

STUDYING THE PROPERTIES OF COCRM0 (F75) DOPED Y USING (P-M) TECHNIQUE

DRHAYDAR H. J. JAMAL AL-DEEN¹, ALI HOBIHALEEM² & AMMAR H. KHILFE³

^{1,2}Assistant Professor, Department of Metallurgical Engineering, Materials Engineering College,
University of Babylon, Babylon, Iraq

³Department of Metallurgical Engineering, Materials Engineering College,
University of Babylon, Babylon, Iraq

ABSTRACT

Cobalt alloys are one of the main groups of metallic materials used as implants. They are numbered among biomaterials of good biocompatibility. Their mechanical properties and corrosion resistance are determined by chemical composition and the technology of production as well.

This study aims to investigate the effect of yttrium addition (0.5, 1 and 1.5 wt %) on properties of CoCrMo alloy (F75) prepared using powder metallurgy technique. The corrosion, wear and compressive behavior were investigated using different examination and test including mechanical test (hardness, compression and wear) and electrochemical test (open circuit and potentiodynamic polarization). The results revealed that the addition of Y has a notable effect on the porosity of sintered CoCrMo causing increasing in porosity. The hardness decreases with increasing Y addition. The addition of Y decreases the compressive strength and it's decreased as addition increased. On the other hand the wear rate of CoCrMo (with and without Y addition) increases as the time and load increase, however, Y addition improve wear resistance, the improvement increased with increasing Y content. The corrosion resistance of F75 alloy was improved by Y addition in both artificial saliva and Hank's solution, the improvement increased as Y addition increased. The corrosion current density for alloys in artificial saliva is lower than that in Hank's solution.

KEYWORDS: CoCrMo alloy, F75 Alloy, Y Addition, Corrosion Resistance, Wear Resistance, Compressive Strength

INTRODUCTION

Implants are fabricated from a wide variety of materials, including metals, polymers, ceramics and their composites. Among these materials, metals are an important group [1]. Cobalt chrome alloys are used widely for medical prosthesis such as hip and knee replacements, dental devices and support structures for heart valves because they have a great biocompatibility and spontaneous chromites formation of a passive layer which provides the material high corrosion resistance [2]. They are used where high stiffness, or highly polished, and extremely wear resistant material is required. Wear resistance, mechanical properties, biocompatibility and corrosion resistance may be influenced by the microstructure which depends on the thermal treatment applied to the material [3].

Yttrium was first discovered by Johan Gadolin. The physical appearance is a bright silvery surface like other metals and it's also prepared as a dark gray to black powder with a bit of shine. Like any other rare earth metals yttrium has many uses and the most common use is in phosphors. A phosphor is a material that shines when struck by electrons.

Yttrium phosphors have long been used in color televisions sets and in computer monitors [4, 5].

No research has focused on Yttrium into CoCrMo matrix to improve the physical and chemical properties without affecting the alloy. This research highlights to improve the mechanical and electrochemical properties of CoCrMo alloy by addition different percentages of yttrium (C1 =0.5% Y, C2= 1% Y, C3= 1.5% Y & A= master alloy).

EXPERIMENTAL PROCEDURE

The material powders used to prepare (F75) CoCrMo alloys in this research are demonstrated in table (1). The average particle size was calculated using Better size 2000 laser particles size analyzer, Handheld (XRF) analyzer type (DS-2000)USA, is used to determine the purity of powders.

Table 1: Purity % and Average Particle Size of Materials

Material (powder)	Purity %	Average Particle Size(μm)	Chemical Composition% F75
Cobalt	99.61	55.56	Balance
Chrome	99.86	40.52	28%
Molybdenum	99.28	20.33	6%
Manganese	99.39	52.31	1%
Nickel	99.44	43.26	0.5%
Silicon	99.11	51.47	1%
Iron	99.77	59.34	0.75%
Carbon	99.44	37.44	0.35%
Yttrium	99.56	31.45	(0.5, 1 & 1.5)%

