Studying the properties of CoCrMo (F75) doped Ge using (P-M) technique

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Abstrac

Cobalt chromium alloys are one of the best alloys used for biomedical applications due to their good wear resistance, high mechanical properties, acceptable bio-compatibility and high corrosion resistance. This study aims to investigate the effect of germanium additive with different percentages on CoCrMo (F75) alloy using powder metallurgy technique. The corrosion, wear and compressive behavior were also 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 Ge has a notable effect on the porosity of sintered CoCrMo causing decreasing in porosity. The hardness increases when Ge is added and it's increased as additives increase. Also the addition of Ge increases the compression strength and it's increased as additives increase. On the other hand the wear rate of CoCrMo (with and without additives) increases as the time and load increase, however it increases with the addition of Ge element and it's increased as Ge additives increase. The corrosion resistance of CoCrMo alloy improved after the addition of Ge in artificial saliva and Hank's solution. Also the corrosion resistance increase as Ge additives increase. The corrosion current for most used alloys in artificial saliva is lower than that for Hank's solution.

Key words: (CoCrMo alloys, F75 alloy, Ge addition, Corrosion resistance, Wear resistance, Compressive strength).

Introduction

In recent decades body implants has became really important using different types of alloys. Implants are fabricated from a wide variety of materials, including metals, polymers, ceramics and their composites. Among these materials, metals are an important group. Metal implants

were first introduced by Lane in 1895 since he discovered metal plate for bone fracture fixation [1]. One of the common alloys known in implant surgery is CoCrMo alloys and this because of its high biocompatibility, high wear and corrosion resistance. 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. In the early progress, metal implants had several issues including corrosion and insufficient strength problems [2].

Most of the research reports that pure porous Co based alloys have a lower resistance to pitting and crevice corrosion than solid materials .Type of metal used in biomedical depends on specific implant applications e.g. stainless steel (316L SS) type is still the most used alloy in all implants division ranging from cardiovascular to otorhinology. However, when the implant requires high wear resistance such as artificial joints, CoCrMo alloys is better served [3].

Germanium was first discovered by the German chemist Clemens Winklerin, it is stable in air and water and it's not affected by acids or alkalis except nitric acid. Germanium is used to make transistors for electronic devices and it's also used in some types of alloys such as phosphor in fluorescent lamps [4]. Some research shows that germanium compounds are effective in health in killing some types of bacteria. Some complex organic germanium compounds are been investigated as possible way for pharmacological treatment and currently is been investigated for use in chemotherapy [5].

No research has focused on Ge into CoCrMo matrix to improve the physical and chemical properties without affecting the alloy. This research highlights to improve the mechanical and electrochemical of CoCrMo alloy by adding different percentages of Germanium (B1=0.5%, B2= 1%, B3= 1.5% & A=master alloy).

2. Experimental and methodology:

The material powders used to prepare (F75) CoCrMo alloys in this research are demonstrated in table (1). The powder sieved with a 200 mesh sieve it’s a normal aperture is 73 μm according to British standard

(410), was calculated using Bettersize 2000 lazer particles size analyzer, Handheld (XRF) analyzer type (DS-2000) American, is used to explain 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 (GSL 1600X) was used to sinter samples from room temperature to 500C° and soaking 2 hr then heating from 500C° 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 are calculated according to ASTM B-328 [7]. Macrohardness Brinell tester which used to measure the hardness of the samples with (31.25)kg/mm^2 as applying weight and the Incubation time was (10 sec) in state applied weight 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:

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

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

$$\textbf{\textit{Wear rate}} = \frac{\textbf{\textit{weigth loss}}(g)}{\rho(\frac{g}{cm^3})} \quad \textbf{... (2)}$$

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

The corrosive behavior of CoCrMo studied in two different solutions (artificial saliva and Hank's solution). The chemical composition of artificial saliva and Hank's solution is illustrated in table (2) and (3) respectively [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 HCO3	1.5
3	NaH2Po4H2o	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	CaCl2	0.14
3	KCl	0.4
4	NaHCO3	0.35
5	Glucose	1
6	MgCl2.6H2o	0.1
7	Na2HPo4.2H2o	0.06
8	KH2PO4	0.06
9	MgSO4.7H2o	0.06

