Investigation of Corrosion Behavior of Cocrmo(F75) Alloy by Using Air Plasma Spray YSZ /Tio_2 as Coating for Biomedical Implant

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Abstract

This research focuses on the synthesis and characterization of a cobalt-chromium-molybdenum (Co-Cr-Mo) alloy prepared using the powder metallurgy technique, followed by coating the alloy with different ratios of Yttrium Stabilized Zirconium (YSZ) and Titania TiO2 using the plasma spray method. The objective is to evaluate the suitability of the coated alloy as a biomedical implant in the human body. The coated samples were subjected to XRD (X-ray diffraction), SEM (scanning electron microscopy), and EDS (energy-dispersive X-ray spectroscopy) analyses. Additionally, corrosion testing was conducted using Hank's solution, contact angle and surface roughness.

Keywords, Air plasma spray, CoCrMo alloy,YSZ ,TiO_2.

Introduction

The CoCrMo alloy illustrates impressive strength, resistance to corrosion, and excellent wear resistance. It is commonly utilized for orthopedic and dental implants. Highly polished components include femoral stems for replacement hips and knee condyles.[1]. When a metal device is implanted into the human body, it is constantly in contact with extracellular tissue fluid. The implant's metal surface gradually dissolves when exposed to the surrounding environment through electrochemical interactions. The initiation of corrosion can be the result of various conditions existing along the implant surface. [2]. Because metals are primarily used in orthopaedics, wear and corrosion must have minimal effects on them before they can be utilized in other practical contexts [3]. The prostheses should have great mechanical resistance in order to solve this issue. Furthermore, it is imperative that prostheses exhibit both superior adherence to the tissue and excellent corrosion resistance in order to establish a stable biological link with the bone [4]. The majority of these issues are related to the metallic implants' surface. As a result, it is required to alter the metallic substrate's surface with particular characteristics that differ from those in bulk [5,6]. To achieve the intended biological interactions and optimal bone formability, this alteration is necessary. Biocompatibility, wear resistance, and corrosion resistance are also necessary in some applications [7]. Many bioactive materials are being investigated for surface modifications of bioimplants in order to prevent unfavorable outcomes such implant surface corrosion hazards, post-surgery infections, lack of biocompatibility, and long-term survivability[8,9]. However, during the past few decades, a number of alloy surface modifications have been made by coating utilizing a variety of processes in an effort to remove the aforementioned drawbacks associated with CoCr alloy medical implants (PVD, CVD, ion implantation, plasma spray). Because of their versatility and effectiveness, bio ceramic materials have found extensive use in bone tissue, biomedicine, dentistry, and medicine. Ceramic materials that have biological origins are far more desired as they can be used in close proximity to living tissues.[10] The bioactive coatings on the metal substrate have drawn researchers' interest recently. Yttrium Stabilized Zirconium (YSZ) is a substance that is frequently utilized as a coating due to its appealing qualities, which include chemical stability and a small influence on inflammation at the implant site [11,12] Nevertheless, they have low wear resistance and shear strength. The ceramic substance titania (TiO2) is typically applied as a coating on the femoral head of hip prosthesis users. For the production of advanced ceramics with improved reliability, fine-grained TiO2 particles with a limited size distribution are preferred [13]. Recently, there has been a surge of interest in studying the biological and physico-chemical properties of fine-grained TiO2 particles. Surface layers of TiO_2 have been applied to metal substrates, demonstrating exceptional biocompatibility. The titania coating has demonstrated impressive bioactivity and the capacity to establish chemical bonds with bone within the body. [14]. Deposited composite coatings with TiO_2 using plasma spraying technology seem desirable to address the mechanical performance and bioactivity concerns of YSZ. The primary conjecture of the research is that including TiO2 into YSZ coating could lead to enhanced efficacy in contrast to a YSZ coating layer that is pure. [15].in 2018 A. Jemat et al study coating by ceramic material (YSZ, TiO_2) and effect on properties [15]. In 2019 J. Barczyk et al focused-on coating by plasma spray by YSZ and to determinate the microstructure and different properties of coating for potential biomedical application [16]. In 2023 Afida Jemat et al This study provides valuable insights into the biocompatibility and bioactivity of the YZP/TiO2 coating, highlighting its potential as an innovative coating material [17].In this research, prepare a CoCrMo (F75) by powder metallurgy and coat it using an air plasma spray with ceramic coating different ratios of YSZ (0,10, 30, 50)wt %, TiO_2. We will then conduct characterization (XRD, SEM, and EDS), corrosion tests, and contact tests on these specimens to evaluate their performance as implants.