Electrical rolling mixer type (STGQM-1/5-2) used in elemental powders mixing process for (5hr). 800MPa was the stress applied on the metallic powders in order to get green compacting samples by using the electric hydraulic press in a cylindrical die in one direction to produce cylindrical samples with a diameter 10mm. Vacuum tube furnace type MTI (GSL1600X) was used to sinter samples from room temperature to 500C° and soaking 2 hr then heating to 950C° and then soaking for 5hr and then slow cooling to room temperature. All samples after sintering process were grinded by using (180, 220, 320, 600, 800, 1000, 1200, 1500, 2000 and 2500) grit silicon carbide papers, then polished with a diamond past of 15 μm to get a bright mirror finish for the final step. Etching was made at room temperature (60ml HCL, 15ml HNO₃. 15ml acidic acid & 15ml water) [6]. After etching process the samples washed with water and dried. The porosity of sintered samples is calculated according to ASTM B-328 [7]. Macrohardness Brinell tester which used to measure the hardness of the samples with (31.25) kg/mm² as applying weight for (10 sec) and ball diameter (2.5) mm The Compression test was run at a constant loading speed of 0.5 mm/ min. The compressive strength is calculated by using the following equations:

$$\text{Compressive strength (MPa)} = \frac{\text{Maxforce(N)}}{\text{crosssectional .area(mm}^2\text{)}} \quad (1)$$

The Wear test had been covered according to ASTM G 99[8].

$$\text{Wear rate} = \frac{\text{weighth loss(g)}}{\rho\left(\frac{\text{g}}{\text{cm}^3}\right)} \quad (2)$$

The microstructure of the sintered samples was observed by optical and scanning electron microscopy.

The corrosion behavior of CoCrMo studied in two different solutions (artificial saliva and Hank's solution). The

chemical composition of both solutions is illustrated in table (2) and (3) [9]. The PH of artificial saliva and Hank's solution at 37C° were 6.7 and 7.4 respectively.

Table 2: Chemical Composition of Artificial Saliva Solution [9]

NO.	Constituent	(g/L)
1	KCl	1.5
2	Na HCO ₃	1.5
3	NaH ₂ PO ₄ H ₂ O	0.5
4	HSCN	0.5
5	Lactic acid	0.9

Table 3: Chemical Composition of Hank's Solution [9]

NO.	Constituent	(g/L)
1	NaCl	8
2	CaCl ₂	0.14
3	KCl	0.4
4	NaHCO ₃	0.35
5	Glucose	1
6	MgCl ₂ .6H ₂ O	0.1
7	Na ₂ HPO ₄ .2H ₂ O	0.06
8	KH ₂ PO ₄	0.06
9	MgSO ₄ .7H ₂ O	0.06

The electrochemical test involved Open circuit potential (OCP) and Potentio dynamic polarization; electro chemical experiments were performed using three electrodes cell containing and electrolytes similar to natural saliva and Hank's solution. The counter electrode was Pt electrode and the reference electrode was SCE and working electrode (specimen) according to the American society for testing and materials (ASTM).The test was conducted by stepping the potential using a scanning rate 0.4 mV/s from initial potential of 250 mV below the open circuit potential and the scan continued up to 250 mV above the open circuit potential. Corrosion rate measurement is obtained by using the following equation [10].

$$\text{Corrosion rate} = \frac{0.13i_{\text{corr}}(E_w)}{\rho \cdot A} \quad (3)$$

Where:

E.W. = equivalent weight (g/eq.)

A= area (cm²)

ρ = density (g/cm³)

0.13 = metric and time conversion factor

i_{corr} = current density ($\mu\text{A}/\text{cm}^2$).

RESULTS AND DISCUSSIONS

The effect of Y content on the porosity of sintered samples shown in figure (1), there is increasing in porosity after sintering, it can be seen that the porosity of sintered samples increases as the Y content increases.

