Synthesis and characterization of porous zirconia parts by nonaqueous electrophoretic deposition technique

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Synthesis and characterization of porous zirconia parts by nonaqueous electrophoretic deposition technique

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Abstract The technological effect of porous implants in biomedical applications has stepped up the look for advanced shaping tools. The present work was mostly concerned on create and control on porosity and surface roughness of zirconia structures that production by electrophoretic deposition (EPD) technique. Distilled water is utilized in this study to help to create the porosity and increase the surface roughness by its addition in little amounts to ethanol suspension. The obtained porous structures were investigated using SEM and AFM analyses. The addition of water affected the properties of the alcohol suspension, reducing the pH and increasing the dielectric constant. The results show that even adding a small amount of water to an electrolytic suspension leads to gas release on the electrode. The resulted zirconia structures showed the 1 ml water addition was the ultimate value to create uniform pores on the deposited part in the case of 0.5 g zirconia powder volume.

1. Introduction

Zirconia is the most distinguished bio inactive oxide ceramics utilized in biomedical uses as they have an attractive mixture of high resistance of wear and corrosion, low friction value and a high value of strength. Zirconia tools have been used in biomedical applications for more than three decades in dental implants and artificial pregnant hip [1]. The success of the clinical process has been detected by implanting zirconia around the world since 1990 [2, 3]. The biological response from zirconia ceramic materials was also pivotal to success in the clinical process of implantation. The events that occur at the front of the physical tissue mainly control the integrity of the implant in the bone [4]. Mostly, it is recognized that a powerful primary connection of osteoblastic cells or their precursors onto biomaterials produces to best bonding between the implant and bone [5]. In this regard, many pieces of research displayed that zirconia implants have good biocompatibility and show cytotoxic properties. If they are added to cell cultures, whichever in nanopowder or monolithic forms [6].

The surface machining process is the first step in designing the implant surface. Previously, researchers were working for long periods following the conventional protocols that were needed for several months for osseointegration [7]. Porosities are significant for the formation of tissue, since they allow the cells emigration and then proliferation in addition to vascularization. Furthermore, a porous surface improves the mechanical interconnecting between the surrounding natural tissue and the implanted biomaterial, imparting higher mechanical stability at this critical necessity [8, 9]. Variations in the roughness of surface implants affect the cells and tissue response by increasing the area of the surface implant close to the bone and in that way developing inserted cells with bone. The implant surfaces have been categorized on various gauges, such as texture, roughness, and irregularity of orientations. Wennerberg and coworkers have classified surface of implants depending on the roughness of surface as (2-3 μm), intermediately rough (1-2 μm), minimal rough (0.5-1 μm) [10].

To manufacture a membrane layer on microporous support or ceramic part for medical applications, the electrophoretic deposition technique appears to be a simple processing procedure. The reason of this due to the electrophoretic deposition suggestions a simple way to control on the morphology and thickness of the deposited film by easy alteration of the applied potential and deposition time [11, 12]. EPD method has attracted a significant deal of care in new time because of its broad zone of uses. EPD can be used for any nanopowder in a colloidal suspension, containing oxides, nitrides, carbides, metals, and polymers. EPD can create parts with an intricate shape, form coatings, and infiltrate (2D) or (3D) woven fibers [13, 14]. The mechanism consists of two stages, at first the electrophoresis process and then the deposition process. Firstly, between the two electrodes, an electric field is applied. The charged particles are suspended in a suitable liquid and traveled in the direction of the electrode. And that has oppositely charge establishing to the electrophoresis stage. The particles collection at the electrode builds a comparatively dense and uniform film and is indicated to the deposition stage. A suspension in a stable form comprising the charged particles is free to transfer an electric field is utilized [15, 16]. Two factors groups determine the characteristics of this technique: 1- associated with the procedure like deposition time and density of the current and, 2- associated with the suspension like viscosity, pH and dielectric constant. The coating's thickness and their morphology intensely depend on the EPD parameters such as the current density and pH of the suspension [17, 18]. During the studies, it was observed that the dielectric constant value of the suspensions must be ranging between 12 and 25 for the deposition process. In suspensions, the dielectric constant values less than 12, the insufficiency of dissociative power stops the deposition. While in suspensions with dielectric constant values higher than 25, electrophoresis is stand up by the decrease in size of the double layer zone, created by elevating the ionic concentration [19].

