Improvement of mechanical properties of CoCr alloys F75 by zirconium oxide addition

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ABSTRACT:
The aim of this study is to investigate the influence of zirconia addition as a particles reinforcement with various percentages (0.5,1,1.5,2,2.5,3,3.5,4,4.5,5 wt. %) on mechanical properties of biomedical CoCrMo alloy ASTM(F75) prepared using powder metallurgy technique (P/M). Samples were sintering and preparing for microstructure observation, macro-hardness tests, dry sliding wear test and compressive test. Increasing the values of hardness significantly as zirconia addition increase from (109HB) of base alloy to (151HB) at (5%) adding of ZrO_2. The wear rate of CoCrMo alloy (with and without additives) increases as the time and load are increased. the wear resistance an increase significantly with zirconia additive compared with base CoCrMo alloy where the volume loss decrease from (0.002 cm^3 of the base) to (0.000671 cm^3) at (2.5% ZrO_2) as minimum of volume loss which consider the best improvement percentage of wear resistance. The compression resistance was increasing by zirconia addition.

Keywords: Powder metallurgy, wear resistance, ASTM (F75) alloy, Zirconia.
DOI Number: 10.14704/nq.2022.20.11.NQ66235 **NeuroQuantology 2022; 20(11): 2380-2388**

INTRODUCTION

Implants use have expanded significantly in recent years, due to the aging of developed-country populations and patients' desire to maintain their current level of activity and quality of life. As a consequence, the need for high-performance implanted biomaterials that can address specific challenges in vascular therapy, cardiology, orthopaedics, spine, trauma, dentistry, and wound care is increasing[1]. Because of CoCr alloys outstanding mechanical qualities, high wear resistance, and superior resistance of corrosion, these alloys have become important metallic biomaterials in the orthopedic, cardiovascular, and dentistry disciplines. When compared to other biometallic materials such as titanium and stainless steels alloys, they exhibit superior wear resistance..[3]. Co28Cr6Mo (F75) alloys are made up of (*27- 30% Cr, 5-7% Mo, 2.5% Ni, 1% Si, 1% Mn, 0.75 Fe, 0.35C, and Co* is balanced) according to (ASTM, 2000)[4]. This alloy is notable for its outstanding corrosion resistance, even in chloride circumstances. This is primarily due to its high bulk chromium content and the surface layer of chromium oxide (Cr_2O_3) [5]. There are many papers focused on the improvement and development of CoCrMo alloys: In 2015, Ammar Hassan Khilfa [6]. Investigated the effects of the addition (0.5, 1, and 1.5) of Y on the wear, corrosion, and compressive strength behavior of CoCrMo (F75) alloys, which were prepared by P/M. This study discovered that the addition of Y causing increasing in porosity, decreasing hardness and compressive strength with increasing of Y addition. The addition of Y improves ware resistance, the improvement increased with increasing content of Y. In 2018, Ekram Abd Al-Razaq Hassani Abtan.[7]. Studied the influence of adding indium (0.5, 1, 1.5, and 2%) on the properties of the ASTM (F75) alloy, which was making by powder metallurgy method. wear behavior and the rate of corrosion were studding by mechanical and electrochemical tests. The study showed a decrease in the porosity an increase in hardness, improved wear resistance, and improved corrosion resistance in both solutions (Hank's solution and synthetic saliva) with increased indium addition.

EXPERMENTAL PART

The powders of materials, which it was used to prepare CoCrMo alloy (F75), are listed in the table (1) that shows powders and its purities with average particle size.

Table (1): Purities and average poetical size of powders.

Powders	Average particle size(μ)	Purity%
cobalt	4.873	99.95
Chromium	10.93	99.95
Molybdenum	12.76	99.9
Nickle	52.31	99.44
Manganese	43.26	99.39
Silicon	51.47	99.11
Iron	59.34	99.78
Carbon	37.44	99.44
Zirconia	0.495	99

Wight powders

Delicate Balance type (L220S– D), with (± 0.0001 accuracy) (German made) was utilized to weight each amount of powders before mixing. This powders were used to prepare F (75) alloy, the composition and code of the alloys which are used in this work are show in Table (2).

Table (2): The Composition and Code of the Alloys.