The electrochemical test involved two different examination and they were: Open circuit potential (OCP) and Potentiodynamic polarization electrochemical experiments were performed in three electrode cell containing and electrolytes similar to nature 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].

$$\textbf{Corrosion rate} = \frac{\textbf{0.13 icoor(Ew)}}{\rho * \textbf{A}} \qquad \textbf{... (3)}$$

Where:
E.W.= equivalent weight (g/eq.)
A= area (cm^2)
ρ= density (g/cm^3)
0.13 = metric and time conversion factor
$i_{corr.}$= current density ($\mu A/cm^2$)

Result and discussion:

The effect of Ge content on the porosity of sintered samples shown in figure (1) and there is decreasing in porosity values of samples after sintering it can be seen that the porosity of sintered samples decreased as the Ge content increases.

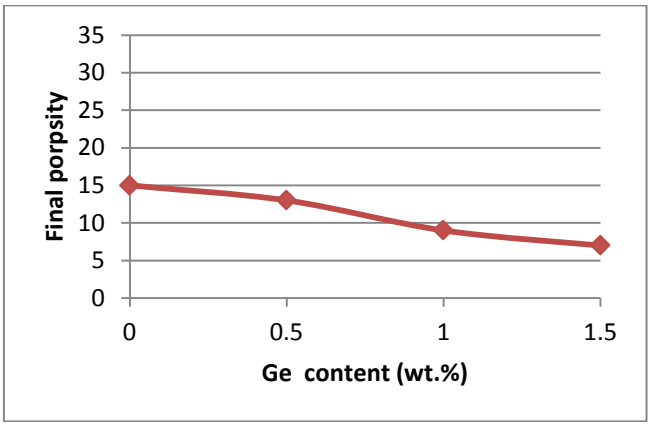


Figure (1) Effect of Ge content on Final porosity for alloys A, B1, B2 and B3.

The hardness values for CoCrMo alloys with Ge additives are higher than CoCrMo alloy as shown in figure (2).

The effect of Ge addition on the rising the hardness values of the samples is attributed to the role of Ge in reducing porosity (figure 1) .In general the hardness of CoCrMo alloys with Ge additives increase as the Ge content increases.

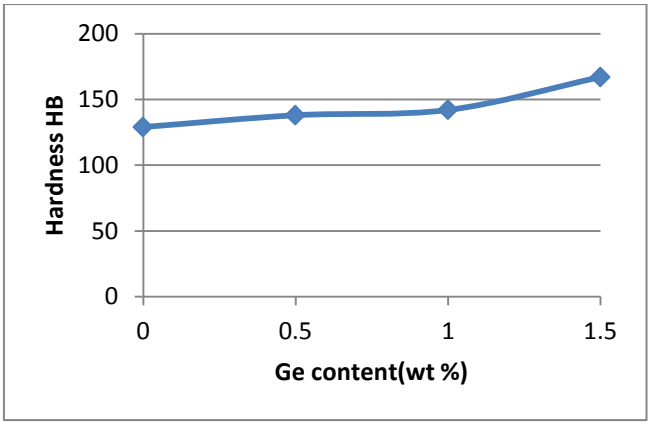


Figure (2) Effect of Ge content on the hardness for A, B1, B2 and B3 alloys.

The compression strength for CoCrMo alloys with Ge additives are higher than CoCrMo alloy, the magnitude for A (292.84) MPa, B1 (407.43)MPa, B2 (509.29)MPa and B3 (687.54) MPa. This is because the alloys with Ge content have a high hardness value compared with A alloy. The reason behind this that the different percentages between the phases of the composed alloy, in addition the porosity of CoCr alloy with Ge additive decreases as the Ge additive increases. These parameters lead to increased hardness as shown in figure (3), therefore the compression strength increase.

