.

Keywords: CoCrMo alloys, F75 alloy, W addition, Corrosion resistance , Powder Metallurgy.

1. Introduction

Biomaterials are the materials which used in the constituents planted into the body as a substitute for unserviceable part in the body. Biomaterials include metals, polymers and ceramics. Lane introduced metal implants in 1895 when he found a metal plate for the fixation of bone fractures. early on, metal implants had several problems including corrosion and lack of strength. [1,2]. Cobalt based alloys are used for different aspects such as economical, industrial and even in health. Cobalt chrome alloys are widely used for medical implant prostheses because they are highly biocompatible and because of the spontaneous formation of passive layers which provide high resistance against corrosion. They are used when high stiffness, or highly polished material is required which is extremely wear-resistant. For many surgical applications such as knee implant, metal-to-metal Hip jointing and dental implants, CoCrMo alloys are the main choice. [3].
Due to their excellent wear and corrosion resistance, CoCrMo alloys are used for medical implants. The CoCrMo alloys are composed of (58.9 to 69.5% Co, 27.0 to 30% Cr, 5.0 to 7.0% Mo) and a small quantity of other elements (Mn, Si, Ni, Fe and C), which complying with ASTM standard of F75 or F1537 for cast and wrought alloys [4]. Currently Co Cr-Mo alloys are useful in orthopedic implants like the replacement of hip and knee joints because of their good wear resistance and corrosion resistance[5,6]. In 2010, Rodrigues focused on powder metallurgical processing of Co, 28%Cr, 6%Mo for dental implants. The results show that the physical, mechanical and electrochemical properties of the alloy are affected by a small variation of the sintering temperature with comparison of samples with different sintering temperatures[7]. In 2013, Xiaoying Li studied the surface modification of a medical grade Co-Cr-Mo alloy by low temperature plasma surface alloying with nitrogen and carbon. The study aimed to improve the hardness, wear resistance and corrosion resistance of alloy (Co-Cr) by plasma surface alloying with nitrogen and with both (carbon and nitrogen) at low temperatures (300 and 400°C). The results showed that the optimized treatment environment have produced very promising surface layers on C-Cr alloy for biomedical applications[8]. In 2020, Xin Dong investigated the influence of microstructure on corrosion behavior of Selective laser melting(SLM) and Cast Co-Cr-Mo-W alloy by using electrochemical techniques. The passive property and non-corrod-ibility of SLM Co-Cr-Mo-W alloy were mainly ascribed to the microstructure (content and structure distribution of precipitates). The higher content of precipitates can cause severe microseggregation phenomenon and form an inhomogeneous structure, which is the main reason for the inferior corrosion resistance. In addition, the segregated large precipitates work as effective micro-cathode, resulting pitting corrosion and increased corrosion rate[9].

2. Experimental Part

Powders and its Tests: Table (1) details the average particle size and purity of the materials powders used in the preparation CoCrMo (F75) alloys

| Material(Powder) | Purity | Average particle size (μm) | Source |
|-----------------|--------|-----------------------------|--------|
| Cobalt          | 99.95  | 16.66                       | Sky, Spring Nanomaterials,Inc/USA |
| Chrome          | 99     | 38.96                       | Sky, Spring Nanomaterials,Inc/USA |
| Molybdenum      | 99.9   | 11.17                       | Sky, Spring Nanomaterials,Inc/USA |
| Manganese       | 99.9   | 6.438                       | Sky, Spring Nanomaterials,Inc/USA |
| Nickel          | 99.9   | 11.11                       | Sky, Spring Nanomaterials,Inc/USA |
| Silicon         | 99     | 22.24                       | Sky, Spring Nanomaterials,Inc/USA |
| Iron            | 99.7   | 6.229                       | Sky, Spring Nanomaterials,Inc/USA |
| Carbon          | 99.8   | 8.105                       | Sky, Spring Nanomaterials,Inc/USA |
| Tungsten        | 99     | 22.72                       | Sky, Spring Nanomaterials,Inc/USA |
2.1. Specimens Preparation