N.	Alloy code	Chemical composition (wt.%)
1	M	F(75) alloy without addition
2	A1	F(75)+0.5% ZrO_2
3	A2	F(75)+1% ZrO_2
4	A3	F(75)+1.5% ZrO_2
5	A4	F(75)+2% ZrO_2
6	A5	F(75)+2.5% ZrO_2
7	A6	F(75)+3% ZrO_2
8	A7	F(75)+3.5% ZrO_2
9	A8	F(75)+4% ZrO_2
10	A9	F(75)+4.5% ZrO_2
11	A10	F(75)+5% ZrO_2

Powders mixing

Wet mixing of powders was accomplished using a planetary automated ball mill, stainless steel balls of varied sizes were employed for 5 hours to provide an even and homogeneous distribution of powder particles, where acetone was added to wet the mixture.

Powders compaction

Mold (12mm) diameter made from stainless steel was employed to execution of the process of compacting by electric-hydraulic press one channel device, type: CT340-CT440, American. (3g) of mixture was compacted with pressure (800Mpa) and holding time was (4min) to create a disk spaceman with a diameter and thickness of 12mm and 4.5mm, respectively.

Sintering

A vacuum tubular furnace was used to conduct the sintering procedure, which included heating the material from ambient temperature to 1100 °C and stay time for 4 h. Afterwards, the furnace was then slowly cooled to room temperature under continued vacuum conditions. Fig (1) that shown the samples after sintering.

Figure (1): The CoCrMo alloy samples after sintering.

Microstructure Characterization

After the sintering process, the samples were grinded by utilizing silicon carbide papers with grits of (320,400,600,800,1200,1500,2000,2500 and 3000), and then polished using a 3µm diamond past and metallographic polishing pads to achieve a dazzling mirror finish for the final stage and its etched by (15ml distilled water, 15ml HNO_3, 15m Acetic acid, 60ml HCl) at ambient temperature[9]. The microstructure was studied using (LOM).

1.1 Mechanical tests

1. Macro-hardness test

The hardness of the samples was determined using a Macro-hardness Brinell tester with an applied load of (*31.25*) kg/mm^2 and a diameter ball of 2.5 mm, with an implantation duration of (10 sec) in the condition of applied weight. Three measurements were collected for each specimen, and the average value is utilized to analysis the alloys' behavior.

2. Dry sliding wear test

After one hour of drying in a drying oven set to 100 °C, the specimens were stored in well-knit boxes lined with material of silica gel to ensure complete drying. This test was conducted employing the pin on disk concept with (350 rpm) and a constant radius (*8 mm*) with various sliding distances and loads (*20N, 25N, and 30N).* Prior to testing, the sample was weighted using a (*0.0001*) precision electric balance. The samples tested were weighted after a period of (*5, 10, 15, 20, 25, and 30*) min, and the volume loss was computed using equation (1). The test procedure has been validated in accordance with ASTM G 99. [8].

$$\text{Volume loss} = \frac{weight\ loss(g)}{\rho(\frac{g}{cm^3})} \quad (1)$$

Where:

Loss of weight (g) = loss quantity after (5, 10, 15, 20, 25, 30 and 40) min.

ρ *= True density.*

3. Compression test

Compression testing was performed in line with ASTM standards at room temperature (D695-85). Using a computerized electronic universal testing equipment, type (WDW 200, No. W1124). The specimen dimensions are (12 *mm* in diameter and 18 *mm* in height), and the specimens were vertically positioned between the jaws to determine compression strength. The experiment was conducted at a constant loading rate of one millimeter per minute. Compressive strength is determined using the following calculations [9]:

$$comperssive\ strength = \frac{\max force(N)}{cross\ sectional\ area\,(mm^2)} \qquad (2).$$

1.2 ESULT AND DISCUSSION

1. Microstructure observation

The microstructure of etched (M, A1, A2, A3, A4, A5, A6, A7, A8, A9 and A10) alloys observed the grain boundary, multiphase and present pores in various size. That shows in Fig (1).

The microstructure of the etched alloys showed multiphase structures in which the CoCr phase is embedded in a uniform matrix (CoCrMo -FCC). Because preparation of spacemen by powder metallurgy method the present pores in different size on the surface of samples are natural manner.

