



# The Role of Uric Acid to Reduce the Corrosion of Co-Cr-Mo Alloy as Joint in Presence of Ca and Vitamin D3

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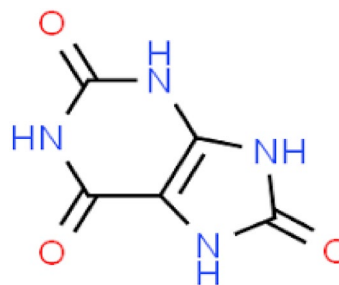
## Abstract

The effect of increasing uric acid which is biologically undesirable had a positive effect on reducing the corrosion of Co-Cr-Mo alloy that used in artificial joint. This investigation was done by the electrochemically study through addition 8 mg/dL uric acid to simulated body fluid (Ringer's solution) at pH = 7.4 and Temp. 37 °C in the absence and presence two concentrations of each Calcium (1500 and 2500 mg/L) and Vitamin D3 (100 and 600 mg/L) representing a normal and mega dose of each drug. The results of corrosion showed that all experimental addition behave as inhibitors by adsorption these molecules on metallic surface to form a layer of coordination complexes (Co<sup>2+</sup>-uric acid and Co<sup>2+</sup>-uric acid) supported by accumulation of organic molecules of D3 to get inhibition efficiency ranged from 98.05 to 99.46%. The characteristic methods were used to support the results of corrosion, where the scanning electron microscopy showed the fully coverage by uric acid molecules and calcium salt as well as D3 molecules with lower defects on the surface of base alloy, atomic force microscopy indicated the adsorption of uric acid, calcium carbonate and cholecalcifero molecules with increasing in maximum height and depth compared with blank as well as increasing in surface roughness that reach to 14.17, 21.53 and 16.76 nm in the presence uric acid alone, uric acid-2500 mg/L Ca and uric acid-600 mg/L D3 respectively compared with 3.107 nm for blank without additives.

**Keywords** Co-Cr-Mo alloy · Uric acid · Joint · Gout · Ca · Vitamin D3

## 1 Introduction

Uric acid is present as urate which is a salt of uric acid and when it is increase in the blood will form crystals; its normal amount is 1.5 to 6.0 mg/dL in blood for women and 2.5 to 7.0 mg/dL for men with the solubility limit of (6.8 mg/dL) and beyond this limit it will form a monosodium urate [1]. Uric acid is a heterocyclic compound has carbon, nitrogen, oxygen, and hydrogen atoms with the formula of C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>O<sub>3</sub> as follow:



The abnormal concentration of uric acid is associated with a different medical conditions and the excess serum accumulation of uric acid can cause arthritis and will precipitate as needle-like crystals in joints and capillaries. The important question in this field is; what can happen for artificial joint in the case of arthritis in the presence of immune drugs?

Many authors studied the effect of drugs on implant including *vitaminD3* by Grzegorz et al. [2], where they showed its positive effect on bone metabolism in

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osteosuppression via the induction of osteoblasts and osteoclasts and continuous bone remodeling around the implant after prosthetic restoration. The analysis of *vitaminD3* effectiveness in bone metabolism, risk of fractures and falls was investigated by Jemina et al. [3] and they concluded that the administration of doses higher than 100,000 IU is considered a megadose. The effect of *Ca* concentration on the bone tissue response to *Ca* incorporated titanium implants was investigated by Byung-Soo et al. [4] through inserting them in the tibia of nine New Zealand White rabbits and they showed by histomorphometrical analyses that there is no significant differences in bone–metal contact, bone area and newly formed bone measurements between implants. In addition, the role of *caffeine* was reviewed by Manuela et al. [5] on Co-Cr-Mo alloy and they showed that caffeine produces an inhibitory effect on the anodic currents due to its adsorption on the surface of the alloy. Temperature is another parameter with an influence on corrosion processes, the effect of *proteins* was investigated by Mohd et al. [6] on Co-Cr alloy and others and they showed the immense influence on the corrosion, biocompatibility and wear properties of implantable metals, where they indicated that proteins inhibit or promote metal degradation, depending on the type of proteins, their concentration and the properties of the implant material, also they showed that the interactions of metal ions with proteins (and amino acids) create colloidal organometallic complexes. The effect of combination *methotrexate* with *glucocorticoid* was studied by Janaina et al. [7] and in general study the corrosion of Co-Cr-Mo alloy in simulated body fluid [8] including the effect of *aspirin*, *paracetamol*, and *mefenamicacid* on this alloy by Zina et al. compared with SS 316L in the absence [9] and presence of *uricacid* with two levels (7 and 12 mg/dL) [10] and also they indicated the inhibitive role of these drugs with uric acid. Non-steroidal anti-inflammatory drugs also studied by Brent et al. [11], but they indicated that the dental implant osseointegration may be affected negatively by an inhibitory effect of non-steroidal anti-inflammatory drugs on bone healing in vulnerable patients. The study in different bio solution was done by Robert et al. [12] including urine, serum and joint fluid by various methods and they showed that Co-Cr-Mo alloy exhibited small passive region in joint fluid and serum, but a much large region for urine. The comparison with other bio implants [13], as well as the effect of arthroplasties on knee joint were achieved by Donatella et al. [14] and they reported the eliciting an immune response whose role in the outcome of the arthroplasty is still unclear. Other corrosion studies including Co-Cr-Mo alloy also done [15, 16], after surface modification by laser [17, 18], effect of *citricacid* [19] which behave as inhibitor. Also, Alenazi investigated about rheumatoid arthritis (*RA*) and its effect for tissue disorder [20]. In this work, (8 mg/dL) of uric acid was added to simulated body fluid to study

the excess of this acid on corrosion of Co-Cr-Mo alloy with some concentrations of *Ca* and *D3* as immune drugs.

## 2 Experimental Part

### 2.1 Materials

Co-Cr-Mo alloys were obtained from “Fusion Frame, Partial Denture” with chemical composition of (Co 62.7, Cr 29.0, Mo 6.0 wt% and remain C, Fe, Si, Mn), Made in Germany, these cylindrical specimens have dimension of (20 mm height and 5 mm diameter). The corrosive medium was Ringer’s injection “BFSBottle” which contain (NaCl 8.6 gm, KCl 0.3 gm,  $\text{CaCl}_2$  0.33 gm and water for injection Q.S). Uric acid was added in concentration of 8 mg/dL, two concentrations of calcium tablets were tested included (1500 and 2500 mg/L) and also two concentrations of vitamin D3 included (100 and 600 mg/dL).

### 2.2 Corrosion Test

The corrosion test was performed by recording open circuit potential (*OCP*) and polarization curves for tested alloy in the absence and presence of different doses of *Ca* using three-electrode cell represented by *Pt* electrode as counter, saturated Calomel electrode (*SCE*) as reference, and Co-Cr-Mo samples as working in Ringer’s solution. All experiments were carried out using Compactstat (Potentiostat/galvanostat), Ivium with controlled software at 37 °C, the data were calculated using Tafel extrapolation method and then corrosion rate and polarization resistance were calculated [21].

### 2.3 Characterization Techniques

Some techniques were used to characterized the corroded surface included field emission scanning electron microscopy from (FEIQUANTA 250, Czech Republic) as well as calculation the particle size. On the other hand the topographical examination and particle analysis was done by an Atomic Force Microscope from (NaioAFM 2022 nanosufr, Switzerland, and ultrasharp Au tip).