Most studies were done to create ceramic using the EPD method by using organic solvents, such as amyl alcohol and dichloromethane. In the case of aqueous EPD, O_2 gases (on the anode) and the development of H2 gas (on the cathode) are often caused by H_2O electrolysis. These bubbles are a source of gas development for initiating defects (voids and pores) in the ceramic mortar through the aqueous EPD method. Thus, the development of gas through aqueous EPD was the most serious problem. It must be installed in the ceramic production or coating formation process for a uniform and dense microstructure [20, 21, 22].

In general, the EPD technique is appropriated method for manufacturing open-porosity ceramic structure with controlled pore size, distribution, and engineering. The route is resilient adequate to be altered considerably to the specific desires of the final product [23].

In this work, porous zirconia parts have been prepared by the technique of EPD. The work was concerned with enhancing the biocompatibility of zirconia parts by increasing the porosity and roughness of its surface through the production process. Unique water additions have been added to zirconia ethanol suspensions to modify the pH and electrical suspension properties. Each deposited part is sintered to characterize the pores.

2. Experimental work

3 mol%Y_2O_3–ZrO_2 (Hongwu International Group Ltd; China; average particle size 70-80 nm) powder was used for the preparation of zirconia samples. Distilled water and ethanol (99.9% C_2H_5OH, Scharlab, Spain) were utilized as a suspension medium. Acetic acid (99.7% CH_3COOH, Hopkin and Williams, Britain) was added to suspensions as a dispersion material to enhance particle charging.

A power supply (TP120-5S, INSTRUMENTS (HK) CO., LTD, China) was used as a DC power supply in the electrophoretic deposition method. The electrophoretic cell was a 50 ml cylindrical glass beaker, and the electrodes were stainless steel (316L) plate with dimensions (2.5 × 1 × 0.1) cm. The distance between the two electrodes was 1.2 cm. The cell of the deposition cell is shown in Figure 1.

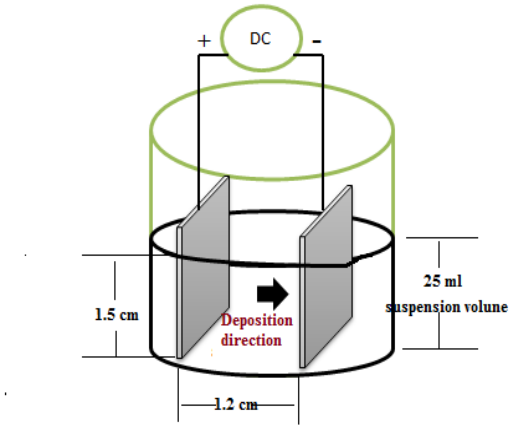


Figure 1. Deposition cell.

Water-based suspensions were used for the production of porous samples, while ethyl alcohol-based suspensions were used for the fabrication of dense samples. The zirconia ceramic powder was added to the solution (0.5 g for each 25 ml) and continuously mixed to form the suspension. Then, a small amount of acetic acid was added to this suspension. Also, this suspension was mixed continuously using a magnetic stirrer (SH-2 model, BestEquip Co., US) for a period of 60 min to complete the dispersion of the zirconia particles. After that, the pH of this suspension was measured using a pen-type pH meter (pH-009(I) meter, POMETER, China) before the process of deposition.

An applied voltage (80V) is utilized in the process and the total process time is 30 minutes. All dimensions of the deposits were determined with a digital micrometer (TERMA, 0-25 mm /0.001 mm, China). The weight of the deposits was determined with a digital Scale (PGW 753e, ADAM Equipment, US). From the measurements of the weight and dimensions of the deposited parts, the rate of deposition was computed through the same period of the deposition for the all experiments in this current study.

To control the amount and size of porosity, which is generated in deposited parts, small amounts of distilled water were added to the ethanol suspension. Acetic acid has been added to the suspension to regulate the pH of the suspension to improve the deposition rate by charging zirconia particles.