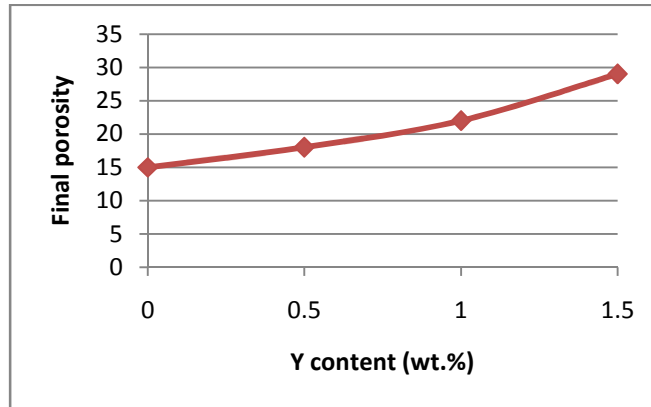


Figure 1: Effect of Y Content on Final Porosity for Alloys A, C1, C2, and C3

The CoCrMo alloys presented significantly higher hardness values in comparison with CoCrMo with Y additive as shown in figure (2), the amount of hardness decreases as the Y content increases. The decreasing of hardness can be attributed to the change of microstructure induced by Y titanium addition. In fact, the lower level of hardness in CoCrMo with Y addition is expected since it is known that the Y addition increases porosity (figure 1) and makes the material more ductile.

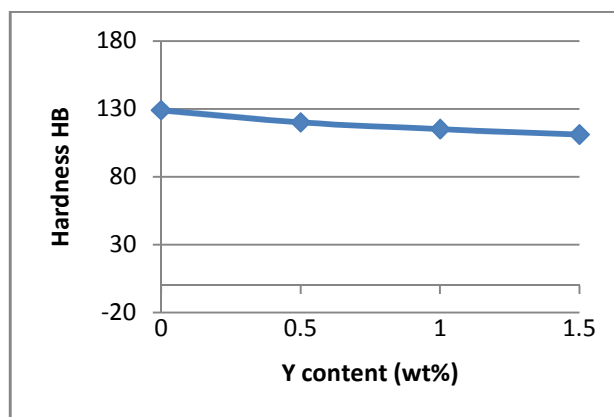


Figure 2: Effect of Y Content on the Hardness for A, C1, C2 and C3 Alloys

The compressive strength for CoCrMo alloys with Y addition are less than master alloy A (figure 3), the magnitude for A (292.84) MPa, C1 (241.91) MPa, C2 (229.18) MPa and C3 (216.45) MPa. This is because alloys with Y addition have low hardness compared with A alloy. In fact this is expected, since yttrium makes the alloy more ductile, therefore the deformation of Y alloys is more than an alloy. If the deformation is high, the area of sample increases, therefore the required stress to achieve a failure condition will decrease. Thus the curve (stress- strain) and compressive strength will decrease compared with A alloy.

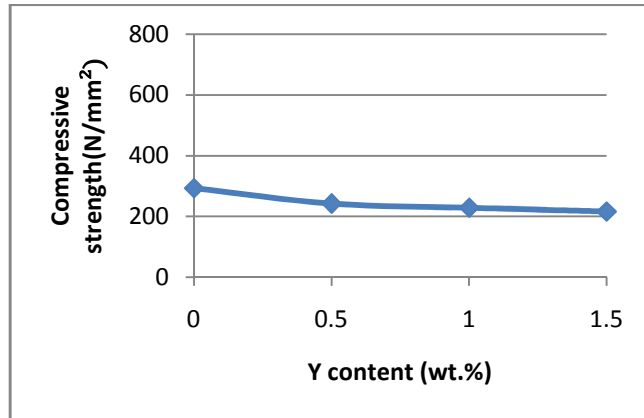


Figure 3: shows Y Content vs. Compression Strength for A, C1, C2 and C3

Samples with (10) mm diameter subjected to wear test under vary loads (1, 2 and 4) N and for different times (5, 10, 15, 20 and 25) min at room temperature. The results have been presented and showed in the following figures:

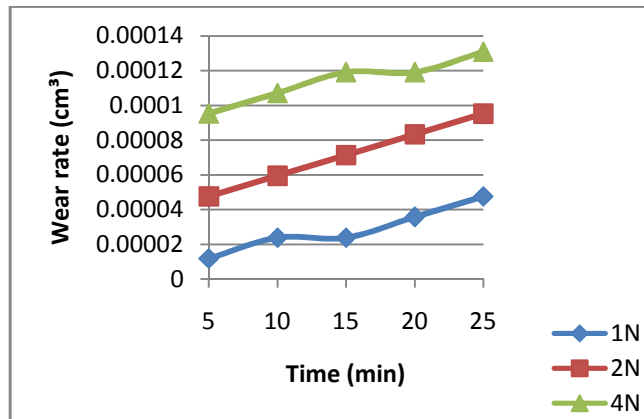


Figure 4: Wear Rate vs. Time for an Alloy under 1, 2 and 4N Load

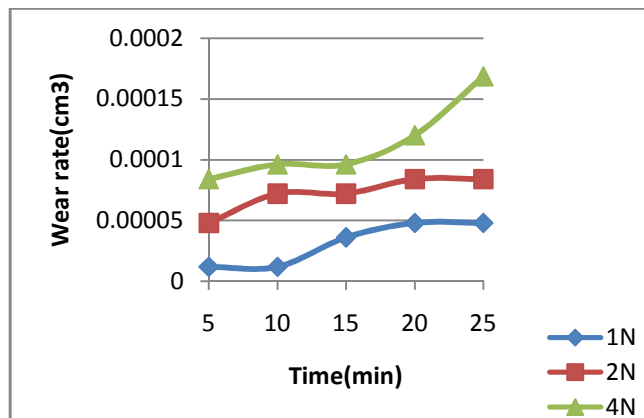


Figure 5: Wear Rate Vs Time for C1 Alloy under 1, 2 and 4N Load

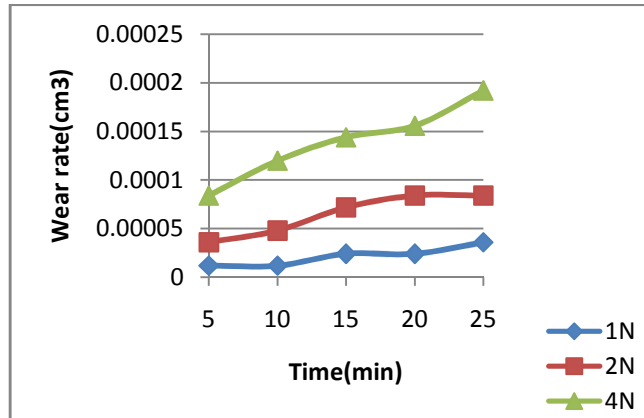


Figure 6: Wear Rate Vs Time for C2 Alloy under 1, 2 and 4N Load

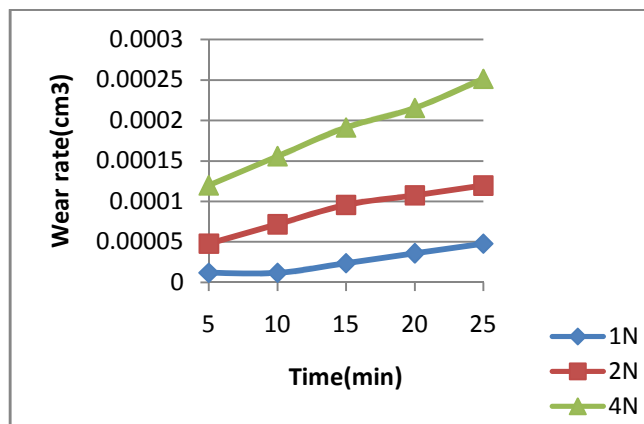


Figure 7: Wear Rate Vs Time for C3 Alloy under 1, 2 and 4N Load

Figure (8) showed the effect of Y addition on the wear rate of A, C1, C2 and C3 alloys under constant load (4N) and constant time (25 min). It can be seen from the mentioned figure that the wear rate increase as the Y content increase. The increases in wear rate is attributed to increase the porosity with increase the Y content, since the friction coefficient decreases with the increasing amount of porosity. The pores play an important role indicating the potential sites of the first micro cracks forming and positively influencing the wear process [11].

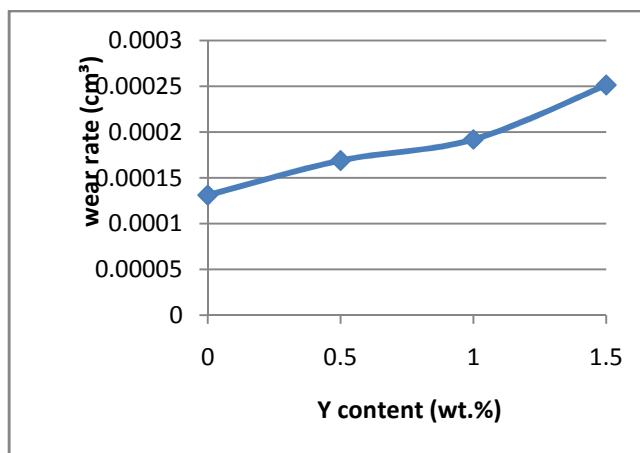


Figure 8: Effect of Y Content on Wear Rate for C1, C2 and C3 Alloys under 4N Load and 25min Time

The OCP-time was measured with respect to SCE in artificial saliva and Hank's solution at $37\pm 1\text{ }^{\circ}\text{C}$ for all tested alloys. Figure (9) shows the evolution of corrosion potential of the alloys throughout time. The time period from (0 to 140) minutes with interval of 5 minutes were potentially reported. The mean values of the OCP were recorded by using two samples for each alloy.

