# Study the effect of adding $TiO_2$ nano-powder on some surface properties of $TiO_2$ thin film prepared on stainless steel substrate

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**Abstract**

In this research $TiO_2$ nano-powder was prepared by a spray pyrolysis technique and then adds to the $TiO_2$ powder with particle size (0.523 µm) in ratio (0, 5, 10, 15 at %) atomic percentage, and then deposition of the mixture on the stainless steel 316 L substrate in order to use in medical and industrial applications.
Structure properties including x-ray diffraction (XRD) and scanning electron microscope (SEM0, also some of mechanical properties and the effect of thermal annealing in different temperature have been studied. The results show that the particle size of a prepared nano-powder was 50 up to 75 nm from SEM, and the crystal structure of the powders (original and nano powder) was rutile with tetragonal cell. An improvement in all the properties after the addition of $TiO_2$ nano –powder was take place.

**Key words**

*$TiO_2$ nano –powder, spray pyrolysis, coating.*

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## دراسة تأثير إضافة مسحوق نانو $TiO_2$على بعض الخصائص السطحية لغشاء رقيق $TiO_2$ مرسب على قواعد من الفولاذ المقاوم للصدأ

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**الخلاصة**

في هذا البحث تم تحضير مسحوقَ نانوي من أوكسيد التيتانيوم $TiO_2$ بطريقة الرش الكيمياوي الحراري spray pyrolysis بعد ذلك تم خلط المسحوق النانو ي المحضر مع مسحوق جاهز من $TiO_2$ أيضا و بحجمِ حبيبيِ بلغ (0.523µ m) و بنسبِ خلط بلغت (0 , 5 , 10 , 15 atom %)، وبعد ذلك ترسيب الخَلِيْطِ على قواعد من الفولاذ المقاوم للصدأِ 316L و المَستعملَة في التطبيقاتِ الطبيةِ والصناعيةِ بشكل واسع. درست الخواص التركيبية باستخدام (XRD,SEM)، أيضا بعض الخواص ميكانيكية، وتأثير التَلْدين الحراري أيضاً في درجةِ الحرارة المختلفةِ. بينت النَتائِجَ بأنّ حجمَ جسيمات المسحوقَ النانو المحضر كَانَ بحدود 50 nm إلى حوالي 75 nm مِنْ فحص SEM ، و تحسن قد حصل في كُلّ الخواص بعد إضافةِ مسحوقَ اوكسيد التيتانيوم النانوي.

## Introduction

Recently titanium dioxide ($TiO_2$) ultra thin films have been investigated with regards to their remarkable optical, electrical and photo electrochemical properties.
A number of methods have been employed to fabricate $TiO_2$ films, including e-beam evaporation [1], sputtering [2], chemical vapour deposition [3] and sol-gel process [4]. Among these methods the sol-gel process is one of the most appropriate techniques to prepare thin film. Structure types of $TiO_2$ in general include (brookite, rutile, anatase).
Applications of $TiO_2$/316 L St.St. like microfiltration media properties, catalytic reactors, catholic protection, and orthopedics.
Contemporary orthopedics commonly uses various types of implants which replace

damaged or malfunctioning parts of the osteoarticular system. The implants are manufactured using a number of construction materials fulfilling specific requirements. To numerous metallic materials belong stainless steel and titanium alloys.

The materials used for the implants working for a long time in a living organism environment ought to be bio-acceptable, resistant to the influence of the tissue environment, and compatible biochemically. Also the implant surfaces are known to be very important, because their chemical, biomechanical, and topographic features influence the behaviour of cells during the initial stage of the implant integration with the surrounding tissues, ultimately determining the speed and the quality of new tissue formation [1, 2].

Physical properties of metallic materials which accelerate the development of bone–implant interactions can be improved by various techniques of surface film engineering, e.g. by the deposition of ultra thin oxide films by the sol–gel method.

The main purpose of the present paper is characterization of new sol-gel derived $TiO_2$ ultra thin films deposited on the surfaces of stainless steel (316L) from normal and nano-powders.

## Experimental Work

This work include many steps;

The first step: preparation of $TiO_2$ nano – powder from an aqueous solution of Titanium chloride ($TiCl_4$). The concentrations was (0.01 M), the acidity was maintained to be 4-5 pH during spraying. The preparing of the nano-powder is made by spray pyrolysis technique. The spraying apparatus was manufactured locally in the university laboratories. In this technique, the prepared aqueous solutions were atomized by a special nozzle glass sprayer at heated collector glass fixed at thermostatic controlled hot plate heater, was used as a carrier gas to atomize the spray with the help of an air blower. The substrate temperature was maintained at 300 °C during spraying.