Experimental part

The sample prepared by powder metallurgy process in an argon environment. ASTM F75 standard of cobalt chromium alloy (CoCr alloy) was used in this study, (60.4% Co, 28% Cr, 6% Mo, 2.5% Ni, 1% Mn ,1% Si, 0.75% Fe, 0.35% C). then the weighted mixture of powder in a planetary automatic a ball mill for five hours to be able to uniform and fine powder particle dispersion. Sample disk with dimensions of 6mm thickness and 12mm diameter created in an electrical hydraulic press by compacting 3.5g of powder combination using cylindrical die in one direction. compacting pressure are equal to 750 MPa. the green compact then sintering in a tube furnace .to prevent samples oxidation, the sintering process carried out in an argon environment. the sintering process carried out in two steps in first step 500ºc for two hours and two step 850°C for six hours, then the sintered samples are allowed to cool in furnace gradually while being continuously purged with argon until they reach room temperature after sintering process,

Coating process

The feedstock powders, YSZ and TiO_2, were combined and ball milled in a ceramic jar with ethanol acting as a dispersant. This process produced YSZ/ (0, 10, 30, and 50) wt% TiO_2 mixing powders. the mean particle size of YSZ is 32.14µm, while the mean particle size of TiO_2 is 45. 55µm.All sintering samples (CoCrMo alloy) were ground using silica carbide sheet with grits of (180,220,32,600 and 800). after that all samples were cleaned with water and dry with methanol and dry with hot air. to obtain roughness required will use sand blast to prepare to coating process by air plasma spray table 1 show parameter of coating process. and the results are compared to the basic sample .X-ray diffraction (XRD)analysis was conducted on finely polished sample to identify the crystal structure of continuous phase. samples were analyzed by scanning electron microscopy (SEM)equipped with energy dispersive X-ray spectroscope (EDS). Table 2 show sample composition and code.

Table 1 parameter coating

	APS parameter
500 A	Electric Current
50 gr/min	Powder feed rate
10 scfh	Carrier gas flow rate
150 psi	Primary gas pressure (Ar)
75 psi	Secondary gas pressure (H_2)
10 cm	Spray distance
5 cm/s	Spray speed
20-40 µm	Coating layer

Table 2 show sample composition and code

Sample code	Sample composition
A	Base (CoCrMO) F75

C1	Coat 100%YSZ
C2	90%YSZ_10%TiO_2
C3	70%YSZ_30%TiO_2
C4	50%YSZ_50%TiO_2

Corrosion experiments are conducted on specimens to better understand the behavior of corrosion in the human body. For this experiment, Hank's Solutions were utilized. As per the ASTM standard, the counter, reference, and working electrodes used were Pt, SCE, and the sample, respectively. For potentiodynamics, the polarization curves were obtained and Utilizing the potential of the anodic and cathodic branches, which is 250 mV lower than the potential of an open circuit, Tafel plots were utilized to calculate the corrosion potential and corrosion current density (I corr.). The scanning was continued up to 250 mV above the open circuit potentials. The corrosion rate was calculated using the following equation[18], whereby

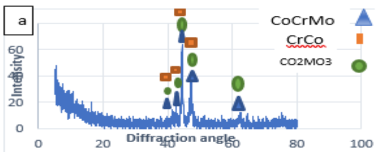
$$\text{Corrosion rate(mpy)} = \frac{0.13\, I_{corr}\,(Ew)}{\rho}$$

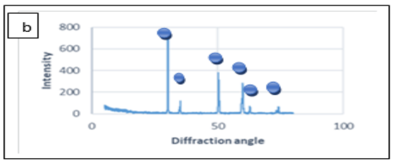
Where Ew. , I corr. , and mpy. , represent the equivalent weight (g/eq.), density (g cm^3), current density (A cm^2), and (mpy) (mills per year) , respectively The metric and time conversion factor equal to 0.13.