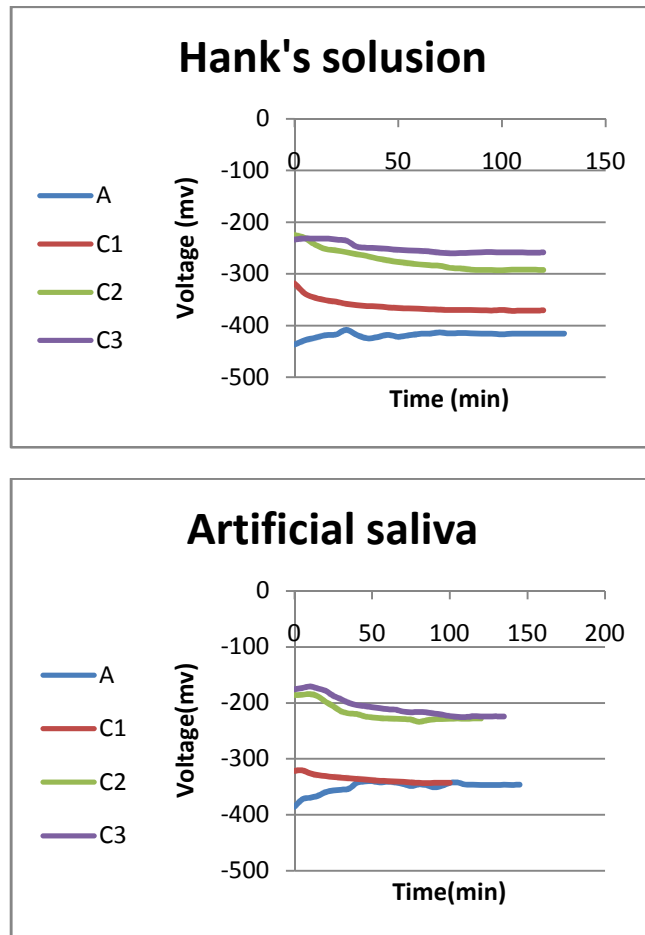


Figure 9: Shows the OCP-Time (a) in Hank's Solution and (b) In Artificial Saliva at $37\pm 1\text{ }^{\circ}\text{C}$ for all Tested Alloys

Figure (9) 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 the corrosion potential increases at a greatest speed in this period in every case study. This initial increasing generally seems to be related to the formation and thickening of the oxide film on the metallic surface, improving its corrosion protection ability. Afterwards the OCP increases slowly because of the growth of the film onto the metallic surface. The second is that the corrosion potential reaches a level from which corrosion potential tends to stabilize. The constant OCP means that there is equilibrium between dissolution and deposition [12].

The data listed in table (4) showed significant improvement in corrosion resistance of CoCrMo alloys with Y additions (C1-176.6%, C2-232% & C3-232%) and the I_{corr} of these alloys ranged between $3.9\text{ }(\mu\text{A}/\text{cm}^2)$ for C1 alloy and $3.23\text{ }(\mu\text{A}/\text{cm}^2)$ for C3 alloy in Hank's solution. It can be noted that the I_{corr} of CoCrMo alloys with Y additions is lower than that for CoCrMo alloy. However the E_{corr} Values for Calloysisgraded from -320.8mV for C1 to -201.6mV for C3 which are greater than E_{corr} for An alloy which is -433.7mV

Table 4: Shows the Corrosion Current (I_{corr.}), Corrosion Potential (E_{corr.}) and Corrosion Rate for all Used Alloys in Hank's Solution at 37 C⁰

