RESEARCH PAPER

# Corrosion Behavior of Ni Cr Mo Dental Alloy Prepared by Powder Metallurgy with Different Zirconium Addition

*Ban Ahmed Shanan [1]*, Ali Hubi Haleem [2], Haydar H.J. Jamal Al-Deen [2]*

[1] *University of Babylon, Iraq*

[2] *Department of Metallurgical Engineering, Materials Engineering Faculty, University of Babylon, Iraq*

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ABSTRACT

Metal-based dental alloy is one of the most widely used materials in dentistry. Alloys of Cobalt-chromium and nickel-chromium have many applications in the field of dentistry besides alloys Gold and precious metals used in this field.Nickel-chromium alloys are common in dental prosthetic applications because they are more economical than gold alloys. In this paper, the effect of adding zirconium on corrosion behavior of a nickel-chromium- molybdenum alloy was studied in saliva solution. Zirconium was added in three percentages (0.4, 0.8, 1.2) %. The alloy was prepared by powder metallurgy method (PM). Open circuit potential, electrochemical, scanning electronic microscope (SEM), and X-ray diffraction tests and inspections were used. The results proved that the addition of zirconium led to an improvement in corrosion resistance by about 81% in (NiCrMo+0.8Zr) alloy compared to the base alloy without the addition of zirconium. The presence of zirconium in the alloy resulted in a refining of the grain size, which improves the properties of the alloy.

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## INTRODUCTION

Nickel-chromium dental alloys have been created as a replacement to the gold-based alloys for crowns and partial dentures, partly due to their excellent characteristics in porcelain fused to metal applications. [1, 2]. Although the main use of zirconium alloy is in nuclear reactors [3], its medical uses have begun to increase recently [4]. Inside the oral cavity, dental tools are subjected to highly severe corrosive conditions. Noble metals are particularly inert in this case due to their excellent corrosion resistance. Their low strength, on the other hand, severely restricts their use in dental device structure. Dental alloys with excellent corrosion resistance and biocompatibility have been developed to overcome these limitations [5]. The bulk composition, microstructure, and development of protective surface oxide mateials all influence corrosion characteristics of nickel–chromium alloys. [6]. These dental alloys are primarily constituted of Cr(11.90-26.30%) and Ni(68-80%), however other elements must be alloyed in order to obtain mechanical strength, porcelain bonding and corrosion resistance. In Ni-Cr alloys, 0.1-14 wt. percent of aluminum, iron, molybdenum, beryllium, silicon, magnesium, carbon, cobalt, niobium, titanium, copper, gallium, tin, and magnesium have been added

* *Corresponding Author Email: ban.ahmad79@yahoo.com*

[7]. Ni-Cr alloy corrosion is characterized by the selective dissolving of nickel-rich grains that differs significantly from the corrosion behavior of Co-Cr alloys [8]. Other elements like carbon, zirconium, and boron are utilized in order to reinforce the grain boundary in the poly-crystalline alloys, and all of those components can affect alloy corrosion resistance, at least in theory [9].

Through a research of the literature, several investigations on dental alloys were discovered. Her-Hsiung Huang investigated the Relationship of the chemical composition with corrosion behavior of Ni-Cr dental alloys in artificial saliva [2]. Mi-Kyung Han *etal*. Have researched the effects of Zr on micro-structure physical characteristics, and corrosion resistance of cp-Ti. As a result of the solid solution strengthening of α-Ti, they discovered that cp-Ti has lower oxidation resistance and hardness than Ti-xZr. [10]. Al-DEEN investigated the influence of zirconium alloying elements(0.5, 1, 1.50, and 2wt%) on aluminum bronze alloy corrosion resistance in (3.50% NaCl and 2M HCl) solutions and discovered that improved zirconium addition reduces corrosion current density, resulting in increased corrosion resistance[11] . Huang studied effects of alloy composition on corrosion behaviors of Ni Cr Mo dental alloy using an artificial saliva solution , where he used nickel alloys with various Cr and Mo ratios and concluded that increasing the Cr ratio of( 21% )and (8%) Mo, this led to larger passive film and this increases corrosion resistance [12]. Silva et.al studied the microstructure and the electrochemical behavior in 0.9% NaCl for two Ni Cr Mo dental alloys and improved that electrochemical parameters depend on recast method, recasting method affects the electrochemical parameters such as current density, passive layer composition and potential stability [13].This study looks at the effects of adding zirconium to a Ni-Cr -Mo dental alloy at three different weight percentages. The corrosion characteristic in the artificial saliva is studied to determine the suitability of provided alloy for use as a restorative material.