Result and Discussion

X-Ray Diffraction analysis

X-ray diffraction analysis was the primary test to assess the microstructure of the researched (A, C1,C2,C3 and C4) alloys because the presence of intermetallic compounds and phase change might also affect the electrochemical characteristics of the aforesaid alloy. A high temperature is required for phase change, because sintering process is diffusion process. Figure (1a) shows the XRD patterns for alloys and after sintering for 2 hours at 500°C and 6hours at 850°C respectively. The X-ray diffraction results of the YSZ/TiO_2 ceramic coatings appear in Fig. 1(b,c,d,e). All of the coatings' diffraction peaks were found to be mostly made of crystalline YSZ, with a consistently high and acute peak intensity. Additionally, the tetragonal peaks have Higher intensity was seen in the XRD pattern for YSZ, signifying the pure phase of the compound and consistent with previous research [19, 20]. ZrTiO4 was a different phase in the XRD pattern that emerged from the reaction of YSZ and TiO2 [15]. This demonstrated that a complete transformation of ($ZrTiO_4$)can be accomplished with larger YSZ-TiO_2 ratios. Consequently, it is possible to achieve the appropriate mechanical and thermal properties of sintered porous ceramics.





)b: XRD patterns for C1 alloy

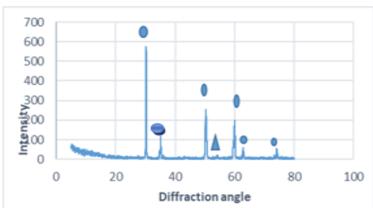
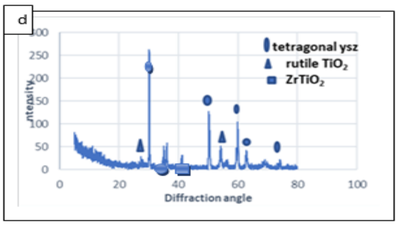
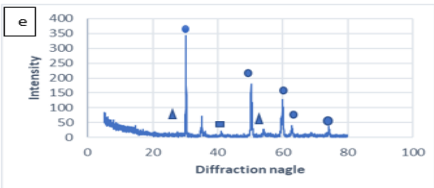


Fig (1)c: XRD patterns for C2 alloy



Fig(1)d: XRD patterns for C3 alloy



Microstructure and phase

Because of this, SEM pictures are very sensitive to chemical composition. According to the microstructure, all of the specimen alloys have more than one phases structure at room temperature, as seen in Fig(2). In contrast to the master sample,

Fig (3) shows the EDS for (A, C1, C2, C3, C4) in the sample. A notice element of F75 means the success of the sintering process. while coating samples show layer coating elements in c1 showed (Zr,Y,O,C) and C2 and C3 showed (Zr,Y,O,C. Ti) and C4 element (Y) hidden this because EDS focuses on a specific area and increasing percentage of TiO_2.