The sintering of the deposited parts is performed using a high-temperature programmable furnace (HUMONLAB model, Germany) at Babylon University / ceramic laboratory. The heating rate was 10°C/min, first holding time at 600^{o}C for 1 hour, the heating continues up at the same rate until it reaches to1500^{o}C. Deposits were held for the second time at 1500 ° C for 2.5 hours, and the samples were left at the furnace for cooling slowly. Microstructural observations of the sintered parts were carried out by SEM (Inspect S50, FEI Co., Netherlands). The surface roughness measurement was carried out by an Atomic Force Microscope (PHYWE/Nano Compact AFM type, UK).

3. Results

The comparison between the deposits made by DC-EPD from the ethanol suspension and the deposits formed from the aqueous suspension at the same voltage (80 V) is manifested in the Figure 2. The dense samples are provided by the ethanol suspension due to no released gases through the deposition process. And that leads to providing high density and homogenous samples, as shown in Figure 2a.

On the contrary, porous samples provided by watery suspensions, as shown in Figure 2b. The porosities advanced as a result of evaporation O_2 and H_2 during the deposition process; which leads to generating bubbles on the deposited layer. The evaporation of O_2 and H_2 prevents the agglomeration of particle and uniform formation of the layer. The particles are taken away as a result of the bubbles ascending.

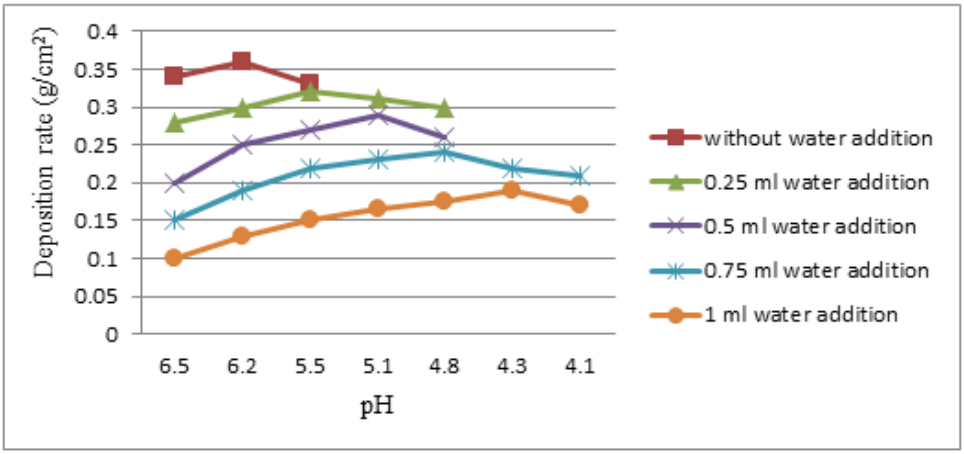
(a) Ethanol suspension (b) Water suspension

Figure 2. Photos of samples that produce from:(a) Ethanol suspension; (b) Water suspension.