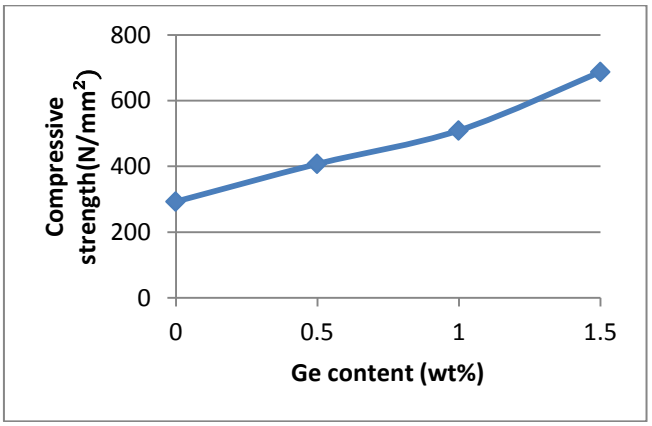


Figure (3) shows Ge content vs compression strength for A, B1, B2,and B3

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:

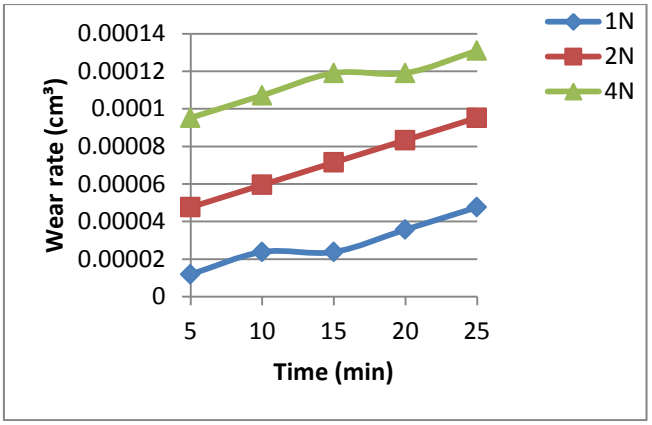


Figure (4) Wear rate vs time for A alloy under 1, 2 and 4N load

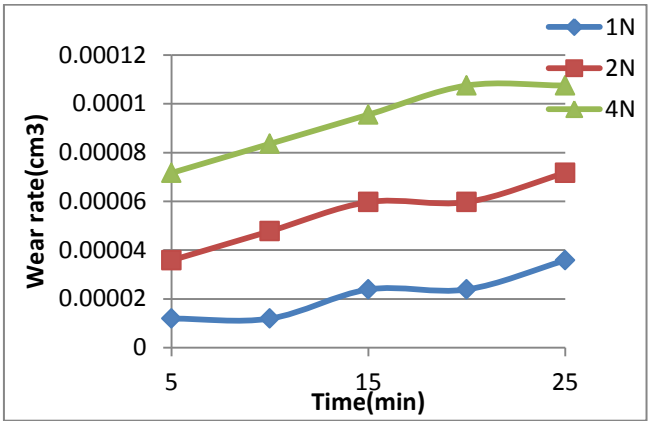


Figure (5) Wear rate vs time for B1 alloy under 1, 2 and 4N load

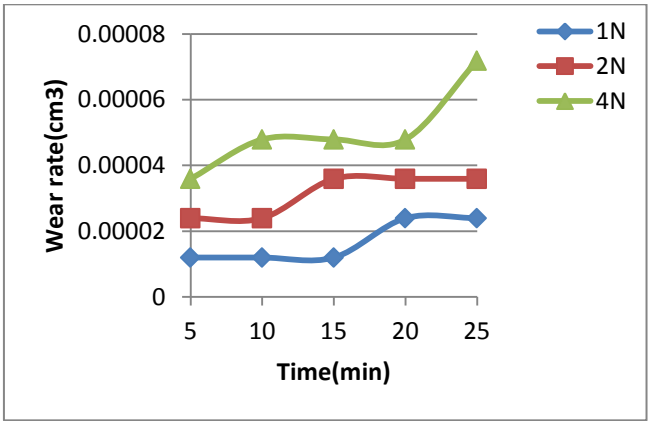


Figure (6) Wear rate vs time for B2 alloy under 1, 2 and 4 N load.