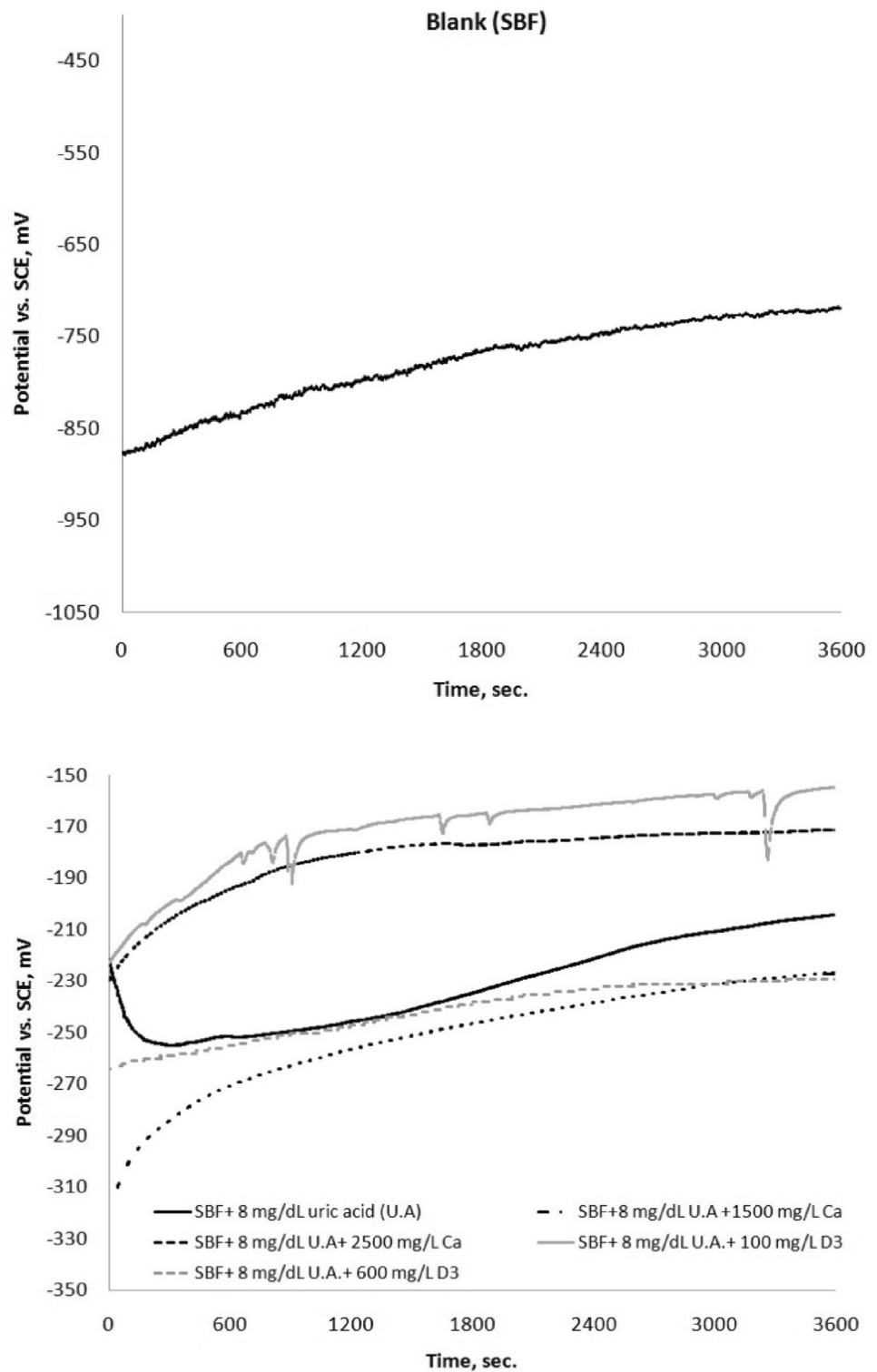
## 3 Results and Discussion

### 3.1 Corrosion Data

The electrochemical behavior of tested alloy in the presence of high level of uric acid and two concentration of each *Ca* and *D3* is presented by *OCP* scan and Tafel plots. The potential-time measurements of these cases are shown in

Fig. 1 which illustrate that the presence of uric acid without and with Ca and D3 shifted the  $E_{oc}$  toward noble direction as in Table 1. The lower concentrations of each drug have nobler potential compared with higher concentration due to increasing the excess accumulation of their molecules over the metallic surface.