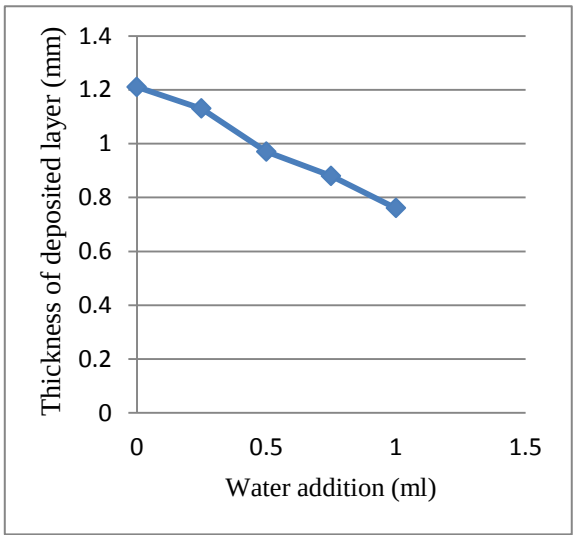
Figure 3 shows the relationship between thickness and deposition rate with water addition to ethanol suspension. The thickness and deposition rate of ZrO_2 tended to decrease with increased added water in the deposition. ZrO_2 was deposited a 0.36 g/cm^2 from ethanol suspension. The deposition rate decreased to 0.32 g/cm^2 when the added water was 0.25 ml, and this reducing was continues with increasing the added water. The reason for this decrease is due to a high dielectric constant of water that led to the change of the electrical properties of the suspension. Dielectric constant values of the used materials are listed in Table 1. The pH and electrical properties of suspension are modified via the addition of acetic acid to enhance the rate of sedimentation. The acetic acid decreased the dielectric constant of suspension and charged the particles of zirconia. In each case of water addition, it can be noted that a higher deposition of the zirconia particles can be obtained at a specific pH value of suspension. At such particular value of pH, the values of the electrical properties of suspension are high; thus the particles of zirconia are deposited and highly packed upon the electrode. The deposition rate reduced beyond reaching the high values, and the reason for that is attributed to the increment in the acidity influence of the adverse impact upon the properties of the deposited suspension, the dielectric constant and pH.

Table 1. Physical properties of accessible materials [24, 25].

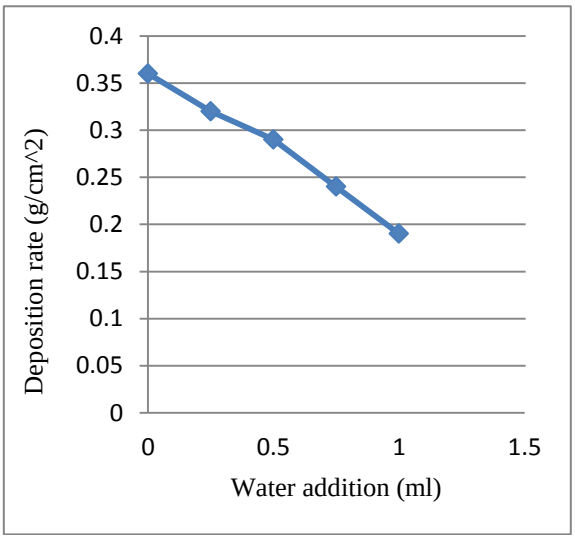
Material	Relative dielectric constant
Zirconia (ZrO2)	12.5 - 26
Water	78.2 - 80
Ethanol	24.55
Acetic acid	6.2



(a)



(b)



(c)

Figure 3. Effect of water on ethanol suspension :(a) Deposition rate with pH of suspension vs. water additions (0, 0.25, 0.5, 0.75, 1) ml; (b) Max thickness of deposited layer at a higher deposition rate. (c) Deposition rate vs. water additions.

Figure 4 shows the pH values that were deposited at much higher rates in each case of water addition. Figure 4 demonstrated that it should add more acid to suspension if increasing the water addition. The acid decreased the dielectric constant of the suspension and thus led to an increase in the deposition rate. That means the suspension should be more acidity to dispersion the ceramic particles.

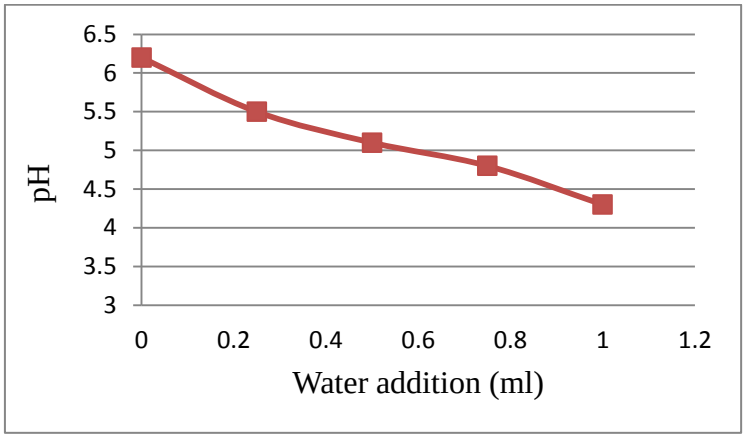
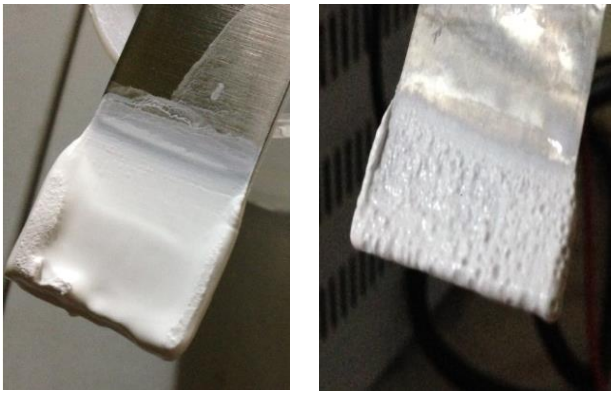