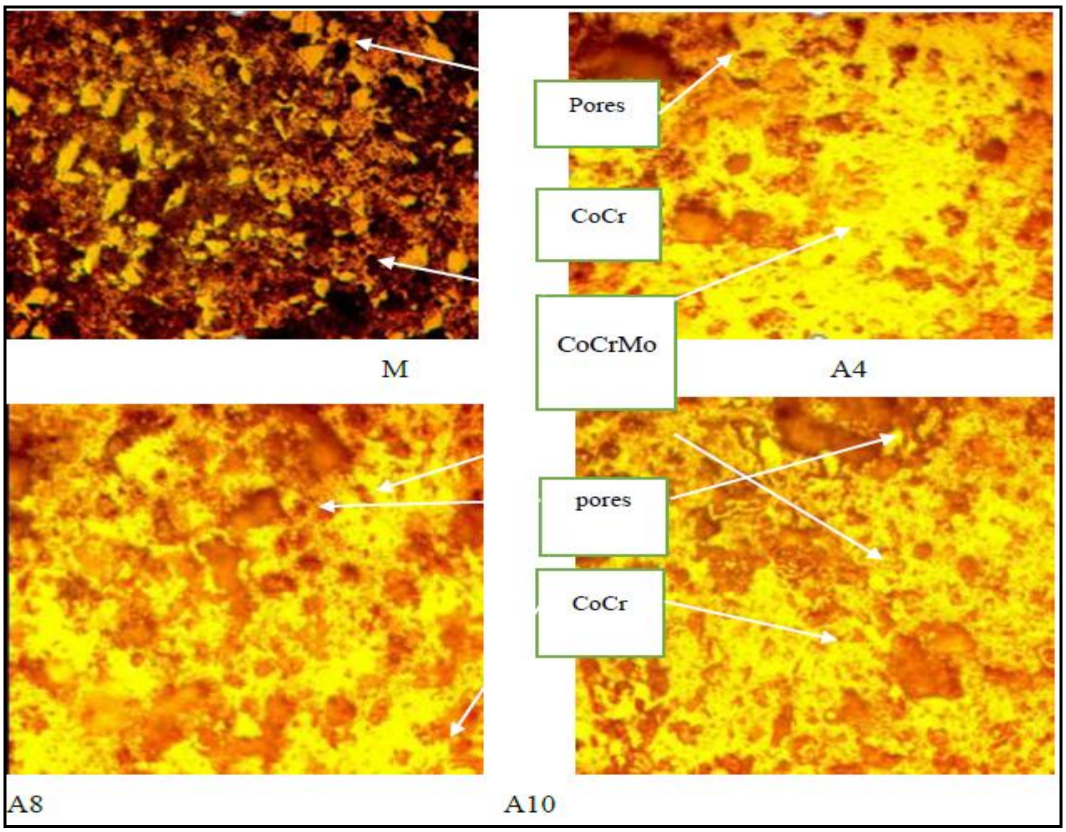


Figure (2): Microstructure for (M, A4, A8, A10) alloys after sintering process**.**

2. Macro-hardness test

The macro-hardness results of all alloy samples are shown in Figure (3).

Figure (3) show that COCrMo base alloy without and with zirconium oxide additive, showed significantly higher values of hardness in comparison with CoCrMo base alloys, values of hardness shown increased gradually with the gradual increased in the addition of ZrO_2. Attributed the rise in hardness to the role of (ZrO2) in the strengthening mechanism whereby these reinforcement particles tend to dampen the matrix phase movement in the vicinity of each particle. In essence, the matrix transfers some pressure applied to the particles, which bear part of the load. Thus, it reduces the movement of the matrix. Segregation of zirconia at grain boundary leads to restrain its movement, which increase of alloy hardness also the hardness increased with the addition of zirconium oxide due to the decrease in the porosity of the alloy.