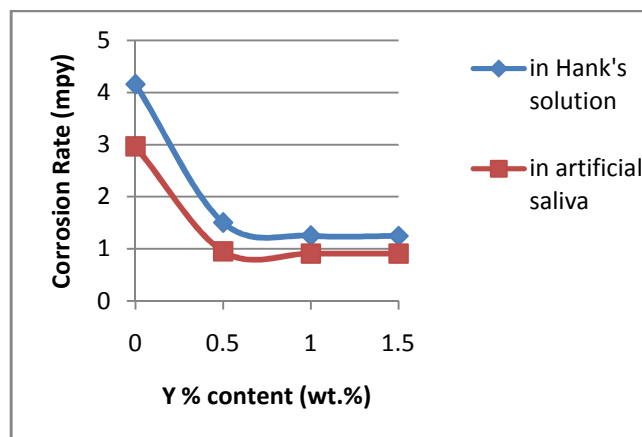
Alloy	Sample Code	I _{corr.} (μA/cm ²)	E _{corr.} (mV)	Corrosion Rate (mpy)	Improvement Percentage%
F(75)	A	10.86	-433.7	4.153833	
C	C1	3.9	-320.8	1.502908	176.6
	C2	3.24	-229.0	1.251389	232
	C3	3.23	-201.6	1.250007	232

There are a noteworthy improvement in corrosion resistance for CoCrMo alloys with Y additives (C1-211.5%, C2-225.2% & C3-228.8%) compared with CoCrMo alloy, I_{corr.} for C alloys ranged between 2.47 (μA/cm²) for C1 alloy and 2.36 (μA/cm²) for C3 alloy in artificial saliva. It can be noted that the I_{corr.} of CoCrMo alloys with Y additives is lower than CoCrMo alloy. However, the E_{corr.} Values for Calloysisgraded from -348.7mv for C1 to -230.2mv for C3

Table 5: Illustrate the Corrosion Current (I_{corr.}), Corrosion Potential (E_{corr.}) and Corrosion Rate for all Alloys Used in This Work in Artificial Saliva at 37 C⁰

Alloy	Sample Code	I _{corr.} (μA/cm ²)	E _{corr.} (mV)	Corrosion Rate (mpy)	Improvement Percentage%
F(75)	A	7.76	-291.8	2.967718	
C	C1	2.47	-348.7	0.952922	211.5
	C2	2.36	-244.9	0.910504	225.2
	C3	2.36	-230.2	0.909452	228.8

The listed data in tables ((4), (5)) cleared that the corrosion current of CoCrMo alloy with Y additives is lower than CoCrMo alloy in artificial saliva and Hank's solution. This can be attributed to the behavior of Y element as a noble element, which enhances the corrosion resistance of CoCrMo alloy. Therefore, the corrosion rate decreases when Y content increase for all samples in two corroded solutions used as shown in figure (10).

**Figure 10: The Effect of Y Content on the Corrosion Rate of A, C1, C2 and C3 Alloys of this Work in Artificial Saliva and Hank's Solution at 37 C⁰**

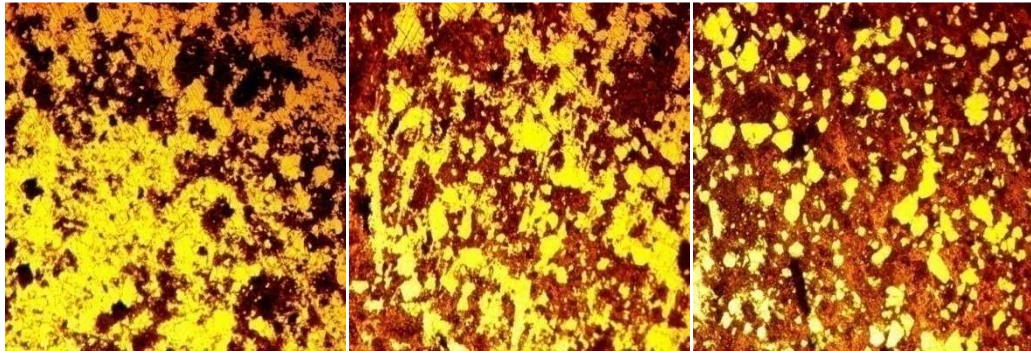


Figure 11: Microstructure for C1, C2 and C3 Alloys after Sintering and Etching (100x)