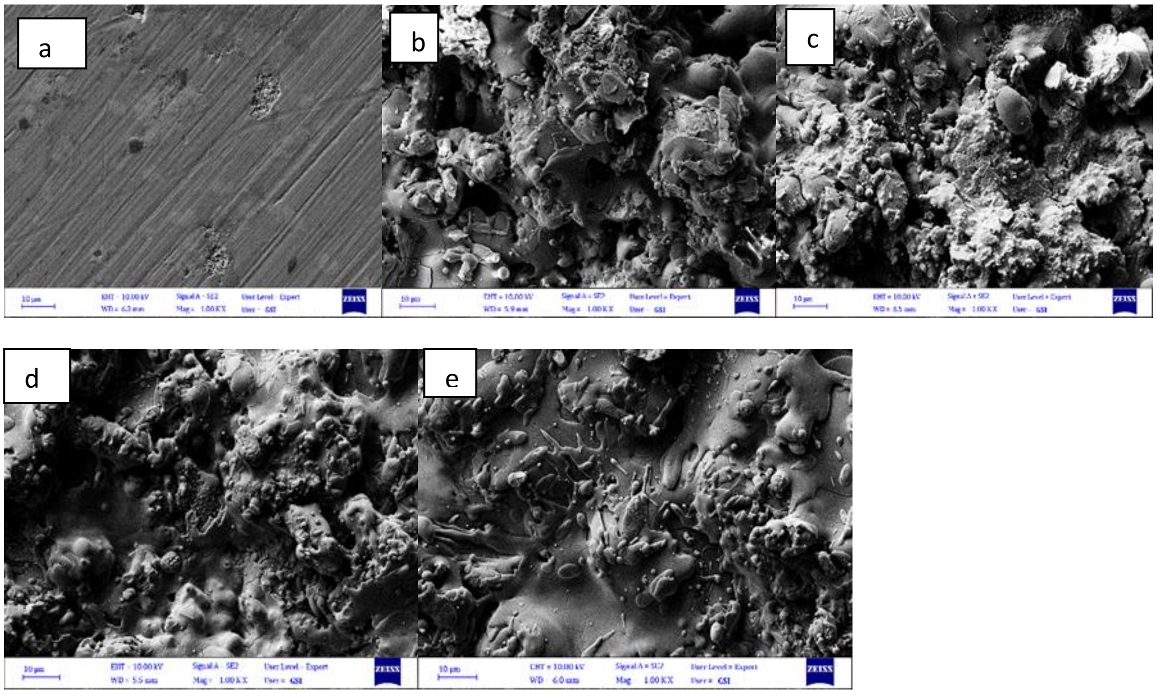


Fig (2) SEM image for A, C1, C2, C3 and C4

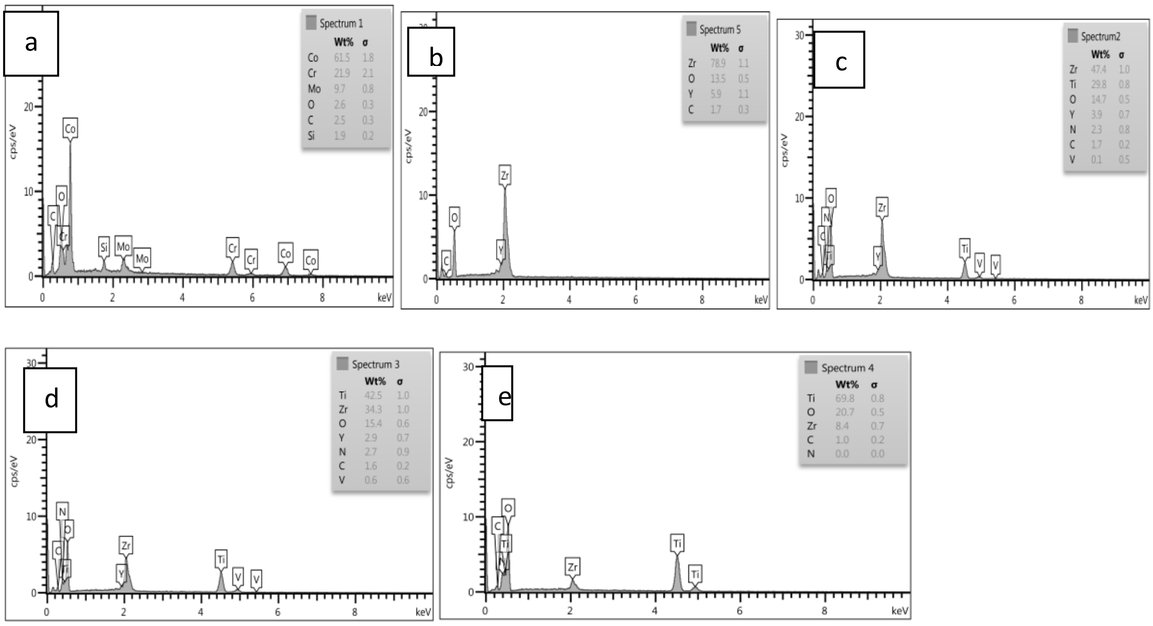


Figure (3) EDS image for A, C1, C2, C3 and C4

Fig(2) displays the SEM views of the surface morphologies of the coatings A, C1, C2, C3, and C4. Splats are seen in typical plasma-sprayed features, and microporosity and cracks on the YSZ/TiO_2 coating are not seen. For YSZ/TiO_2 composite coatings, these particles subsequently spread out, flattened, and quickly formed. They then cooled and consolidated to create the lamellar [21]. The lack of a clear interface between the coating and substrate, however, indicated good interfacial locking [22]. When compared to coatings without TiO2, the deposition layer of coatings with TiO2 content had a more homogeneous and denser microstructure overall.

The corrosion tests

Open circuit potential (OCP)

For every alloy that was tested, the OCP-time in the Hanks solution was calculated at 37°C in relation to SCE. as depicted in Fig4. In this test, the time spanned from 0 to 160 minutes, with a 5-minute interval. Numerous conclusions can be drawn from the aforementioned figure, which shows how the open circuit potential (OCP) changes over time.

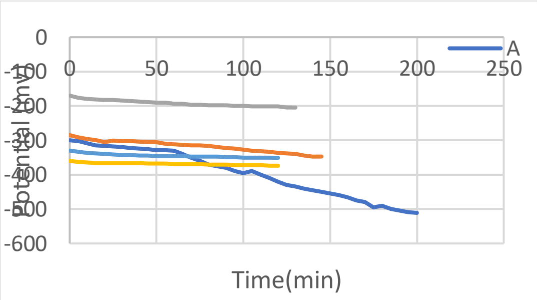


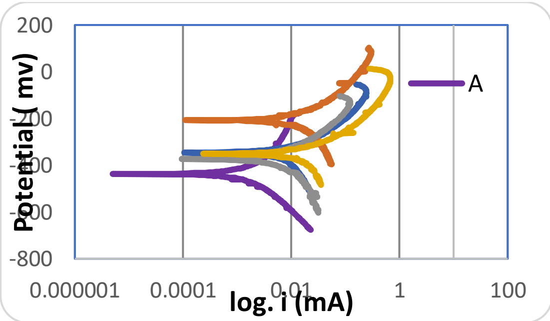
Figure (4) the OCP-time for the alloys A, C1, C2, C3and C4 in Hanks Solution.

The changment in open circuit potential over time help us in estimate the corrosion behavior since OCP is correlated with the type of reactions that occur at the electrodes surface when it comes into contact with a corrosion medium [23] Fig. (4) compares the uncoated and coated sample with YSZ and different TiO_2 percentage **(0,10,30,50)% in** composite coating as shown in fig.