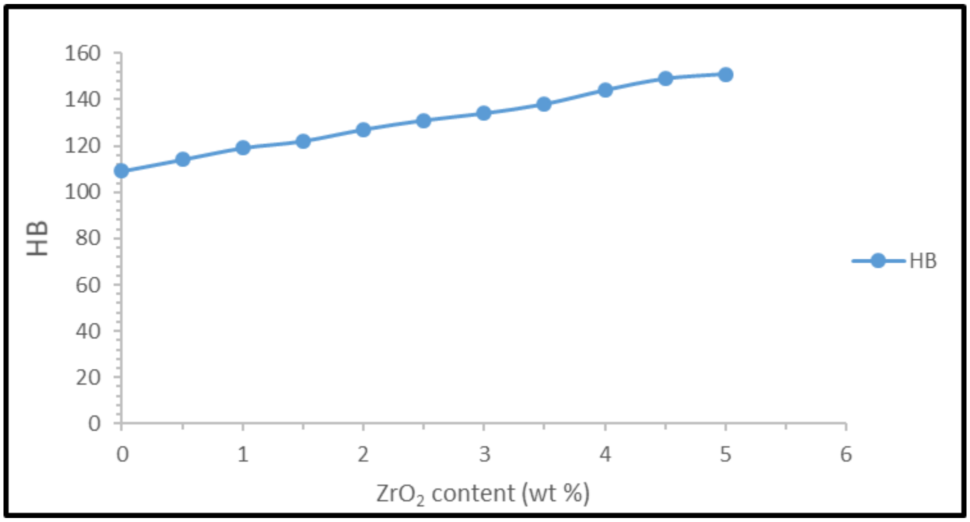


Figure (3): Effect zirconia content on hardness for CoCrMo alloy.

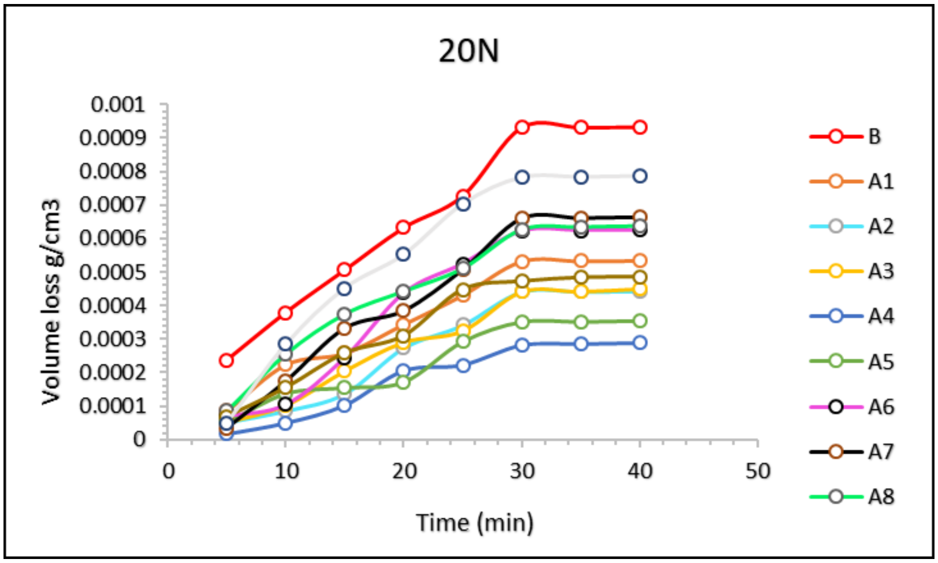
The table (3) shows the percentage of improvement in the hardness values of the alloy CoCrMo with the addition of zirconium oxide, where the percentage of improvement of hardness increases with the increase in the addition of zirconia, and the highest percentage of improvement is at the highest percentage of zirconia addition due to the relatively high percentage of ceramic particles (ZrO_2) present in the alloy, which bear part of the applied load and are segregation at grain boundaries to impede Its movement, which gives the least porosity in the alloy.

Table (3): Macro-hardness and improvement percentage of all alloy.

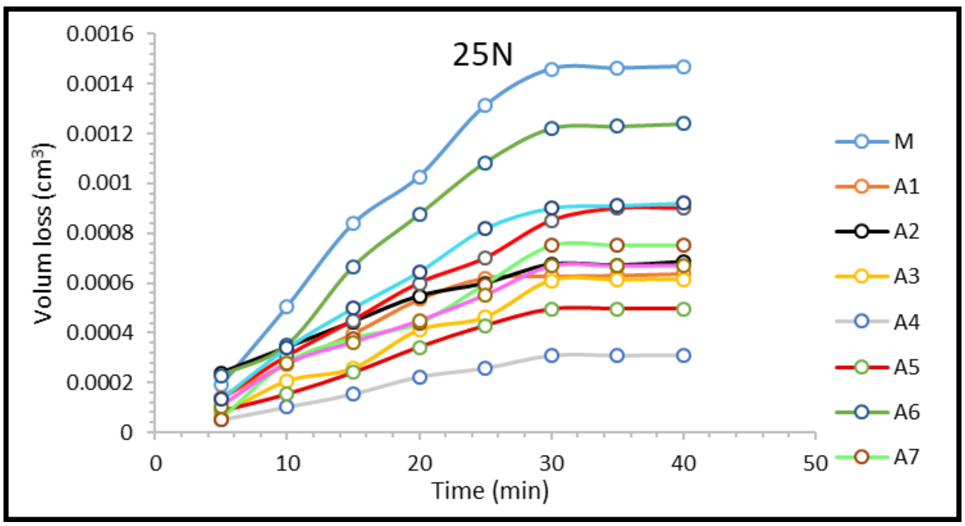
Alloys	Hardness	Improvement percentage %
B	109	-----
A1	112	2.75
A2	116	6.4
A3	122	11.9
A4	127	16.5
A5	131	20.1
A6	134	22.9
A7	138	26.6
A8	144	32.1
A9	149	36.6
A10	151	38.5