**Fig. 1** Potential-time plot of blank and for effect of uric acid

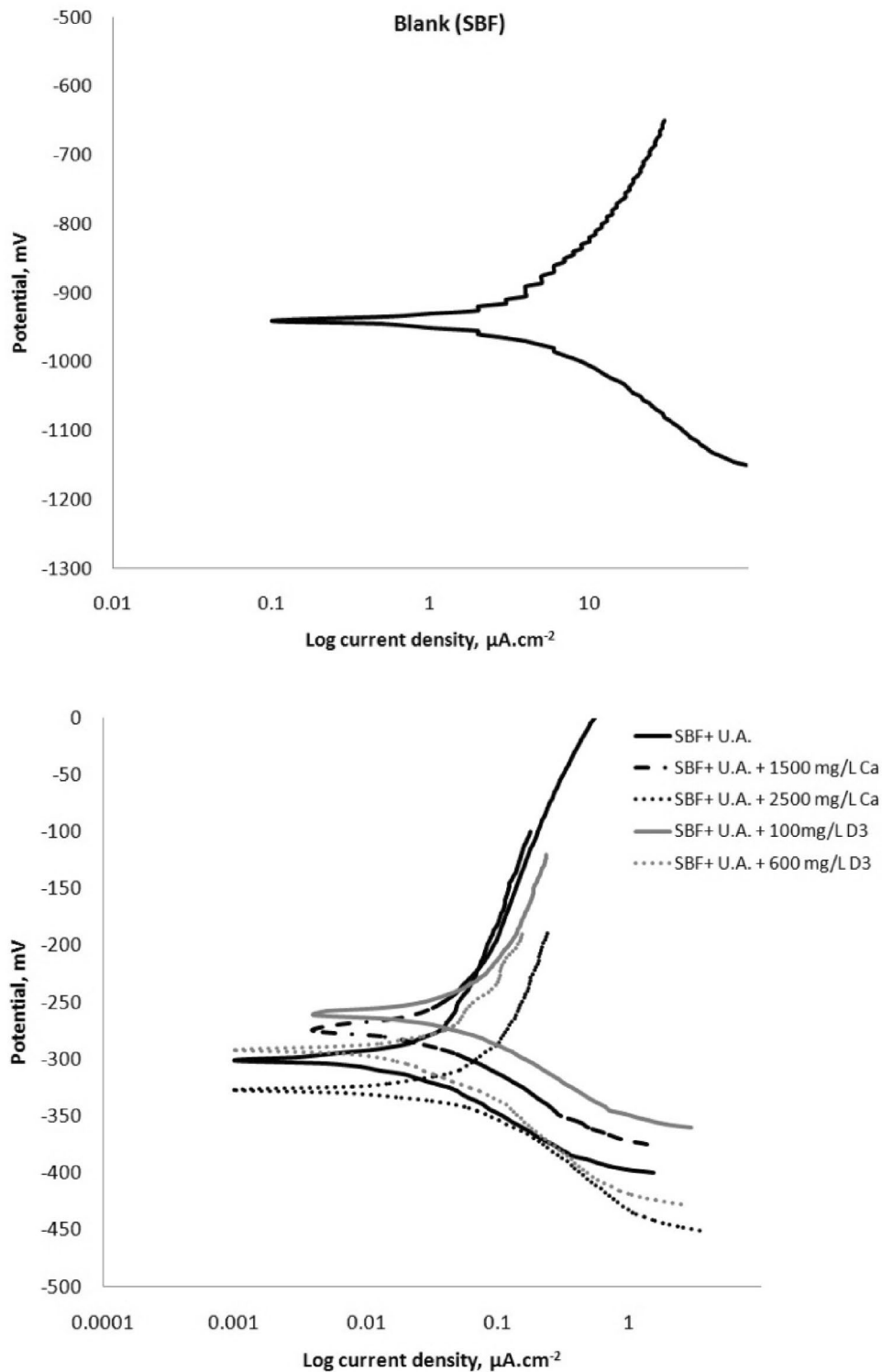


The Tafel plots of the effect for uric acid are shown in Fig. 2 indicating that addition of uric acid without and with Ca and D3 shifted the corrosion potential toward more noble values with clear decreasing in corrosion current densities especially for uric acid without drugs to give the lowest corrosion rate ( $C_R$ ) and highest polarization resistance ( $R_p$ ) (see

**Table 1** The value of OCP in the presence of uric acid

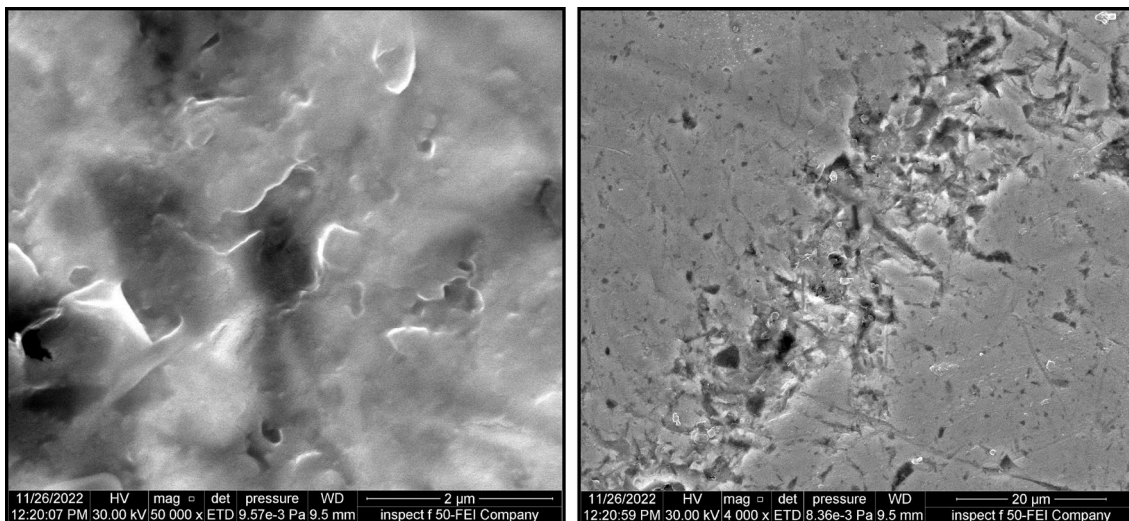
Conc. of u.a. in mg/L	$E_{oc}, mV$	Conc. of Ca, mg/L	$E_{oc}, mV$	Conc. of D3, mg/L	$E_{oc}, mV$
0	- 719	u.a. + 1500	- 171	u.a. + 100	- 155
8	- 204	u.a. + 2500	- 227	u.a. + 600	- 229

**Fig. 2** Tafel plots of blank and for effect of uric acid in SBF



**Table 2** Corrosion data for effect of two doses of Ca and D3 with uric acid on corrosion of Co-Cr-Mo alloy in SBF

Conc., mg/L	$-E_{corr}$ (mV)	$i_{corr} \times 10^{-3}$ (mA/cm <sup>2</sup> )	$-b_c$	$+b_a$	$C_R$ (mm/y)	$R_p \times 10^3$ ( $\Omega$ cm <sup>2</sup> )	$IE$ (%)
			mV/dec				
Blank (SBF)	938	3.752	153	280	4.04	11.45	–
SBF+uric acid	302	<b>0.02024</b>	<b>66</b>	<b>116</b>	<b>0.022</b>	<b>902.46</b>	99.46
SBF+u.a.+1500 mg/L Ca	<b>273</b>	0.03697	83	183	0.040	670.66	99.01
SBF+u.a.+2500 mg/L Ca	328	0.07303	94	252	0.079	407.06	98.05
SBF+u.a.+100 mg/L D3	<b>261</b>	0.04668	72	148	0.050	450.55	98.76
SBF+u.a.+600 mg/L D3	294	0.03473	92	153	0.037	718.31	99.07



**Fig. 3** FESEM of corroded alloy in SBF

Table 2) that calculated according to the following formula using the equivalent weight ( $e$ ) and density of alloy ( $\rho$ ), and Tafel slopes ( $b_c$  and  $b_a$ ) [22, 23]:

$$C_R = 0.13 \times i_{corr} \left( \frac{e}{\rho} \right) \tag{1}$$

$$R_p = \frac{b_c \times b_a}{2.3 \times i_{corr}(b_c + b_a)} \tag{2}$$

This behavior is attributed to the nature of uric acid molecule with active centers on nitrogen and oxygen atoms to be good adsorbed on metallic surface of alloy especially without Ca and D3 that hinder the getting full coverage by uric acid molecules. On the other hand, the study of the implant-related inflammatory arthritis by Thomas Dorner showed that immune activation play a vital role in introduction of arthritis by an implant in addition to producing wear debris by metallic biomaterials included free metallic ions, organometallic complex, inorganic metal salts and oxides [24].

The full coverage by uric acid can be seen through the lowest values of Tafel slopes that give indication to reduce

both the dissolution of metals and reduction of oxygen at the alloy’s surface.

This inhibitive role of uric acid with drugs lead to calculate inhibition efficiency ( $IE\%$ ) using the current density in case of additives compared with current density of blank as follow [25]:

$$IE\% = \left[ 1 - \frac{i_{corr,with\ additives}}{i_{corr,blank}} \right] \times 100 \tag{3}$$

The results show the getting excellent inhibition for alloy surface in the presence of three additives and the best inhibition was for presence uric acid without drugs due to coordination complexes that may be formed between the uric acid molecules and released ions from base alloy.