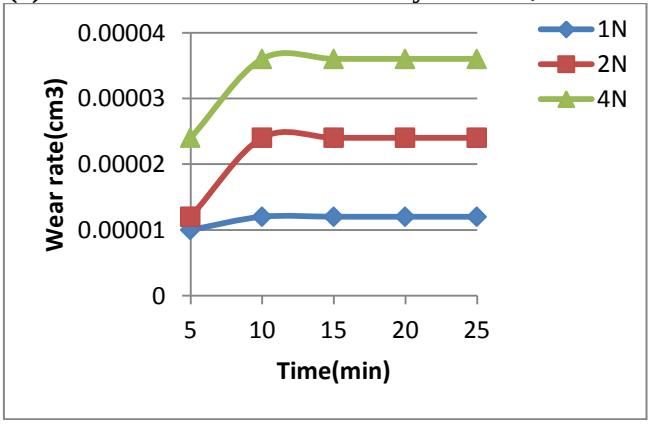


Figure (7) Wear rate vs time for B3 alloy under 1, 2 and 4N load

It can be noted from figure (8) which showed the effect of Ge content on the wear rate of B1, B2 and B3 alloys under constant load (4N) and constant time (25min), the wear rate decrease as the Ge content increase.

The reason behind this reduction in wear rate belongs to the Ge addition reduces the porosity and increases the hardness so the wear rate will be reduced.

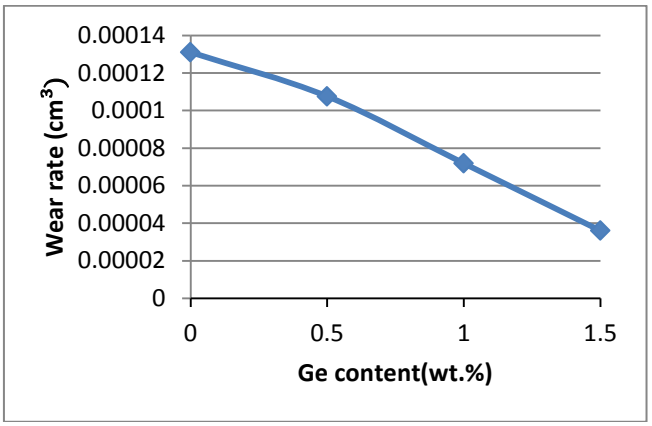
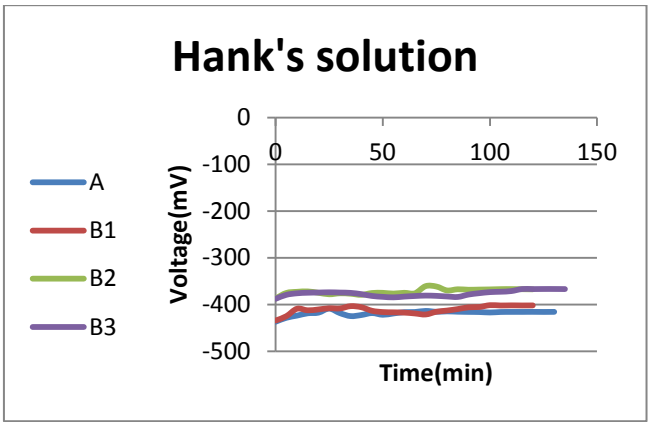


Figure (8) The effect of Ge content on wear rate for B1, B2 and B3 alloys under 4N load at 25min time.

The OCP-time was measured with respect to SCE in artificial saliva and Hank's solution at 37±1 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 and with interval of 5 minutes were potentially reported. The mean values of the OCP were recorded by using two samples for each alloy.