Figure 4. pH values for max deposition rate vs. water addition.

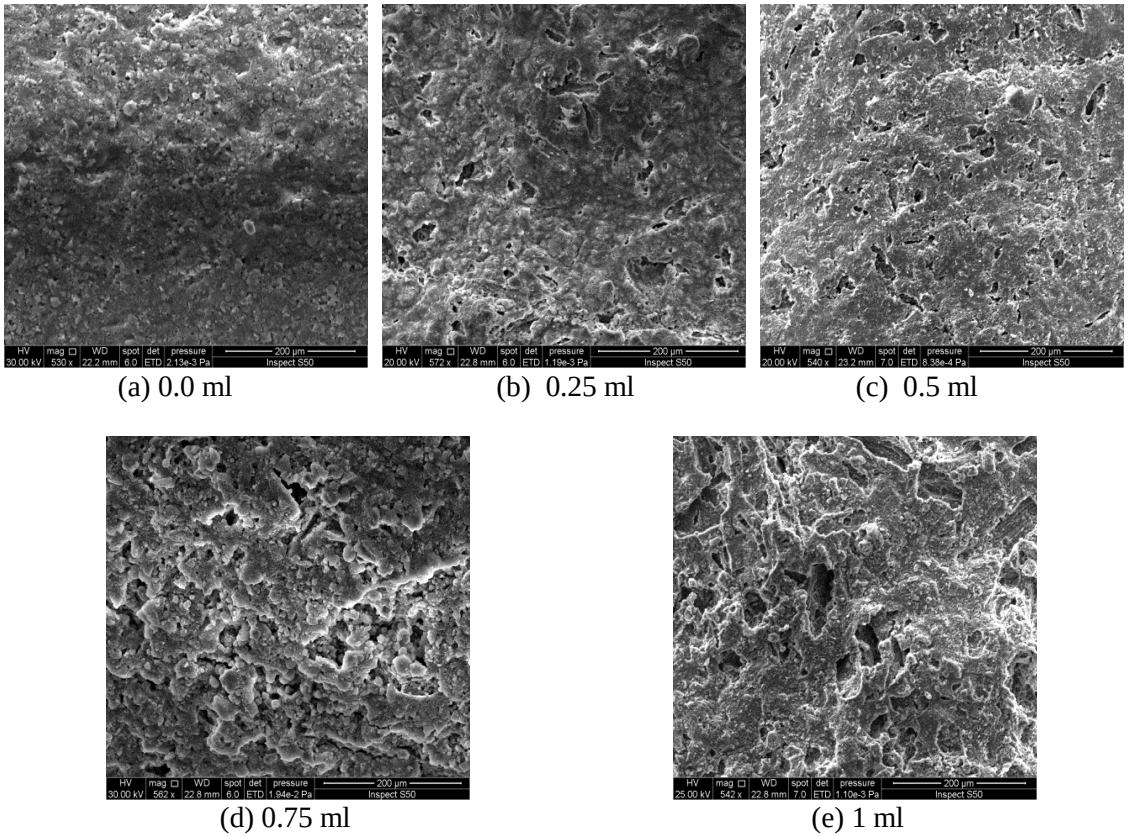
It should be noted that adding more than 1 ml of water alters the chemical and physical properties of the suspension, due to dissociation of water and an increase in the amount of hydrogen and oxygen, which affects the charge and stabilizes the suspension particles. The unstable suspension that produced an irregular deposition for the sample [20] is elucidated in the Figure 5. It's thought that the reason for this is the adverse influence of water on the properties of suspension, particularly on the acidity and dielectric constant [24, 25].