(4) the stable potential after 150 minutes of immersion of the coated sample and 200 min, for uncoated sample in hanks solution. It can be observed from fig. (4) that there is a significant toward higher (OCP) for coated sample compared with uncoated sample. The OCP for C1 (-150)mv while for A reach to(-500) which mean that composite coatings have more noble potential and stabilities behavior than uncoated sample these result are similar to[23]

Electrochemical Tests

Hank's solution at pH 7.2 was subjected to corrosion behavior analysis using potentiodynamic polarization. The Tafel extrapolation method was then used to investigate the potentiodynamic curves. The Hank's solution was utilized for immersing the substrates before conducting corrosion tests. Fig.(5) depicts the polarization curve

In order to ensure corrosion resistance in an aqueous environment, it is crucial for the YSZ film to have a uniform structure, free from any structural defects like pinholes, pores, and cracks, and firmly attached to the substrate. Therefore, only the samples that exhibit noticeable corrosion enhancement are presented here. Corrosion assessment has been carried out through potentiodynamic polarization tests.
The variations in corrosion resistance can be attributed to the compactness of the film and its internal structure. Various studies have been conducted on doped zirconia coatings on CoCrMo alloy using different methods, yielding conflicting results. Some researchers have found that the air plasma spray technique resulted in the formation of uneven, porous coatings. Presented here are the values for corrosion current (Icorr), corrosion potential (Ecorr), and corrosion rate (C.R.) for Table 3.