## MATERIALS AND METHODS

*Samples Preparation*

The approach of powder metallurgy (PM) utilized to manufacture the samples that include the following steps:

Table 1. Purity % and Average Particle Size of the Materials.

| Powder | Purity % | Average Particle Sizes |
|---|---|---|
| Ni | 99.9 | 23.53 |
| Cr | 99.9 | 38.95 |
| Mo | 99.95 | 19.76 |
| Co | 99.68 | 18.46 |
| Zr | 99.99 | 14.23 |

Table 2. Chemical composition of specimens.

| Code | Alloy Composition |
|---|---|
| A | Ni-21%Cr-2%Mo-2%Co |
| A1 | Ni-21%Cr-2%Mo-2%Co-0.4Zr |
| A2 | Ni-21%Cr-2%Mo-2%Co-0.8Zr |
| A3 | Ni-21%Cr-2%Mo-2%Co-1.2Zr |

*Powder preparation*

There are several tests performed on the powders before they are used in the alloy. The powders (Ni, Cr, Mo, Co, Zr) used in the production of the alloy must be prepared and tests carried out before using them. The particle size of the powders are examined by a device laser particle size analyzer and distilled water as medium of dispersion. The Table 1 showed purity of powders and the particle size.

*Mixing and Compacting powders*

To obtain homogeneity and uniform distribution of the used powders, a mixing process is required. The mixing process was carried out by electric rolling mixer type (STGQM-1/5-2) and to ensure better mixing of the powders, steel balls of different sizes were used. A small amount of alcohol is added to the powders to avoid friction and oxidation during a 6-hour mixing period. After the mixing process is completed, the powder is compacted into a stainless steel die specially designed for the required samples with dimensions thickness and diameter respectively (4mm, 13mm). Compacting was carried out with a compacting pressure of 650 MPa using electric uniaxial hydraulic press. The chemical composition of specimens has been listed in Table 2.

*Sintering process*

The sintering process follows the compacting process of the samples using a tube furnace in presence of inert argon gas. Fig. 1 shows sintering mechanism.

The sintered samples need grinding and polishing processes for the purpose of conducting tests on them. The grinding process is done by silicon carbide grinding papers of different grit

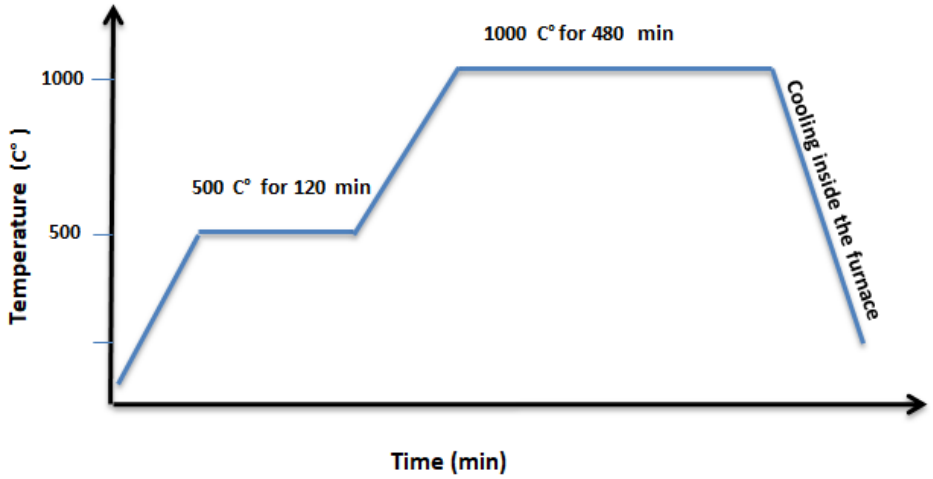


Fig. 1. Sintering program.

Table 3. The artificial saliva composition [15].

| No. | Constituents | g/l |
|---|---|---|
| 1 | NaCl | 0.40 |
| 2 | KCl | 0.40 |
| 3 | $CaCl_2.2H_2O$ | 0.906 |
| 4 | $NaH_2Po_4.2H_2O$ | 0.69 |
| 5 | $Na_2S.9H_2O$ | 0.005 |
| 6 | Urea | 1 |

values (400, 600, 800, 1000, 1200, 1500, 2000, and 2500). The polishing is done by using a piece of cloth on which diamonds) 15 µm( are placed.

*The samples testes*

The X-Ray diffractometer type (shlmadzu XRD-60000) using for the analysis of phases of the alloys.