(a) (b)

Figure 5. Deposited layers from (a) ethanol- 1 ml water addition. (b) ethanol -1.25 ml water addition.

Figure 6 shows SEM images for deposited parts that are resulting from the addition of water to the ethanol suspension. The addition of water even in a small amount to the ethanol suspension leads to release gases on the electrode through the deposition process. So, we resorted to adding water in a small amount to the ethanol suspension. The influence of adding water to the ethyl alcohol suspension was clarified through the SEM pictures in figure 6 when adding 0.25 ml water, notice the appearance of some pores when compared with SEM image in a case without water addition. But this porosity was a small size, as shown in Figure 6b. Increasing the amount of added water (0.5, 0.75 and 1 ml) increased the size of pores, and the reason was increased gas release at the electrode, this can be shown in Figures 6c, 6d, and 6e. In the case of addition 1 ml water, the size of big pores was nearly 100 μm. And that attribute to release more gasses at an electrode [20].



(a) 0.0 ml (b) 0.25 ml (c) 0.5 ml

(d) 0.75 ml (e) 1 ml

Figure 6. SEM image of a zirconia surface with water addition.

AFM was utilized to characterize the water addition to ethanol suspension on the surface of deposited parts. Figure 7 shows the roughness value of the outer surface for samples that deposition from suspensions with different water amounts. It can be observed that the roughness value for a sample with 0.25 ml added to water in suspension has a higher roughness compared with the sample without any additional water. Also, Figure 7 shows that increasing the water addition amount to the zirconia suspension leads to increase surface roughness, which leads to release gases on the electrode and formation of porosity which affects the stacking of particles on an electrode [22]. This is consistent with the SEM images in Figure 6.

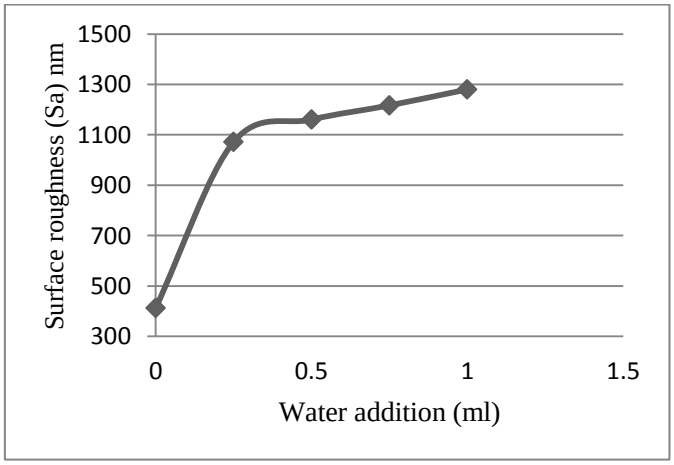


Figure 7. Surface roughness.

Figure 8 shows the topography of a ~ 50×50 µm for the surface of zirconia by EPD technology with additional variables that resulting from the amount of water to the suspension. From the AFM

topographic images, increased differences between the maximum and minimum height at surface topography are observed.