Figure(5) depicts the polarization curve for the alloys A, C1, C2, C3and C4 in the Hanks solution.

Table(3): Alloys in Hanks Solution at 37°C: Corrosion Current (Icorr), Corrosion Potential (Ecorr), and Corrosion Rate (C.R.)

sample	code	Current	E	Corrosion rate (mpy)	Improvement percentage %
Base	A	21,793	-188.6	16.797	--
YSZ	C1	6.96	-347.2	5.359	68
90%YSZ-10TiO_2	C2	8.6	-204.8	6.622	60.5
70%YSZ-30TiO_2	C3	3.6	-373.9	2.772	83.4
50%YSZ-50TiO_2	C4	4.45	-351	3.427	79.5

The variation in values is influenced by multiple factors, including the choice of ceramic materials, porosity, and the coating method. It should be noted that corrosion values of the coating are not solely dependent on the amount of TiO_2 present in the coating, but are also influenced by other factors. These factors can be attributed to variations in microstructural differences, porosity levels, and phase distribution within the coating. However, it is important to acknowledge some limitations in the measurement process of the coating. Measurements should be taken near the center of the ceramic coating, and indentations should be parallel to the substrate to ensure accurate results. Otherwise, the creation of cracks during the measurement process may pose difficulties."

Contact Angle

The bioactivity and wettability of implant surfaces have been established in order to confirm the surface's hydrophilic/hydrophobic character, which influences the implant's performance. The contact angle value, as an indicator of surface wettability and its biocompatibility [24], in fig. (6) shows contact angle value.

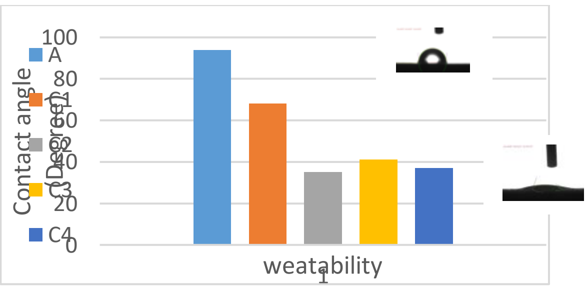


Fig.(6) contact angle for A,C1,C2,C3,and C4

In general, hydrophobic materials are usually characterized by a large contact angle (>90°), whereas a low contact angle characterizes hydrophilicity (<90) the greater the angle, the greater the hydrophobicity of a material. Or other word SAMs were created with varying wettability's: hydrophobic (CA 80°), moderately wettable (CA 48 – 62°), and hydrophilic (CA 35°). [25,26]

Surfaces made of biomaterials with low CAs may not always be more biocompatible. Adequate equilibrium between hydrophilic and hydrophobic surface entities is necessary for blood-contacting devices and tissue engineering substrates. This is because surfaces that are too hydrophobic can increase cell affinity and decrease biocompatibility, while surfaces that are too hydrophilic can hinder cell-cell interactions, which are crucial in tissue engineering. [26,27].

Atomic Force Microscope (AFM)

The depth morphology and surface roughness of both the coated and uncoated substrates were analyzed using an atomic force microscope (AFM), as depicted in Fig (8). The Table (4) shows the value of surface roughness of the samples, and as we note, roughness increases after coating, which is common in coating characterization.

Table (4) shows value of surface roughness

sample code	Surface roughness
A	163.6nm
C1	361.7nm
C2	245.2 nm
C3	316.9nm
C4	252 nm