Field Emission scanning electron microscopy (FE-SEM) and EDX: Following polishing, the samples were etched using an etching solution at room temperature (100 ml $HNO_3$, 10 ml HF). The microstructure was estimated using FESEM. EDX used to know the chemical composition in a specific area of the samples and through which the phases present in the alloy can be estimated. Then the samples are washed with water and dried.

*Electro-chemical Tests*

*Open Circuit Potential (OCP)*

Specimen are placed in a beaker containing 500 ml of salvia solution. The sample is connected to one of the voltmeter sensors and is called the working electrode. The calomel electrode is utilized, which represents a reference electrode, which is connected to the other sensor of the voltmeter. The readings are recorded after every five minutes until the voltage is stabilized at a certain reading.

*Potential-dynamic polarization test*

The test was carried out according to ASTM (GS-87), where the calomel electrode is reference electrode, platinum electrode is a counter electrode, and the sample is working electrode. The sample is immersed in corrosive solution salvia with PH 5.79 at 37 C0, the test is performed by a potentiostat (Winking M Lab 200). Through Tafel extrapolation curves we get the corrosion current density (icorr) as well as corrosion potential at a scan rate of + 1.0mV / sec. The dynamic polarization curve usually uses a semi-logarithmic scheme consisting of an anodic part and a cathodic part as a result of the electrochemical reactions that occur between the sample and the corrosive medium (Saliva). The open circuit voltage of the specimen is used to determine the beginning and end of the anodic and cathodic reaction by adding ± 0.250 volts. The corrosion rate calculated by following Eq. 1[14].

$$\text{Corrosion rate (mpy)} = 0.13\frac{I_{corr(Ew)}}{A.\rho} \quad (1)$$

Where: 0.13=metric and time conversion factor, I corr.= Current density (µA/cm$^2$) E.W= equivalent weight (g mol$^{-1}$), ρ=density (g/cm$^3$), A= exposed specimen area (cm$^2$), mpy= Corrosion rate (mils penetration per year).

## RESULTS AND DISCUSSION

*XRD Test*

After performing X-ray test of the sintered samples, the ($Cr_3Ni_2$, $MoNi_4$) phases appeared, in

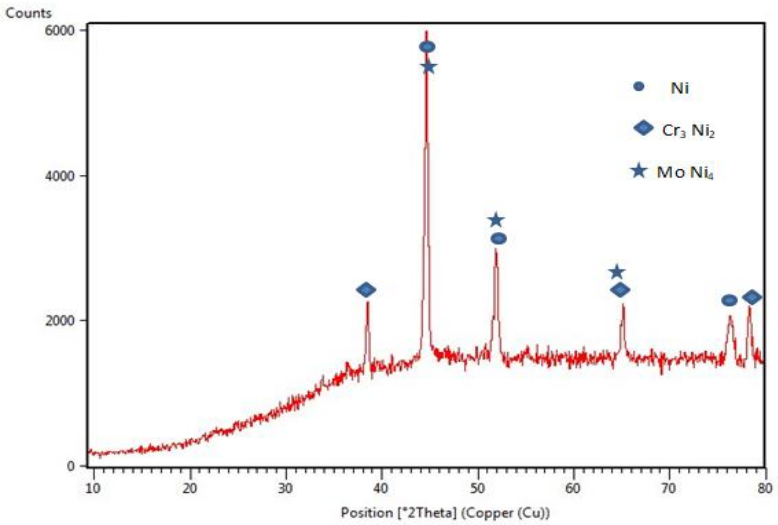


Fig. 2. The XRD analysis of alloy.

addition to the presence of the nickel phase. This indicates that the sintering process is successful (Fig. 2).

*Open Circuit Potential (O.C.P)*

When the samples are immersed in the corrosive solution (saliva), a reaction will happen on the surface of the specimen and as a result of this reaction we will get a potential called open circuit potential. Cathodic and anodic reactions occur and an oxide layer forms on surface, but this layer is unstable and prone to breakage, so the potential increases when the layer is formed and decreases when the oxide layer is broken, and this is the reason for the curvature fluctuation of the open circuit potential .When the cathodic and anodic reactions are equal, we get a constant value of the potential as a result of the formation of protective oxide layer on surface of sample to be constant and the free energy equals 0. It was notice from the Fig.3 the open circuit potential of alloy with and without the addition