The inhibitive role of combination between uric acid and added drugs can be discussed as follow: where the two main components of calcium supplements are carbonate and citrate, and may be gluconate and lactate, but the  $CaCO_3$  is the cheapest and often it is a good first choice as in the present work. In spite of poorly solubility of

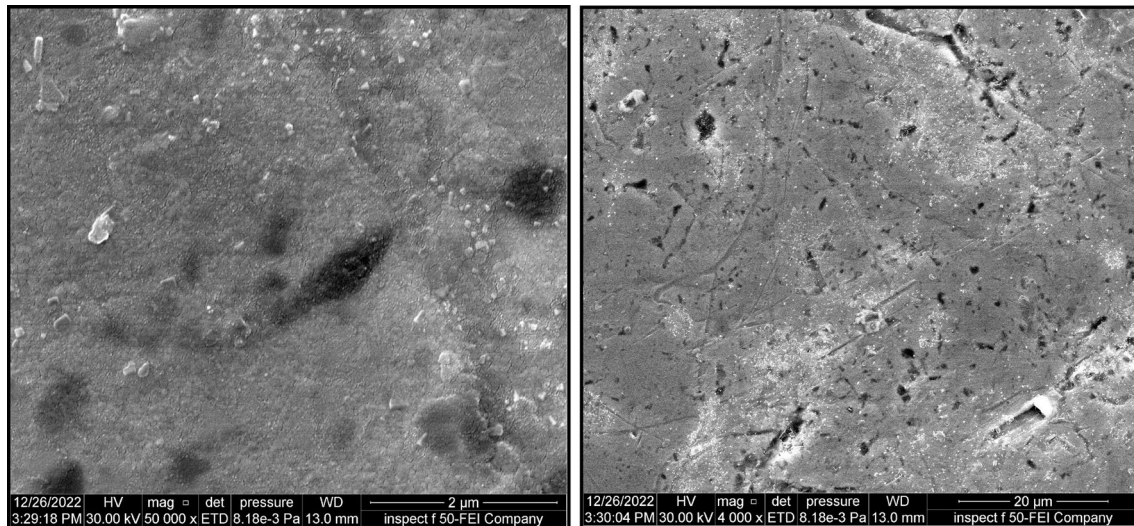


Fig. 4 FESEM of corroded alloy in presence of uric acid only

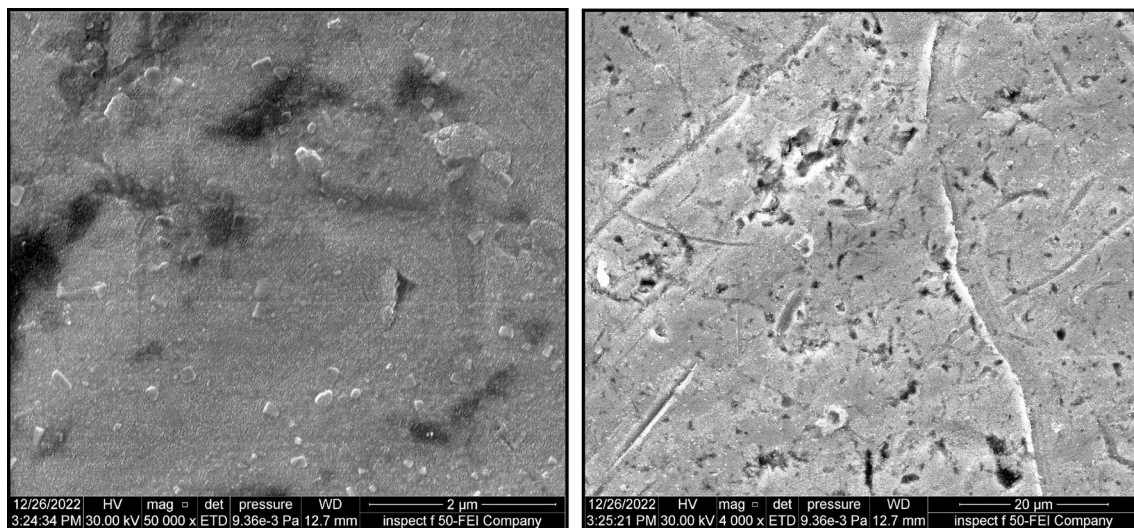


Fig. 5 FESEM of corroded alloy in presence of uric acid-Ca

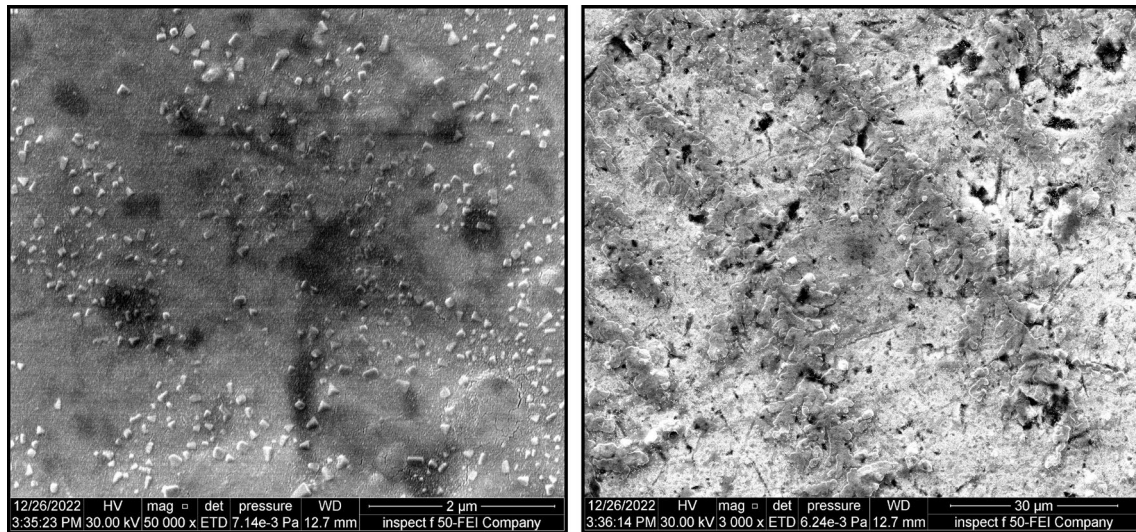
$CaCO_3$  in pure water, it will dissolve in human body fluid as follow:



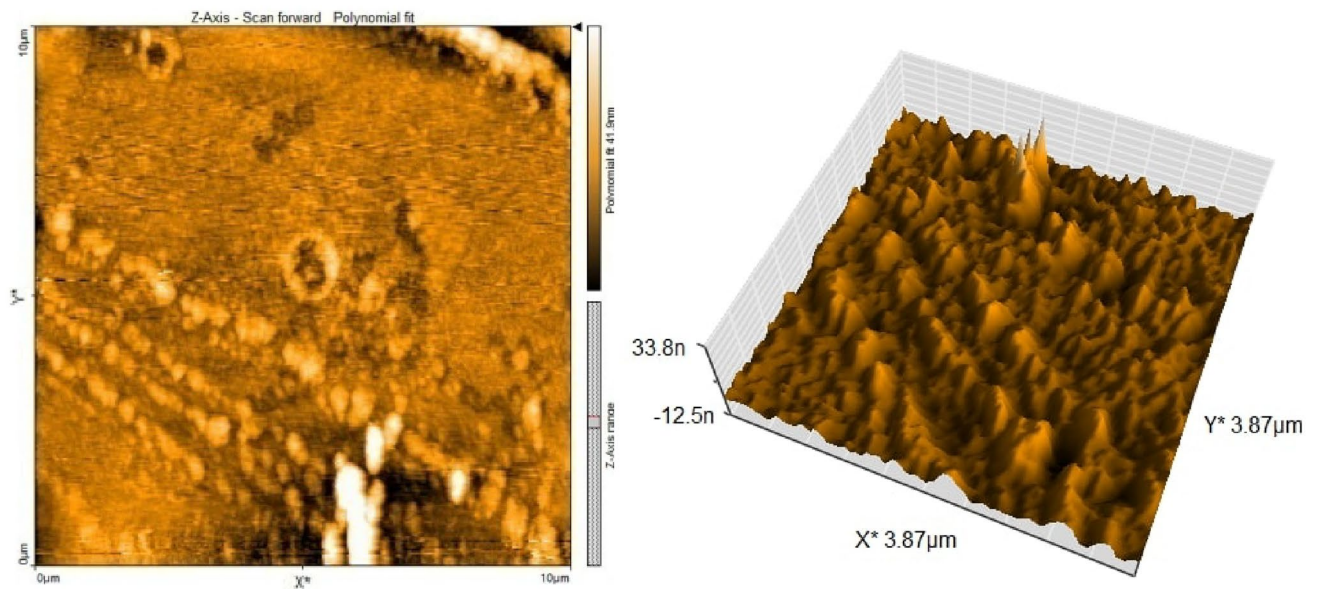
The later ( $CO_3^{2-}$ ) can combine with hydrogen ion to form bicarbonate, and then to form carbonic acid as follow:



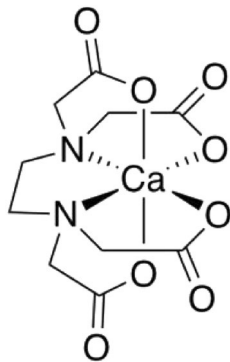
Calcium ions can be adsorbed on the surface and because of the large size of ( $Ca^{2+}$ ), it has high coordination numbers to form structure of the polymeric  $[Ca(H_2O)_6]^{2+}$  center in hydrated calcium chloride and can be deposited to represent a sufficient cathodic sites on the alloy's surface. In addition, it can form complexes with uric acid molecules such as a complex between ( $Ca^{2+}$ ) and EDTA as in following form, to act a cover on the metallic surface:



**Fig. 6** FESEM of corroded alloy in presence of uric acid-D3



**Fig. 7** 2D and 3D images for alloy surface in SBF



On the other hand, vitamin *D3* is an organic molecule and it can behave as inhibitor and in the metabolic process, it is converted into the new form (i.e., from Cholecalciferol to Calcifediol and Calcitriol) through livers and kidneys, respectively, as follows:

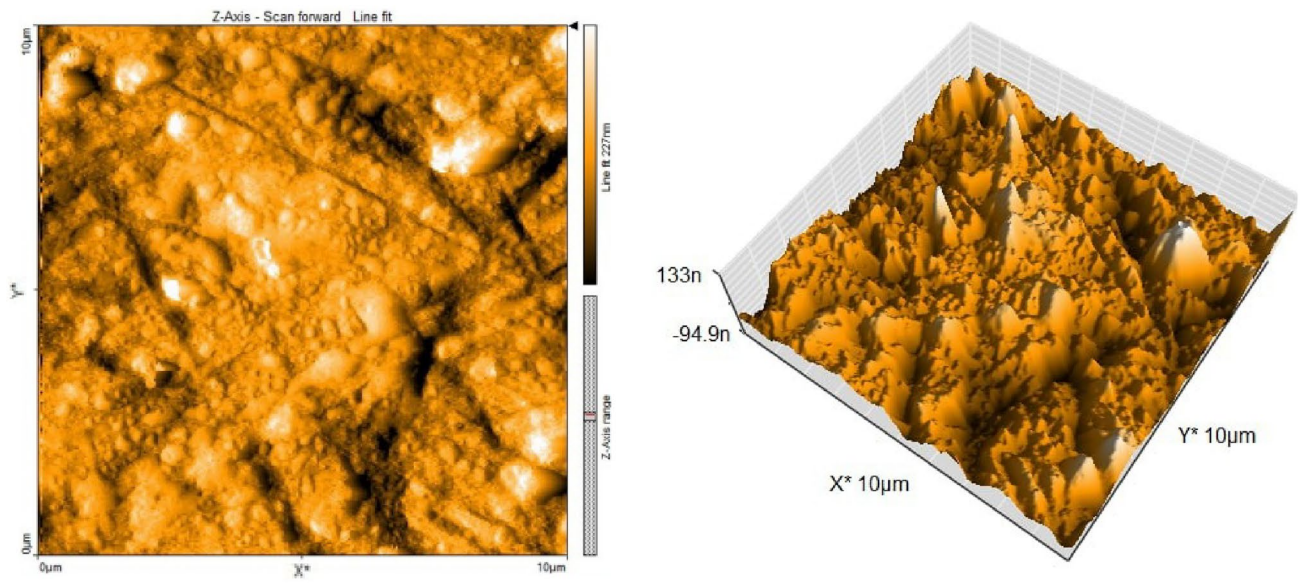


Fig. 8 2D and 3D images in presence of uric acid

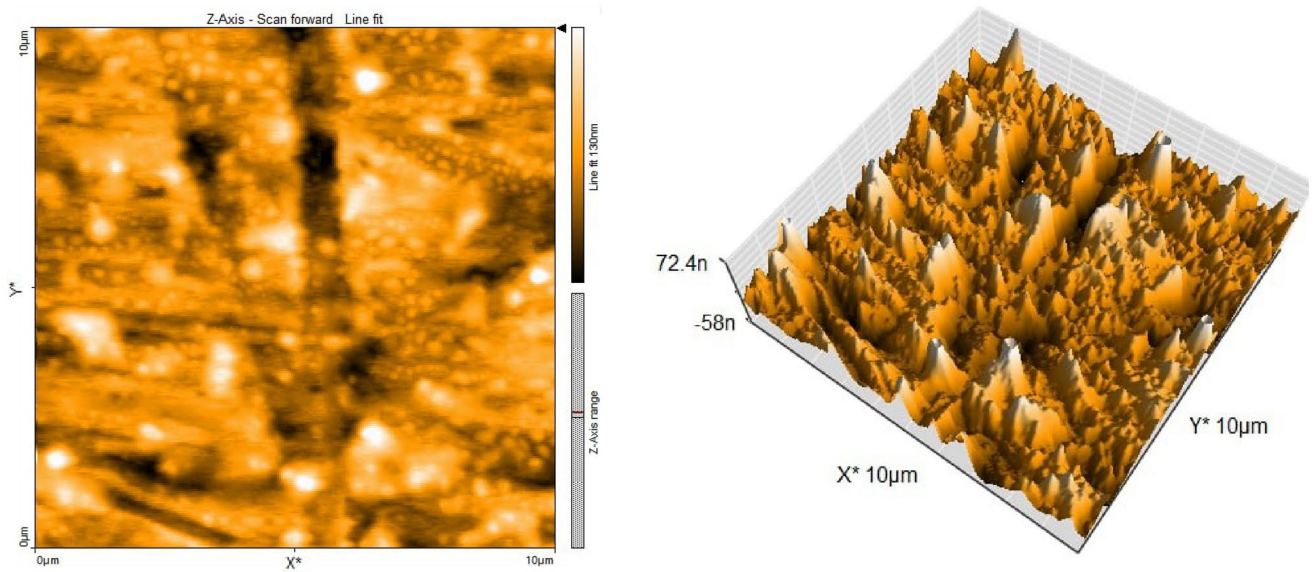
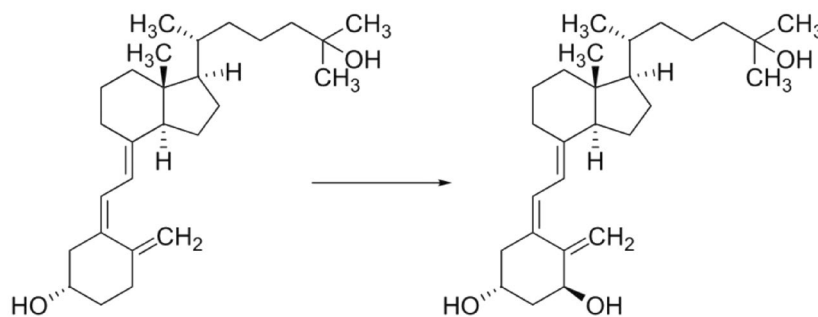
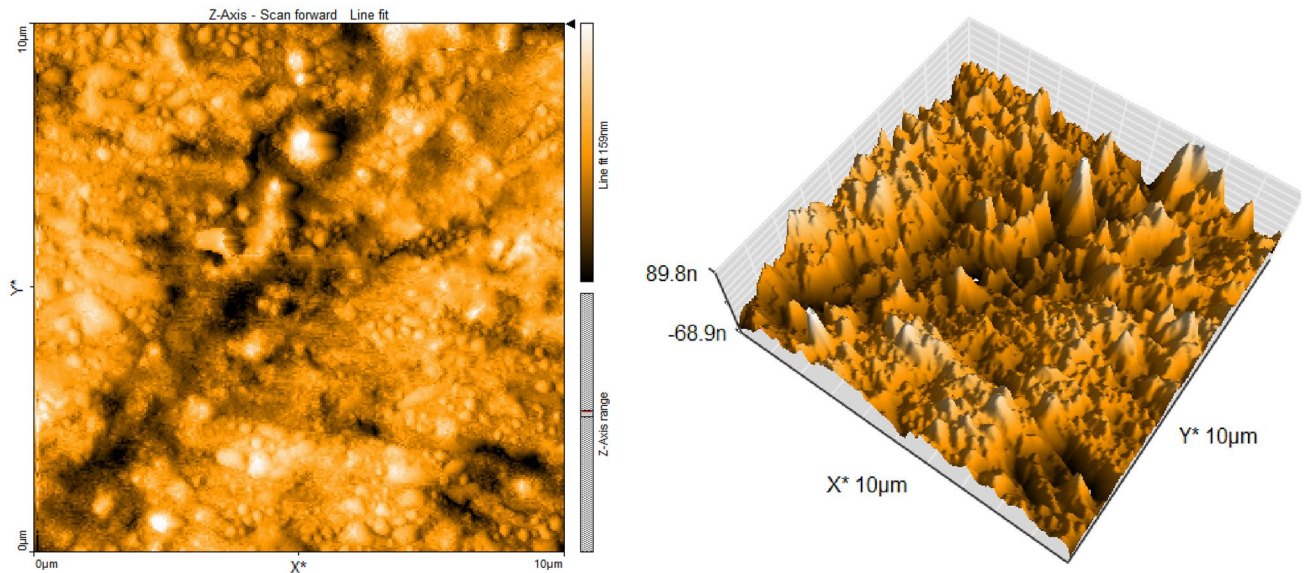