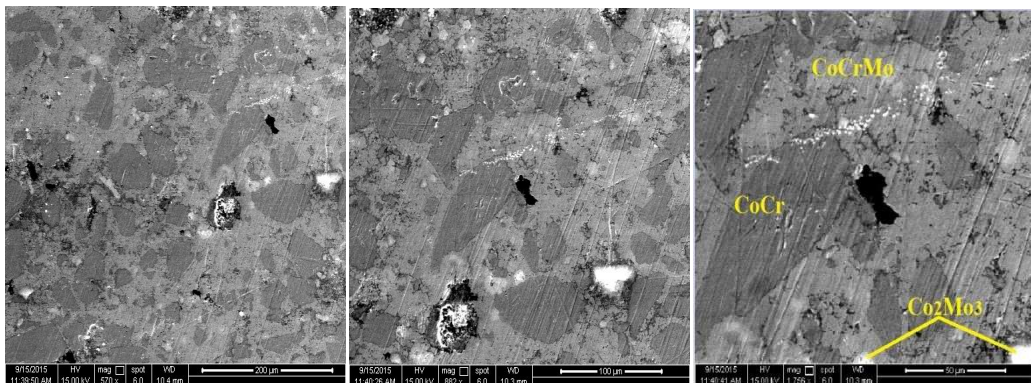


Figure 12: SEM Images for Etched C3 Alloy with Different Magnification

CONCLUSIONS

The addition of Y has a notable effect on the porosity of sintered CoCrMo alloys, also Y addition leads to increasing the porosity. The hardness decreases with addition and increase Y content. The addition of Y decreases the compressive strength and it's decreased as addition increase. The Wear rate of CoCrMo (with and without addition) increases as the time and load is increased. The wear resistance decreased with addition of Y element and it's decreased as Y increase. The corrosion resistance of CoCrMo alloy improved after the addition of Y in both artificial saliva and Hank's solution. The corrosion resistance increase as Y addition increase. The corrosion current for most used alloys in artificial saliva is lower than that for Hank's solution.

REFERENCES

1. H. Hermawan, D. Ramdan and J. R. P. Djuansjah, "Metals for Biomedical Applications". Faculty of Biomedical Engineering and Health Science, University Teknologi Malaysia. Chapter 17, 2011
2. H. Hermawan, D. Dubé and D. Mantovani. "Developments in metallic biodegradable stents". Acta Biomaterial, 2010, 6, 1693
3. M. Walter. "Benefits of P/M Processed Cobalt-Based Alloy for Orthopaedic Medical Implants", Carpenter Technology Corp., Wyomissing, PA, USA, 2006
4. chemistryexplained.com/elements/T-Z/Yttrium. foundations and applications(cited 2015)
5. L. Hanyi, W. Fuhui and B. Linxiang. "Effect of yttrium on the hot-corrosion resistance of sputtered Co-Cr-Al

- coatings". Elsevier materials science and engineering, Vol: 123, P: 123-128, 1990
6. T. Odahara, H. Matsumoto and A. Chiba "Mechanical Properties of Biomedical Co-33Cr-5Mo-0.3N Alloy at Elevated Temperatures" Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan 2008
 7. ASTM B-328" Standard Test Method for Density, Oil Content, and Interconnected Porosity of Sintered Metal Structural Part and Oil – Impregnated Bearing "ASTM international, 2003
 8. A. S. Hemza " study of micro structure , corrosion and dry sliding wear of copper – aluminum- nickel shape memory alloys " , MS.C thesis , materials engineering college , university of Babylon / Iraq , 2013.
 9. N. M. Dawood, ' Preparation And Characterization Of Bio Nitinol With Addition Of Copper' , PhD. thesis, materials engineering department , university of technology/ Iraq , 2014
 10. H.H. jaber, "The Effect of Addmixed Ti on Corrosion Resistant of High Copper Dental Amalgam" journal of Babylon University, vol. 22, no. 2.pp. 413-421, 2014
 11. Tripathy, "Effect of Microstructure on Sliding Wear Behaviour of Modified 9Cr-1Mo steel" , MS.C thesis , Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, 2011
 12. N. K. Sarkar and E. H. Greener, "Corrosion behavior of Tin-containing Silver-mercury phase of dental amalgam", J Det Res, Vol: 53, No: 4, P: 925-932, 1974