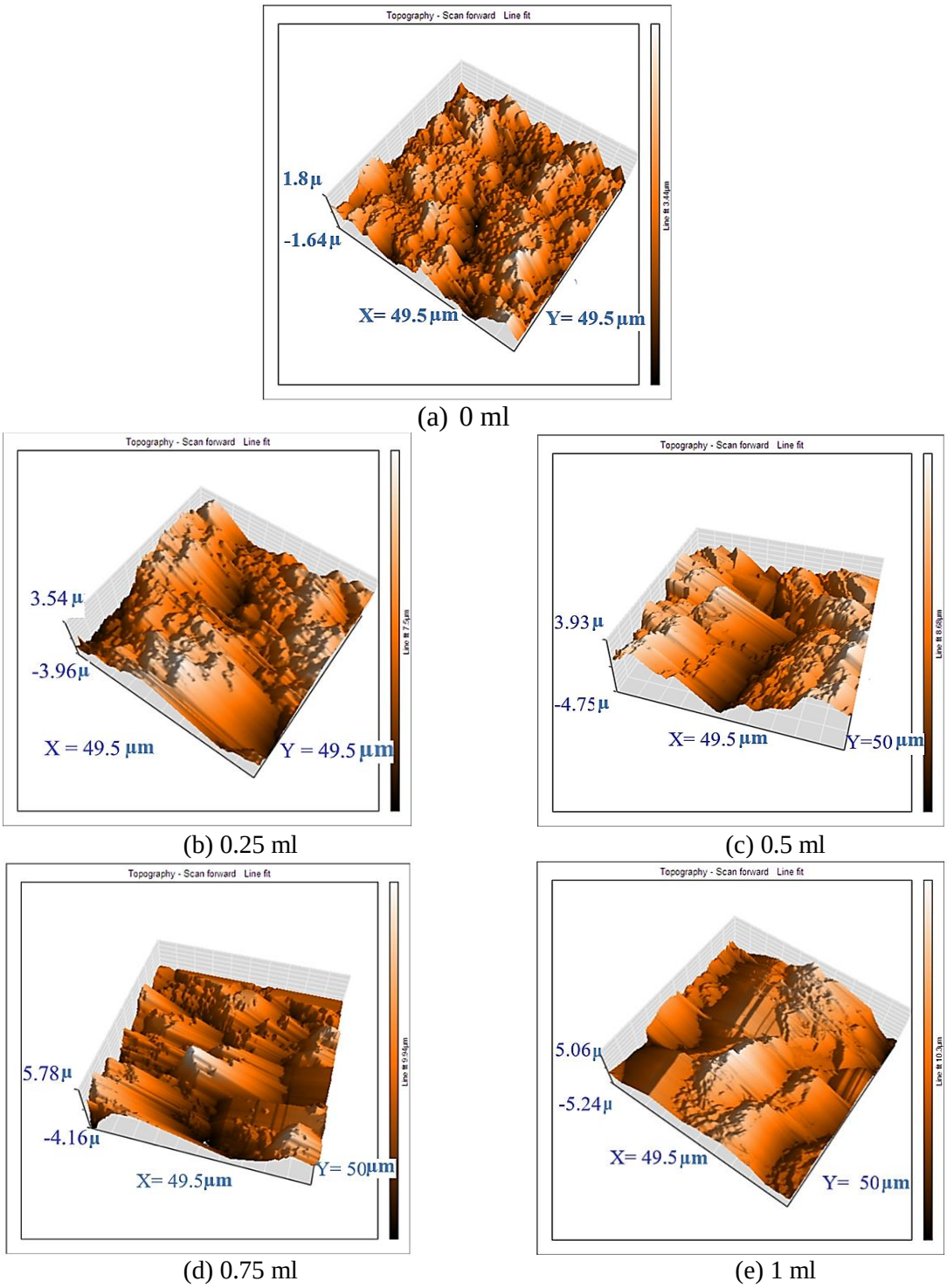


Figure 8. AFM topography images for Zirconia samples with water addition.

4. Conclusions

1. The amount and size of pores (diameter 1-5 mm, as shown in Figure 2B) in the parts deposited by the aqueous EPD process are high and uncontrollable. The pores created by the aqueous

EPD process impact negatively on the mechanical properties of the deposited part. Therefore, the pore production method must be controlled to obtain the required pores.

2. The presence of a slight quantity of water in the ethanol suspension created pores in the deposited part resulted from the released gases on the electrode. The increase in the water amount leads to further increases in the amount and size of the formed pores.
3. The additional amount of water affects the suspension properties (pH and dielectric constant) and then affects the precipitation process. The suspension features can be modified and improved by adding acid, but there is a certain amount, and any extra amount will impact negatively on the deposition process.
4. The addition of water does not only affect porosity formation but also increases the surface roughness of the deposited part.

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