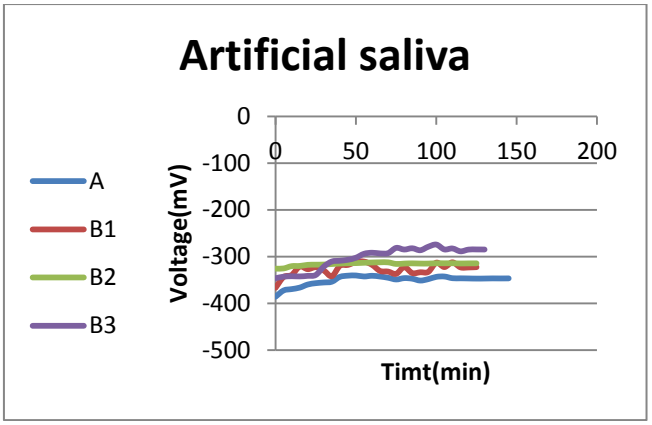


Figure (9) shows the OCP-time (a) in Hank's solution and (b) in artificial saliva at 37±1 C° for all tested alloys

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 Ge additives (B1=56.6%, B2=125.5% &B3=128%) and the $I_{corr.}$ of these alloys ranged between 6.9 ($\mu A/cm^2$) for B1 alloy and 4.7 ($\mu A/cm^2$) for B3 alloy in Hank's solution. It can be noted that the $I_{corr.}$ of CoCrMo alloys with Ge additives is lower than that for CoCrMo alloy. However the $E_{corr.}$values for B alloys is graded from -446.5mV for B1 to -410.8mV for B3 which are greater than $E_{corr.}$for A 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 C_0.

Alloy	Sample code	Icorr. ($\mu A/cm^2$)	Ecorr. (mV)	Corrosion Rate(mpy)	Improvement percentage%
F(75)	A	10.86	-433.7	4.153833	
B	B1	6.9	-446.5	2.657625	56.6
	B2	4.78	-419.1	1.844086	125.5
	B3	4.7	-410.8	1.820806	128

There are a noteworthy improvement in corrosion resistance for CoCrMo alloys with Ge additives (B1= 169%, B2=274.6% & B3=289.4%) compared with CoCrMo alloy, $I_{corr.}$ for B alloys ranged between 2.87 ($\mu A/cm^2$) for B1 alloy and 1.96 ($\mu A/cm^2$) for B3 alloy in artificial saliva. It can be noted that the I_{corr} of CoCrMo alloys with Ge additives is lower than CoCrMo alloy. However the $E_{corr.}$values for B alloys are graded from -369.4mV for B1 to -343.3mV for B3.

Table (5) Illustrate the corrosion current (Icorr.), corrosion potential (Ecorr) and corrosion rate for all alloys used in this work in artificial saliva at 37 C0.

Alloy	Sample code	Icorr.($\mu A/cm^2$)	Ecorr. (mV)	Corrosion Rate (mpy)	Improvement percentage%
F(75)	A	7.76	-291.8	2.967718	
B	B1	2.87	-369.4	1.105424	169
	B2	2.07	-327.5	0.798589	274.6
	B3	1.96	-343.3	0.762604	289.4

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

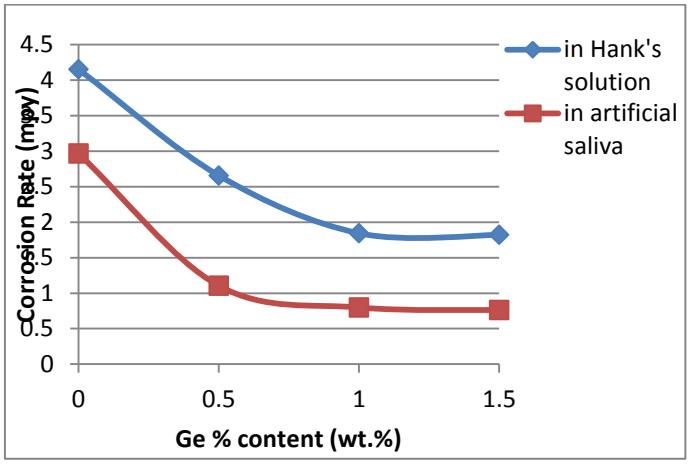


Figure (10) The effect of Ge content on corrosion rate of A,B1,B2 and B3 alloys in artificial saliva and Hank's solution at 37 C°.