2. Dry sliding wear test

The samples with a diameter of (*12*) mm are subjected to dry wear test under various load *20, 25* and *30* N for various times (*5, 10, 15, 20, 25, 30, 35, 40*) min, were chosen constant load and different times according to several experiments.



(a)



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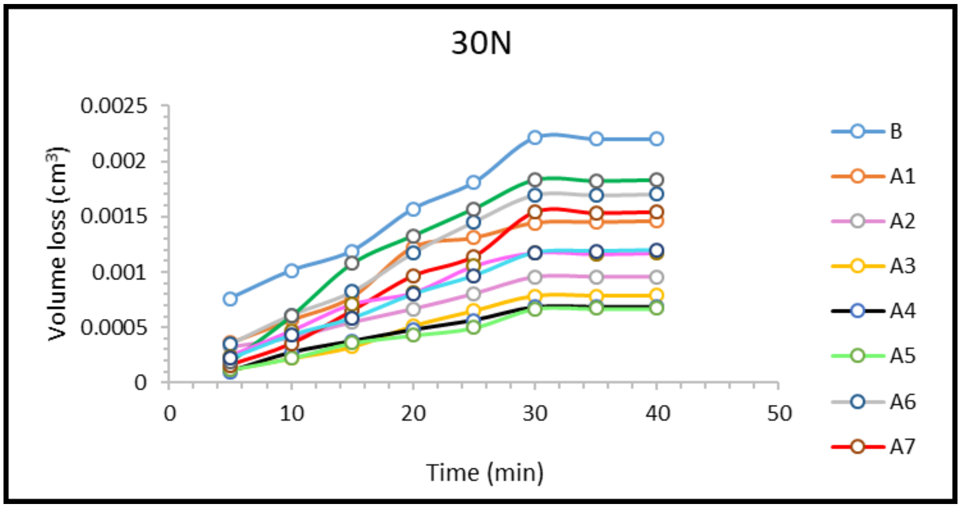

(c)

Figure (4.12): Volume Losses vs. Time for CoCrMo base Alloys and CoCrMo –xZrO_2 under (20, 30 and 30N) Loads.

The Figure (4) was shown the relationship between the loss of volume for CoCrMo base alloy without additions & with additions (0.5, 1, 1.5, 2,2.5,3, 3.5, 4, 4.5, 5% wt. ZrO_2) versus time under various load (20,25 and 30 N) From this figure, it's clear that weight loss gradually increased with increasing time regardless of the chemical composition and microstructure of alloys, this because of the increasing of friction at the surface as the load increase. In addition, increasing of wear rate with time of all samples is because more friction time leads to remove more material from the surface. It can be noted the behavior of the volume curve with time, the volume loss increase initially with time until reach study state, the asperities of the surface will be removed during sliding indicating the increase in the volume loss (wear rate) of the specimens and the increasing in the frication coefficient, when all asperities removed the friction coefficient reach constant value, consequently the volume loss reach constant value with time.

From Figure (4) It is possible to note the lower volume loss of CoCrMo alloys with the ZrO_2 additives (For all loads) compared to the CoCrMo base alloy, this attributed to restricts of matrix movement and grain boundaries by zirconium oxide particles added to base alloy which caused increase hardness, thus increase wear resistance and decrease volume loss.