Atomization rate was about (1 nm/s) with (0.5 ml/min) of flow rate. The distance between the collector and spray nozzle was kept at (5 cm.) The spray of the aqueous solution yields the following chemical reaction [5]:

$$TiCl_4 + 2H_2O \longrightarrow TiO_2\downarrow + 2Cl_2\uparrow + 2H_2\uparrow \quad (1)$$

The second step: making ready $TiO_2$ fine size powder by analyzing particle size by using SHIMADZU SALD2101 device, and mixing the fine powder with prepared nano-powder at different percentage as shown in Table (1)

The third step: preparing specimens 316L Stainless Steel substrate with dimension ($5*1*0.3\ cm^3$) for coating. The samples was ground with emery papers from (200-1000), and then clean by ethanol and acetone. And taking its weight before and after coating. The surface roughness (Ra) was done by using roughness tester type TR 200 before and after coating Fig. 1.

The forth step: deposition of the thin film by mounting the blend solvent [Ethanol, Isopropanol and powder mixture] on the surface of Stainless Steel and enter the sample to the furnace at three different temperatures (600,700,800°C) in order to formation the coating.

The fifth step: is the measurement which includes:

1-$TiO_2$ film thickness was calculated from the relation below, and it was found to be about 0.1µm [6]:

$$\mathbf{t} = \Delta m/\rho' A \qquad (2)$$

where $\Delta m$ is the mass changes of the substrate before and after deposition ,$\rho'$ is theoretical density of $TiO_2$ film and A is substrate area .

2- X-ray diffraction with diffractometer type CuKα ( λ = 1.5406 Å ), the scanning speed was 3%. The data was compared with that ASTM (21-1276 ) card .To determine the (a- and c-lattice constant) from X-ray spectrum were using the following formulas were used [7,8]:

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (3)$$

Where (hkl) are Miller indices, d-space (inter planer space) which can be calculated from the well-known BRAGG's law:

$$n\lambda = 2d_{(hkl)} \sin\theta \qquad (4)$$

The preferred plane (hkl) in polycrystalline coat in which there is maximal growth (preferred orientation) can be described by texture coefficient [7,8]:

$$Tc(hkl) = [I_m(hkl)/I_{ASTM}(hkl)] \ / \ [(1/M)\sum I_m(hkl)/I_{ASTM}(hkl)] \qquad (5)$$

Where $T_C(hkl)$ is the texture coefficient of the (hkl) plane, $I_m$ is the measured intensity, $I_{ASTM}$ is the American Standard for Testing Materials ASTM standard intensity of the corresponding powder and M is the number of reflections observed in the X-ray diffraction trace.

3- The vickers microhardness was performed with (5g load) by using following reaction[9]:

$$H.v = 1854.4p/d^2 \qquad (6)$$

where p is the load and d is the average diameter of the trace.

**Results and Discussion**

Fig.2 shows the X-ray diffraction chart of titanium oxide original powder (normal) in the (a) and in (b) prepared

***Table.1: Components of the powder mixtures are used***

| Sample No. | $TiO_2$ at% (Normal powder) | $TiO_2$ at% (prepared nano powder) |
|---|---|---|
| $X_0$ | 100 | 0 |
| $X_5$ | 95 | 5 |
| $X_{10}$ | 90 | 10 |
| $X_{15}$ | 85 | 15 |

***Fig.1: Measurement of roughness***

titanium oxide nano- powder by spray pyrolysis , the crystal structure of the powders (original and prepared nano powder )was rutile with tetragonal unit cell where we note a significant change in the high of peaks between the record and the original and can explain it to the nature of the nano particles of the powder that product.

Table (2) shows the values of lattice constants with compared with reference values, according to the card ASTM (21-1276) and after applying the equations, showing that the values change in the lattice constant (a and c) be positive any increase in the lattice constants compared with standard values and a decrease in the constants (a and c) compared with standard values. Also from the chart of X-ray diffraction, were calculated the values of texture factor (Tc) from equation (5), the results show that the value of the texture factories of the nano-powder closer to the ideal values and different from the original powder (natural), because of the nature of the nano-structure of powder.