Powder metallurgy technique was used to prepare the specimens under an Argon atmosphere. The first stage of the preparation is to calculate the weight of powder by using Sensitive Balance type (L220S–D), Germany, with (± 0.0001 accuracy), when the main mixture of F75 contains (60.4% Co, 28% Cr, 6% Mo, 2.5% Ni, 1% Mn, 1% Si, 0.75% Fe, 0.35% C). Then, mixing the weighted powders by planetary automatic ball mill. Steel balls with different diameters have been used for 5 hours in order to get fine and homogenous distribution of powder particles. In an electrical hydraulic press, the (4g) powder mixture was compacted by using cylindrical die (one direction) to produce a disk sample with a dimension of 13mm in diameter and 5mm in thickness, that samples used for (corrosion, hardness, and microstructure). Lubricant of graphite has been used for the die walls from inside to reduce the friction during the pressing process. The compacting pressure was 750 MPa. A tube furnace was used to sinter the green compacted samples. The sintering process was performed in an argon atmosphere to inhibit the specimens oxidation. Where the sintering process includes heating the green compact from room temperature to 500°C with a heating rate of 20°C/min and soaking for 2 hours at 500°C, then heating from 500°C to 850°C and then soaking for 6 hours at 850°C, and in the final stage, the sintered samples were left in the furnace to cool down slowly with a continuous pump of argon until reaching room temperature. Table (2) clarifies the code and composition of the alloys which are used in this work.

Table (2): The code and composition of alloys

| NO | Alloy Code | Chemical Composition (wt.%) |
|----|------------|-----------------------------|
| 1  | A          | F75 Base alloy              |
| 2  | C1         | F75 + 0.5% W                |
| 3  | C2         | F75 + 1% W                  |
| 4  | C3         | F75 + 1.5% W                |

Fig (1): Heating cycle in sintering
3. Tests:

3.1. Light Optical Microscope (LOM)

The sintered specimens were grinding with SiC paper grits as (180, 400, 600, 800, 1000, 1200, 1500 and 2000) and then it polished by using a diamond solution (1 µ). The samples were etched at the room temperature by (15mL HNO3, 15mL Acetic acid, 60mL HCL, and 15mL distilled water) [10].

A microscope type (BEL PHOTONICS) was used.

3.2. Macrohardness Measurement

The macrohardness Brinell test includes the use of load (62.5kg/mm²) on the specimen to measure its hardness by a carbide ball diameter of (2.5 mm) for (10 sec). The average value used was taken for three readings for each specimen to analysis the behavior of the alloys.

4. Corrosion Test

4.1. Open Circuit

The electrolytic cell is used a capacity of 500 ml. The samples of this tests were immersed in the Ringer solution. By use of a saturated calomel electrode the potential of the working electrode is measured (SCE).

Between the working electrode and the reference electrode a voltmeter is connected saturated. Open circuit potential measurement for each sample was performed for three hours.

After immersion the sample in solution the first record was taken immediately then the voltage was monitored for the required period of test at an interval of (5min).

4.2. Electrochemical Tests

Because of the importance of the CoCrMo alloys and their use as implants within the human body, corrosion tests should be done on specimens to determine the behavior of corrosion of specimens in the human body.

In body solution Ringer's solution, the corrosive behavior of CoCrMo was studied. Ringer's solution have chemical composition as illustrated in table (3).

| NO | Constituent     | (g/L) |
|----|----------------|-------|
| 1  | NaCl           | 6     |
| 2  | NaC3H5O3       | 3.2   |
| 3  | KCl            | 0.4   |
| 4  | CaCl2,2H2O     | 0.27  |
5. Results:

5.1. Light Optical Microscope

Figures (2,3,4,5) illustrate the microstructure of etched master alloy A and C1,C2 and C3 with (0.5, 1 and 1.5)%wt of tungsten after sintering with different magnifications.

As shown in the previous figures, the microstructure for mentioned alloys showed grain boundaries, pores with different size in addition to present phases.