Table (4): Volume loss and Improvement percentage of all alloy

alloy	Volume loss (cm^3)	Improvement percentage %
B	0.0022	------
A1	0.00146	33.6
A2	0.000956	56.5
A3	0.000786	64.2
A4	0.000685	68.8
A5	0.000671	69.5
A6	0.0017	22.7
A7	0.00154	30
A8	0.00183	16.8
A9	0.00117	46.8
A10	0.001	54.5

Table (4) shows the volume loss values of base alloy and CoCrMo with zirconia addition and improvement percentage of base alloy with (ZrO_2) addition. Volume loss of base alloy is (0.002 cm^3), which decrease with adding zirconium oxide particles to it. the volume loss of CoCrMo-0.5ZrO_2 alloy is (0.00146) with improvement percentage (33.6%) and decreasing continuous with gradual increased addition of ZrO_2 with increasing of improvement percentage even arrives addition ratio to 2.5% of zirconia (A5 alloy) with maximum improvement (69.5%) and minimum in loss of volume (0.000671cm^3), then occur drop in the wear resistance where increase volume loss with decreasing improvement percentage after pass this addition.

3. Compressive test

The results of the compressive strength test are illustrated in Figure (5).

The strength of compressive values of the CoCrMo alloy with the addition of zirconia are higher than its value for the base alloy, due to the reinforcement mechanism by large particulate composite. The hard and stiff zirconium oxide particles dispersed in the ductile matrix bear a fraction of supply load, which restrain matrix movement around each particle, also decreases of porosity when zirconia additive to base alloy leads to increase compressive strength.

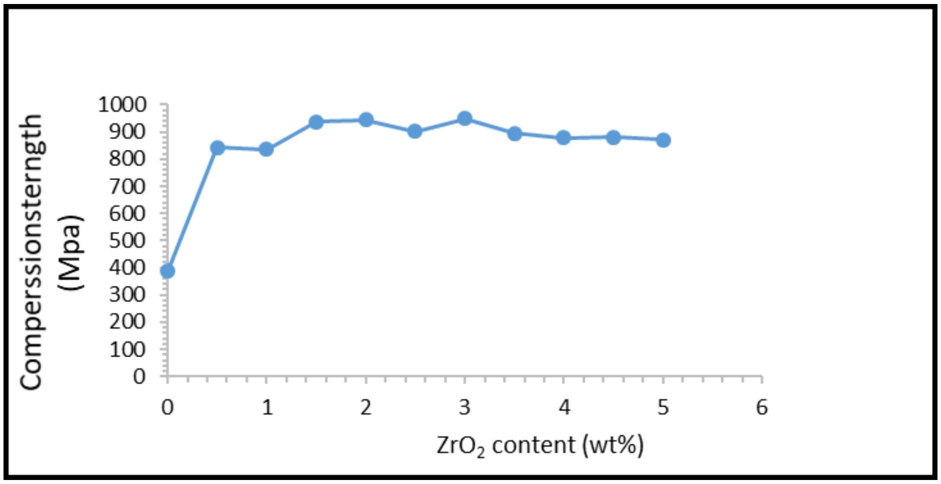

Figure (5): compressive strength for CoCrMo alloy (without and with ZrO_2).

Table (5) demonstrates the compressive strength magnitudes of base alloy without and with zirconia addition and improvement percentage compared with base alloy. B alloy with (388.41Mpa) value of compressive strength, increase this value to (841.99Mpa) when trace addition of zirconium particles (0.5%) with high improvement percentage (116.5%) and increasing continuous with gradual increased addition of ZrO_2 particles with increasing of improvement percentage even arrives addition ratio to 3% of zirconia (A6 alloy) with maximum compressive strength(949Mpa) and improvement (144.4%), then occur drop in the values of compressive strength and decreasing improvement percentage after pass this addition.

Table (5) the compressive strength and improvement percentage of all alloy.

samples	Compressive strength(MPa)	Improvement percentage %
B	388.41	------
A1	841.99	116.7
A2	835.10	115
A3	937.75	141.4
A4	942.97	142.7

A5	902.31	132.3
A6	949.6	144.4
A7	893.8	130.11
A8	877.09	125.8
A9	880.6	126.7
A10	871	124.2

1.3 Conclusions

1- Adding zirconium oxide to the base alloy leads to an increase in the hardness values compared to the base alloy, where the hardness increases with the increase in the ratio of addition.

2- Wear resistance of the CoCrMo alloy increases with addition of zirconia compared with base alloy, where the best wear resistance at (A5) alloy.

3- The values of compressive strength increase with addition zirconia to the CoCrMo base alloy and the best compressive strength value at (A1) alloy.

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