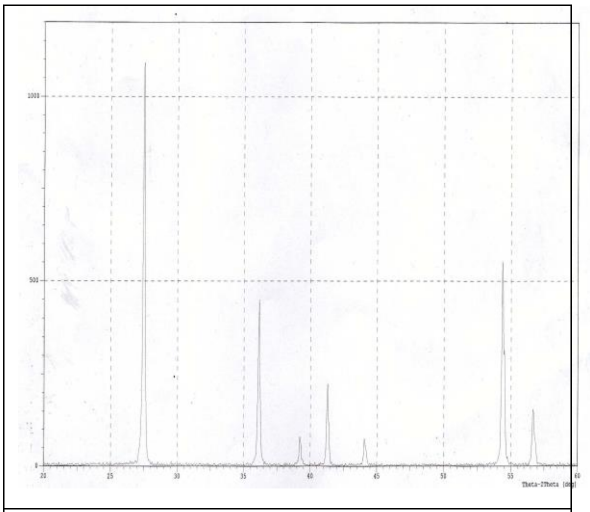
*Table 2: Lattice constants*

| structure | a(nm) | c(nm) |
|---|---|---|
| Standard ASTM(21-1276) | 4.5933 | 2.9592 |
| (Normal powder) | 4.5821 | 2.9537 |
| (prepared nano powder | 4.5962 | 2.9605 |
| | Δa (nm) | Δc (nm) |
| (Normal powder) | +0.0112 | +0.0055 |
| (prepared nano powder) | -0.0029 | -0.0013 |

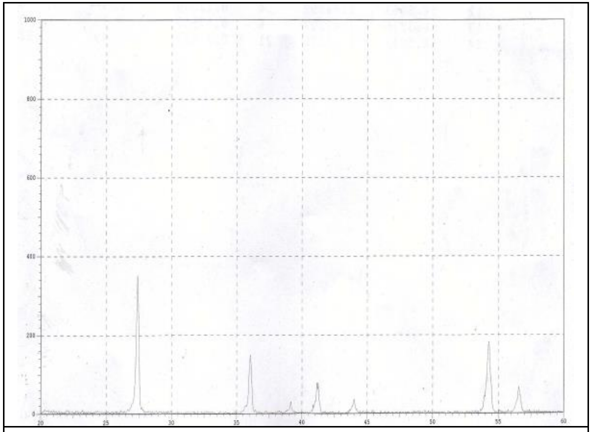
Fig.3 shows in (a) SEM image of the prepared nano powder, and its demonstrate that granular shape with particle size (50 up to 75 nm) while the particle size of powder used in the original work is up to 0.523 microns as shown in(b).
Fig.4 shows the weight difference before and after coat treatment, its shown increases because of two factors which are, the first one a resulting from the increased in the adding nano-powder percentage to the original powder , and the second factor is to increase the temperature of the heat treatment that create from increasing the diffusion. Values of the increase in the gained weight on the surface related to nano-powder percentage that increases the propagation into the base and thereby increase the weight [2, 3, and 11].

***Table (3): The texture coefficient of prepared and normal powders***

| Structure | Tc |
|---|---|
| (Normal powder) | 1.1912 |
| (prepared nano powder) | 1.0548 |