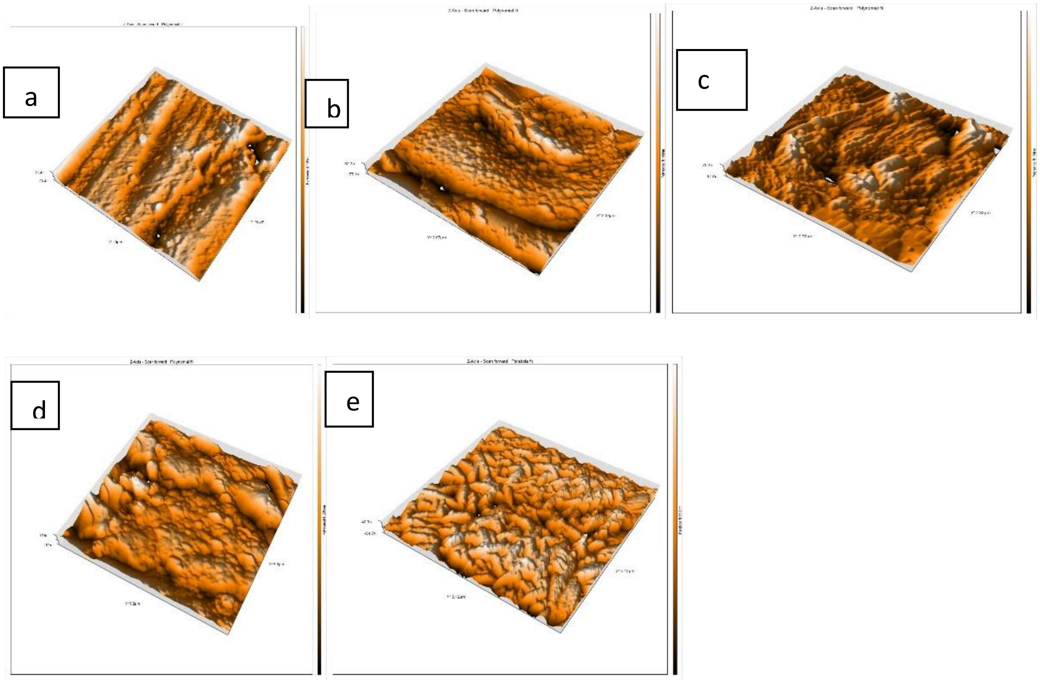


Fig.(8) surface roughness for A,C1,C2,C3,and C4

Roughness of implants' surfaces has an impact on protein adsorption, cell adhesion, and proliferation, suggesting that higher surface roughness allows for more space for biomaterial interactions. It is desired for the bone cells to connect with rough surfaces [28].

conclusion

This research aimed to study the corrosion behavior of a CoCrMo alloy using a YSZ/TiO_2 coating by atmospheric plasma spraying for biomedical implant applications. The metal powder manufacturing technique was employed to prepare the alloy, followed by the application of the YSZ/TiO_2 coating layer using plasma spraying. The composition and chemical structure of the coated samples were characterized using analyses such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Corrosion tests were conducted using Hank's solution.

Key findings and recommendations of the research are as follows:

1. The YSZ/TiO_2 coating layer exhibited promising results in improving the corrosion resistance of CoCrMo alloy. The coating applied using plasma spraying technique resulted in the formation of a homogeneous and cohesive coating layer on the metal surface, thereby enhancing its corrosion resistance.

2. The coated layer achieved a homogeneous distribution of chemical components, indicating the quality and consistency of the deposition in terms of chemical composition.

3. The results demonstrated significantly reduced corrosion in the coated alloy compared to the uncoated alloy, indicating an improvement in corrosion resistance.

4. The use of YSZ/TiO_2 coating by atmospheric plasma spraying is recommended as an effective method for enhancing the corrosion resistance of CoCrMo base alloys.

5. Contact angle analysis was performed on the YSZ/TiO_2 coating on the CoCrMo alloy, and an increase in the contact angle was observed. This result indicates an improvement in surface wetting and a reduction in the water spreading effect on the coating. It can be concluded that the coating exhibits excellent hydrophobic surface properties.

6. The surface roughness of the coating sample increases compared with the uncoated sample,

which leads to an enhancement of biomaterial interactions.

In conclusion, this study recommends the use of a YSZ/TiO_2 coating by atmospheric plasma spraying as a promising approach to improving the corrosion resistance of CoCrMo alloys. These findings can serve as a basis for future developments in the field of corrosion and ternary alloys applications.

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