Fig. 9 2D and 3D images in presence of uric acid-Ca







**Fig. 10** 2D and 3D images in presence of uric acid-D3

**Table 3** AFM data of effect of uric acid (u.a) in SBF

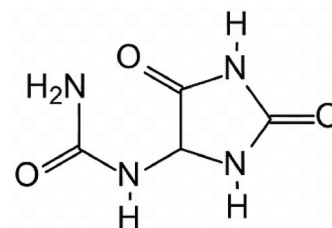
Parameter, nm	Blank	8 mg/dL u.a	u.a. + 2500 mg/L Ca	u.a. + 600 mg/L D3
Root-mean-square height ( $S_q$ )	3.978	18.02	25.64	20.57
Maximum peak height ( $S_p$ )	13.37	37.36	45.61	49.28
Maximum pit depth ( $S_v$ )	9.784	39.53	60.58	44.57
Maximum height ( $S_z$ )	23.16	76.89	106.2	93.85
Arithmetic mean height ( $S_a$ )	3.107	14.17	21.53	16.76

These two products after converting step are released into the circulation especially at the surface of implant to defense against microbial invaders by stimulating the innate immune system. The new forms have hydroxyl group and can easily adsorbed on the metallic surface, and can attain a full coverage for metallic surface and isolate it from surrounding to help in a capsulation process in shorter time. At the same time, these products can coordinate with uric acid molecules to form big polymeric organic molecules to achieve good coverage and protection for metallic surface.

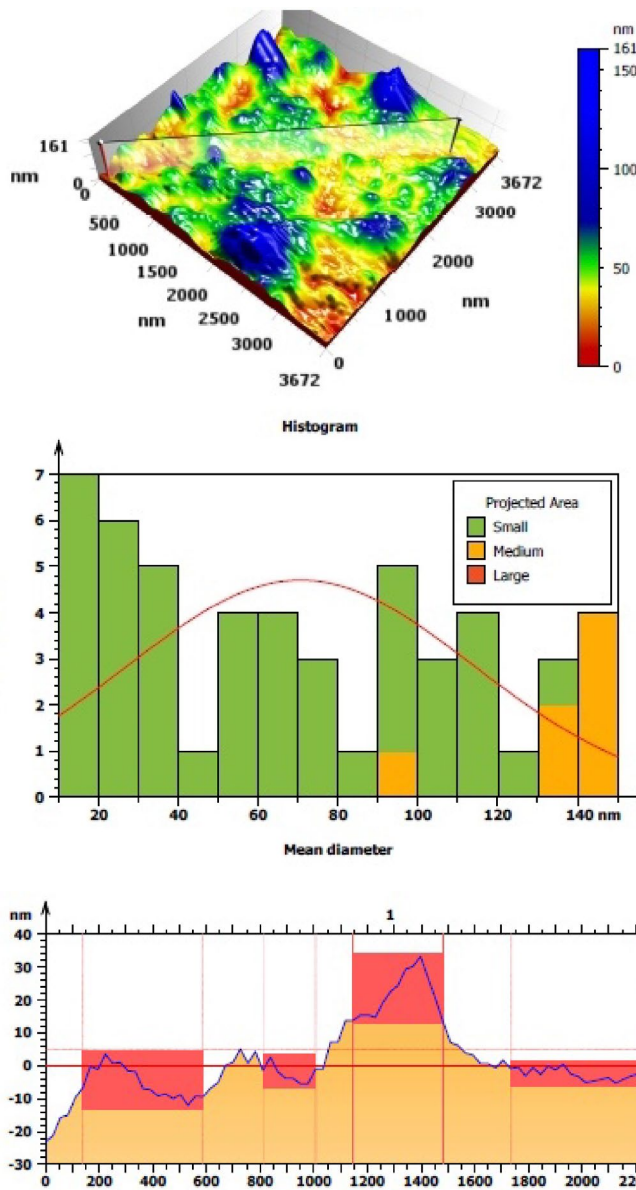
### 3.2 FESEM Data

The examination by FESEM was done for the metallic surface in the absence and presence of 8 mg/dL uric acid, 8 mg/dL uric acid-2500 mg/L Ca and 8 mg/dL uric acid-600 mg/L D3 as shown in Figs. 3, 4, 5, 6 respectively. The full coverage by uric acid molecules and calcium salt as well as D3 molecules is very clear with lower defects on the surface of base alloy compared with the appearance of anodic and cathodic sites for blank. Therefore, the surface is represented

inhibited in (Figs. 5 and 6) compared with corroded one in (Fig. 3) with highly damages and pits. Here, we cannot see the needle-like structure for uric acid due to presence of metal ions ( $Co^{2+}$  and  $Cr^{3+}$ ) surrounded the implant that may form coordination complex (organometallic complex) especially after opening the ring in uric acid as follow:



The cobalt and chromium are easy produce coordination complexes, where the Co may be form metallodendrimer structure as shown by Jasmina et al. when they study the properties of dendritic cobalt (II) salicylaldimine DNA biosensor [26]. Also, Cr can produce complexes with good



<b><i>Number of particles</i></b>	93
<b><i>Coverage</i></b>	37.07%
<b><i>Density</i></b>	6,897,727 P/mm <sup>3</sup>
<b><i>Mean diameter</i></b>	173.7 nm
<b><i>Mean height</i></b>	12.48 nm

Fig. 11 Particle analysis for surface in presence of uric acid

properties as indicated by Anamaria et al. when they study chromium (III) complex with flavonoids that have pharmacological properties such as anticoagulant, antitumoral and anti-inflammatory [27].