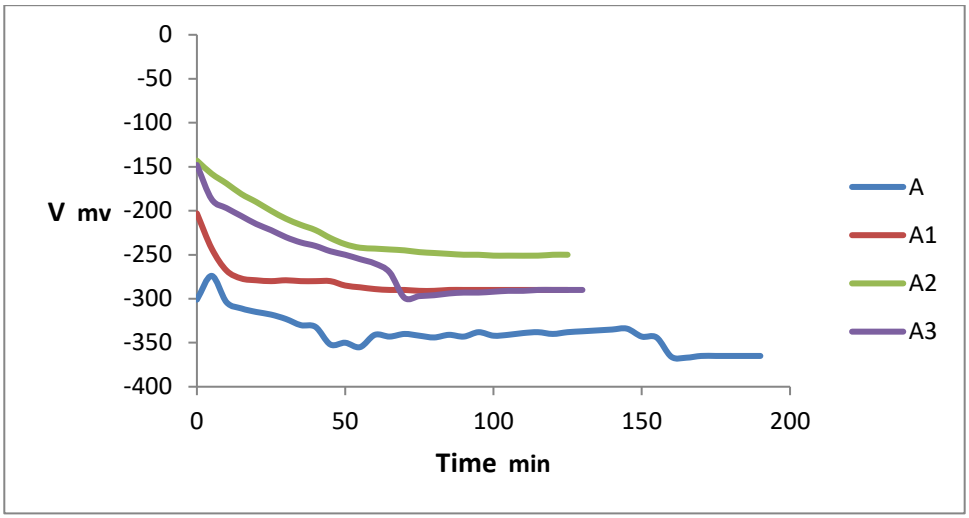


Fig. 3. Curve of O.C.P for A, A1, A2, A3, and A4 alloys in saliva.

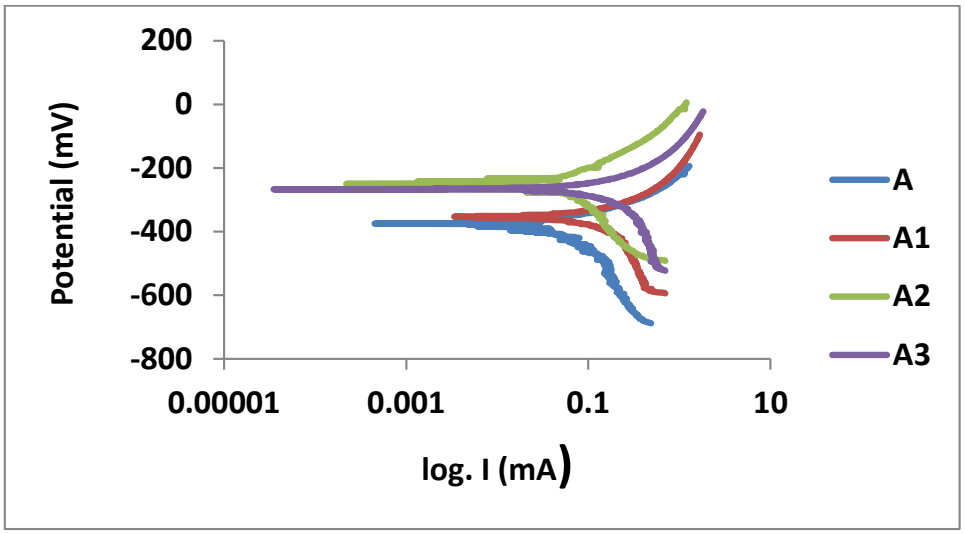


Fig. 4. The ( P.D.P ) curve for all alloys(A,A1,A2,A3,A4).

of zirconium(A1,A2,A3), when adding zirconium, the alloy will become more noble compared to the base alloy .The most negative potential means that the oxide layer is not enough to protect the metal.

*Potential-dynamic polarization (P.D.P)*

Fig. 4 shows the polarization curve for samples (A, A1, A2, A3) at 37 °C in artificial saliva solutions. Through polarization curve, it was notice that the addition of zirconium led to an improvement in corrosion resistance, and this is due to the fact that the presence of zirconium in the alloy led to stabilization of protective oxide layer on surface[15]. When zirconium is added to the alloy, the corrosion rate improves attributable to rise in the corrosion potential (Ecorr) and a reduce in current density (Icorr )[16], Table 4 . The dissolution of the alloy decreases when zirconium is added, so the corrosion current density will decrease when zirconium is added, and this is consistent with [11, 17].