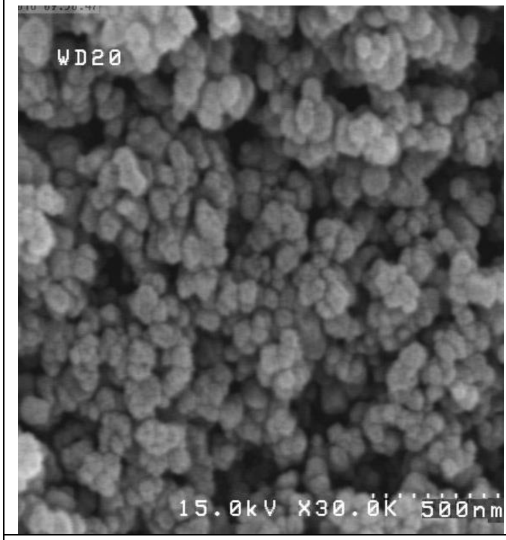
***(a)Normal powder***



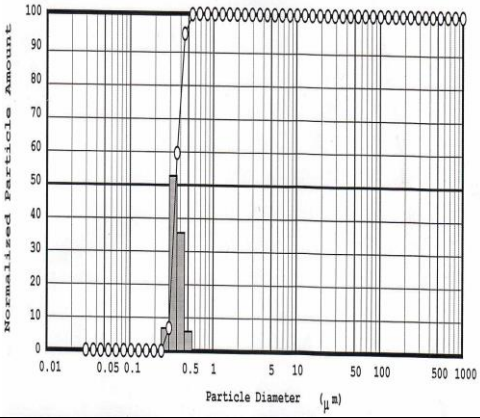
***(b)Nano-powder***

***Fig. 2:** X-ray diffraction chart of titanium oxide original powder*

Fig.5 shows a marked decrease in the values of surface roughness of the samples with the increase in the proportion of nano-powder added and the temperature and that these results resemble the results of some researchers, nano-powder is works to re-fining the structure [9, 11].
The value of Vickers micro hardness of 316L stainless steels was190kg/mm$^2$ and agree with [10], the Vickers micro hardness of the $TiO_2$ coats was shown in Fig.6.
The value of micro hardness measurement for the coating was ranging from (400 kg/mm$^2$) to more than (600 kg/mm$^2$) and as shown, and this result are also similar to the results of other researchers [4, 12].




*(a)SEM picture of $TiO_2$ nano powder(prepared powder)*




*(b)Particle size analyzing of $TiO_2$ (original powder)*

*Fig.3: SEM image of the prepared nano powder*

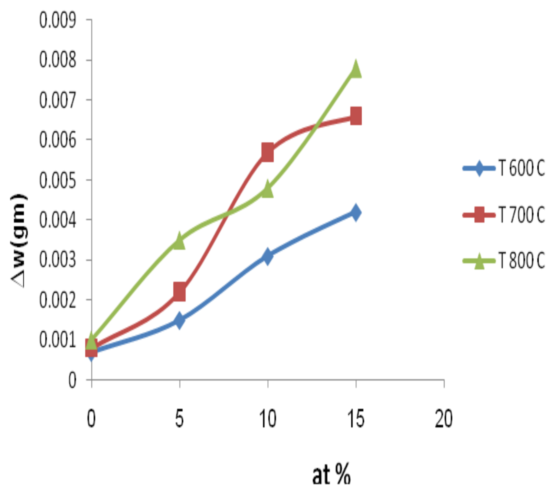



*Fig.4: Sketch of the relation of weight change and $TiO_2$ nano –powder atomic percentage*

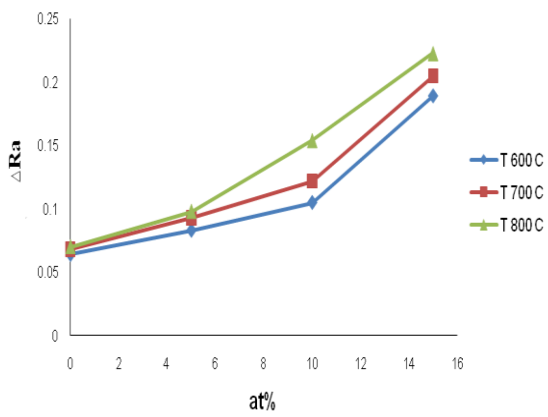



*Fig.5: Sketch of the relation of roughness changing and $TiO_2$ nano –powder atomic percentage*

## Conclusions

1 – We can be prepared nano powder of metal oxide such as titanium oxide using the spray pyrolysis properly.

2 - Can be used titanium dioxide plus titanium dioxide nanoscale in engineering applications in general and surgery orthopedic in particular.

3-To obtain advanced results it must be adding a proportion of nanoscale powder to powder the original (normal).

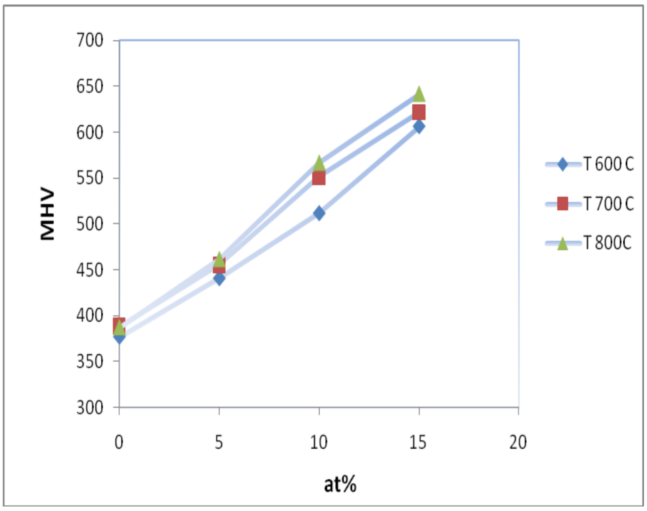



***Fig.6: Vickers micro hardness of the $TiO_2$ coats***

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