### 3.3 AFM Data

The morphological investigation can be estimated by AFM images as shown in Figs. 7, 8, 9, 10 for surface as blank and for three additive cases showing the height and valleys of the

adsorption on the surface by uric acid, calcium carbonate and cholecalciferol molecules. The deposition and adsorption of molecules are clear from the white spots in 2D images for three additive cases, the data of this analysis are shown in Table 3 that indicate the increasing in maximum height and depth compared with blank (Fig. 7) as well as increasing in surface roughness. The increasing in roughness is indication to increasing in the valleys and humps as depth and height, especially in case of uric acid-Ca due to mountains of calcium carbonate at a different area (i.e., accumulation of

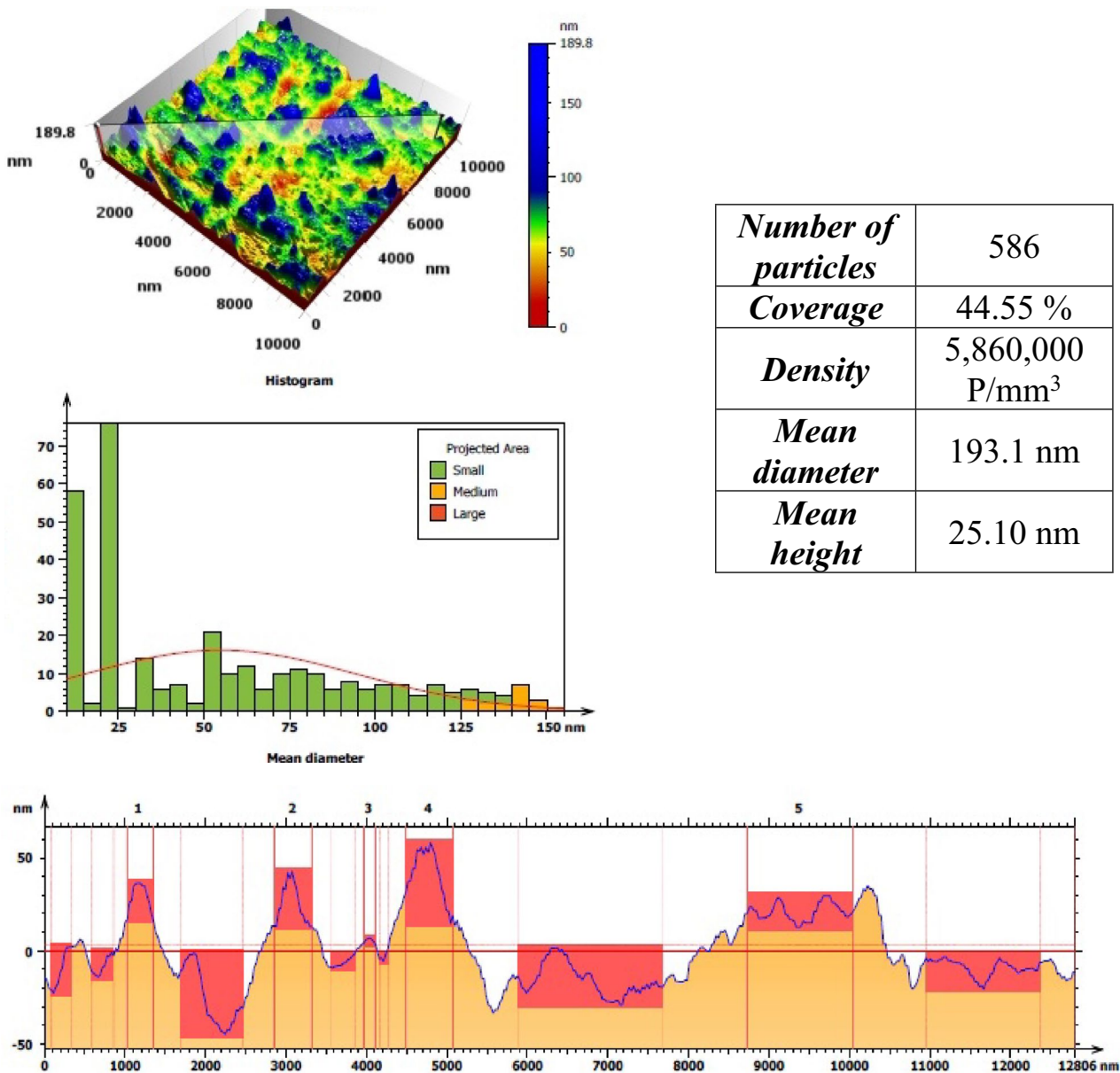


Fig. 12 Particle analysis in presence of uric acid + 2500 mg/L Ca

calcium carbonate salt), while the increasing in valleys and humps in the case of uric acid-D3 is due to bulk molecules of vitamin D3 that form mountains like structure by Calcifediol and Calcitriol molecules.

Particle analysis for the effect of uric acid can be seen in Figs. 11, 12, 13, compared with the blank (Fig. 14); No. of particles and density were decreased, while the mean diameter and mean height were increased. The

comparison among the three case of uric acid can be seen that the highest no. of particles was for uric acid-Ca due to small size of inorganic molecules that give more coverage. The highest density was for uric acid-D3 because of bulk molecules of D3, while the most height was for uric acid-Ca case that forms mountains structure.