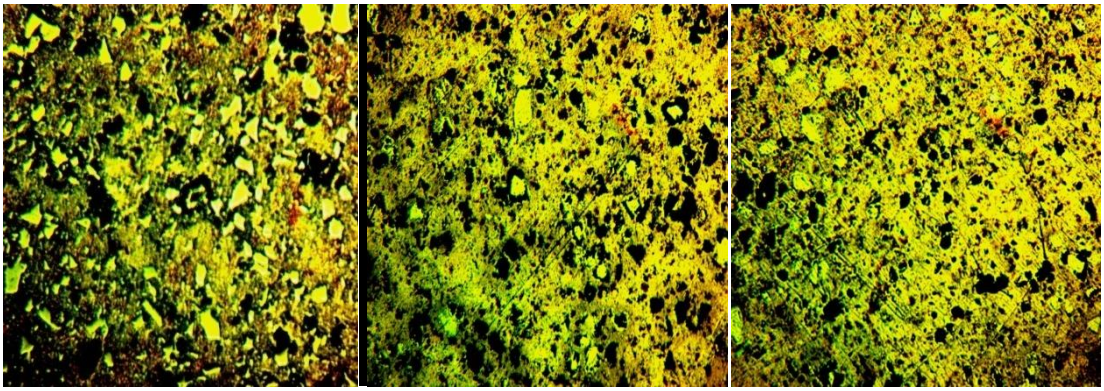


Figure (11) Microstructure for B1, B2 and B3 alloys after sintering and etching (100x)

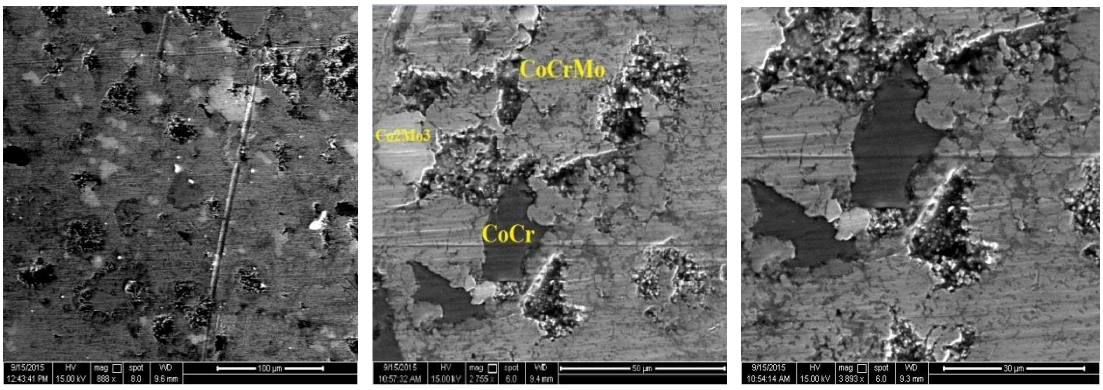


Figure (12) SEM images for etched B3 alloy with different magnification.

4. Conclusion

The addition of Ge has a notable effect on the porosity of sintered CoCrMo alloys. Also Ge addition resulted in decreasing the porosity. The hardness increases when Ge is added and it's increased as additives increase. The addition of Ge increases the compression strength and it's increased as additives increase. The Wear rate of CoCrMo (with and without additives) increases as the time and load is increased. The wear resistance inccreased with the addition of Ge element and it's increased as Ge additives increase. The corrosion resistance of CoCrMo alloy improved after the addition of Ge in artificial saliva and Hank's solution. The corrosion resistance increase as Ge additives increase. The corrosion current for most used alloys in artificial saliva is lower than that for Hank's solution.

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