*FESEM*

After samples were prepared, FE-SEM was

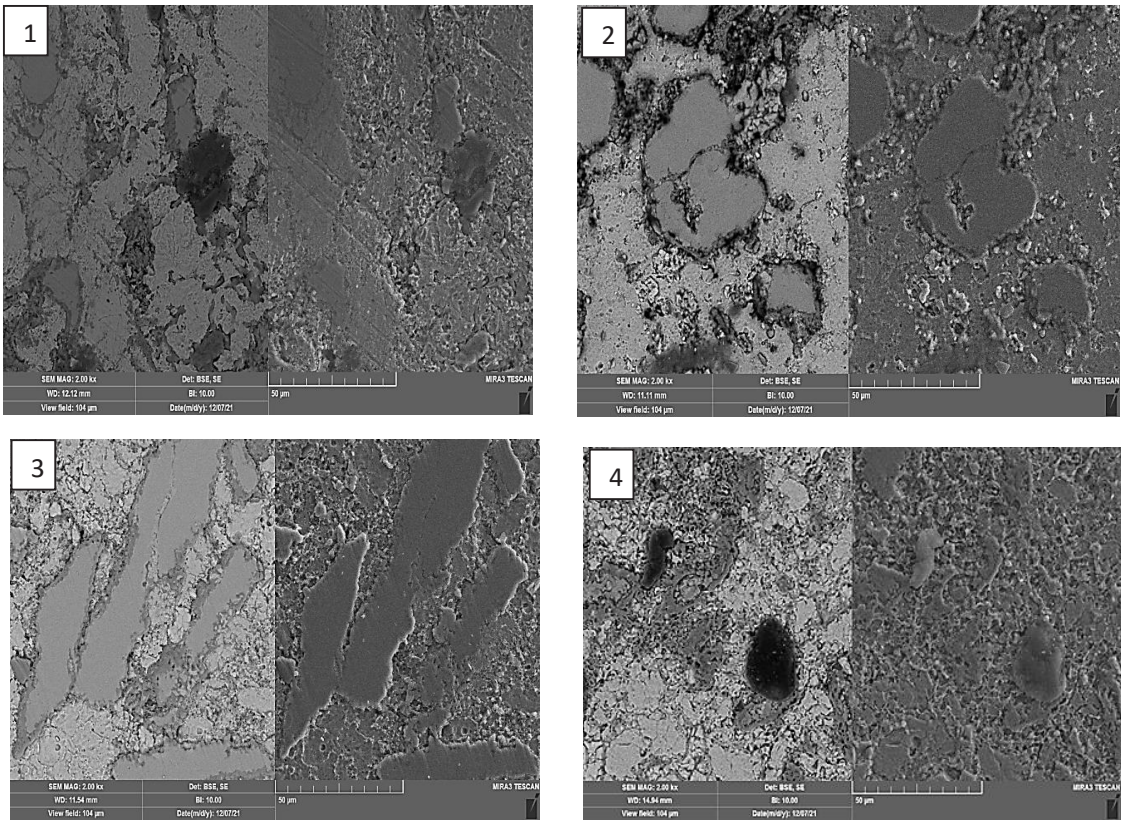


Fig. 5. FESM Images of 1) A 2) A1 3) A2 4) A3.

Table 4. Corrosion data in Saliva at 37 °C.

| Sample code | I corr. ($\mu$A/cm$^2$) | E corr. (mV) | E.W (g mol$^{-1}$) | Corrosion rate(mpy) | Improvements % |
|---|---|---|---|---|---|
| A | 31.80 | -386.6 | 21.10 | 10.030 | |
| $A_1$ | 13.90 | -347.5 | 21.16 | 5.709 | 43% |
| $A_2$ | 4.85 | -251.5 | 21.21 | 1.806 | 81% |
| $A_3$ | 17.16 | -265.7 | 21.27 | 5.855 | 41% |

tested. The form and size of the grains have a significant influence on the material's behavior. Fig. 5 shows the microstructure of the alloy (A, A $_1$, A2, A3). It was notice that the presence of zirconium has refined the grain size of the alloy compared to base alloy and this agrees with[18].

## CONCLUSION

The present study included effects of adding zirconium to the alloy in different proportions. Through the tests conducted on the samples, it was concluded that:

1- The open circuit potential becomes more positive when Zr is added which means the alloy is more noble.

2- The addition of zirconium improved the corrosion rate from a value of )10.030) mpy in alloy A to a value of (5.709, 1.806,5.855)mpy in alloy (A1,A2,A3) respectively.

3- The presence of zirconium reduced the dissolution of the ions in the solution, which had resulted in decreasing corrosion rate and an improvement in properties of the alloy.

4- The best corrosion resistance in $A_2$ alloy, where the emprovment in corrosion resistance equal to 81% than base alloy .

5- From the microstructure, it has been noted that addition of zirconium had led to a refinning of particle size, so the process of ion dissolution is more difficult.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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