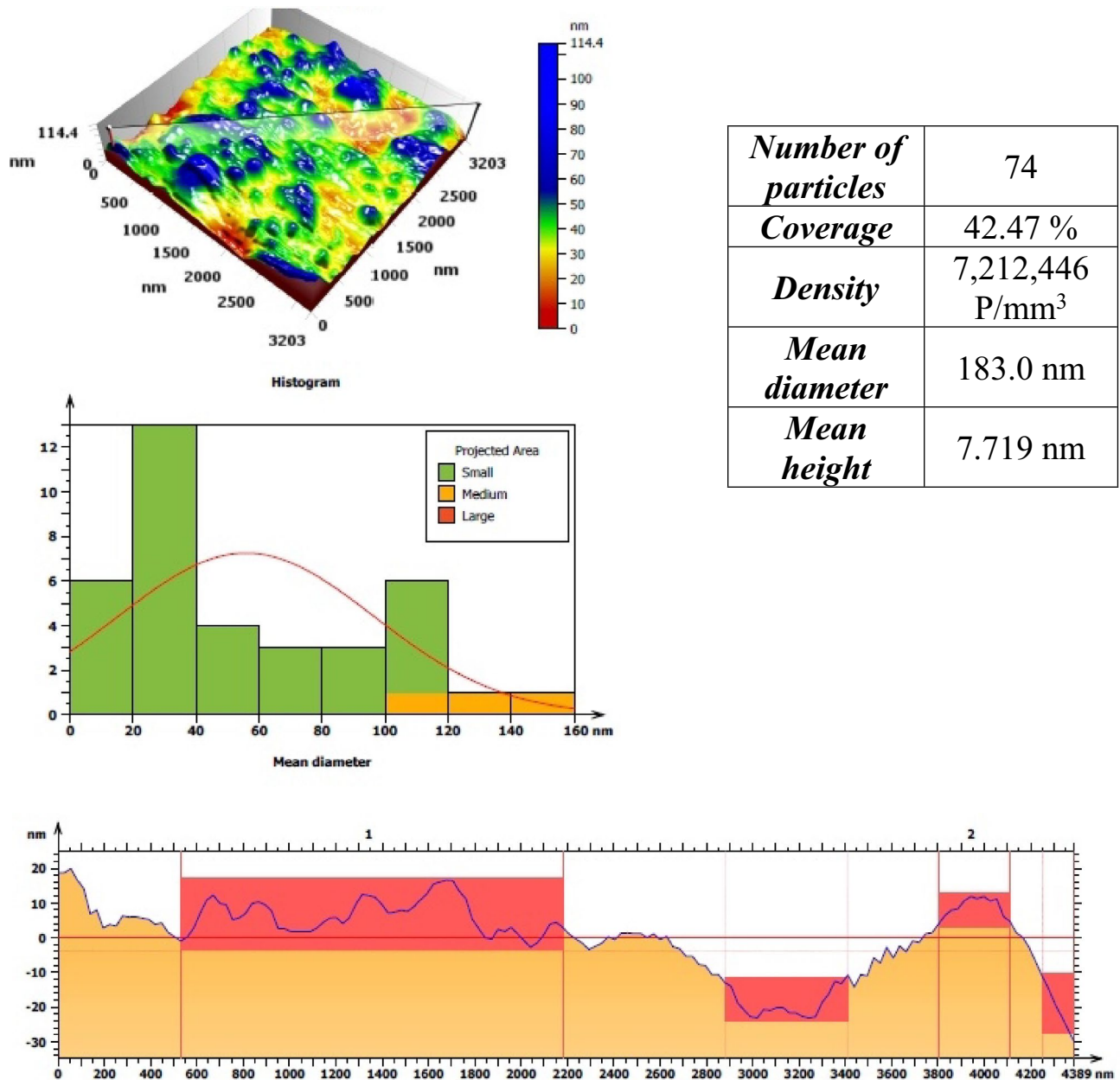


Fig. 13 Particle analysis in presence of uric acid + 600 mg/L D3

### 4 Conclusion

This study is concerned to the effect of increasing the level of uric acid in body due to gout disease which is represent as biological risk, but it was chemical requirement to reduce the corrosion or dissolution of bio implant such as Co-Cr-Mo alloy in the current work.

Five cases were investigated for increasing uric acid in body included: 8 mg/dL uric acid, uric acid with two different of calcium supplement and uric acid with two concentrations of vitamin D3 as immune drugs. All cases showed good corrosion inhibition for base alloy through adsorption these additives by their electronic functional groups that attract to positively charged surface to form some organometallic complex.

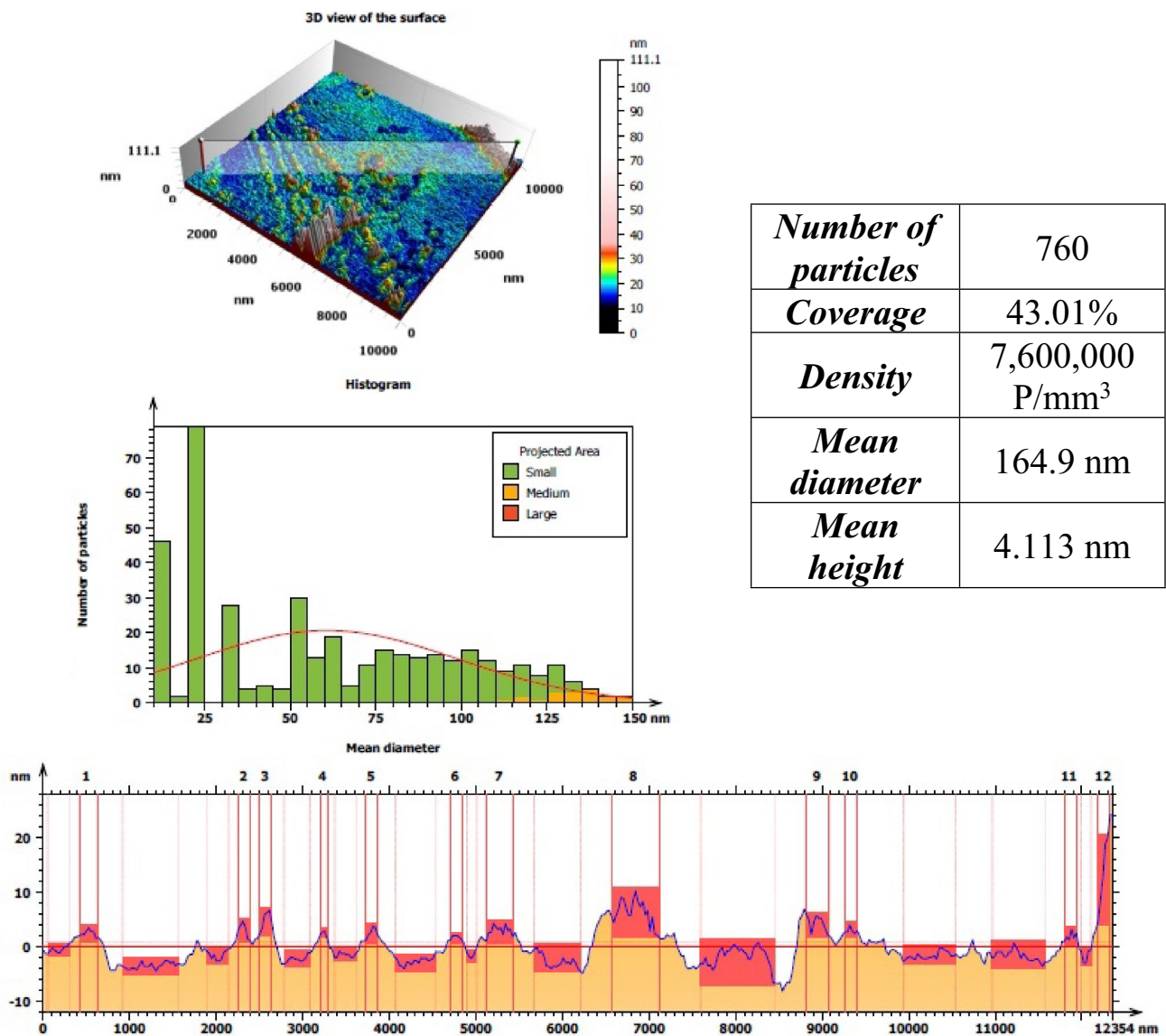


Fig. 14 Particle analysis for alloy's surface

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**Data Availability** All data generated or analyzed during this study are included in this published article.

## Declarations

**Competing interests** The authors have not disclosed any competing interests.

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