The microstructure of etching A, C1, C2 and C3 appeared a multiphase structure in which CoCr phase are embedded in uniformly matrix (CoCrMo-f.c.c) these result are similar to [12].

There are many pores with different size can be seen on the surface, that is a natural manner since the samples were prepared by powder metallurgy technique [13].

Fig (2): Microstructure for A alloy after sintering and etching with different magnifications

Fig (3): Microstructure for C1 alloy after sintering and etching with different magnifications
5.2. Hardness

The hardness value of CoCrMo alloys increases with increasing Tungsten addition as shown in figure (6). Where, the hardness of the Master alloy (A) is 86.16 and it increased to 87.3 for C1 alloy, then it increased to 88.5 for C2 alloy and then to 97 for C3 alloy. This confirms the role of adding tungsten in obstruction the movement of dislocations and therefore increased alloy hardness. These results are compatible with [9]
5.3. Open Circuit Potential

For all alloys tested, the OCP-time in the Ringer solution was measured at 37 ±1°C with respect to SCE. The evolution of corrosion alloys can be shown here as (and it is shown in Figure 7) The time period from (0 to 160) minutes and the interval was 5 minutes.

The above figures shows the variation of open circuit potential (OCP) with time from which several deduction can be made. The first is that during the first 30 minutes were studied noted the corrosion potential increases at a greatest speed in this period in most case study. This initial increased generally has been shown to be due to the formation and thickening of the oxide film on the metallic surface, resulting in improved corrosion. Afterwards, because of the growth of the film onto the metallic surface so the OCP increases slowly .The second is that when the corrosion potential reaches the stabilize level. The constant OCP means that there is equilibrium between dissolution and deposition [14].
5.4. Electrochemical Tests

It's noted in Figure (8) which refer to the polarization curve of (A) alloy in Ringer’s solution. In cathodic polarization, the current of corrosion decreases with increasing voltage until it reaches the lowest possible value. In anodic polarization, the current of corrosion increases with increasing voltage until it reach voltage at which it decreases suddenly as result to the formation of passive film and with increasing voltage passive film broke and the current increases too.

Figure (8) which represent polarization curve for C1, C2 and C3 alloys in Ringer’s solution with a tungsten ratio 0.5%, 1% and 1.5% respectively, it's clear from figure that the current density decreased excessively after addition of tungsten, So improvement Improvement percentage of corrosion rate as shown in table (4) for C1 is 42.2 but after addition W with 1% the improvement percentage increased and the corrosion current decreased(10.48) and improvement percentage increase to 59.5 for C2 and the best improvement percentage for C3 which reached to 68.1, this results due to the role of tungsten as a noble metal contributed in reduce corrosion rate as controlled the anodic and cathodic polarization parameters.

Fig (8): Potential-dynamic polarization curve for A, C1, C2 and C3 alloys in ringer's solution
Table (4): The polarization parameters of A, C1, C2 and C3 in Ringer’s solution

| Alloy | Icorr(μA/cm²) | Ecorr(mV) | Corrosion Rate(mpy) | Improvement percentage | ba | -bc |
|-------|--------------|-----------|---------------------|-----------------------|----|-----|
| A     | 17.67        | -341.8    | 13.49               | 60.1                  | 52.7 |
| C1    | 10.48        | -428.3    | 7.801               | 42.2                  | 41.9 | 46.1 |
| C2    | 7.07         | -489.4    | 5.458               | 59.5                  | 29.7 | 33.7 |
| C3    | 5.84         | -426      | 4.310               | 68.1                  | 14.2 | 19.9 |

Fig (9): The effect of W content on the corrosion rate of A, C1, C2 & C3 alloys of this work in Ringer’s solution at 37°C.

6. Conclusions

1. Results shown that CoCrMo alloy can produce successfully by powder metallurgy

2. The hardness increased form (86.16 HB) for master alloy to (97 HB) for 1.5 % wt of W.

3. In Ringer’s solution however, the most improvement percentage in corrosion rate was (68.1) with a 1.5% wt of W addition to the master alloy which reduced the corrosion rate from 13.49 to 4.310 (mpy).

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